Biomaterials Plenary

Room: 609 - Session BP-SuA

Biomaterials Plenary Session - Global Health Technologies

Moderator: B.D. Ratner, University of Washington

3:00pm **BP-SuA1 Paratransgenic Strategies for Control of Vector-borne Diseases: Rewards and Risks**, ***R.V. Durvasula***, *I. Hurwitz, S. Matthews*, University of New Mexico School of Medicine **INVITED**

The last decade saw vector-borne disease emerge as an urgent global health concern. Malaria, leishmaniasis, dengue fever, African trypanosomiasis, and Chagas disease place over sixty percent of the world's population at risk with nearly 740 million new cases. The mainstay of vector-borne disease control has been pesticide-based vector eradication. Pesticides were responsible for dramatic reductions of malaria in India during the 1950's and 60's. More recently, the Southern Cone Initiative against Chagas disease achieved spectacular reductions in South America. Unfortunately, such reductions may be temporary. Progress can be retarded by twinned factors: vector resistance and cost. In addition, pesticides pose a significant hazard to human health and the environment. These limitations have inspired new strategies for prevention and control, such as genetic modification of insect vectors to reduce their competence to transmit a target pathogen. This goal has been pursued via two approaches: modification of the vector genome and paratransgenesis, which involves genetic manipulation of symbiotic bacteria resident in vectors. Although proof of concept for both of these approaches has been achieved in laboratory studies, field application remains a possibility with many attendant risks. Paratransgenesis has been proposed as a strategy for the control of Chagas disease, a parasitic illness endemic to Central and South America. The WHO estimates that 8 - 11 million people are currently infected and 25 million are at risk for the disease. Chagas disease can be chronic and debilitating, with infected persons suffering cardiac, gastrointestinal, and neurological damage. Because neither vaccine nor treatment exists for the chronic stage of the disease, controlling transmission has been a priority. Chagas disease is transmitted to humans by obligate blood-feeding insects, the triatomines (order Hemiptera, family Reduviidae). The causative agent of the disease, the parasite Trypanosoma cruzi, lives in the gut of the triatomine and is transmitted via a fecal droplet deposited by the bug after a blood meal. In the paratransgenic strategy, the symbiotic bacterium, Rhodococcus rhodnii, which lives in the Chagas disease vector, Rhodnius prolixus, has been transformed with a series of expression plasmids to export molecules that are toxic to the parasite, T. cruzi. Laboratory lines of R. prolixus carrying cecropin A-producing symbionts have been reared which are refractory to T. cruzi infection. Field use of this approach will rely on natural coprophagic spread of symbionts by R. prolixus. A fake fecal preparation termed CRUZIGARD has been made and impregnated with engineered symbionts. Under closed cage and greenhouse conditions, CRUZIGARD- mediated delivery of transgenic bacteria to target populations of R. prolixus has been demonstrated. A paratransgenic approach to another important vector-borne disease, visceral leishmaniasis, is also under development. Soil-borne bacteria isolated from the sandfly vector, P. argentipes, in Bihar, India have been transformed to export molecules to larval and adult stages of sandflies with the aim of disrupting the cycle of Leishmania donovani. The paratransgenic approach has the potential to reduce pathogen transmission. Because it involves release of engineered microbes, aspects of field release impacting the environment merit investigation. An analysis of risks versus benefits of these strategies and the role for other delivery strategies of foreign genetic material will be presented.

3:40pm **BP-SuA3 Engineering New Diagnostics for Global Health**, ***W.R. Rodriguez***, Harvard Medical School **INVITED**

More than 70% of the 40 million people living with HIV infection worldwide do not know they are infected, and do not have access to the critical blood tests--CD4 cell counts and HIV RNA levels—essential for effective treatment. Diagnosis of tuberculosis, which kills 9,000 people per day, remains rooted in a 19th century test--light microscopy--and as a result, nearly half of TB cases go undiagnosed. Malaria diagnostics, also dependent on microscopes, are insensitive and difficult to implement. Are these engineering problems? How can advances in microfabrication, MEMS, microfluidics, and nanosensing be extended to global health problems? Are technical solutions to the unforgiving challenges of monitoring disease in poor countries within reach? Through a case history of a CD4 cell counting device, I will review the product specifications of the most urgently needed diagnostic devices for global health; review current efforts in microscale and nanoscale diagnostics, and their application to diseases like AIDS, TB and malaria; and discuss the biological, technical, product development, intellectual property, funding, and commercialization challenges to unleashing the potential of microscale technologies for global health.

4:20pm **BP-SuA5 Development of a Point-of-Care Diagnostics System for the Developing World**, ***P. Yager***, University of Washington, *G. Domingo*, PATH, *C.F. Battrell*, Micronics, Inc., *W. Mahoney*, Nanogen, Inc., *P. Stayton*, University of Washington **INVITED**

Microfluidics and related fields have progressed to the point that one can now tackle the technical challenges of miniaturizing complex bioassays for use in point-of-care diagnosis. The potential for improving health is great, but in the developing world the final system must be simple, robust, operable without the need for supporting infrastructure, and extremely inexpensive. We are engaged in a 5-year project for development of such a diagnostic system for use in the developing world. Supported by the Bill & Melinda Gates Foundation's Grand Challenges in Global Health initiative, this is a team effort led by the University of Washington that includes PATH, Nanogen, Inc., and Micronics, Inc. In many resource-limited settings, patients presenting with fever are treated on the basis of a presumptive clinical diagnosis due to unavailability of complex diagnostic assays, and the patients are, therefore, often treated incorrectly. The initial focus of this project is on a panel of tests for detection (from a few drops of blood) of a range of infectious agents that cause rapid-onset fever: malarial parasites, the bacteria Salmonella typhi and Rickettsia, and viruses including those that cause dengue, measles and influenza. The technical aim is to develop an integrated system that includes a portable battery-powered reader and small disposable single-use microfluidic cards; the cards allow the system to perform both immunoassays and nucleic acid amplification assays on this panel of infectious disease targets simultaneously and within a few minutes. The instrument itself remains dry; the disposable card is pre-loaded with all necessary reagents (in either dry or wet form) to perform in parallel both immunoassays for antigens and pathogen-specific IgM levels and amplification and detection of both RNA and DNA from pathogens. Optical imaging of absorption is used for the immunoassays, and fluorescence is used for the nucleic acids. After adding the sample, the card will be inserted into the reader, which activates the fluid movements, thermal cycling, and other preparatory and analytical activities. The disposable card will contain molecular systems for sample concentration and controlled delivery of reagents, and will be made of cost effective materials for low-cost volume production. All reagents on the card will be storable at ambient conditions for at least 1 year. This platform eventually is intended to ultimately accommodate a wide range of analytical panels tailored for region-specific and disease-specific diagnostic problems.

The Industrial Physics Forum 2007: The Energy Challenge

Room: 602/603 - Session IPF-SuA

Automotive Energy

Moderator: J. Hobbs, American Institute of Physics

3:00pm **IPF-SuA1 Technology, Economics, and Policy of Hydrogen and Fuel Cells**, ***D. Dresselhaus***, Massachusetts Institute of Technology **INVITED**

The history of alternative transportation fuels is largely a history of failures. None has overcome the institutional, financial, and technological inertia of gasoline and diesel. Only ethanol made from corn is gaining market share in the US - thanks to large federal and state subsidies and a federal mandate. What are the prospects of alternative low-carbon fuels, especially biofuels, electricity and hydrogen? Is California's low carbon fuel standard a model for orchestrating the transiton to alternative fuels? Is hydrogen different? Might hydrogen and fuel cells succeed on a grand scale, where others have not? If so, how might this unfold? What role do hybrid vehicles play in this process? This presentation will address the technology, economics, and policy of hydrogen and fuel cells, and will explore possible and likely outcomes.

3:40pm **IPF-SuA3 Frontiers, Opportunities and Challenges for a Hydrogen Economy**, ***J.A. Turner***, National Renewable Energy Laboratory **INVITED**

Energy is one of the most important issues facing our world today; in fact, in today's society energy is as important as food and water. Humankind finds itself faced the challenge of how to continue to power society, particularly in the face of the rapidly growing economies of emerging nations like India and China, and yet answer questions of sustainability, energy security, geopolitics and global environment. One of the major issues facing America and most other countries in the world is how to supply a transportation fuel, an energy carrier to replace gasoline. Hydrogen as an energy carrier, primarily derived from water, can address issues of sustainability, environmental emissions and energy security. The "Hydrogen Economy" then is the production of hydrogen, its distribution and utilization as an energy carrier. While the vision of a hydrogen economy has been around for over 130 years, the most recent push to use hydrogen as an energy carrier came as part of a US Presidential Initiative, announced in the 2003 State of the Union Address. It is important that we consider hydrogen in tandem with other technologies as an alternative to the once-abundant hydrocarbon resources on which our society depends. This talk will introduce sustainable energy systems, including fuel cell technology and discuss the vision, the barriers and possible pathways for the production and implementation of hydrogen into the energy infrastructure.

4:20pm **IPF-SuA5 The (Re) Electrification of the Automobile**, ***M.A. Tamor***, Ford Research and Advanced Engineering **INVITED**

It is easily forgotten that a century ago electric vehicles had a dominant market share over steam and internal combustion automobiles. While quiet, clean and reliable, the EV was challenged by range and performance limitations, and eventually done in by the electric self-starter …. one of the first electrified features! Driven in large part by the quest for improved fuel efficiency and emissions – and accelerated by design opportunities and attractive customer features – the re-electrification of motor vehicle is now progressing rapidly. Electrified functions range from the mundane, such as power steering and engine coolant pumps, through a spectrum of hybrid powertrain concepts and on to a resurgent interest in all-electric vehicles. Each incremental function and additional load increases the demand for efficient and cost-effective energy storage and is driving new, sometimes divergent, battery requirements. The hybrid electric vehicles available today are all what might be called "power hybrids" that have been optimized to achieve impressive fuel efficiency with minimum battery energy capacity – and so minimum battery weight and cost. Driven by commercialization of HEVs, rapid progress on batteries and power electronic systems paves the way to two revolutions in the motor vehicles: First, is the proposal to shift a significant fraction of propulsion energy from petroleum fuel to electricity by "plugging in." The "plug-in" HEV is an "energy hybrid" that by definition requires a much larger battery, and creates a new connection that allows motor vehicles to exploit the efficiency and diversity of the electric grid. While not overwhelmingly attractive in the present economy of still-cheap oil and fossil fuel-generated electricity, the plug-in hybrid could prove critical to closing the gap between a limited supply of renewable fuel and ever-growing transportation needs. Second, with no rigid connections between the various powertrain elements, the series HEV – "power" or "energy" - enables re-engineering of the motor vehicle including its shape, structure, materials and manufacturing. In short, the re-electrification of the automobile is enabled by progress in battery technology, but itself may enable revolutions in the nature and the economics of personal transportation.

5:00pm **IPF-SuA7 General Motors' Perspective on New Transportation Technologies**, ***J. Bereisa***, General Motors Corporation **INVITED**

Will review the rationale behind and the progress made in fuel cell cars and the hydrogen economy and specifically highlight technical progress achieved in fuel cell vehicles, remaining challenges and issues related to creating the hydrogen refueling infrastructure.

Applied Surface Science

Room: 610 - Session AS-MoM

Quantitative Surface Analysis I. Electron Spectroscopies: (Honoring the contributions of Martin Seah, NPL, and Cedric Powell, NIST)

Moderator: D. Gaspar, Pacific Northwest National Laboratory

8:00am **AS-MoM1 Quantitative Surface Analysis - Applying Thirty Years of Progress and Addressing New Analysis Needs*, D.R. Baer*,** Pacific Northwest National Laboratory **INVITED**

Over the past thirty plus years, advances in instrumental capability, analytical approaches and the establishment of data bases have significantly improved the reliability of instrumentation and the possible accuracy of surface analysis. The significant contributions of Cedric Powell, Martin Seah along with those of many others provided the foundation for many of these advancements and served to establish many of the elements of surface analysis as it is currently practiced. From the prospective of the growth of the use of techniques such as XPS and based on the number of surface analysis systems available around the world, it is clear that use of the methods is increasing and many users are no longer experts. At the same time, many of the pioneering researchers who have made these advancements possible and who have the greatest knowledge about the techniques are at or nearing retirement age. Thus, we currently face two different but related challenges. First, we need to establish ways to efficiently transfer the important analytical knowledge to new and often less expert analysts. Second, new types of materials make additional demands on the analytical capabilities and it is important for a new generation of researchers to pick up the challenge. This talk will note some aspects of the progress and address the current challenges from the view of a nanotechnology project manager, the use of surface analysis in a DOE User facility (the Environmental Molecular Sciences Laboratory, EMSL), and from the view of a participant in two committees developing surface chemical analysis guides and standards. From the viewpoint of a project manager, it is useful to extract as much information as possible form the techniques being used. For some nanomaterials, this often requires application of multiple techniques, sophisticated analysis of some types of data and allowing the analysis of data from one method to inform the data collection and analysis of other types of data. In the EMSL we find that we are in a constant education mode teaching users about how to plan experiments, handle samples, collect and analyze data to obtain the desired information. The ASTM Committee E42 on surface analysis is currently working on a variety of consensus guides to enable new users to apply the experience of topical experts to analyze some type of samples and problems.

8:40am **AS-MoM3 Some Highlights and New Directions in Quantitative AES and XPS*, C.J. Powell*,** National Institute of Standards and Technology **INVITED**

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been productive tools for a large variety of scientific and technological purposes since commercial instruments became available almost 40 years ago. Elemental identification is relatively easy but quantitative measurements (e.g., identification of chemical state, determination of chemical composition, and measurement of film thicknesses) can be more difficult. I will give a brief overview of advances that have been made to calibrate instruments, assess surface sensitivity, and account for elastic scattering of the signal electrons. NIST databases are now available that provide XPS data, inelastic mean free paths, effective attenuation lengths (EALs), and elastic-scattering cross sections.[1] A new NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) was recently released.[1] I will describe two applications of SESSA, one to assess the distinguishability of N composition profiles in SiON films on Si by angle-resolved XPS[2] and the other to determine EALs for photoelectrons in SiO_2.[3] Small systematic differences between the SESSA results and experimental data give new insights into photoelectron excitation and transport. Finally, I will describe results from a VAMAS project to assess the magnitude of uncertainties in XPS peak intensities associated with different techniques and procedures for background subtraction.

[1] http://www.nist.gov/srd/surface.htm.

[2] C. J. Powell, W. S. M. Werner, and W. Smekal, Appl. Phys. Letters 89, 172101 (2006).

[3] C. J. Powell, W. S. M. Werner, and W. Smekal, Appl. Phys. Letters 89, 252116 (2006).

9:20am **AS-MoM5 The Bulk Ratio Method for Determining Surface Enhancement Using Auger Analysis*, J.D. Geller*,** Geller MicroAnalytical Laboratory, Inc.

Enhanced surface layers on stainless steel are engineered to provide improved corrosion resistance and reduced surface reactivity. Stainless steel can be electropolished and chemically treated in such a way that the surface finish is improved while enhancing the chromium levels near the surface. This modification is thought to increase corrosion protection and produce less gas stream particulates for semiconductor applications. The surface analysis techniques of x-ray photoelectron (XPS) and Auger electron spectroscopy (AES) have been used for decades to characterize the effects of these treatments by observing the near surface chemistry. International standards and practices (Sematech, ASTM F-1402-92 and SEMI 2335b), for AES and others for XPS, have been written to guide the analyst on how to calibrate their instruments, as well as collect and reduce the data. The test results most often examined are the oxide depth and maximum Cr to Fe ratio. Improved standard practices are necessary to reduce the variability that is seen between instruments and between laboratories for measuring the ratios. The variability likely stems from the use of sensitivity factors that are not representative of the host instrument and the improper selection of standards. The Bulk Ratio Method is a new approach which provides the same numerical value of chromium enhancement from data collected and reduced using either relative intensities or sensitivity factors. The Bulk Ratio can be easily calculated from historical data collected on different instruments and laboratories.

9:40am **AS-MoM6 Investigation of Average Matrix Relative Sensitivity Factors in Auger Electron Spectroscopy*, M. Suzuki*,** *K. Mamiya, N. Urushihara, N. Sanada,* ULVAC-PHI, Inc., Japan*, D.F. Paul, S. Bryan*, Physical Electronics

Auger electron spectroscopy (AES) is widely used for surface elemental analysis of the outer several nm of a material surface. Quantification is performed by converting signal intensities to elemental concentrations with relative sensitivity factors (RSF's). In practice, elemental RSF (ERSF) or atomic RSF (ARSF) tables are utilized in AES quantification. However, ISO18118:2004[1] recommends adopting an average matrix RSF (AMRSF), which includes corrections of matrix effects that are affected by elastic scattering, backscattering, inelastic mean free paths and atomic densities. In this study we calculate AMRSF's for the primary electron accelerating voltages of 3 kV, 5 kV, and 10 kV according to ISO18118 from experimentally obtained ERSF's. Comparing AMRSF's and ERSF's, there are greater differences for main group elements than for transition elements. For main group elements, AMRSF values are smaller than ERSF's for second row elements, while they inversely correlate for fifth and sixth row elements. So far, ERSF's for AES quantification have been provided as a database for primary electron energies less than 10 kV. Higher voltages, such as 20 kV or 30 kV, are in common use today in field emission AES instruments in order to achieve high spatial resolution. Thus RSF's for primary voltages higher than 10 kV are strongly desired for quantification of small areas. Therefore, we have extended AMRSF's for higher than 10 kV using Ichimura-Shimizu's backscattering factors[2] and Gryzinski's ionization cross-sections.[3] The former ones are assumed to be extrapolatable for higher than 10 kV.[4] In order to examine the validity of these calculations, experimentally obtained AMRSF's for 3 kV and 5 kV are compared with those calculated for 10 kV AMRSF's, showing good agreement. In the presentation, concentrations derived from AMRSF's will be compared with those from ERSF's for several kinds of compound materials.

[1] ISO 18118:2004, Surface chemical analysis - AES and XPS- Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials.

[2] S. Ichimura, R. Shimizu, and J. P. Langeron.

[3] M. Gryzinski, Phys. Rev. A336, 138 (1965).

[4] S. Tanuma, private communications. (to be submitted to J. Surf. Anal.).

10:20am **AS-MoM8 Quantitative Surface Chemical Microscopy*, J. Walton*,** The University of Manchester, UK **INVITED**

X-ray photoelectron spectroscopy is widely regarded as a mature technique, with a large instrument base, not restricted to specialist laboratories. One of the reasons for this is the apparent ease of quantification compared with other surface analytical techniques, and its ability to provide chemical state information. Yet comparison of quantified data between different instruments is still problematic. A procedure will be described for determining the instrument response function for selected modes of operation to allow quantification using theoretically determined sensitivity factors, enabling transfer of results between instruments. XPS is much less frequently used in imaging mode, which was originally developed as a guide for small area analysis. However, the consequence of the acquisition of single energy images is that the aspects that make XPS spectroscopy appealing, ie ease of quantification and provision of chemical state information, are not available, since quantification requires peak area measurement after a suitable background subtraction and chemical state information is often dependent on resolution of overlapping photoelectron peaks. These limitations can be overcome by acquiring a spectrum at each pixel in an image, known as spectromicroscopy, so that the accepted processing procedures used in spectroscopy may be applied to the spectrum image data set. The acquisition of spectrum image data sets which may consists of 1000 images each containing 256 by 256 pixels presents further challenges for the analyst charged with the interpretation of thousands of spectra with low signal/noise. The use of multivariate statistical analysis to reduce the dimensionality of the data and to improve signal/noise will be demonstrated. Procedures will then be described to characterise the instrument performance in imaging mode, and to apply a modified quantification procedure to obtain atomic concentration images. Further, it will be shown that by maintaining the relationship between images and spectra so that pixels may be classified by chemistry, leads to improved curve fitting, and provides an alternative to multivariate curve resolution in visualizing physically meaningful spectra. Finally the ability to obtain spatially resolved nanostructural information will be discussed.

11:00am **AS-MoM10 Quantitative Characterization of Nb SRF Accelerator Cavity Surfaces Based on the Work of Seah and Powell**, ***M.J. Kelley***, *H. Tian*, College of William & Mary, *C.E. Reece*, Thomas Jefferson National Accelerator Facility

In the very first figure in the first paper to appear in Surface and Interface Analysis, Seah and Dench displayed the kinetic energy dependence of the electron IMFP in solids. They and others, especially Cedric Powell, have pursued this issue relentlessly. Their work was seminal, pointing to the opportunity for non-destructive depth profiling by tracking emission from a particular element core level while varying photon energy. The opportunity was a motivation for construction of photoemission beamlines at synchrotron sources. We have used the soft x-ray undulator line (X1B) at National Synchrotron Light Source to study the near-surface structure of niobium. Niobium is the material of construction for superconducting radio-frequency (SRF) cavities at the heart of most new particle accelerators. The International Linear Collider is proposed to comprise some 16,000 Nb SRF cavities. The microwave rf penetrates only a few tens of nm into the Nb surface, lending great importance to optimizing it. Much is determined by the final post-fabrication steps, typically chemical etching or electropolishing followed by low temperature baking. While many characterization techniques can be applied, variable photon energy XPS has the added advantage that it does not alter the material examined. A specimen can therefore be examined at successive treatment stages, followed by SRF performance measurements.

11:20am **AS-MoM11 Formation of Ultra Thin Oxide Free Protective Coatings on Chromium and 316 L Stainless Steel from Etidronic Acid**, *S.L. Johnson*, ***P.M.A. Sherwood***, Oklahoma State University

We have reported many examples of how thin (10nm or less) oxide free films can be formed on a number of metals. In this work we report how the use of etidronic acid (1-hydroxyethylidene-1,1-diphosphonic acid (hydroxy-ethyl diphosphonate or HEDP)) can form such films, providing an example of how an organophosphorus acid can form thin oxide free films in addition to the films previously reported for phosphorus acids. The films formed were produced on the surface of metallic chromium and on 316 L stainless steel by treatment by 3 molar etidronic acid using an anaerobic cell and a"bench" treatment. Core level and valence band X-ray photoelectron spectroscopy (XPS) were used to study the films formed. Compositional variations were interpreted through the use of band structure and X-alpha calculations. Valence band photoemission spectra interpreted in this manner were found to be effective in understanding subtle differences in the resulting surface chemistry as well as in identification of the various phosphates structures. The chromium foil experimental results indicate that the etidronate broke up and formed a phosphide on the surface. The anaerobic cell treatment of the chromium foil produced an extremely thin layer which consists of a phosphate which appears characteristic of chromium orthophosphate indicating that the etidronate molecule did not remain intact. Polished 316L stainless steel treated in 3 M etidronic acid formed a thin film when using the "bench"treatment, but a film characteristic of etidronate when the anaerobic cell was used. This thin etidronate film result shows that oxide-free etidronate films can be formed on stainless steel which may find application in implant fabrication.

11:40am **AS-MoM12 X-ray Photoemission Analysis of Chemically Treated CdZnTe Semiconductor Surfaces**, ***A.J. Nelson***, *A.M. Conway, R.A. Bliss, C Evans, J.L. Ferreira, R.J. Nikolic, S.A. Payne*, Lawrence Livermore National Laboratory

Device-grade $Cd_{(1-x)}Zn_xTe$ was subjected to various chemical treatments commonly used in device fabrication to determine the resulting microscopic surface composition/morphology and the effect on contact formation. Br:MeOH (2% Br), N_2H_4, NH_4F/H_2O_2, and $(NH_4)_2S$ solutions were used to modify the surface chemistry of the $Cd_{(1-x)}Zn_xTe$ crystals. Scanning electron microscopy was used to evaluate the resultant surface morphology. Angle-resolved high-resolution photoemission measurements on the valence band electronic structure and Zn 2p, Cd 3d, Te 3d, O 1s core lines were used to evaluate the chemistry of the chemically treated surfaces. Metal overlayers were then deposited on these chemically treated surfaces and the I-V characteristics were measured. The measurements were correlated to understand the effect of interface chemistry on the electronic structure at these interfaces with the goal of optimizing the metal/$Cd_{(1-x)}Zn_xTe$ Schottky barrier for radiation detector devices.

This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

Electronic Materials and Processing

Room: 612 - Session EM-MoM

Organic Materials and Devices

Moderator: D.J. Gundlach, National Institute of Standards and Technology

8:00am **EM-MoM1 An Organic Interlayer for Organic Thin Film Transistor**, ***H.H. Lee***, *S.Y. Park, K.H. Kim, T. Kwon*, Seoul National University, Korea

An organic interlayer between source/drain metal and semiconductor is introduced for the purpose of improving the performance of pentacene-based organic thin film transistor (OTFT). The formation and patterning of both the interlayer and the source/drain electrode is accomplished by a one-step bilayer transfer with 'rigiflex' lithography. The interlayer organic material should be chosen in such a way that the HOMO level of the organic lies between the metal work function and the HOMO level of the organic semiconductor. It is shown that the use of the interlayer of m-MTDATA for the cop-contact OTFT results in a more than one order of magnitude improvement in the effective mobility and also in the on-off current ratio. The main reason for the improvement can be attributed to a recuction in resistance.

8:20am **EM-MoM2 Changing Band Offsets in Copper-Phthalocyanine to Copolymer Poly(Vinylidene Fluoride with Trifluoroethylene) Heterojunctions**, ***J. Xiao***, *A. Sokolov, P.A. Dowben*, University of Nebraska-Lincoln

Copper phthalocyanine (CuPc) is an organic semiconductor with a small instantaneous dipole, while poly(vinylidene fluoride with trifluoroethylene), P(VDF-TrFE), is a ferroelectric polymer with a strong intrinsic (reversible) dipole. We explored the band offsets of CuPc deposited on crystalline P(VDF-TrFE) copolymers through combined photoemission and inverse photoemission studies at different temperatures. We also fabricated a thin film CuPc to crystalline ferroelectric copolymer P(VDF-TrFE) heterojunction diode. The formation of a diode is expected from the band offsets between the two molecular systems. Dipole interactions are implicated at the interface between CuPc and P(VDF-TrFE), and affect the band offsets and resultant diode properties: the diode current is adjusted by application of an electric field, which in turn may be affected by the dipole orientation.

8:40am **EM-MoM3 Control of the Molecular Orientation of Thin Films of a Solution Processable Organic Semiconductor**, ***L.J. Richter***, *A.J. Moad, B.H. Hamadani, O.D. Jurchescu, D.J. Gundlach*, National Institute of Standards and Technology, *S. Subramanian, J.E. Anthony*, University of Kentucky

Considerable interest has developed in the potential of macro-electronics enabled by low-cost manufacturing techniques such as roll-to-roll printing. Solution-processable small molecule based semiconductor films are emerging as a viable candidate for the active layer in thin film transistors (TFTs). The performance of TFTs fabricated from fluorinated 5,11-Bis(triethylsilylethynyl)anthradithiophene (diF-TESADT) are strongly dependent on processing conditions and the chemical treatment of the contacts. High performance devices can be fabricated with Au contacts treated with perfluorinated-bezenethiol PFBT. We report on the structure of thin films of diF-TESADT, formed on both Au and SiO_2 substrates, as a function of substrate treatment and film thickness. Both spectroscopic ellipsometry and infrared absorption are use to assess the molecular orientation in the films. In films formed on PFBT treated Au, the orientation is found to be consistent with the bulk crystal structure, with a near optimal orientation of the pi-stacked conjugated cores in the channel of the transistor, consistent with the observed good device performance.

9:00am **EM-MoM4 Interfacial Influences and Electron-Injection Mechanisms of Tris-(8-Hydroxyquinoline)-Aluminum Doped with Cesium-Derivatives In Organic Light Emitting Devices**, ***M.-H. Chen***, *C.-I. Wu, Y.-J. Lu, C.-C. Wu*, National Taiwan University

The cesium-derivatives (Cs2CO3, CsF and CsNO3) have been investigated as a dopant in tris-(8-hydroxyquinoline)-aluminum (Alq3) or a thin electron injection layer in organic light emitting devices. Unlike low work function metal which would be evaporated from a complex deposition process, the cesium-derivatives have a very simple deposition process and are easy to handle. By using ultraviolet and x-ray photoemission spectroscopy, the properties of electronic structures and the interface chemistry are studied. The paper presents the investigation of interfacial interactions and electron-injection between cesium-derivatives and Alq3. According to our results, the Fermi level of Alq3 after doped with cesium-derivatives shifts inside the gap toward the lowest unoccupied molecular orbital (LUMO) as a result of the charge transfer from cesium atom to Alq3, showing that electron-injection ability would be improved as a result of strong n-type doping effect. It is noteworthy to emphasize that through the ultraviolet and x-ray photoemission spectroscopy measurement, Cs2CO3 does not decompose during evaporation with various evaporation rates and pressures. The relatively abrupt decreasing in vacuum level is found via UPS, which can be explained by charge exchanges and a strong dipole field at the interface with deposition of cesium-derivatives. Moreover, doping cesium-derivatives into Alq3 not only reduces the electron-injection barrier height, but also increases the carrier concentration for current conduction. We also demonstrate that the interfacial chemical reaction leads to the excellent electron injection efficiency.

9:20am **EM-MoM5 Ultraviolet-Enhanced Device Properties in Pentacene-Based Thin-Film Transistors**, ***J.M. Choi***, *D.K. Hwang, J.H. Kim, S. Im*, Yonsei University, Republic of Korea

Pentacene thin–film transistors (TFTs) have attracted much attention due to their unique potentials. Nevertheless, there are still several issues to be considered before the TFTs are launched into real applications. Among these issues, the ultraviolet (UV)-induced degradation of pentacene is probably the most immediate and serious. However, in the present study we unexpectedly found that a lower energy UV radiation could rather be advantageous. Since this finding is quite surprising and may be applicable to the improvement of the performance of pentacene TFTs, we report on the contrasting effects of deep and shallow UV on the device performance of pentacene-based TFTs. Furthermore, we also fabricated the low-voltage high-gain pentacene-based inverter using a thin polymer/high-k dielectric through UV treatments. A substrate of 200 nm-thick SiO_2 or 450 nm-thick poly-4-vinylphenol (PVP) on p^+-Si (~0.01 Ωcm) was adopted for the gate dielectric and gate electrode in the present TFTs. The pentacene channel layers of 50 nm thickness were then patterned on the substrate by the thermal evaporation at RT. Subsequently, Au was evaporated onto the pentacene channels through a source/drain mask at RT (top-contact mode). Under the illumination of 254 nm-UV the TFTs showed degraded mobility and lowered saturation current. It is because the high energy UV degraded the crystalline quality of the pentacene channel as confirmed by optical absorption technique. However, under 352 nm UV the pentacene devices rather exhibited the enhancement of saturation current and also a positive shift of the threshold voltage (V_T), maintaining their mobilities. We also found that these UV-induced advantages were more clearly obtainable from the TFTs with polymer dielectric where extra negative charges are generated to exist as permanent form at the pentacene/polymer interface while those charges are not necessarily fixed at the pentacene/SiO_2 interface. Through inverters fabricated by illuminating 352nm-UV onto the load-TFT to selectively adjust its V_T, we also could achieve a stable high-gain low-voltage inverting within the input voltage (V_{in}) range of 0 ~ -6 V. We thus conclude that illuminating a low energy UV on the TFT with pentacene/polymer dielectric interface is a simple promising way of enhancing the general performance of pentacene TFTs and controlling their V_T that enables to achieve stable pentacene-based inverters as well.

9:40am **EM-MoM6 High Efficient Organic Light-Emitting Devise with MoO3**, ***C.-T. Lin***, *G.-R. Lee, C.-I. Wu, T.-Y. Cho, C.-C. Wu*, National Taiwan University, *T.-W. Pi*, National Synchrotron Radiation Research Center, Taiwan

Two high efficient devices will be discussed in this paper. The first is ITO/MoO3/N,N -diphenyl-N,N -bis(1-naphthyl)-1,1 -biphenyl-4,4 -diamine (NPB) based organic light emitting diodes (OLEDS). Current-voltage characteristics (I-V) and quantum-efficiency (?-J) measurements show the improvement of device performance with insertion of thin MoO3 between ITO and NPB. Ultraviolet photoemission spectra (UPS) and core-level x-ray photoemission spectra (XPS) data show that MoO3 would catch electrons from NPB and results in p-type doping in NPB. In addition, there is a significant structure transition from insulating MoO3 to metallic MoO2. As a result of high work function MoO2 in anode structure and p-type doping NPB, holes can easily be injected from ITO to NPB. The second efficient devices relate to MoO3/metal structures in tandem OLEDS. Non-stoichiometric MoO3 films consist of defect states due to O defects which pins the Fermi level in the forbidden gap. I-V characteristics show that with the MoO3 hole injection layer between anode and NPB, the current efficiency is almost identical, regardless the choice of anodes. We further investigation the interaction between low work function metals and MoO3. According to UPS and XPS results, low work function metals would easily get O atoms from MoO3, resulting in the transition to MoO2 and the increase in conductivity at the same time. The high work function of MoO3 can be tuned to relatively low work function of MoO3/Al, Mg anode. These results show that MoO3 can act as a effective hole injection layer in OLEDS, a charge generation layer in tandem OLEDS, and a high ohmic contact of metal/MoO3 in top-emitting OLEDS.

10:20am **EM-MoM8 Electronic Transport Processes in Polymer Transistors**, ***R.A. Street***, *M.L. Chabinyc, J.E. Northrup*, Palo Alto Research Center **INVITED**

Solution deposited polymer thin film transistors have mobility reaching of order 1 cm2/Vsec making them interesting for applications such as flat panel displays. The increase in mobility is a result of new materials synthesis and an understanding of how the surface energy of the deposition surface controls the structural order of the film. A polymer such as polythiophene is highly anisotropic and conduction occurs essentially in a single 2-dimensional sheet of polymer next to the dielectric interface. Band conduction, coupled with a simple density of states model to account for disorder effects, are able to explain the main features of the electronic transport, based on theoretical calculations of the electronic structure. The upper limits on the mobility, of about 10 cm2/Vs can also be estimated from calculations. Although polymer semiconductors cannot be doped by conventional atomic substitution, doping is possible by the incorporation of molecular impurities, and allows further test of transport models. We describe a particular case of acceptor doping with ozone and show that the transport models are able to explain the results and that acceptor binding energies can be deduced. In common with other disordered semiconductors, polymer TFTs exhibit electrical bias stress effects, which induce a change in the threshold voltage due to trapping in states that communicate weakly with the conduction holes. Electrical stress measurements in polythiophene TFTs show properties with a wide range of time constants. The threshold voltage shift increases as a power law in time and in gate voltage. However, after a few days of stress, the threshold voltage shift stabilizes because there is a thermally activated recovery mechanism. The physical mechanisms of the bias stress effects, and whether they are intrinsic to the polymer semiconductor, will be discussed.

11:00am **EM-MoM10 Relationship between the Morphology, Contact Resistance and Field-Effect Mobility in Poly(3-hexylthiophene) based Field-Effect Transistors**, ***K.A. Singh***, *G. Sauve, R. Zhang, R.D. McCullough, L.M. Porter*, Carnegie Mellon University

In this study we report on the interdependence of morphology, mobility, and contact resistance in field effect-transistors (FETs) based on poly(3-hexyl thiophene) (P3HT) as the active layer. Bottom-contact FETs with Pt electrodes were fabricated with channel lengths varying from 3 to 40µm.The P3HT films were deposited using a solvent-assisted drop casting technique. Atomic force microscopy images indicate that P3HT self assembles into a lamellar structure consisting of nanorods, which contribute to high field-effect mobilities. Our AFM images, along with prior X-ray data,[1] show that an increase in the molecular weight of the polymer leads to an increase in the size of the self-assembled nanorods, leading to higher crystallinity of the polymer. Our results show that both the mobility and the contact resistance depend strongly on the molecular weight, or morphology, of the polymer. For example, at a gate voltage of -80V, the mobility increased from 0.03 to 0.16$cm^2V^{-1}s^{-1}$ and the contact resistance decreased from 2.2 to 0.4MΩ when the molecular weight was increased from 5.5 to 11Kg mol^{-1}. These mobility values were obtained after correcting for the contact resistance. The results also show a dependence of the mobility and the contact resistance on the gate voltage: The contact resistance decreased from 1.2 to 0.4MΩ with an increase in gate voltage from -20 to -80V; the mobility correspondingly increased by a factor of 8. The dependence of the mobility on the gate voltage is attributed to the presence of traps that limit the charge transport. The effect of mobility on contact resistance can be explained by a diffusion-limited charge injection theory.[2] In summary, our results expand on prior individual studies, primarily on Au/P3HT, that indicate a correlation between mobility and either the contact resistance[3] or molecular weight[1], to a systematic study on Pt/P3HT transistors. Future experiments with higher molecular-weight P3HT are also planned for comparison.

[1] R. Zhang, B. Li, M.C. Iovu, M. Jeffries-EL, G. Sauve, J. Cooper, S. Jia, S. Tristram-Nagle, D.M. Smilgies, D.N. Lambeth, R.D. McCullough, and T. Kowalewski, J. Am. Chem. Soc. 128[11], 3480(2006)

[2] V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bassler, J. Appl. Phys. 84[2], 848(1998)

[3] B. H. Hamadini and D. Natelson, Appl. Phys. Lett. 84[3], 443(2004).

11:20am **EM-MoM11 Potential Profile Evolution in Static and Dynamic Junction Light-Emitting Electrochemical Cells**, ***L.S.C. Pingree****, D.B. Rodovsky, G.P. Bartholomew, D.S. Ginger*, University of Washington

Recently, there has been a renewed interest in light-emitting electrochemical cells (LECs) as methods for improving upon their transient performance and lifetimes have emerged. Such devices promise one-step junction deposition and very little dependence upon the electrode materials due to ionic-assisted injection. However, with this renewed interest in LECs, the debate over the appropriate model for their ionic concentration profiles and the underlying charge transport mechanisms has become more important. Three models for device operation have been independently developed,[1,2,3] however, direct evidence of the accuracy of these models through potential profiling has yet to be reported in the literature. In this talk, we present experimental data using Scanning Kelvin Probe Microscopy (SKPM) to directly image the potential profile in planar (gap width ~15 µm) operating LECs. We examine both dynamic junction LECs and chemically-fixed LECs, and find that in the dynamic junction LECs, > 90% of the potential drops near the cathode. This profile develops within 10’s of seconds of applying a potential across the planer devices, and evolves very little with time. In the chemically fixed LEC’s we find that the potential is initially dropped at the contacts and that the potential profile evolves over minutes to hours in time, dependent upon the ion concentration. Once steady-state is achieved, the majority of the potential is dropped in a similar manner to the dynamic junction LEC. We deduce that the low ionic conductivity of the counter-ions in the chemically-fixed system retards this evolution. Furthermore, we show direct evidence for the accuracy of a primarily p-type model with the emitting junction near the cathode and relatively small electric fields across the bulk of the device.[3]

[1] Pei et al. Science (1995)

[2] deMello et al. Phys. Rev. B (1999)

[3] Leger et al. J. Appl. Phys. (2005).

11:40am **EM-MoM12 Rubrene Polycrystalline Transistor Channel Achieved through In-Situ Vacuum Annealing**, ***S.W. Park****, S.H. Jung, J.M. Choi, J.M. Whang, J.H. Kim, S. Im*, Yonsei University, Republic of Korea

Semiconducting organic materials have attracted much attention during the last and even this decade, because of their potentials toward low temperature-, low cost-, and flexible substrate-based electronics. The most popular organic semiconductor is pentacene which has a high field effect mobility exceeding 1 cm^2/Vs in the form of a channel of a thin-film transistor (TFT). Among the promising candidate materials, rubrene is also attracting recent interests because in single crystal form it shows a very large field-effect mobility (up to 20 cm^2/Vs). For practical applications, several groups have also studied crystalline thin film phase. But it has been found not easy to get a good crystalline rubrene thin film unlike the case of pentacene, although other group could obtain a good crystalline phase film through a solution-process-involving technique.[1-3] We have studied the crystalline thin film fabrication by thermal evaporation, that may be more compatible with device patterning. In the previous work,[4] we have obtained a rubrene thin film which has an amorphous-crystalline mixed phase on SiO_2 substrate. The film thus contained crystal domains of few hundred diameters embedded in amorphous matrix. In the present work, based on our new findings, we report on how to increase the crystal domain size so that the mobility of a rubrene-TFT may be maximized on SiO_2 dielectric. Initially, amorphous rubrene thin film was obtained on 200 nm-thick SiO_2/Si substrate at 40 ^{o}C in a vacuum chamber by thermal evaporation but in-situ long time post-annealing at the elevated temperatures of 60 ~ 80 ^{o}C transformed the amorphous phase into crystalline. Based on an optimum condition to cover whole channel area with polycrystalline film, we have fabricated a rubrene-TFT with a relatively high field effect mobility of 0.002 cm^2/Vs, on/off ratio of ~ 10^4 and a low threshold voltage of -10V.

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[2] S. Seo, B. Park, and P. G. Evans, Appl. Phys. Lett. 88, 232114 (2006).

[3] N. Stingelin-Stutzmann, E. Smits, H. Wondergem, C. Tanase, P. Blom, P. Smith and D. Deleeuw, Nature. Mater. 4, 601 (2005).

[4] S. Park, J. Whang, J. Choi, D. Whang, M. Oh, J. Kim, S. Im, Appl. Phys. Lett. 90, 153512 (2007).

In-situ Electron Microscopy Topical Conference

Room: 618 - Session IE-MoM

Structure-Property Characterization

Moderator: S. Kodambaka, University of California, Los Angeles

8:00am **IE-MoM1 The TEAM Project and its Potential for In-Situ Experimentation**, ***U. Dahmen***, Lawrence Berkeley National Laboratory **INVITED**

Advanced electron microscopes give us unprecedented views of materials and their unusual behavior on the nanoscale. It is possible to observe how a nanocrystal grows or melts or changes its structure atom by atom, or to investigate the structure of nanocrystals embedded in microcrystals. However, until now, electron microscopes have remained limited by lens aberrations. As it becomes possible to overcome this limitation with aberration correcting optics, a broad range of new possibilities for research and discovery by high resolution imaging opens up. The improved instrument resolution, contrast and sensitivity create the opportunity to directly observe the atomic-scale order, electronic structure, and dynamics of individual nanoscale structures. To take advantage of this opportunity, the TEAM project (Transmission Electron Aberration-corrected Microscope) brings together several microscopy groups in a collaborative effort to jointly design and construct a new generation microscope with extraordinary capabilities. Led by the National Center for Electron Microscopy, the project involves several Department of Energy research efforts and commercial partners. After its completion in 2009, the instrument will be made available to the scientific user community at the National Center for Electron Microscopy. The vision for the TEAM project is the idea of providing a sample space for electron scattering experiments in a tunable electron optical environment by removing some of the constraints that have limited electron microscopy until now. The resulting improvements in spatial, spectral and temporal resolution, the increased space around the sample, and the possibility of exotic electron-optical settings will enable new types of experiments. The TEAM microscope will feature unique corrector elements for spherical and chromatic aberrations, a novel AFM-inspired specimen stage, a high-brightness gun and numerous other innovations that will extend resolution down to the half-Angstrom level. The most important scientific driving force that emerged from a series of workshops is the need for in-situ experiments to observe directly the relationship between structure and properties of individual nanoscale objects. Successive instruments built on the TEAM platform would provide unique experimental capabilities to probe dynamics and mechanisms of reactions such as catalysis in a gaseous environment, or the effects of gradients in temperature, composition, stress, magnetic or electric fields. This talk will highlight some recent discoveries in nanoscale materials science using high resolution electron microscopy and outline some research opportunities for future users of TEAM instrument.

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8:40am **IE-MoM3 Dynamic Studies of Magnetization Reversal Processes and Future Prospects for In-Situ TEM**, ***B. Kabius****, A.K. Petford-Long*, Argonne National Laboratory **INVITED**

The rapid increase in information storage density, memory density and speed have been brought about in part by the development of new materials, often consisting of layered structures, with properties that are engineered by controlling the microstructure and chemical profile. The layer thicknesses are of the order of a few nanometers, and the deposition techniques used tend to give polycrystalline films, resulting in variations in properties across the structures. One of the most spectacular examples is the development of devices based on the giant magnetoresistance (GMR) phenomenon, such as the spin-valve and the spin-dependent tunneling junction used for read heads or magnetoresistive random access memories. In addition, patterned single layer structures are of importance for both media and memory applications. The behavior of these materials relies on the local magnetic domain structure and magnetization reversal mechanism, and one of the techniques enabling micromagnetic studies at the sub-micron scale is Lorentz transmission electron microscopy (LTEM) which allows the magnetic domain structure and magnetization reversal mechanism of a FM material to be investigated dynamically in real-time with a resolution of a few nm. We have used LTEM and in-situ magnetizing experiments to study magnetization reversal in a range of materials including spin-tunnel junctions and patterned thin film elements. Quantitative analysis of the Lorentz TEM data has been carried out using the transport of intensity equation (TIE) approach. Studies of active spin valves have shown the way in which the magnetization reversal process depends on applied current. In addition to the local variations in the magnetic properties induced by the microstructure of the films, further variations arise when the films are patterned to form small elements and results will be presented for a range of structures patterned both from single layers and from device structures. Results of further in situ experiments to measure the local tunneling properties of magnetic tunnel junctions will also be presented. Recent progress in electron beam instrumentation is expected to have a strong impact on in-situ TEM, especially LTEM. E.g., correction of chromatic aberration is at present under development within the frame work of the TEAM project. The benefits of this novel corrector for in-situ experiments will be discussed.

9:20am **IE-MoM5 Understanding Dislocation Dynamics and the link to Macroscopic Properties**, ***I.M. Robertson***, *G. Liu, B. Clark, B. Miller*, University of Illinois **INVITED**

The behaviour of dislocations under an applied load and their interaction with obstacles, such as grain boundaries, precipitates, voids etc., can be revealed be conducting deformation experiments in real time in situ in the transmission electron microscope. Linking the insight gained form such studies to macroscopic measurements of property changes remains challenging but significant progress has been made. It will be shown that grain and twin boundaries serve as sources and sinks for, and barriers to perfect and partial dislocations. From information learned from these studies, criteria for the transfer of slip across grain boundaries and interfaces have been established. However, the microstructure is not static and evolves with increasing strain. For example, the process of slip transmission can result in the destruction of the grain boundary locally and this influences subsequent deformation activity. These observations provided a basis for developing strategies for incorporating grain boundary effects in large-scale predictive models of mechanical behaviour. Studies of the interaction of dislocations with precipitates with different interfacial character as a function of temperature have revealed a rich variety of complex dislocation-precipitate interactions and by-pass mechanisms. The interaction type depends on the particle coherency and size, the nature and Burgers vector of the dislocation, the geometry of the interaction, the number of interactions, and the test temperature. It is also possible and common for multiple slip systems to interact with the particle consecutively or simultaneously and this changes the nature of the interactions. The number and complexity of the interactions and the richness of the possibilities have significant implications for current models of mechanical properties of precipitate-hardened systems. This paper emphasizes what can be learned from conducting dynamic experiments in the electron microscope and how such insights can and are being used as a basis for formulating physically-based constitutive relationships to predict macroscopic mechanical properties of thin and thick films.

10:20am **IE-MoM8 Structure and Structural Transitions of Supported Nanoparticles and In-Situ RHEED Observations**, *K. Sato, W.J. Huang,* ***J.M. Zuo***, University of Illinois, Urbana-Champaign **INVITED**

Understanding different structures of nanoparticles and their transition can have a large impact on our ability to self-assemble controlled nanostructures and understanding properties of nanoparticles. Small nanoparticles of a few nanometers in diameter are difficult to characterize by traditional surface characterization techniques. Here we report two recent developments in nanoparticle characterization. The first is an in-situ RHEED characterization of the size dependence of structural transition from multiply-twinned particle (MTP) to epitaxial face centered cubic (FCC) nanocrystal for Ag nanoparticle formed on Si(001) surfaces. The transition from MTP to nanocrystals was promoted by post-deposition annealing. Clear particle size dependence is found in the epitaxial formation temperatures (T_E), which is about 2/3 of the calculated, size-dependent, melting temperature (T_M) for particles larger than 2 nm in diameter. For smaller nanoparticles, T_E is about the same as T_M. Once nanocrystals are formed, they decay and disappear in a narrow temperature range between 794 and 849 K. No evidence of nanocrystal melting was detected from the RHEED observation. In the second study, we show that coherent electron diffraction patterns recorded from individual nanocrystals are very sensitive to, and can be used to study, the structures of nanocrystal surfaces. We use this to study the bond-length dependent atomic contractions in Au nanocrystals 3 to 5 nm. Evidences of inhomogeneous surface relaxation will be presented.

11:00am **IE-MoM10 In-Situ Hot-Stage TEM of Interface Dynamics and Phase Transformations in Materials**, ***J.M. Howe***, *A.R.S. Gautam, S.K. Eswaramoorthy*, University of Virginia **INVITED**

In-situ transmission electron microscopy (TEM) is an indispensable tool for determining the behavior of materials and interfaces under actual experimental conditions. This paper focuses on the results from in-situ heating experiments performed on nanoparticles in the TEM, using either high-resolution TEM (HRTEM) imaging or energy-dispersive X-ray spectroscopy (EDXS). Three different types of transformations and the fundamental processes associated with them are discussed. These include the atomic-level dynamics of an order-disorder interface near equilibrium in a Au-Cu alloy nanoparticle, the mechanisms of migration and coalescence of Au-Cu alloy nanoparticles supported on an amorphous-C thin-film, and the nucleation and growth behavior of phases and how elements partition between them in partially molten Al-Cu-Mg-Si nanoparticles in near-equilibrium and highly undercooled conditions. Some of the major results from these studies are summarized as follows. For the order-disorder interface near equilibrium in a Au-Cu alloy nanoparticle, it was found that both the interphase boundary position and thickness fluctuate with time and that the behavior of the disordered side of the interphase boundary differs from that of the ordered side. These features can be explained in terms of the physical properties of the different phases and the energetics of the interphase boundary. In the case of two Au-Cu alloy nanoparticles supported on an amorphous-C thin-film, it was found that Ostwald ripening and particle motion occur simultaneously, through collective surface fluctuations and a directed diffusional flux between the two particles. This flux becomes directly visible during coalescence, where redistribution of mass on the large particle is also revealed. In the partially molten Al-Si-Cu-Mg alloy nanoparticle, it was found that the solid Al phase is completely wet by the liquid and therefore cannot nucleate heterogeneously on the Si phase or oxide surface. Because heterogeneous nucleation is eliminated, it was possible to directly determine the metastable liquidus and solidus phase boundaries in the undercooled liquid by EDXS, in addition to the compositions across the solid Si-liquid interface. This research was supported by NSF under Grants DMR-9908855 and DMR-0554792.

11:40am **IE-MoM12 Design and Development of an Environmental Cell for Dynamic In Situ Observation of Gas Solid Reactions at Elevated Temperatures**, ***P.V. Deshmukh***, *P.E. Fischione, C.M. Thomas, J.J. Gronsky*, E.A. Fischione Instruments, Inc.

In situ monitoring of events in transmission electron microscopy provides information on how materials behave in their true state in the presence of various gases, under varying conditions of temperature and pressure. These results are usually different from static, post-reaction observations.[1, 2,3] To facilitate applications that demand in situ observations, a transmission electron microscope specimen holder has been developed. This holder incorporates a gas flow and heating mechanism along with a window-type environmental cell. A controlled mixture of up to four different gases can be circulated through the cell. The specimen can be heated up to a temperature of 800 °C using a carbon dioxide laser. This heating technique provides major advantages over conventional heating methods in terms of product life, specimen heating time and design size. The cell design incorporates a 200 micron high chamber enclosed between a pair of 20 nm thick silicon nitride windows. The chamber can accommodate a specimen or a grid having a diameter of 3 mm and thickness in the range of 50 to 100 microns. The volume for the gas environment within the chamber is approximately 0.7 mm^3 and the gas path length is less than 0.1 mm. This holder has been designed by incorporating cutting edge heating and MEMS technology to achieve excellent resolution along with a low thermal drift. Successful application of this holder would provide scientists with an economical alternative to dedicated transmission electron microscopes for a vast array of in situ applications including understanding the basic material properties, catalysis reactions, semiconductor device development, and nano structure fabrication.

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[3] I M. Robertson and D. Teter, Controlled Environmental Transmission Electron Microscopy, Microscopy Research and Technique, 42, 260, 1998.

The Industrial Physics Forum 2007: The Energy Challenge

Room: 602/603 - Session IPF-MoM

Energy Efficiency

Moderator: J. Hobbs, American Institute of Physics

8:00am **IPF-MoM1 Solar Photovoltaics: At the Tipping Point**, ***L. Kazmerski***, National Renewable Energy Laboratory **INVITED**

The prospects of current and coming solar-photovoltaic (PV) technologies are envisioned, arguing this solar-electricity source is at a tipping point in the complex worldwide energy outlook. The co-requirements for policy and technology investments are strongly supported. The emphasis of this presentation is on R&D advances (cell, materials, and module options), with indications of the limitations and strengths of crystalline (Si and GaAs) and thin-film (a-Si:H, Si, Cu(In,Ga)(Se,S)$_2$, CdTe). The contributions and technological pathways for now and near-term technologies (silicon, III-Vs, and thin films) and status and forecasts for next-generation PV (organics, nanotechnologies, non-conventional junction approaches) are evaluated. Recent advances in concentrators, new directions for thin films, and materials/device technology issues are discussed in terms of technology evolution and progress. Insights to technical and other investments needed to tip photovoltaics to its next level of contribution as a significant clean-energy partner in the world energy portfolio. The need for R&D accelerating the now and imminent (evolutionary) technologies balanced with work in mid-term (disruptive) approaches is highlighted. Moreover, technology progress and ownership for next generation solar PV mandates a balanced investment in research on revolutionary (long-term) technologies (quantum dots, multi-multijunctions, intermediate-band concepts, nanotubes, bio-inspired, thermophotonics, . . .) having high-risk, but extremely high performance and cost returns for our next generations of energy consumers. This presentation provides insights (some irreverent, some entertaining) into how this technology has developed---and where we can expect to be by this mid-21st century.

8:40am **IPF-MoM3 The Physics of Terrestrial Concentrator Solar Cells with Over 40% Efficiency**, ***R.R. King***, *D.C. Law, K.M. Edmondson, C.M. Fetzer, G.S. Kinsey, H. Yoon, D.D. Krut, J.H. Ermer, R.A. Sherif, N.H. Karam*, Spectrolab, Inc. **INVITED**

Solar cell efficiency is one of the most enabling device parameters for widespread implementation of solar electricity generation on Earth, since high efficiency dramatically reduces not only the cell area needed to generate a given power, but also the cost of all area-related components in a photovoltaic system. The efficiency of a solar cell with a single energy band gap E_g in unconcentrated sunlight is quite limited by fundamental considerations, such as thermalization of photogenerated electrons and holes, non-absorption of low energy photons, and the limited quasi-Fermi level splitting at one sun. Multijunction concentrator cells are able to overcome these fundamental efficiency limits, and as a result have attracted much attention recently for cost-effective terrestrial photovoltaics. If the subcell bandgaps for the multijunction solar cell are chosen from metamorphic semiconductors that are lattice-mismatched to the growth substrate, theoretical efficiencies can be raised even higher than for lattice-matched designs. Advances in the design of metamorphic subcells to reduce carrier recombination and increase voltage, wide-bandgap tunnel junctions, metamorphic buffers to transition to the lattice constant of the active subcells, concentrator cell anti-reflection coating and grid design, and integration into current-matched 3-junction cells have resulted in new heights in solar cell performance. A metamorphic $Ga_{0.44}In_{0.56}P$/ $Ga_{0.92}In_{0.08}As$/ Ge 3-junction solar cell has reached a record 40.7% efficiency at 240 suns, under the standard reporting spectrum for terrestrial concentrator cells (AM1.5 direct, low-AOD, 24.0 W/cm^2, 25°C). This metamorphic 3-junction device is the first solar cell to reach over 40% in efficiency, and has the highest solar conversion efficiency for any type of photovoltaic cell to date. Experimental lattice-matched 3-junction cells have now also achieved over 40% efficiency, with 40.1% measured at 135 suns. The multijunction structure of these cells and their operation at concentration allow efficiencies substantially above the Shockley-Queisser limit[1] of 30% for a single-band-gap device at one sun, and above the theoretical limit of 37% for single-band-gap cells at 1000 suns,[2] to now be achieved in practice.

[1] W. Shockley and H. J. Queisser, J. Appl. Phys., 32, 510 (1961).

[2] C. H. Henry, J. Appl. Phys., 51, 4494 (1980).

9:20am **IPF-MoM5 Thermoelectrics and Waste Heat Recovery**, ***L.E. Bell***, BSST LLC **INVITED**

Thermoelectric (TE) devices are reversible, solid-state heat engines. When a temperature difference is applied across a TE array, electric power is produced; and when electric power is applied, a portion of the array cools (sinks thermal power) and another portion heats (produces thermal power). Increased needs to lower energy costs and reduce green house gas emissions have renewed interest in the technology. TE applications have been limited most importantly by lower conversion efficiency, but also by the cost of the materials and systems. Recent advances in performance through the development of more efficient thermodynamic cycles, laboratory demonstrations of improved materials, and the availability of more comprehensive design tools, have increased interest in the application of the technology for power generation uses. The recent recognition of the need to reduce CO$_2$ emissions has renewed interest in TE technology with respect to waste heat harvesting from vehicle exhaust. Since the 1960's, TEs have been employed in critical military and space applications where their demonstrated ruggedness and maintenance-free operation has outweighed energy conversion efficiency limitations. Target applications are small to midsize (up to 40 kW) sources of exhaust waste heat and include: vehicle exhaust residential, commercial, and industrial fuel-fired heating systems; diesel powered electric generators; and other similar applications. TE technology is evolving to the point where systems with conversion efficiencies of 6% to possibly 20% are being investigated. Prospects for successful implementation of TE technology for waste heat recovery to reduce CO$_2$ and other green house gas emissions are discussed for a range of business sectors for which the technology appears attractive. Examples of current approaches to implementation are given, along with estimates for critical system characteristics including projected size, weight, efficiency, and rough costs. Important current programs funded by various U.S. and foreign government agencies are described and their level of technical and commercial readiness are assessed.

10:20am **IPF-MoM8 Current Status of Solid State Lighting**, ***S. Nakamura***, University of California, Santa Barbara **INVITED**

The light emitting diode (LED) takes electrical energy and converts it to bright bluelight. The light generation is very energy efficient (60%), which is much better than normal incandescent bulb (5%). The light is generated inside of a crystal of gallium nitride (GaN), and it only requires a 3-volt battery. The efficiency of white LEDs that use blue LEDs will become higher, almost close to 100% (currently 150 lm/W). Then, all of the conventional lighting, such as incandescent bulbs (10 lm/W), fluorescent lamps (70 lm/W), and others, would be replaced with the white LEDs in order to save energy and resources. Also, these white LEDs would be operated by a battery powered by a solar cell in the daytime. So, it means that this lighting would be operated with clean energy thanks to its high efficiency and low voltage operation. In the developing countries, there is no electricity and no light at night. However, white LEDs operated with a small battery powered by a solar cell in the daytime could be used as a light source in those developing countries.

11:00am **IPF-MoM10 Emerging Energy Policy on Capitol Hill**, ***M. Kenderdine***, GTI **INVITED**

Marine Biofouling Topical Conference

Room: 609 - Session MB+BI-MoM

Biological Interactions at the Marine Interface

Moderator: M. Grunze, University of Heidelberg, Germany

8:00am **MB+BI-MoM1 Surfaces and Signals: Dissecting Surface Properties for Controlling the Settlement and Adhesion of Algae**, ***J.A. Callow***, *M.E. Callow*, University of Birmingham, UK **INVITED**

All man-made structures in marine or freshwater environments suffer from the problem of 'biofouling'- the unwanted growth of bacteria (as biofilms), algae (diatoms and seaweeds) and invertebrates (e.g. barnacles, tube-worms). Most current, commercial antifouling strategies use biocide-containing coatings, which are subject to increasingly stringent environmental restrictions. Alternative coating technologies that do not require biocides either invoke 'deterrence' to prevent organisms from sticking in the first place, or the 'non-stick' or 'foul-release' principle to facilitate the detachment of adhered organisms under moderate shear stress. The search for 'environmentally-friendly' solutions has stimulated basic research efforts in an attempt to understand which interfacial properties (e.g.

roughness, wettability, charge, friction, elasticity) are important in influencing the adhesion of fouling organisms. This has been facilitated by the advent of novel technologies, such as various forms of lithography, and self-assembly, which enable the production of test surfaces with systematic variations in structure and properties at the micro- and nano-scales. Motile marine organisms such as spores of Ulva, are highly selective in their choice of a suitable surface for settlement. Therefore, one approach to developing practical coatings based upon 'deterrence' is to try to destabilize the surface cue-sensing mechanisms of the organism. The aim of this presentation is to illustrate how spores of the green alga Ulva, and the diatom, Navicula respond to surfaces presenting a range of well-characterised interfacial properties. Examples will be taken from collaborations developed within the ONR Marine Coatings programme and the EC Framework 6 Integrated Project 'AMBIO' (Advanced Nanostructured Surfaces for the Control of Biofouling).

8:40am **MB+BI-MoM3 Cationic Peptide SAMs for Biofouling Studies**, ***B. Liedberg***, *P. Nygren, M. Östblom, Y. Zhou, T. Ederth*, Linköping University, Sweden **INVITED**

Positively charged peptides have been synthesized in our laboratory with the purpose of investigating their anti-biofouling potential. The peptides contain a common leading sequence of Cys(Gly)$_2$ where the cysteine residue offers an convenient handle for oriented attachment to gold. The functional part of the peptides (7-mers) consists of alternating ArgTyr, LysTyr, LysTyrGly as well as mixed layers of ArgTyr and a filling Cys(Gly)$_3$ peptide. The peptide layers have been prepared from aqueous solutions and were characterized with respect to layer thickness, conformation and long-term stability in artificial seawater (ASW) using null ellipsometry and infrared spectroscopy. The peptide layers were also examined with respect to settlement of Ulva linza zoospores. The functional ArgTyr, LysTyr, LysTyrGly peptides displayed enhanced settlement as compared to reference surfaces/coatings. Moreover, the settlement on the ArgTyr layer was greatly increased as compared to the other peptide layers, and the amount of settled spores increased with increasing fraction of the ArgTyr. Most importanty, however, the Ulva spores seemed to settle in a side-on conformation on the ArgTyr layer with their flagella (swimming arms) intact. This mode of settlement has not been observed before. Pre-incubation of the Ulva spores in a solution containing the ArgTyr peptide also influenced the subsequent attachment of the spores to polystyrene in a concentration dependent manner. The ArgTyr peptides in solution seemed to stimulate the settlement up to a concentration of ca. 20 µM above which the number of settled spores started to fall. Microscopic examination of the remaining spore solution after settlement suggests that this is due to an increase in spore death. Thus, the Arg residues in the ArgTyr peptide are believed to convey a membrane-associating effect which seems to have a deterring effect upon settling organisms. Complementary experiments on diatoms (a cell surrounded by a silica shell) revealed that these species settle in a non-selective manner on the different peptides. In addition, ongoing experiments using QCM to study vesicle adsorption onto the peptide layers give support to the suggested peptide-membrane association meachanism that resulted in an abnormal, side-on, attachment of Ulva spores. Interestingly, recent preliminary experiments using barnacle cyprids revealed marginal settlement on the ArgTyr peptide layer.

9:20am **MB+BI-MoM5 Mechanics of Barnacle Glue Surfaces and Relation to Foul Release**, ***G. Walker***, University of Toronto, Canada **INVITED**

Recent results concerning the mechanics of barnacle release will be discussed. The fracture mechanics of a whole barnacle will be examined in the context of nanoscale defect formation that is predicted by theory and structures that are observed in the natural cements.

10:20am **MB+BI-MoM8 Understanding Biofouling Mechanisms In Situ: Molecular Level Studies on Polymer Surface Structures in Water and Polymer-Protein Interactions**, ***Z. Chen***, University of Michigan **INVITED**

Biofouling, the growth of barnacles, seaweeds, tubeworms and other marine organisms on the hulls of ocean-going vessels, causes many problems for the US government including extra financial burdens, excessive consumption of energy, and contamination of the environment. Minimally adhesive polymers or polymers from which foulants can be easily removed are being developed as coatings for use in the marine environment. The possibility to use materials with biocides for marine anti-biofouling purposes have also been explored recently. In our group, a second-order nonlinear vibrational spectroscopic technique, sum frequency generation (SFG) vibrational spectroscopy, has been applied to study surface structures of polymer materials which may be developed as fouling control/release coatings in water, to study interactions between polymer surfaces and biological molecules in situ, and to study how biocides which are being developed for marine anti-biofouling purposes interact with cell membranes. Other techniques such as attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), quartz crystal microbalance (QCM), atomic force microscope (AFM), and contact angle goniometer have been used as supplemental tools in such studies. The polymers which have been studied include model polymers such as polymethacrylates, model poly (dimethyl siloxane) (PDMS), commercial PDMS samples, as well as newly developed anti-biofouling polymer coatings. We elucidated that different polymer surfaces exhibit varied restructuring behaviors in water. To understand polymer surfaces in aqueous environments, it is necessary to investigate them in situ. By examining interfacial protein structures, we showed that different polymer surfaces mediate differed molecular interactions with adhesive proteins of marine organisms. Detailed structural information of proteins at the polymer/protein solution interface can be deduced. In addition, we elucidated the molecular interactions between biocides or polymers containing biocides and cell membranes. Such studies provide molecular level information regarding surface - biological molecule interactions, aiding in the design of coatings with improved anti-biofouling property.

11:00am **MB+BI-MoM10 Surface Tension and Bacterial Attachment Revisited: The Effect of Components of Interfacial Tension**, ***L.K. Ista***, *B.P. Andrzejewski, K. Artyushkova, D.N. Petsev, G.P. Lopez*, The University of New Mexico

Bacterial adhesion to surfaces is controlled by the relative strengths of interfacial tensions: those between the bacterium and the surface, the bacterium and the liquid and the surface and the liquid. Models of precisely which properties of the substratum and bacteria most profoundly and predictably affect the attachment of bacteria to a sold surface, as well as methods for accurately and predictively measuring these interfacial tensions, abound, but, to date, none is, in and of itself, sufficient to accurately predict bacterial attachement. A well defined and characterized series of self-assembled monolayers (SAMs) of ω-terminated alkanethiolates on gold were used to systematically explore the effect of the various surface energetic components (e.g. polar, non-polar, electron donating and accepting) of solid substrata on the attachment of the marine bacterium, Cobetia marina. The surface energy of the SAM surfaces was calculated from contact angle data obtained from several different solvents and using different models for calculation, to determine which of these methods most accurately predicted bacterial adhesion. It was discovered that a combination of factors, specifically, the hydrophobicity and Lewis acidity of a surface, promoted the greatest adhesion to these surfaces. A model for adhesion of C. marina has been derived using this measurement. The general applicability of this model to organisms of different surface compositions and environmental niches has been explored. General and specific trends for bacterial adhesion will be discussed.

11:20am **MB+BI-MoM11 Interface Chemistry and Mechanics of Barnacles**, *G.H. Dickinson,* Duke University Marine Laboratory*, D. Ramsay, J.N. Russell, Jr.,* U.S. Naval Research Laboratory*, D. Rittschof,* Duke University Marine Laboratory*,* ***K.J. Wahl***, U.S. Naval Research Laboratory

Barnacles adhere to all kinds of surfaces in the ocean. These animals settle as larval cyprids, and attach by exuding a protenaceous adhesive. Only recently, with the study of soft and transparent release coatings, has the investigation of the adhesive mechanisms of the barnacle base plate become accessible. We are employing a combination of optical and mechanical spectroscopy to understand the near surface properties of barnacles. Here we report on studies of Amphibalanus amphitrite (little striped barnacle) using a combination of micro-Raman and Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopies, Atomic Force Microscopy (AFM), and micromechanical compression testing to investigate base plate chemistry and mechanics. For barnacles grown on release surfaces, two base plate phenotypes are found - those with a 'hard,' thin adhesive morphology, and those with 'gummy' or compliant adhesive morphology. Micro-Raman, ATR-FTIR, and AFM spectroscopies show significant differences in the protein structure and mineralization of hard and gummy. ATR-FTIR spectroscopy of hard and gummy barnacles, with and without seawater present, showed strong time-dependent responses during reattachment. Mechanical differences between hard and gummy base plates were examined using a custom instrumented flat-punch mechanical tester. The base plate mechanical properties of composite moduli are of order 2 to 5 GPa, with statistically lower modulus for gummy barnacles. The overall flexibility of the barnacle base plate was similar for both hard and gummy barnacles, due to compensating morphologies. Release properties will be discussed in relation to base plate morphology and flexibility.

MEMS and NEMS

Room: 615 - Session MN-MoM

Materials Processing, Characterization and Fabrication Aspects

Moderator: A.V. Sumant, Argonne National Laboratory

8:00am **MN-MoM1 Materials for the Realization of High Performance Radio Frequency MEMS Devices**, ***S.P. Pacheco,*** Freescale Semiconductor, Inc., *G. Piazza*, University of Pennsylvania **INVITED**

RF MEMS technology has rapidly evolved and matured over the last decade. More than 60 companies are currently involved in RF MEMS development with around 25% shipping commercial products or samples to customers. According to industry projections, by 2009, the RF MEMS market will break the $1 billion barrier with about 40% of the total market dominated by Bulk Acoustic Wave (BAW) devices.[1] Major opportunities for other RF MEMS devices will continue to expand as the rest of the market hits its stride in terms of both high-volume and high-end applications as issues with reliability, packaging, and CMOS integration are solved. The remaining market will be split between micro-mechanical resonators and oscillators for consumer and IT applications and RF MEMS switches for military applications and RF Test and Automated Test Equipment (ATE). This paper will describe proven material systems that are being presently commercialized as well as examine innovative materials that are starting to gain popularity for RF MEMS micro-resonators and switches. Benefits and challenges associated with each of these material systems will be presented. Topics such as CMOS/MEMS monolithic integration as well as the use of high acoustic velocity materials such as silicon carbide and diamond-like films for the realization of high performance, compact frequency references will be discussed. Additionally, the introduction to CMOS-compatible, low-loss GHz-range bandpass filters based on piezoelectric aluminum nitride contour-mode MEMS resonators will be covered. Piezoelectricity is also being investigated as an actuation mechanism for RF MEMS switches that would allow handset front-end compatible bias voltages in the 2-4 V range. Lastly, packaging breakthroughs using wafer-level techniques, including 3-D integration and surface micromachining, have the potential to enable low-cost, high-reliability, high-performance RF MEMS devices.

[1] J. Bouchaud, B. Knoblich, RF MEMS Market and Industry Overview, WTC - Wicht Technologie Consulting, Munich, http://www.wtc-consult.de.

8:40am **MN-MoM3 Nano-Scale, Directional Contact Metal Transfer in Hot-Switched MEMS Actuators**, ***Z. Yang***, *D. Lichtenwalner*, *A. Kingon*, North Carolina State University

We have investigated failure mechanisms of metal-contact Micro-electro-mechanical Systems (MEMS) switches using a new accelerated lifetime test facility. The facility utilizes a double-contact upper cantilever from commercial MEMS contact switches, and tests these against bottom gold contact pads within a modified AFM. After a number of switching cycles, both the upper contacts and bottom electrode were characterized by atomic force microscopy (AFM). In this paper, a new phenomenon we term "nano-scale, directional contact metal transfer" during hot switching is reported. The material (gold) in the contact area transfers between the bottom contacts and upper contacts during hot-switching, following the electric field direction. The field-directional transfer was confirmed by DC signal (open circuit voltage, Voc = 6 V) test and reversed DC signal (Voc = -6 V) test. It has been found that the material transfer process is accelerated with the increase of cycling number. Volume analysis of the damaged contact area shows that using an AC signal (with the amplitude of Voc = 6 V) yields an order of magnitude less material transfer damage than DC current, and the material transfer under AC does not have any directional characteristics. This indicates that under the condition of "hot-switching", signal type (AC/ DC; biased or not) may have a significant effect on MEMS switches' failure mechanism. Different material transfer related theories and models are reviewed and examined. A new micro-contact degradation mechanism is proposed.

9:00am **MN-MoM4 Growth of AlN by Pulsed Laser Deposition and Reactive Sputtering Techniques and Fabrication of RF MEMS Resonators**, ***S. Hullavarad***, University of Alaska Fairbanks

AlN is a desirable piezoelectric material for MEMS and NEMS resonators and micro-switches for high frequency filtering applications. The theoretical maximum frequency of AlN is >180 GHz, as opposed to <60 MHz for PZT. The Young's modulus of bulk ceramic AlN at 25°C is 345 GPa, and the density is 3260 kg m-3. This compares to a Young's modulus of 56 GPa for thin film PZT, and a density of 7600 kg/m3 measured for bulk PZT. Additionally, AlN is better suited for the integration of MEMS devices into silicon-based electronics due to its complete compatibility with conventional silicon technologies.[1] In this work, the growth of AlN by Pulsed Laser Deposition method and comparison of properties of AlN thin films with reactive sputter deposition method will be presented. The fabrication and performance of MEMS resonators on AlN thin films deposited by both Pulsed laser deposition and sputtering techniques on substrates consisting of Pt/SiO2/Si structures will be discussed. Special emphasis will be given to the quality (thermal stability, stress) of SiO2 (thermal or PECVD) used as a support layer in fabrication of MEMS resonators. The results obtained by Rutherford Back Scattering Spectroscopy and X-Ray Diffraction techniques to understand the structural stability, composition, crystalline quality of SiO2, Pt and AlN films will be discussed. The quality factor of the resonators in air and vacuum will be compared. It will be shown that the crystalline quality of the films affects the actutation properties of the resonator beams.

[1] S.S.Hullavarad, B. Nagaraj, V.N.Kulkarni, S.Dhar, R.D.Vispute, T. Venkatesan, K.A. Jones, M. Derenge, T. Zheleva, M. Ervin, A. Lelis, C.J. Scozzie, D. Habersat, A.E. Wickenden, L. Currano, M. Dubey, J. Electronic Materials 35, 777 (2006) - A short review.

9:20am **MN-MoM5 Science and Technology of Piezoelectric/Diamond Hybrid Heterostructures for High Performance MEMS/NEMS Devices**, ***O. Auciello***, *A.V. Sumant*, *J. Hiller*, *B. Kabius*, Argonne National Laboratory

A new generation of low power microelectromechanical and nanoelectromechanical system (MEMS/NEMS) devices will require new materials and the integration of dissimilar materials, and new micro and nanofabrication processing techniques to achieve high device performance. Most MEMS devices are currently based on silicon because of the available surface micromachining technology. However, the poor mechanical and tribological properties of Si are not suitable for many high-performance MEMS/NEMS devices, such as resonators and switches. A novel ultra-nano crystalline diamond (UNCD) material developed in thin film form at Argonne exhibits exceptional mechanical and tribological properties that make UNCD a suitable material for a new generation of high-performance MEMS/NEMS devices. Piezoelectric-based MEMS attracts much attention due to their high sensitivity and low electrical noise in sensing applications and high-force output in actuation applications. Piezoelectric Pb(ZrxTi1-x)O3 (PZT) thin films have been intensively investigated over the past decade due to its potential applications in a wide variety of devices, such as non-volatile ferroelectric memories and piezoelectrically actuated MEMS/NEMS devices, which can be actuated at comparatively lower voltages (5-10 V) to those actuated by electrostatic action that required higher voltages. Therefore, the integration of functional PZT thin films with the UNCD-based MEMS/NEMS structures opens up the tantalizing possibility of advanced MEMS/NEMS devices. However, the integration of PZT and UNCD is challenging, mainly due to the PZT/UNCD interface and the need to grow PZT at high temperature in oxygen in the presence of a carbon-based material such as diamond. We will review in this paper the fundamental and applied materials science performed in our laboratory to achieve integration of PZT as a piezoelectric actuation material and UNCD as a mechanically superior platform for MEMS/NEMS, and the development of fabrication processes to produce high-performance hybrid PZT/UNCD MEMS.NEMS devices. We will also present data from test of hybrid PZT/UNCD piezo-actuated resonator structures.

This work was supported by the US Department of Energy, BES-Materials Sciences, under Contract DE-AC02-06CH11357.

9:40am **MN-MoM6 NEMS Resonators of Carbon Nanotube Network and Metal-Carbon Nanotube Composites**, ***J.H. Bak***, *Y.D. Kim*, *B.Y. Lee*, *S.S. Hong*, *Y.D. Park*, Seoul National University, Korea

We present nanomechanical torsional resonator and doubly-clamped beam resonator structures fabricated from aluminum-carbon nanotube (CNT) and palladium-CNT composites. In addition, we realize nanoelectromechanical systems (NEMS) structures suspended by self-assembled carbon nanotube network on GaAs surface by adopting highly selective wet-etching and reactive ion etching techniques. Carbon nanotubes have been spotlighted for its great potential as a promising material as well as a future candidate material for nanoelectronics, with CNT's unique electrical and mechanical properties. NEMS structure combined with CNT can be applied to elucidate the nanotube's physical properties as well as further applications. Furthermore, metallic based NEMS resonator structures are of interest due to higher optical reflectivity, ductility, and conductivity compared to insulator- and semiconductor- based NEMS structures. The resonators are electrostatically driven and are detected at room temperatures under moderate vacuum conditions using optical modulation techniques. From identifying fundamental flexural and rotational modes as well as applying continuum mechanics equations, we observe a significant enhancement of the Young's modulus in metallic resonators structures with added CNTs.

We will also discuss the characterization of mechanical properties of the structures by AFM force deflection spectroscopy and compare the two characterization techniques.

10:20am **MN-MoM8 Addition and Removal of Stress to Drastically Tune Frequency and Quality Factor of Nanomechanical Resonators**, ***S.S. Verbridge***, *D. Finkelstein Shapiro, H.G. Craighead, J.M. Parpia*, Cornell University

We have used optical drive and detection to study the mechanics of flexural nanostring resonators. Beam stress in devices made of both silicon and silicon nitride is tuned by macroscopically bending the resonator chip, resulting in a drastic tuning of the frequency of the correctly oriented doubly clamped beams. Frequency tuning by as much as several hundred percent is achieved with this technique. Over this wide range of frequency tuning, quality factor is also observed to be tuned by as much as several hundred percent. Highly stressed devices display the highest quality factors, and we therefore conclude that stress can be used as a parameter to increase device performance by increasing both resonant frequency as well as quality factor. Frequency can be drastically tuned and quality factor positively impacted by the addition of both tensile, as well as compressive stress. We discuss the sources of dissipation for these devices, and demonstrate a high tensile stress doubly-clamped beam resonator with sub-micron cross-sections, and a quality factor of 390,000 at 3.7 MHz, in vacuum, and at room temperature. The high frequency and quality factor exhibited by the high stress devices, as well as the significant tuning attained with the chip-bending technique, should prove useful for applications of nanomechanical resonant devices.

10:40am **MN-MoM9 Noise Temperature and Thermodynamic Temperature of Ultrasensitive Cantilevers Below 1 K**, ***A.C. Bleszynski***, *W.E. Shanks*, Yale University, *B. Ilic*, Cornell University, *J.G.E. Harris*, Yale University

Micromechanical systems can be fabricated with the sensitivity necessary for detecting ultra-small forces arising from quantum mechanical effects. We use cantilevers as torsional magnetometers to study the magnetic properties of systems mounted directly on a cantilever. Our goal is to study persistent currents in normal metal rings. The properties of these currents remain an outstanding controversy in mesoscopic physics. As with all sample-on-cantilever arrangements, there are two distinct temperatures that determine the performance of the experiment: the cantilever's Brownian motion temperature (T_n) and the temperature of the sample mounted on the cantilever (T_s). T_n is associated with a single macroscopic degree of freedom extended over the length of the cantilever. T_s on the other hand is associated with the very large number of microscopic degrees of freedom in the sample. For a high-Q cantilever, T_n, which sets the cantilever's ultimate force sensitivity, is in weak contact with the thermal bath at temperature T_b. T_s is in contact with the bath via phonon conduction through the cantilever. This contact can also be weak for a small, electrically insulating cantilever at low temperatures. It is thus a priori uclear whether in a practical experiment T_s and T_n will equilibrate with each other or even with T_b. It is also unclear how they will respond to a localized heat source, e.g. a laser used to monitor the cantilever's motion. We have used our sample-on-cantilever system to realize two primary thermometers to measure both T_n and T_s. We infer T_n by monitoring the cantilever's Brownian motion and T_s from the critical magnetic field of a superconducting sample mounted on the cantilever. We find that for modest laser powers incident on the sample, these two temperatures stay equilibrated to each other and to T_b down to 300mK. For higher laser powers T_s and T_n remain equal to each other but are hotter than T_b. The temperature difference is well-described by a simple model of phonon transport along the cantilever beam. We have also fabricated single crystal silicon cantilevers with integrated micron-scale metal rings. We have demonstrated attonewton force sensitivity with these devices and will present measurements of the rings' susceptibility in the normal and superconducting states.

11:00am **MN-MoM10 Process Development and Material Characterization of Polycrystalline BiTe and PbTe Thin Film Alloys on Si for MEMS Thermoelectric Generators**, ***I. Boniche***, University of Florida, *B.C. Morgan, P.J. Taylor*, U.S. Army Research Laboratory, *C.D. Meyer, D.P. Arnold*, University of Florida

Numerous opportunities exist in commercial and military applications for thermoelectric (TE) energy scavengers to act as integrated power sources. Bulk TE materials and modules are commercially available but are often tailored for heating/cooling applications, rather than power generation. Additionally, these bulk technologies limit the miniaturization of TE modules. This work seeks to develop and characterize vapor-deposited polycrystalline TE thin films on Si substrates for integration with MEMS devices, specifically investigating Bi_2Te_3 and PbTe alloys for both room and high-temperature applications. P-type polycrystalline Bi_2Te_3 and PbTe films from 0.4 µm to 9 µm thick have been successfully deposited on bare and etched Si, thermally oxidized Si, and Si/SiO_2 substrates with patterned metal traces. The films were vapor-deposited in UHV using congruent sublimation of the solid-source parent compounds. Fundamental microfabrication techniques for Bi_2Te_3 films, such as patterning and metallization, have recently been developed to augment previous work on PbTe alloys.[1] Dry etch rates of 0.4 µm/min and 0.7 µm/min were obtained for Bi_2Te_3 and PbTe, respectively. Wet etch rates of ~3 µm/min were achieved using bromine-based chemistries, but at the expense of mask undercut. Films have been characterized electrically using van der Pauw and transfer length method test structures. As-deposited resistivity was 23 mΩ-cm for Bi_2Te_3, and 126 mΩ-cm for PbTe films. Contact resistivities of 2x10^{-4} Ω-cm^2 were achieved for Cr/Pt/Au on Bi_2Te_3, and 4x10^{-4} Ω-cm^2 for Cr/Au on PbTe. The Seebeck coefficient was measured to be 94 µV/K for Bi_2Te_3 and ~100 µV/K for PbTe alloys. Analytical modeling of in-plane MEMS TE generators showed that film resistivity is a limiting factor for power generation. Various post-deposition annealing treatments were explored to reduce film resistivity, and thus enable higher power delivery. The results show that successive rapid thermal annealing in nitrogen at 400°C can reduce the resistivity of PbTe. The integration of these materials into prototype generator structures will also be discussed, particularly towards developing fabrication compatible TE, heat exchanger, and mechanical MEMS structures.

[1] I. Boniche, et al, PowerMEMS Conf., Nov. 2006.

11:20am **MN-MoM11 Fabrication of Metal-based High Aspect Ratio Microscale Structures by Compression Molding**, ***J. Jiang***, *F.H. Mei, W.J. Meng*, Louisiana State University

Metal-based high aspect ratio microscale structures (HARMS) are basic building blocks for metallic microdevices such as micro heat exchangers[1,2] and micro electromagnetic relays.[3,4] Metallic microdevices may function better when subjected to high stresses, high temperatures, and other harsh conditions. Metal-based HARMS can be fabricated by combining X-ray/UV lithography and electrodeposition, following the Lithographie/Galvanoformung (LiG) protocol.[5] Such primary HARMS made by LiG are expensive. In comparison, production of secondary HARMS by molding replication from HARMS inserts is fast and simple.[5,6] We have demonstrated successful molding replication of HARMS in Pb[7] Al[8], and Cu.[9] Molding replication of metal-based HARMS entails extensive plastic deformation within the molded metal. Understanding the mechanics of microscale compression molding is important for accurately assessing the capabilities and limitations of this technique. The present paper summarizes our results on instrumented compression molding of Pb, Al, and Cu as a function of the molding temperature. Measured molding responses are rationalized with companion elevated-temperature tensile testing of metals using a simple mechanics-based model of the micromolding process. The present results suggest that stresses on the insert during micromolding are determined primarily by the yield stress of the molded metal at the molding temperature and the frictional tractions on the insert sidewalls. Additional factors of complication during high temperature micromolding will be discussed.

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[4] J. D. Williams, W. Wang, Microsystem Technologies 2004, 10, 699

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[8] D. M. Cao, W. J. Meng, Microsystem Technologies 2004, 10, 662

[9] D. M. Cao, J. Jiang, W. J. Meng, J. C. Jiang, W. Wang, Microsystem Technologies 2007, 13, 503.

11:40am **MN-MoM12 Process Characterization of Vapour Phase Sacrificial Etching**, ***A. O'Hara***, *G. Pringle, M. Leavy*, MEMSSTAR, UK

The manufacture of MEMS devices has primarily used processes and techniques developed for the semiconductor industry. The process characterization is well established for these methods and are then adapted to the MEMS structure. One process unique to MEMS manufacture is isotropic etching of a sacrificial layer. Historically these processes have been developed using wet etch methods, stagnant gas techniques or gas flow processes with limited process capability. Wet processing and stagnant gas processes employ a one process fits all approach. However, it is seen that different MEMS structures require significantly different process optimization and control. Using memsstar systems for etching, based on controlled continuous flow technology CCFT the process is optimised to the structure being etched. In this example for XeF_2 etching, a carrier gas is employed to transport a precise flow of XeF_2 to the process chamber. The flow of the carrier gas determines the flow of the XeF_2. When etching a structure with a large open access to the sacrificial material the etch is seen to be transport limited. The etch rate is dependent on the flow of XeF_2 into the chamber, the higher the flow the higher the etch rate. When the open access to the sacrificial material is very limited the etch is seen to be reaction limited. In this case the etch rate is dependent on the partial pressure of the XeF_2, the higher the partial pressure the higher the etch rate. Using controlled continuous flow of the process gases combined with fine chamber pressure control the sacrificial etch process can be tuned to the MEMS structure being manufactured. Experimentation with different structures is discussed to show that the etch process performance and process window varies depending upon the mechanical materials and dimensions.

Nanometer-scale Science and Technology

Room: 616 - Session NS-MoM

Nanoscale Assembly and Manipulation I

Moderator: L.E. Ocola, Argonne National Laboratory

8:00am **NS-MoM1 On-Surface Synthesis of Metallo-Porphyrin Nanotubes by Vacuum Sublimation onto Noble Metals Substrates**, *M. Trelka, C. Urban, D. Ecija,* Universidad Autonoma de Madrid, Spain, *P. de Mendoza,* Insituto Catalan de Investigaciones Quimicas (ICIQ), Spain, *J.M. Gallego,* Insituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *R. Otero,* Universidad Autonoma de Madrid, Spain, *A. Echavarren,* ICIQ, Spain, ***R. Miranda***, Universidad Autonoma de Madrid, Spain

Molecular electronics is a promising alternative for the continuing miniaturization of electronic devices. The capability of synthesizing and depositing molecular wires on solid surfaces is a key step within this context. The majority of the most promising current candidates to molecular wires, such as carbon nanotubes, DNA strands or individual polymer molecules, are too large and fragile for depositing them on solid surfaces by in-vacuum sublimation. Other kinds of wet deposition methods, such as drop-casting, are not so well controlled, which, in turn, hinders the understanding and design of their conductivity. Since the molecular mass of the chemical species well-suited for deposition on solid surfaces by in-vacuum sublimation is limited, one could envisage a mechanism to grow the polymeric molecular wires by depositing smaller subunits that would subsequently assemble into the polymer on the surface. This approach has successfully been used to steer the assembly of organic molecules into 1D structures. The 1D molecular wires so created are mostly like 'ribbons', due to the fact the molecules tend to lie flat on the surface to maximize substrate-adsorbate interaction. The on-surface synthesis of molecular wires with more complex geometrical shapes, such as tubular or cylindrical, has only been described for the case of carbon nanotubes, and only on surfaces covered with catalytic nanoparticles or on silicon carbide surfaces, where the constituent carbon for the nanotube growth arises from bulk segregation. The aforementioned ideal situation in which molecular subunits assemble into 1D structures with cylindrical symmetry has not been described so far in the literature. In this work we describe the growth of 1D tube or cylinder-looking structures obtained after deposition of a metallo-porphyrin (Zn-Tmp) on the noble-metal surfaces Au(111) and Cu(100) by vacuum sublimation with the substrate held at room temperature (RT). Our experiments indicate that the 'nanotubes' are only a meta-stable structure, since they disassemble into flat-lying Zn-Tmp monomers upon annealing to 500 K. The disassembled Zn-Tmp adsorbates are tightly bound to the surface, as evidenced by the fact that they can be easily imaged by Scanning Tunnelling Microscopy even at room temperature, and the difficulty to manipulate them even under the harsher tunnelling conditions. Two mechanisms for such a phenomenon will be discussed.

8:20am **NS-MoM2 Interactions of Nanoparticles with a Dewetting Solid Film**, ***J.S. Palmer***, *P. Swaminathan, J.H. Weaver*, University of Illinois at Urbana-Champaign

Capillary forces at the interfaces between particles, fluids, and solid substrates lead to the self assembly of structures during liquid film evaporation. We introduce a related process that involves nanoparticle assembly during dewetting and sublimation of a solid thin film. Metal atoms evaporated onto condensed inert gas films form clusters that can be delivered to a substrate of choice by subliming the film. Warming leads to hole formation at defects or grain boundary triple points and surface tension causes hole spreading and film breakup. For Au on Xe we show that, as for liquids, the physics underlying aggregation involves capillary forces as films dewet amorphous carbon substrates. The cluster mobility reflects the dynamics of the boundary of the retreating solid film and results in the formation of nanostructures, whose sizes and densities are controlled by adjusting the film thickness. Kinetic Monte Carlo simulations reproduce the experimentally-observed shapes and distributions and provide insight into the particle assembly process. In contrast to liquid films, particle motion is limited to the dewetting front where capillary forces drive cluster aggregation. This nanoparticle assembly process is not limited to noble metals on rare gas films but occurs in a variety of systems where particles are deposited onto thin volatile films, e.g. II-VI semiconductor particles and condensed CO_2 layers.

8:40am **NS-MoM3 Solidification and Melting of Mercury in Nanotube Cavities**, ***A. Kutana***, *K.P. Giapis*, California Institute of Technology

We present molecular dynamics simulations of solidification and melting of mercury nanoparticles inside carbon nanotubes as a function of nanotube diameter. The mercury liquid is described by an ab initio potential for mercury dimer, rescaled to match the experimental density at 300K and melting point of mercury. The liquid-wall interactions are optimized based on the wetting angle of a mercury drop on graphite. The liquid-solid phase transition is marked by a discontinuity of the energy when monitored as a function of temperature. A significant depression of the melting point of mercury nanoparticles is predicted as the nanotube diameter decreases from 5.4 nm to 1.4 nm. The transition is less pronounced in smaller tubes, as the limit of one-dimensional system is approached. Below the freezing point, the crystal structure of solid nanoparticles is represented by a set of concentric shells in small nanotubes, while larger nanotubes show multiple domains with bulk crystal structure. Above the melting point, the central part of the nanoparticle is amorphous, while the liquid within a few atomic layers of the wall remains partially ordered. Near-wall liquid density profiles exhibit oscillation with the amplitude that increases as the tube diameter becomes smaller. In overall, the ordering inside nanotube cavities is stronger in comparison with the liquid near a flat wall. The contact angles are predicted to be larger inside nanotubes than on flat graphene sheets, indicating less favorable conditions for wetting on concave surfaces.

9:00am **NS-MoM4 Template Guided Self-Assembly of Metal Oxide Quantum Dots**, ***Y. Du***, *I. Lyubinetsky, D.R. Baer,* Pacific Northwest National Laboratory, *J.F. Groves*, University of Virginia

This talk reports the use of focused ion-beams (FIB) to direct the self-assembly of Cu_2O quantum dots (QDs) on $SrTiO_3$ (100) substrates via point implants of Ga^+. Oxygen plasma-assisted molecular beam-epitaxy (OPA-MBE) is used to grow Cu_2O QDs. It is found that, for high FIB implant dose ($>10^{18}$ ions/cm^2) and large interdot spacing (~1000 nm), multiple QDs can be formed preferentially on the edges of FIB modified pits. For lower doses ($<10^{15}$ ions/cm^2) and/or smaller interdot spacings (~100 nm), individual QDs nucleate first within the pits. Under carefully controlled conditions, the separation and arrangement of the Cu_2O QDs follows the FIB patterned template. This study finds that the FIB directed self-assembly technique works for different FIB doses, interdot spacings and deposition thicknesses, suggesting that this method is robust and flexible. Examination of QD growth on low-dose implant surfaces revealed a multi-step growth process. To further interpret the low dose implant results, calculations of total free-energy changes have been performed to study the differences between nucleation on a flat substrate surface and nucleation within a surface pit. This analysis shows that nucleation within a pit is almost always energetically favorable. In some special cases, assuming the pits have an inverted pyramidal shape, calculations show that island formation within the pits lowers the system total free-energy from the beginning of growth, i.e. there is no critical radius or energy barrier before a stable nucleus can be formed. Continued study of directed self-assembly of metal oxide quantum dots should lead to better understanding of the creation of well ordered, precisely controlled, high density QD arrays, ultimately contributing to the development of next generation nanoelectronic, magnetic, and optical devices.

9:20am **NS-MoM5 A Generic Method for Coupling Quantum Dots to Biomolecules**, ***A.S. Blum***, *C.M. Soto,* Naval Research Laboratory, *C.D. Wilson,* SAIC, *K.E. Sapsford,* George Mason University, *J.L. Whitley,* SAIC, *A. Chatterji, J.E. Johnson,* Scripps Research Institute, *B.R. Ratna*, Naval Research Laboratory

We present a new technique that allows the generic coupling of quantum dots to any biomolecule without the use of specially engineered domains. Using well-developed chemistry short histidine-containing peptides can be conjugated to lysine-containing protein scaffolds to controllably attach quantum dots (QDs) to the scaffold. This technique was used to bind quantum dots from aqueous solution to both chicken IgG and Cowpea mosaic virus (CPMV), a 30 nm viral particle. These quantum dot-protein assemblies were studied in detail. The IgG-QD complexes were shown to retain binding specificity to their antigen after modification. The CPMV-QD complexes have a local concentration quantum dot greater than 3000 nmol/mL, and show a 15% increase in fluorescence quantum yield over free quantum dots in solution.

9:40am **NS-MoM6 Luminescent Nanocrystals Labelled Beads for Directed Patterned Assembly**, *E. Fanizza,* Università di Bari, Italy, *L. Malaquin,* LPN CNRS, France, *T. Kraus, H. Wolf,* IBM Research GmbH, Zurich Research Laboratory, Switzerland, *M. Striccoli, A. Agostiano,* ***M.L. Curri***, CNR Italian National Research Council IPCF, Italy

Polystyrene (PS) beads have been functionalized with luminescent (CdSe)ZnS core shell type nanocrystal (NC), generating a versatile core-shell type of material, able to combine the size dependent optical property of (CdSe)ZnS NCs with the versatility and prompt processability for assembly of micrometer sized PS beads. The novel colloidal nanocomposite system has been fabricated by using a layer-by-layer (LbL) approach.[1] Polystyrene beads have been firstly coated with polyelectrolyte (PE) layers and subsequently functionalized with fluorescent (CdSe)ZnS nanocrystals, synthesized following established procedure with minor adjustment. The obtained luminescent NC functionalized beads have been subsequently assembled onto patterned polydimethylsiloxane (PDMS) substrate by means of a capillary force induced process,[2] thus providing an original example of physical directed assembly. Here the patterned stamp, fabricated with a top-down approach, act as template for the construction of well-defined discrete nanoscale structures at two- and three dimensions. The ordered fluorescent nanoparticle arrangement has been successful preformed by using two different patterns. A precise positioning of the PS functionalized beads has been achieved. Such original structures based on colloidal particles, which now carry the unique spectroscopic signatures of the luminescent NCs, are of considerable interest either in optoelectronic systems, and the ability to assembly and precisely positioning the functionalized nano-object into ordered assembly the venue to their prompt integration in bio-engineering due to their potential application in multiplexed bioassays, medical diagnostic, drug screening.[3]

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[3] The partial support of the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120) MIUR SINERGY programme (FIRB RBNE03S7XZ) is gratefully acknowledged.

10:20am **NS-MoM8 Selecting and Driving Nanoscale Assembly in Monolayer Films through Tailored Intermolecular Interactions**, ***T.J. Mullen***, *C. Srinivasan, M.J. Shuster, J.N. Hohman, M.W. Horn, A.M. Andrews, P.S. Weiss*, Penn State University

Active chemical surfaces that selectively capture and separate specific analytes from competitive environments are useful for detecting and isolating complex biological molecules as well as small molecules found in chemical weapons and toxic industrial waste. The development of self- and directed assembly strategies is key to the fabrication of molecularly precise structures for such applications. As the dimensions of patterned surface structures have decreased to the sub-100 nm scale, traditional lithographic techniques have not demonstrated the ability to fabricate reproducible structures over larger areas with molecular-scale organization. We have developed, utilized, and evaluated self- and directed nanoscale assembly strategies to fabricate, to register, and to functionalize chemical surface structures at the supramolecular 1-100 nm scale. We will highlight two hybrid soft-lithography strategies - microdisplacement printing and microcontact insertion printing - where monolayers with specifically tuned intermolecular interactions were engineered and the chemical and physical properties of the resulting patterned structures were characterized on both the ensemble and the molecular scales. Additionally, we will demonstrate that these chemical films can be functionalized with small-molecule probes that selectively capture large biomolecules while resisting nonspecific binding.

11:00am **NS-MoM10 Assembly and Transfer of Functional Nanoparticle Arrays**, ***H. Wolf***, *T. Kraus, L. Malaquin, A. Decker, H. Schmid,* IBM Research GmbH, Zurich Research Laboratory, Switzerland, *N.D. Spencer*, Swiss Federal Institute of Technology, Switzerland**INVITED**

Nanoparticles provide multiple properties that make them potential building blocks of novel optical and electronic devices. Significant progress has been made in the bulk synthesis of nanoparticles with controllable composition, shape, structure, and size. However, in general the products are disordered colloidal suspensions or powders, whereas devices usually require ordered arrangements of particles on a substrate. Self-assembly processes can order large numbers of particles in parallel on surfaces, but they usually provide only dense regular arrays without the long-range order required for large-scale integration. In addition to particle order, also the particle-substrate junction is often crucial for device performance, and the reliable creation of well-defined particle-surface interfaces remains a challenge. We will show in this talk how directed self-assembly can be combined with a transfer step to produce arbitrary patterns of nanoparticles on a substrate. The combined process, called "SATI" for "Self-Assembly, Transfer and Integration", maintains the advantages of self-assembly but relaxes the requirements on the substrates, and is more flexible than single-step self-assembly. Directed self-assembly uses a topographically or chemically patterned template to assemble nanoscale objects. Compared to template-free self-assembly it has less requirements and restrictions with regard to the assembled object. It is not limited to regular patterns but still a highly parallel process. Directed self-assembly comes at the cost of producing a template. However, the template can be re-used or fabricated as a low-cost replica of a topographical master made by standard top-down patterning techniques. After assembly, the nanoscale objects are printed in the transfer and integration steps onto the target substrate, retaining the parallel nature of the process. The transfer requires to tailor adhesion in a way that makes the nanoparticles leave the template or intermediate carrier and stay on the target substrate. Further processing of the arrays allows to exploit the specific particle functionality, e.g. as a catalyst, optical activity, or simply as a resist.

11:40am **NS-MoM12 Cyanuric Acid and Melamine on Au(111): Structure and Energetics of Hydrogen Bonded Networks**, *W. Xu,* ***M. Dong***, *H. Gersen, E. Rauls, T. Linderoth, F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

Supramolecular chemistry based on non-covalent interactions is a powerful synthetic tool for the preparation of complex molecular architectures. In particular hydrogen bonds are considered to be useful for controlling molecular self-assembly due to the reversibility, specificity, directionality, and co-operative strength of this class of interactions. The highly specific interaction between the molecules Cyanuric Acid (CA) and Melamine (M), based on three complementary hydrogen bonds, is a key structural motif in supramolecular chemistry. Here we investigate the adsorption and co-adsorption M and CA on a Au(111) surface under Ultra High Vacuum conditions using Scanning Tunneling Microscopy with submolecular resolution. In addition to the expected structure with a 1:1 CA:M ratio, we identify a novel phase with 1:3 CA:M ratio formed upon sequential deposition. The hierarchy of binding energies for homo and heteromolecular dimers as well as for the observed network structures has been evaluated through theoretical modeling by the SCC-DFTB method, rationalizing the experimental observations.

Plasmonics Topical Conference

Room: 619 - Session PL-MoM

Plasmonic Nanostructures and Plasmon Manipulation

Moderator: J.V. Coe, The Ohio State University

8:00am **PL-MoM1 Local and Surface Plasmon Couplings on Ag Nano-Sheet Composed of 2D Crystallized Ag Nanoparticles**, ***K. Tamada***, *K. Michioka, X. Li, Y. Ikezoe, M. Hara*, Tokyo Institute of Technology, Japan

In this paper, we present our latest result concerning the coupling between propagating surface plasmon on flat gold surface and local plasmon on silver nanoparticles. The silver nanoparticles are deposited on the substrate as 'nano-sheet' composed of two dimensional crystalline layer fabricated at air-water interface, in which the distance between the particle cores is controlled accurately by the thickness of the shell layer and the compressions (e.g., core diameter: 3.7nm, core distance between neighboring particles : 6.6nm). We found the silver nano-sheet deposited on glass to exhibit a significant shift of plasmon absorption band in UV-vis-Near-IR spectra to the longer wavelength (c.a. 50nm), while the peak width was rather reduced (sharpened) in the sheet formation. We determined the dielectric constant of the silver nano-sheet by Kramers-Kronig analyses of the UV-vis-Near-IR spectra, and compared with the value obtained from the SPR angle shift on gold substrate. The SPR curves are broadened distinctively depending on the thickness of sandwiched dielectric layer (in our study, alkanethiol self-assembled monolayers or Langmuir-Blodget films are utilized to control the distance between the nano-sheet and the gold substrate), which evidences the dipole coupling between the gold substrate and the silver nano-sheet. By use of this ideal nanostructual material, we examined several fundamental issues concerning the propagating and the local surface plasmons and their coupling effect on the optical responses.

8:20am **PL-MoM2 Photochemical Synthesis of Shape Controlled Gold Nanoparticles: A Deeper Insight on the Growth Mechanism**, ***M.L. Curri***, *T. Placido, R. Comparelli, M. Striccoli,* National Research Council CNR IPCF Italy, *D. Cozzoli,* National Nanotechnology Laboratory Lecce Italy, *A. Agostiano,* National Research Council CNR IPCF Italy, *G. Capitani,* Università di Bari, Italy, *F. Giannici*, Università di Palermo, Italy

Au nanoparticles are of great interest due to their unusual physical and chemical properties with respect to their bulk equivalent. The field has recently experienced significant growth because of advances in the reproducible synthesis of Au nonspherical nanoparticles with tunable plasmon resonances, and applications of plasmon-resonant nanoparticles in nanophotonics, chemical sensing, and biomedical engineering.[1] Current research has been focused on one-dimensional nanoparticles such as nanorods (NRs) since the morphological anisotropy results in very complex physical properties.[2] Water soluble Au nanospheres and nanorods have been synthesized by using various methods such as templating,[3] photochemistry,[4] seeding[5] and electrochemistry.[6] In this work, we propose a Ag ion mediated photochemical synthesis of gold nanoparticles (NPs) in micellar template under UV irradiation. We performed a systematic study on the role of Ag+ ions in directing the growth of Au NRs, in order to elucidate the mechanism that produces anisotropic particles rather than spheres. The samples have been characterized by UV-Vis-NIR absorption spectroscopy, High Resolution Transmission Electron Microscopy (HR-TEM), Energy Dispersive Spectrometry (EDS), Inductively Coupled Plasma (ICP), and Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) measurements. Moreover the size and shape distribution has also been investigated by statistical analysis of the experimental data. The overall obtained results allowed us to finely tune the size and the shape distribution of gold NPs and to propose a reasonable mechanism describing the role played by silver ions in directing the growth of gold NRs.[7,8]

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[7] This work was financially supported by the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120)) and by MIUR SINERGY programme (FIRB RBNE03S7XZ).

8:40am **PL-MoM3 Plasmonics: A Route to Optical Metamaterials and Nanoscale Optical Devices**, ***H. Atwater***, California Institute of Technology **INVITED**

The rapidly developing field of plasmonics has captured the imagination of physicists, chemists and engineers because of the unique ability to control optical dispersion and localize light in metallodielectric materials at nanoscale dimensions. Many ideas are currently being generated by researchers, which may ultimately enable plasmonic components to form new metamaterials designs and also building blocks of a chip-based optical device technology with potential imaging, spectroscopy and interconnection applications in ultramicroscopy, computing, communication and chemical/biological detection. In this talk I will describe recent opportunities presented by new plasmonic components including i)design of metal-insulator-metal metamaterials that facilitate dispersion control to enable very high positive as well as negative effective refractive index in the visible and near infrared ii) Si CMOS compatible light near-infrared light sources for coupling into plasmonic networks iii) plasmon-enhanced emission from quantum dots, and iv) active plasmonic devices based on electro-optic and all-optical modulation of plasmon propagation. Finally, amid the exuberance currently felt by plasmonics researchers, it is worthwhile to ponder the potential technological and scientific limitations that we currently face, and how we might take the next steps toward integrated plasmonic circuit and system technologies with compelling applications.

9:20am **PL-MoM5 Surface Plasmon Propagation and Detection**, ***A. Hohenau***, Karl-Franzens University, Graz, Austria **INVITED**

Surface plasmons are hybrid modes of electrons and photons at the interface of a metal and a dielectric. Confinement to two dimensions, resonant field enhancement and femtosecond lifetimes are properties that boost the interest in surface plasmons in a variety of fields as meta-materials, near field optics or molecular spectroscopy. In this talk I will focus on the concepts for the realization of two-dimensional optics with surface plasmons. Basic elements for surface plasmon optics can be realized by nano-fabrication of metal surfaces or local variations of dielectric host media. I will present and discuss the peculiarities of the different approaches to achieve reflection, refraction, wave-guiding of surface plasmons as well as schemes for their integrated detection.

10:20am **PL-MoM8 Plasmon Hybridization: Understanding the Nature of Plasmons in Complex Nanostructures**, ***P. Nordlander***, Rice University **INVITED**

The recent observation that certain metallic nanoparticles possess plasmon resonances that depend very sensitively on the shape of the nanostructure has led us to a fundamentally new understanding of the plasmon resonances supported by metals of various geometries. This picture- "plasmon hybridization",[1] reveals that the collective electronic resonances in metallic nanostructures are mesoscopic analogs of the wave functions of simple atoms and molecules, interacting in a manner that is analogous to hybridization in molecular orbital theory. The plasmon hybridization picture can be applied to an entire family of plasmonic nanostructures of various geometries, such as "nanoshells", "nanoeggs", "nanorice", nanoparticle aggregates, and finite nanoparticles interacting with extended substrates such as metallic films and wires.[2] The approach can also be used to provide a microscopic understanding of the plasmon in highly irregular nanostructures such as "nanostars",[3] electromigrated gaps in bowtie junctions,[4] and individual and concentric nanorings. The new theoretical insight gained through this approach provides an important conceptual foundation for the development of new plasmonic structures that can serve as surface plasmon resonance (SPR) sensors and as substrates for surface enhanced spectroscopies such as surface enhanced Raman scattering (SERS) or surface enhanced infrared absorption spectroscopy (SEIRA), subwavelength plasmonic waveguides, and nanoantennas for on-chip communication.

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11:00am **PL-MoM10 Fabrication of Large-Area Patterned Nanostructures for Optical Applications by Nanoskiving**, ***Q. Xu***, *J. Bao, R.M. Rioux, R. Perez-Castillejos, F. Capasso, G.M. Whitesides*, Harvard University

Patterned arrays of metallic nanostructures have many applications in photonics. E-beam lithography or more complicate photolithography such as extreme ultraviolet or x-ray lithography has been applied for the generation of test nanostructures, but they are complex, expensive, not applicable to non-planar surfaces, and incompatible with many materials. Cost-effective and convenient methods for fabrication of patterned metallic nanostructures over the large (mm^2) areas required for applications in nanophotonics are much needed. In this work, we demonstrate the fabrication of arrays of closed and open, loop-shaped nanostructures over a large area (~9 mm^2) by a simple technique (nanoskiving) that combines thin-film deposition by metal evaporation with thin-film sectioning. This method combines deposition of thin metallic films by e-beam evaporation, with nanometer-thick sectioning by ultramicrotome. These arrays of metallic structures fabricated by nanoskiving serve as frequency-selective surfaces at mid-infrared wavelengths. Experiments with structures prepared using this technique demonstrate that a closed-looped structure has a single dominant resonance regardless of the polarization of the incident light, while open structures have resonances that are anisotropic with respect to the polarization of the electric field. Finite-Difference Time-Domain (FDTD) simulations reproduce the scattering spectra of these FSS, provide an explanation of the wavelength of the experimentally observed resonances, and rationalize their polarization dependence based on the patterns of current induced in the nanostructures. Because the thin, polymer slabs containing the nanostructures have some mechanical strength; their manipulation allows the fabrication of certain types of arrays of nanostructures, including those in layers or stacks, which is difficult to fabricate by other conventional methods. We demonstrated the fabrication of multilayered nanostructures containing arrays of U-shaped metallic nanostructure with a layer of parallel nanowires on top, in which nanowire acted as a mid-IR wire grid polarizer to filter the two resonant peaks excited by incident p-polarized light. The ability to fabricate and manipulate free-standing metallic nanostructures will find applications in the fabrication of materials with negative index of refraction, and of three-dimensional metamaterials.

11:20am **PL-MoM11 Extraordinary Transmission and Enhanced Emission with Metallic Gratings having Converging-Diverging Channels**, *S. Chen*, ***A. Battula***, University of Texas at Austin

Transmission metallic gratings having the shape of converging-diverging channel (CDC) gives an extra degree of freedom to exhibit enhanced transmission resonances. By varying the gap size at the throat of CDC, the spectral locations of the transmission resonance bands can be shifted close to each other and have high transmittance in a very narrow energy band. Hence, the CDC shape metallic gratings can lead to almost perfect transmittance for any desired wavelength by carefully optimizing the metallic material, gap at the throat of CDC, and grating parameters. In addition, a cavity surrounded by the CDC shaped metallic grating and a one-dimensional (1D) photonic crystal (PhC) can lead to a enhanced emission with properties similar to like a â?~laserâ?T. The large coherence length of the emission is achieved by exploiting the coherence properties of the surface waves on the gratings and PhC. The new multilayer structure can attain the spectral and directional control of emission with only p-polarization. The resonance condition inside the cavity is extremely sensitive to the wavelength, which would then lead to high emission in a very narrow wavelength band. Such simple 1D multilayer structure should be easy to fabricate and have applications in photonic circuits, thermophotovoltaics and potentially in energy efficient incandescent sources.

11:40am **PL-MoM12 Biodetection by Nanoscale 2-D Plasmonic Crystal**, ***A. Valsesia,*** European Commission - Joint Research Centre, Italy, *F. Marabelli,* University of Pavia, Italy, *P. Colpo, G. Ceccone, F. Rossi*, European Commission - Joint Research Centre, Italy

Optical detection is a technique of choice for the development of label-free biosensor to detect molecular interactions. In particular methods exploiting the Surface Plasmon Resonances (SPR) of uniform metal films such as gold or silver have become more and more important from the scientific and the commercial point of view. Moreover, the development of advanced surface nanostructuring techniques has allowed the fabrication of biosensing surfaces based on the Localized-SPR (L-SPR) effect. On the other hand the ability to create controlled chemical nanopatterns on the sensor surfaces and to create functional nanostructures is a crucial step for the controlled immobilization of the biomolecular probes in order to optimize their surface bioactivity as well as for the coherence effects on the optical response. In this work we propose a novel optical based biosensing platform combining the sensitivity characteristic of both localized SPR and physico-chemical nanopatterned surfaces. The fabrication method is based on the combination of cold-plasma processes and colloidal lithography techniques. The fabrication process is briefly the following: a layer of Poly Acrylic Acid (PAA) is plasma deposited on a transparent glass slide and nano-structured through a Polystyrene colloidal mask. As the second step, a Gold film is deposited through the residual colloidal mask by Physical Vapor Deposition in order to create a gold matrix surrounding the polymeric nanodomes. Finally the residual colloidal mask is removed by ultrasonic bath. The resulting surface is a 2-D crystal constituted by PAA nanodomes surrounded by Gold matrix (2-D Plasmonic Crystal - 2D-PlC). The 2D-PlC was optically characterized by Angle Resolved - Micro Reflectometry in the spectral range between 400 nm and 1200 nm, inside a continuous flow liquid cell. The micro-reflectance spectra showed different angle dependent absorption resonances attributed to the Surface Plasmon Polaritons - Bloch Waves (SPP-BW) generated at the gold-polymer and gold-ambient (air or liquid) discontinuities and replicated in the Brillouin Zone by the presence of the 2-D crystal. We demonstrated that the SPP-BW resonances are sensitive to the absorption of proteins on the 2D-PlC and the results were confirmed by X-ray Photoelectron Spectroscopy analysis of the surface. The fabricated nanostructured surfaces promise to be an ideal platform for ultra-sensitive label-free biodetectors.

Plasma Science and Technology

Room: 606 - Session PS1-MoM

Plasma Modeling

Moderator: C.C. Hsu, University of California at Los Angeles

8:00am **PS1-MoM1 Mechanisms of Surface Roughness Formation and Evolution during Plasma Etching**, ***G. Kokkoris***, *V. Constantoudis, G. Boulousis, P. Angelikopoulos, E. Gogolides*, NSCR Demokritos, Greece

The control and understanding of roughness formation during plasma etching is of primary importance in micro- and nano-fabrication technology. In one hand, the roughness of the surfaces of fabricated features may degrade electrical, optical or other device performance. On the other hand, there are beneficial effects of high surface roughness, e.g., in the fabrication of super-hydrophobic surfaces.[1] In this work, a stochastic (Monte Carlo) simulator is used for the study of the surface roughness formation and evolution during plasma etching. The etched film is represented by cells. Shadowing and reemission of particles are taken into account. The trajectory of each particle is calculated until sticking on a cell. The interaction of the particles with the cells is defined by the sticking probability and the etching yield. The focus of the simulation is on Si etching by fluorine-containing plasmas. A common finding of past works devoted to investigation of roughness origins on plasma etched Si surfaces was the increase of the surface roughness, i.e., the root mean square roughness, versus etching time.[2,3,4] In a previous work[2], by using a (1+1)D stochastic simulator, we also demonstrated that the experimentally observed dual scale roughness is captured by a simple model including reactive neutral species, ions and etch inhibitors; the latter may come from sputtering of the electrode and the reactor-wall (hard inhibitors). In this work, we attempt to quantitatively reproduce all surface roughness parameters, e.g., correlation length, by a) refining model parameters, b) including another type of etch inhibitors (soft inhibitors) produced in the bulk phase of the plasma reactor, c) taking into account surface diffusion, and d) using a (2+1)D simulation tool. Atomic Force Microscope (AFM) images of Si surfaces etched by SF_6 plasma are characterized and compared to the simulation results.

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8:20am **PS1-MoM2 Molecular Dynamics Simulation of Hydrogen Induced Damage to Si and SiO_2 Substrates during Reactive Ion Etching (RIE) Processes**, ***T. Takizawa,*** Osaka University, Japan, *S. Kobayashi, T. Tatsumi,* Sony Corp., Japan, *S. Hamagushi*, Osaka University, Japan

As the dimensions of transistors diminish in Ultra-Large-Scale Integrated (ULSI) circuits, "small" damage to the substrate materials caused by plasma etching during chip fabrication processes can have adverse effects on chip performance. In the present work, we investigate damage to Si and SiO_2 caused by energetic hydrogen injections in, for example, a reactive ion etching (RIE) process of Si with a gas containing HBr, using classical molecular dynamics (MD) simulations. In this work, we performed MD simulations of energetic hydrogen injections into Si and SiO_2 substrates and measured penetration depths of H atoms and also reaction characteristics, e.g., bond formation of injected hydrogen with substrate atoms, as functions of the injection energy in the range of 50 -200eV. As injected species, we examined both atomic and molecular hydrogen, i.e., H and H_2. It is usually difficult to determines penetration (implant) depth profiles for hydrogen experimentally, so these MD simulation may give good insight into such problems. It was found that the average penetration depth is essentially proportional to the injection energy. For Si and SiO_2 substrates, hydrogen is found to penetrate deeper in Si than in SiO_2 for the same injection energies. The penetration depth has been also found to depend only on the impact energy of each H atom whether it is injected as a hydrogen atomic or part of a hydrogen molecule. As to reaction characteristics, in the case of a SiO_2 substrate, the majority of injected hydrogen atoms are bound with substrate oxygen atoms, generating hydroxyl groups. In this case, H_2 molecules are hardly formed. Similarly, in the case of a Si substrate, the majority of injected hydrogen atoms form Si-H bonds. However, in this case, H_2 molecules can be also generated in the Si bulk. These MD simulations are based on a newly developed classical interatomic potential functions for Si, C, O, F, and H systems. The model potential functions were developed from data obtained from the density functional calculations based on Gaussian03 (B3LYP), a first-principle simulation code. We are also in the process of evaluating sputtering yields of SiOCH by energetic injections of fluorocarbon radical ions, i.e., CF_x^+. Details of such reactions will be also discussed.

8:40am **PS1-MoM3 Vertically Integrated Computer Aided Design for Devices Process**, ***T. Makabe****, Keio University, Japan **INVITED**

We had our opportunity to propose a relaxation continuum (RCT) model for a low temperature radio-frequency plasma in 1988 in GEC.[1] In 2000 we presented a vertically integrated computer aided design for device processes (VicAddress) in RGD.[2] With the aid of VicAddress described by a hybrid model consisting of the RCT model and particle model, a series of modeling has been carried out for the prediction and the design for a space- and time-resolved plasma structure, sheath dynamics of reactive species, a feature profile evolution, and the damage to a lower level device element during plasma etching.[3] These are a typical example of the multi-scale system. In this talk, we will review the dry etching of dielectric SiO2 in CF4/Ar[4] and organic low-k material in N2/H2[5] under competitive processes among charging, deposition, and etching at each of local positions of a geometrical structure by considering two-layers, intrinsic (or mixing layer) and an overlaying polymer layer in a two-frequency capacitively coupled plasma on the basis of a database of etching yield. Also a Si deep etching with several hundreds of micrometers such that used in MEMS fabrication is predicted under an effect of plasma molding, and the effect of ions, F-

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* 2006 Plasma Prize Winner

radicals, and oxygen radicals on the feature profile is investigated in SF6/O2 in 2f-CCP.[6]

[1] T. Makabe, 41st GEC (Minneapolis)(1988).

[2] T. Makabe, 22nd Int. Symposium on Rarefied Gas Dynamics (Sydney) (2000).

[3] T. Makabe and Z. Petrovic, "Plasma Electronics: Applications in Microelectronic Device Fabrication", Taylor & Francis (New York) (2006).

[4] T. Shimada, T. Yagisawa, and T. Makabe, Jpn. J. Appl. Phys. 45, 8876 (2006).

[5] K. Ishihara, T. Shimada, T. Yagisawa, and T. Makabe, Plasma Physics and Controlled Fusion, 48, B99 (2006).

[6] F. Hamaoka, T. Yagisawa, and T. Makabe, IEEE TPS (accepted for publication).

9:20am **PS1-MoM5 Ion Energy and Angular Distributions into Small Features in Plasma Etching Reactors: The Wafer- Focus Ring Gap[1]**, ***N.Y. Babaeva***, *M.J. Kushner*, Iowa State University

The termination of the edge of the wafer in reactive ion etching is important to obtaining uniform reactants across the entire substrate. This goal is often complicated by the necessary mechanical gap between the edge of the wafer and the terminating structures, such as the focus ring. Plasma penetration into the gap is of concern due to the likelihood of depositing particle forming materials and erosion. We previously showed that the ratio of the Debye length (or sheath thickness) to the width of the wafer-focus ring gap (WFG) is an important parameter: small ratios allow penetration of plasma species in the WFG.[2] As a result, orientation of the electric field, ion trajectories and ion energy and angular (IEAD) distributions are functions of this ratio as well as the details of the geometries and materials. In this talk, we extend that study with a computational investigation of ion energy and angular distributions into the WFG. The model used in this investigation is a 2-dimensional plasma hydrodynamics model utilizing an unstructured mesh to resolve the small structures of the WFG. A Monte Carlo simulation was added to the model to track the trajectories of the ions and neutrals while capturing their gas phase collisions and interactions with the surface. Electric potentials as a function of phase from the unstructured mesh are interpolated onto a fine rectilinear capable of resolving the WFG to facilitate a rapidly executing MCS. The consequences of voltage waveform, frequency and geometry of the WFG on IEADs inside the gap (e.g., incident on the lower edge of the wafer bevel) will be discussed for RIE plasmas sustained in fluorocarbon gas mixtures at tens of mTorr.

[1] Work supported by the Semiconductor Research Corp. and the National Science Foundation.

[2] N. Y. Babaeva and M. J. Kushner, "Penetration of Plasma into the Wafer-Focus Ring Gap in Capacitively Coupled Plasmas", to appear in J. Appl. Phys. (2007).

9:40am **PS1-MoM6 Effect of Dual Frequency Bias on Ion Energy and Angular Distribution and Feature Profile in a Capacitively Coupled Plasma Reactor*, K. Bera***, *S. Rauf, K. Collins*, Applied Materials, Inc.

Capacitively coupled plasma reactors are commonly used in dry etch processes. Control of ion energy and angular distribution function (IEADF) is key to achieving desired etch profile in a plasma reactor. Dual frequency bias combining medium frequency (MF) and high frequency (HF) can be used to modulate the ion energy distribution. Understanding the effect of MF and HF mixing on IEADF is crucial for etch profile control. MF and HF bias are mixed in this investigation, and the mixing effect is characterized for IEADF and etch profile. Plasma simulations have been conducted using the Hybrid Plasma Equipment Model, while a string-based model is used for feature profile simulations. Interaction between ions and electric field modulation across the sheath determined the ion energy and angular distribution. A mono-energetic peak is observed using HF bias while ion energy distribution is broader using MF bias. DC bias is comparable at HF and MF bias for a given RF voltage. Plasma density with MF bias is smaller than that with HF bias. Mixing of MF and HF leads to lower DC bias and lower ion energy. The plasma density distribution and sheath structure are observed to change as the MF voltage is increased relative to HF bias for a given total MF + HF voltage. Ion flux at the wafer is determined by the plasma profile while the local sheath dynamics control the ion energy and angular distribution. Ion flux and IEADF are calculated near the center, middle and edge of the wafer, which are then input into a feature profile model. The feature profile model includes mechanisms for Si and mask etching. The etch depth and selectivity are calculated at the above three locations on the wafer for various mixtures of MF and HF biases. The etch profile is tuned using the mixing of MF with HF bias. Based on etch depth variation across the wafer, etch profile uniformity is calculated. Profile tilting is observed at locations where sheath is non-planar and the ion angular distribution is asymmetric. Various process-kits are evaluated to minimize profile tilting.

10:20am **PS1-MoM8 Modeling of a Dual-Coil and Dual-Flow Inductively Coupled Plasma Reactor**, *C.C. Hsu*, ***V. Le***, *J.P. Chang*, University of California at Los Angeles

The ion flux spatial profile and the etching by-products transportation are among the most important characteristics for plasma processes. The above characteristics need to be well-tailored in order to achieve the desired etching process performance, such as the uniformity and the etched feature profile. A numerical model has been developed to investigate how the processing parameters affect the plasma characteristics and how these characteristics in turn alter the spatial distribution of the plasma species. This numerical model is a two dimensional fluid model of an inductively coupled plasma in mixtures of chlorine, oxygen, and argon. It has been setup to resemble a simplified commercial etching tool, AMAT DPS-II^{TM}, used for 300 mm wafer shallow trench isolation (STI) processes. This tool is equipped with dual-coil and dual-flow arrangements allowing for additional etching process control. It was shown in this model that the spatial profile of the inductively coupled power deposition can be altered by changing the current ratio of the outer and the inner coils of the dual-coil (DC ratio). This change in turn altered the spatial profile of the ion flux and the plasma species densities. For example, by increasing the DC ratio, the center-to-edge ratio of the Cl radical and the ion flux to the wafer surface decreased. The model was then used to interpret the spatial variation and the variation among different operating conditions of a number of STI etched feature profiles obtained by an AMAT DPS-II^{TM} with chlorine-based chemistries. The model qualitatively explained the spatial variation of the etched depth and the side wall angles of the etched profiles. One example was to explain the consistently positive center-to-edge variation of the etched profile sidewall angel using the center-high by-products density obtained by this fluid model. The effect of the flow to the dual-flow gas feed on the by-products transportation and distribution will also be discussed.

10:40am **PS1-MoM9 Prediction of Feature Profile Evolution of Deep Si Etching under Effect of Plasma Molding in 2f-CCP in SF$_6$/O$_2$*, F. Hamaoka***, *T.Y. Yagisawa, T. Makabe*, Keio University, Japan

Deep-RIE is widely used in MEMS fabrication. In large-scale etching, plasma molding is one of the important issues.[1] In our previous study, the influence of the ion transport under the distorted electric field, i.e., plasma molding, on the anisotropic Si etching was numerically investigated without considering the neutral reaction.[2] In this study, we numerically investigate the feature profile evolution of deep Si etching on the MEMS scale in a 2f-CCP in SF$_6$/O$_2$ under competition between Si etching by ions and F radicals and passivation layer formation by O radicals, including the effect of plasma molding. In SF$_6$(83%)/O$_2$ at 300 mTorr, for only physical SF$_5^+$ ion etching of Si, the etching is enhanced at the bottom corner due to the distorted ion incidence on the wafer under the plasma molding. In the case of RIE caused by both SF$_5^+$ ions and F radicals without passivation layer formation, the influence of the plasma molding on the feature profile is not observed because of a much higher etching rate of Si by F radicals than that by SF$_5^+$. However, the bowed and undercut profiles appear significantly at the sidewall and near the silicon-mask interface. Finally, we estimate the feature profile evolution of Si by RIE with the passivation layer formed by O radicals. Under the presence of the plasma molding, the removal of the passivation layer by energetic ions at the bottom corner is strengthened by the effect of excess ion flux with distorted angular distribution. On the other hand, an insufficient amount of ions leads to less efficient removing the passivation layer at the center of the bottom. The chemical etching rate of Si layer for F radicals is much higher than that of passivation layer. Thus, when the passivation layer is removed by SF$_5^+$ion impact, the etching of Si is enhanced by addition of F radicals. As a result, this indicates that anisotropy of the etching profile is not achieved especially at the bottom in SF$_6$(83%)/O$_2$ at 300 mTorr.[3] Further investigation will be given for influence of the percentage of Oxygen on anisotropic feature profile on the MEMS scale in the 2f-CCP system.

[1] D. Kim and D. J. Economou, IEEE. Trans. Plasma Sci., vol. 30, no. 5, pp. 2048-2058, 2002.

[2] F. Hamaoka, T. Yagisawa, and T. Makabe, Jpn. J. Appl. Phys., vol. 46, no. 5A, pp. 3059-3065, 2007.

[3] -, IEEE Trans. Plasma Sci., (accepted for publication), Oct 2007.

11:00am **PS1-MoM10 Prediction of Feature Profile Evolution in Shallow Trench Isolation Etching*, J. Hoang***, *C.C. Hsu, J.P. Chang*, University of California at Los Angeles

Predictive modeling of feature profile evolution is critical to understand the complex plasma-surface interactions and aid the design of etch chemistry and development of etch systems. In this work, a direct simulation Monte Carlo (DSMC) method is used to develop a simulator that predicts profile evolution during shallow trench isolation etch (STIE) in Cl-based plasmas. Due to the discretized cells inherent in the model, a segmented surface advancement algorithm was developed to capture surface normals and particle fluxes. Plasma parameters such as particle densities and mean ion energy are determined from a reactor scale model, while ion energy distribution (IED) and ion angular distribution (IAD) are verified by a particle-in-cell (PIC) model.[1] A fractional factorial design of experiments determined major processing parameters affecting profile evolution in a Cl$_2$, O$_2$, and N$_2$ plasma in a dual coil inductively coupled plasma reactor. Out of seven parameters investigated, chamber pressure and DC ratio (current ratio of inner and outer coils) had the most effect on the feature side wall angle

(SWA), one of the most critical parameters defining the success of STIE. Additional experiments were performed to assess the effect of O_2 addition as well as to ascertain the effects of source power and DC ratio. Scanning electron microscopy (SEM) was used to assess the profile evolution in various plasma chemistries under different etch conditions. Slight microtrenching was observed in features etched by pure chlorine (no O_2) and was accurately predicted by the profile simulator, sampling only ions (Cl^+), neutral etchants (Cl), and a minute ratio of neutral passivants (e.g. $SiCl_2$). Changes in plasma density and substrate bias (translating to ion energy) were found to significantly alter the sidewall tapering and etch depth. The profile simulator captured these changes by determining the full-width half maximum of the IAD as a function of substrate bias and adjusting the neutral to ion ratio which is affected by pressure and source power. The erosion of the hard mask during STIE was found to occur in a high density plasma under high substrate bias, affirming an etching threshold energy of the hard mask, and the simulator successfully predicted the double facets on the hard mask and the resulting profile.

[1] A. C. F. Wu, M. A. Lieberman, and J. P. Verboncoeur, Journal of Applied Physics 101, 056105 (2007).

11:20am **PS1-MoM11 Investigation of Source and Bias Pulsing for High Aspect Ratio Silicon Etching**, ***G. Wenig***, *A. Kersch, W. Jacobs, S. Barth, A. Henke, J. Sobe, A. Steinbach, S. Wege*, Qimonda, Germany, *M. Reinicke*, Dresden University of Technology, Germany

Silicon etching based on a HBr/O2/NF3 plasma generated in a dual (2 and 60MHz) frequency capacitively coupled MERIE plasma reactor is used to fabricate DRAM trench capacitors. To maintain a constant capacitance per memory cell an optimum aspect ratio and trench shape with respect to capacitance and cost has to be achieved. In this contribution a high aspect ratio silicon etch selective to an oxide mask is studied with respect to the influence of pulsing the rf sources on the ion energy and angular distributions. Particle-in-cell and efficient hybrid fluid-kinetic simulations are used to investigate the consequences of source and bias pulsing. Both methods use identical ion-neutral collision models. The required differential cross sections have been computed ab initio. Charge exchange processes are treated with a constant charge exchange probability. The resulting ion and neutral distributions are used as input for a Monte Carlo simulation of particle transport in the trench. Pulsing frequencies, duty cycles, and phase shifts are varied separately. Modeling results and experimental data show the beneficial effects of pulsing on etch results.

11:40am **PS1-MoM12 Global Plasma Simulations using Dynamically Generated Chemical Models**, ***J.J. Munro***, *J. Tennyson*, University College London, England

Extensive molecular data is a key requirement in understanding modern technical plasmas. Here we present a method for coupling molecular data with chemical models and a global plasma simulation to enable rapid testing and evaluation of new plasmas. A global plasma model (GLOBAL_KIN[1]) is extended using an expert system 'Quantemol-P' to enable ad-hoc simulations using new plasma recipes. A set of atomic and molecular species to be considered in the plasma simulation is specified by the user. The expert system generates a complete set of reaction pathways for both the gas and surface reactions in a plasma. This set is pruned by discarding un-physical reactions and reaction data not appropriate to technical plasmas. Where data exists, a rate is calculated for the reaction at the plasma temperature so its importance can be evaluated. Where no data exists, a set of heuristics is used (based upon reaction type) to evaluate the reaction's importance. A user can adjust the species, gas phase reactions, surface reactions and plasma properties to control the simulation. The reaction list is populated with a database of molecular parameters and cross-sections; missing data can be calculated using a further expert system 'Quantemol-N'.[2] This applies the R-Matrix method, which has proven highly accurate for electron-molecule interactions.[3] In instances where this R-Matrix method does not apply, other methods such as the Binary Encounter Bethe model[4] maximize the range of cross-section data available. The method allows for rapid investigation of new plasma recipes with a greater level of flexibility than previously achievable. A simple plasma-etch example is presented to demonstrate the system.

[1] D.S. Stafford and M.J. Kushner, O2(1-delta) Production in He/O2 Mixtures in Flowing Low Pressure Plasmas, J. Appl. Phys. 96, 2451(2004).

[2] J. Tennyson, D.B. Brown, J.J. Munro, I. Rozum, H.N. Varambhia and N. Vinci, Quantemol-N: an expert system for performing electron molecule collision calculations using the R-matrix method, J. Phys. Conf. Series, (in press).

[3] H.N. Varambhia and J. Tennyson, Electron collision with HCN and HNC molecules using the R-matrix method, J. Phys. B: At. Mol. Opt. Phys. 40, 1211-1223 (2007).

[4] W. Hwang, Y.-K. Kim and M.E. Rudd, New model for electron-impact cross sections of molecules, J. Chem. Phys. 104(8), 2956-2966 (1996).

Plasma Science and Technology

Room: 607 - Session PS2+MS-MoM

Plasma Etching for Advanced Interconnects I

Moderator: V. Ku, Applied Materials

8:00am **PS2+MS-MoM1 Challenges for Microwave Plasma Etching of Low-k Dielectrics**, ***T. Nozawa***, *M. Inoue, T. Nishizuka*, Tokyo Electron LTD Japan **INVITED**

Meeting post 32 nm etch process integration requirements with porous SiCOH and conventional plasma sources is a challenge as the SiCOH surface is decomposed by reactions induced by electron, ion, radical and UV radiation exposure. This exposure is inherent to most plasma systems making it difficult to achieve both high precision and damage free etching. Neutral beam etching has been developed to provide ion and UV radiation free and therefore damage free etching processes. Neutral beam etching by itself lacks the benefits of energy and chemistry control afforded by in-situ plasma processes. A Radial Line Slot Antenna (RLSA) driven surface-wave-plasma at 2.45GHz generates very high density plasma with high electron temperature in a region limited to just below the dielectric plate through which microwave pass. Both chemistry and energy control are achieved with the RLSA configuration. Plasma is transported to the wafer by diffusive transport through a low electron temperature region. An electronegative precursor gas (e.g., C4F8) is injected into the low electron temperature region so that dissociation is not excessive and a substantial negative ion population is generated near the wafer. An RF bias frequency 400kHz through the wafer provides ion acceleration without plasma generation. The combination of the low electron temperature electronegative downstream plasma with the low driving frequency facilitates charge damage free etching for all process conditions. Another consequence of the combination of plasma conditions near the electrode is that physical damage of SiCOH material is eliminated and k-value increase is minimized. This is achieved through dissociation control which results in the population reduction of small very reactive species such as H* and F* and the retention of sidewall polymer integrity. The unique plasma characteristics of the RLSA system will be described in this presentation with an emphasis on process performance for post 32 nm node CMOS fabrication.

8:40am **PS2+MS-MoM3 High Frequency Capacitively Coupled Plasma for Low Ion Energy Dual Damascene Etching**, ***A. Marakhtanov***, *E.A. Hudson, K. Takeshita, O. Turmel*, Lam Research Corp.

Capacitively coupled discharges are widely used for semiconductor processing, especially in the area of dielectric etching. With a wide range of film materials and complex stacks including multiple mask layers, advanced dielectric etch processes require tight control of plasma parameters, such as ion flux, radical composition, and ion energy distribution (IED). This paper presents IED measurements and patterned-wafer etch results as a function of RF bias excitation frequency applied to the wafer electrode. The aim is to produce the optimal IED for etching of soft materials, such as low-k dielectrics commonly used in Dual Damascene interconnect schemes. One key challenge arises in the trench etch step, which requires a vertical etch profile in the low-k film. But the process must avoid corner faceting of any exposed via holes or of the hard mask layer which defines the initial trench pattern. Faceting would cause an increase in via or trench critical dimension, respectively. The competing requirements of vertical profile and minimal faceting define a fairly narrow range of acceptable ion energies for the process. If power is held constant, higher RF driving frequencies typically produce plasmas with higher densities and lower potentials, and enable operation at lower pressure. Both the mean ion energy and width of the IED reaching the wafer tend to decrease as the wafer bias frequency increases. For frequencies too low, the width of the IED is too large and faceting is induced by the high energy ions. For frequencies too high, the mean IED is too low to etch the low-k film with a vertical profile and acceptable rate. Results show that the necessary IED for these applications can be obtained by applying 60MHz to the wafer electrode.

9:00am **PS2+MS-MoM4 Energy Distribution of Bombarding Ions, Etch Selectivity and Profile Control in Plasma Etching of Dielectrics**, ***F.L. Buzzi***, *Y.-H. Ting, A.E. Wendt*, University of Wisconsin-Madison

The energy distribution of bombarding ions during plasma etching of dielectrics for microelectronics manufacturing affects both selectivity to photoresist and the profile shape of the etched feature. Here we examine the role of ion bombardment making use of an ability to produce either a narrow ion energy distribution (IED) at a specified energy, or a two-peaked distribution in which the energy and relative flux of the two peaks can be controlled. A system has been developed for manipulating the IED at the substrate during plasma etching by controlling the voltage bias waveform of the RF bias applied to the substrate. The output of a waveform generator drives a broadband power amplifier connected to the electrode, and is programmed in an iterative process to produce the desired substrate wave form. The iterative feedback process has recently been automated so that arbitrary waveforms can be quickly achieved. Waveforms to produce ions at the substrate with energies greater than 500 eV in single-peaked or two-peaked IEDs are now routinely produced, and are applied to etching of silicon dioxide in fluorocarbon-based gas mixtures. Prior studies with a single-peaked IED at energies below 200 eV showed significant improvements in etch selectivity compared to a sinusoidal bias producing a broad IEDF (Wang and Wendt, 2001, Silapunt et al., 2003). In this study, we will report on a systematic characterization of IED effects on blanket and patterned wafers. Results include the following: 1) effect of ion energy on photoresist and oxide etch rates for the narrow single-peaked IED at high energy, 2) effect of ion energy on photoresist roughening/distortion, to explore evidence of improved performance with higher energy ions, and 3) systematic study of the asymmetric bimodal IEDs as a function of the relative ion fluxes at the two energies, to examine the effect on etch rates for oxide and photoresist and etched feature profiles. The plasma system is equipped with a helicon plasma source operating at 13.56 MHz. The substrate electrode accommodates 4" diameter wafers, and is equipped with helium backside cooling and a thin film laser interferometer to monitor etch rates of blanket films. The chamber walls are heated externally to minimize process drift associated with wall temperature changes during plasma operation.

9:20am **PS2+MS-MoM5 Etch Plasma Chemistry and Film Variability Effects on Dual Damascene Patterning of Porous Ultra-low k Materials**, ***C.B. Labelle***, AMD, Inc., *J. Arnold*, IBM Research, *H. Wendt*, Infineon Tech., *R.P. Srivastava*, Chartered Semicon. Mfg Ltd., *K. Kumar, Y. Choi, H. Yusuff, S. Molis, C. Parks, C. Dziobkowski, M. Chace, A. Passano, L. Tai*, IBM Microelectronics, *D. Kioussis*, AMD, Inc., *J. Yamartino, D. Restaino, L. Nicholson*, IBM Microelectronics

Porous ultra low k dielectrics (k < 2.5) are being integrated into current and future technology nodes. A large focus of the integration of these films has been on the sensitivity of the films to compositional modification (i.e., carbon depletion) during resist strip in the dual damascene patterning scheme. As porous ultra low k dielectric strip processes have evolved and matured, new sensitivities have emerged which affect successful integration. This paper will discuss a case where, in a via-first-trench-last dual damascene integration scheme, the plasma chemistry used during via etch has been found to affect the profiles after trench etch when etching porous ultra low k dielectrics ("ULK via/trench interaction"). Modifications to the via etch plasma chemistry can be made to bring the trench profile back to target, but repeatability of the success of these workarounds is key. Variability in the film composition through the bulk of the film can also instigate post-etch profile changes or exacerbate the etch plasma-induced via/trench interaction. Data will be shown demonstrating the sensitivity of the etch processes to film composition variability. Possible mechanisms for the ULK via/trench interaction will also be discussed.

9:40am **PS2+MS-MoM6 Surface Roughening Mechanisms during Porous SiOCH Etching Processes**, *F. Bailly*, CNRS/IMN - France, ***T. David***, CEA/LETI-MINATEC - France, *T. Chevolleau, M. Darnon*, CNRS/LTM - France, *C. Cardinaud*, CNRS/IMN - France

Introducing dual damascene structures for the interconnections has been a means of improving their electrical performances. However, lowering the effective dielectric constant remains a major stake. Increase the porosity of the dielectric material or remove the trench bottom etch stop layer are some solutions. As a result, the trench etch process is stopped into the porous material which may lead to a tricky trench bottom roughness. In addition, sidewall metal diffusion barriers have to be thinned down to keep the copper line resistance low. In this context, the trench bottom roughness may also affect metal barrier coverage. In this study, roughness of dielectric materials is characterized by SEM and AFM after partial etching. Dielectric etching is known to be controlled by the thickness and composition of a fluorocarbon overlayer which depends on the plasma characteristics (etch chemistry…) and on the materials properties (composition, porosity,…). Thereby, in order to understand the mechanisms controlling the porous SiOCH roughening, different etch plasmas have been performed on materials with different percentages of porosity (7, 25 and 30%). For a high polymerizing ($CF_4/Ar/CH_2F_2$), a low polymerizing (CF_4/Ar) and a pure physical sputtering plasma (Ar), surface composition has been characterized by quasi in situ XPS and the roughness has been studied as a function of the etched thickness. Those experiments highlight different trends. Firstly, the 7 % porous SiOCH does not exhibit any significant roughness whatever the etching plasma (rms roughness = 0.5nm). Secondly, porous SiOCH with a higher porosity (25 and 30%) is roughened when exposed to fluorocarbon based plasmas. The resulting roughness increases linearly versus the etched thickness in the range of a tenth of nanometers. This increase is fast when the concentration of fluorocarboned species at the etched surface is low, while a higher amount of fluorocarboned species limits it. At last, sputtering of porous SiOCH using a pure Ar plasma, namely the absence of fluorocarboned species at the etched surface, leads to a surface as smooth as the pristine material (rms roughness = 0.2 nm). Those results highlight the critical role of porosity and the presence of fluorocarboned species on the dielectric surface roughening. On the basis of those observations, a hypothesis will be proposed for the initiation and maintaining of the dielectric roughness.

10:20am **PS2+MS-MoM8 Design for Manufacturability through Design-Process Integration**, ***A. Neureuther***, University of California, Berkeley **INVITED**

Exploratory prototype Design for Manufacturing (DFM) tools and methodologies are described. Examples will include new platforms for collaboration on process/device/circuits, visualization/quantification of manufacturing effects at the mask layout level, and fast/approximate physical modeling for first-cut design decisions. The examples have evolved from research supported over the last several years by DARPA, SRC, Industry and the U.C. Discovery Program on aberrations, illumination, polarization, CMP, plasma etching and device variation. DFM tools must enable complexity management with very fast approximate models across process, device and circuit performance with new modes of collaboration. Circuit Designers have good complexity management skills can add value by participating in this collaboration. Collaborations can be promoted by supporting multiple views of the trade-offs in terms of the natural intuitive parameters of each collaborator. Many of the nonidealities of manufacturing can be expressed at the mask plane in terms of lateral impact functions. This allows visualization and quantitative assessment of effects that are not easily captured even with large sets of design rules. Pattern Matching and Perturbation Formulation have promising exceptional speed and adequate accuracy for implementing these lateral impact assessments.

11:00am **PS2+MS-MoM10 Feature Profile Simulation for Organic Low-k Etching in 2f-CCP in H_2/N_2**, ***T.Y. Yagisawa***, *T. Makabe*, Keio University, Japan

As the size of ULSI continuously shrinks up to 45 nm in 2010 and multi-layer interconnect with more than 12 layers is applied, RC (resistance-capacitance) signal delay should be made smaller to meet the demand for higher performance of signal transmission. The dielectric constant of interlayer dielectric (ILD) can be reduced by lowering electric polarizability of the material. Alternatively introducing nano-holes within the material to reduce its density, decreases the k value. Increasing porosity is considered as a promising candidate for obtaining low-k ILD, though it may bring up new serious problems in its processing. Materials with low dielectric constant tend to possess poor mechanical strength and adhesiveness to the wire. In addition, low-k dielectric has low heat conductance and low resistance against heat, which makes it difficult to go through the post annealing in back-end processes. Currently, H_2/N_2 plasma is developed as the most suitable tool for the etching of organic low-k material. The etching profile is determined under the balance among isotropic etching by reactive H radical, physical sputtering by energetic ions and surface protection by the deposition of N radical. In order to attain the optimal profile, detailed understanding of these elements throughout the whole plasma etcher is strongly required. We have developed an integrated simulation consisting of the flux-velocity distribution of reactive species and the feature profile evolution of organic low-k etching in two frequency capacitively coupled plasma (2f-CCP) in the admixture of H_2/N_2.[1] In the present study, we will first estimate the density of reactive species, such as H, N and NH_x radicals, generated mainly via direct dissociation from parent gas molecules. Further, the effect of dissociation degree on the etching profile will be discussed as a function of the mixture ratio of feed gases.

[1] K. Ishihara et. al., Plasma Physics and Controlled Fusion, 48, B99 (2006).

11:20am **PS2+MS-MoM11 Removal of Scallops formed during Deep Via Etching for 3D Interconnects**, ***Y.-D. Lim***, *S.-H Lee, C.-H. Ra, W.J. Yoo*, Sunkyunkwan University, Korea

Three dimensional (3D) integration using chip-to-chip interconnects is currently receiving great attention since it can bring about substantial advantages in high packing density, low power consumption and high speed operation over planar circuits integration. Deep etching of high aspect ratio vias is known be the most critical step to realize the 3D interconnects. When the Bosch process which alternately introduces SF6 for isotropic etching and C4F8 for sidewall passivation is implemented to form deep via holes, the formation of scallops along the sidewall is unavoidable and poses a serious obstacle to scale down design rule in this scheme. In this work, we investigated methods to remove scallops using post O2 based plasma treatment assisted by subsequent HF based wet etching treatment, when inductively-coupled plasma etching had been applied to form various via hole sizes down to 2.5um with depths up to 100um. According to the experimental results, the removal of scallops was dependent on the via hole size, the orientation of scallop directed out of the sidewall, the combination of the post plasma etching chemistry and the subsequent wet etching chemistry, and the profile of etched structure. Furthermore, it was found that the removal of scallops is more effective for vias of larger and for more vertical structures. The technology developed in this work was proven to be suitable for subsequent electroplating of Cu interconnects.

11:40am **PS2+MS-MoM12 High-rate Deep Anisotropic Silicon Etching with the Expanding Thermal Plasma Technique**, ***M.C.M. van de Sanden***, *M.A. Blauw,* Eindhoven University of Technology, Netherlands, *F. Roozeboom,* NXP Semiconductors Research, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Emerging microsystem and 3D interconnect technologies require high anisotropic etch rates to accommodate Si etch depths exceeding 200-300 µm and aspect ratios higher than 10. Using inductively coupled plasma (ICP) reactors there has been a steady improvement of the performance of deep anisotropic Si etching, however, it is unclear whether sufficiently high etch rates can be obtained by continuous innovation of the existing ICP technology. Following our work on high-rate deposition of a wide variety of materials, we have explored deep anisotropic Si etching with the expanding thermal plasma (ETP) technique using fluorine-based chemistries. The ETP technique consists of a remote high-density plasma source and due to a low downstream electron temperature (< 0.3 eV) it has a good control of the plasma chemistry and ion energy. Both a cryogenic etching process and a time-multiplexed etching process were developed using SF_6-O_2 and SF_6-C_4F_8 etch chemistries, respectively. The ion energy was controlled by employing several substrate biasing schemes, including rf and pulse-shape biasing. In this contribution we will present data on etch rates, anisotropy, and selectivity with regard to the hard mask and it will be demonstrated that etch rates up to 12 µm/min and selectivities higher than 300 can be obtained by the ETP technique. Insight in feature profile control will also be presented and it will be shown that feature profiles are comparable to those obtained with ICP reactors. This novel, ETP-based deep anisotropic silicon etching technique might therefore be an attractive alternative for the fabrication of silicon microstructures with high-aspect-ratio features.

Advanced Surface Engineering

Room: 617 - Session SE-MoM

Hard and Nanocomposite Coatings: Synthesis, Structure, and Properties

Moderator: M.S. Wong, National Dong Hwa University, Taiwan

8:00am **SE-MoM1 Thermal Stability of TiAlSiN and CrAlSiN Thin Films**, ***Y.-Y. Chang***, *C.-P. Chang,* Mingdao University, Taiwan, *S.-M. Yang,* National Chung Hsing University, Taiwan, *D.-Y. Wang,* Mingdao University, Taiwan, *W. Wu*, National Chung Hsing University, Taiwan

Binary CrN and ternary TiAlN coatings attracted considerable industrial interest, because of their excellent tribological performance and high oxidation resistance at high temperature. Recently, TiAlSiN and CrAlSiN coatings have been developed in order to possess high hardness and good chemical stability at temperature exceeding 1000 °C. These properties are very important in developing new generation superhard and wear-resistant coatings for high speed and dry machining applications. In this study, a series of CrN, TiAlN, TiAlSiN and CrAlSiN coatings were deposited onto silicon substrate by a cathodic arc evaporation system using a lateral rotating arc source. Owing to the different oxidation behavior and decomposition of CrN, TiAlN, TiAlSiN and CrAlSiN coatings, the as-deposited films were annealed at 900 °C and 1100 °C in air atmosphere for duration of 2 hours. During the annealing process, Ti, Al, and Si would diffusion outward to form the oxidative layers of Al_2O_3, TiO_2, and SiO_2 or others at high temperature. Cr, Al, and Si would diffusion outward to form the oxidative layers of Al_2O_3, Cr_2O_3, and SiO_2 or others at high temperature. Therefore, the mechanical property varied with the phase segregation via heat-treatment caused the deposited films destruction. The correlation between oxidative layer and the deposited films will be discussed. The chemical depth profile of the deposited coatings was determined by Secondary Ion Mass Spectrometry (SIMS). X-ray diffractometry was performed using PANalytical X'pert Pro diffractometer with a high resolution ? goniometer and Cu radiation in both glancing angle and high-angle configurations for phase identification. The microstructure was investigated by field emission gun high resolution transmission electron microscopy (FEG-HRTEM, FEI Tecnai G^2 20 S-Twin) equipped with an energy-dispersive x-ray analysis spectrometer (EDS), operated at 200 keV for high-resolution imaging.

8:20am **SE-MoM2 Si Influence on Thermal Stability, Microstructure, and Hardness of Arc Evaporated Ti-Si-N Thin Films**, ***A. Flink***, Linköping University, Sweden, *J. Sjölen, T. Larsson, L. Karlsson,* SECO Tools AB, Sweden, *L. Hultman*, Linköping University, Sweden

$Ti_{1-x}Si_xN_y$ ($0 \leq x \leq 0.22$) thin solid films were deposited by arc evaporation onto WC(Co) and c-BN substrates. Elastic recoil detection analysis revealed an N increase with increasing Si content. X-ray diffraction and transmission electron microscopy showed that as-deposited films contain a NaCl-structure phase with a lattice parameter similar to TiN, 4.24 Å. The films exhibited a competitive columnar growth mode where the structure transits to a defect-rich feather-like nanostructure with increasing Si content. As-deposited TiN exhibited random crystallographic orientation, which gradually changed to an exclusive <200> texture for x>0.05. The highest hardness, 42.8±2.1 GPa, was achieved for x=0.14, which was significantly higher than 29.8±1.5 GPa for TiN. The hardness increase is attributed to solid-solution and defect hardening. The hardness was retained for an annealing temperature of 1000°C for $0.05 \leq x \leq 0.10$, but decreased to below 28 GPa for all other compositions due to recrystallization within the cubic state together with Co and W interdiffusion from the substrate via the grain boundaries. Furthermore, the Si content decrease for the films annealed at 1000°C to x=0.14. Residual stresses were measured with the $\sin^2\psi$-method and differential scanning calorimetry was performed in order to investigate phase transformations.

8:40am **SE-MoM3 Nanostructured PVD Hard Coatings in Industrial Research and Application**, ***J. Vetter***, Sulzer Metaplas GmbH, Germany **INVITED**

The improvement of the overall coating performance of wear protecting PVD coatings concentrates to achieve lower friction values, better thermal stability , optimization of hardness and toughness and higher oxidation stability. The aim of these improvements is to get a higher performance of tools and parts of components. Nowadays composite materials having structures in the nanometre dimensions are in the scope of industrial applications. Different coating architectures were developed in industrial scale: isotropic composites coatings, gradient nano composite coatings and nano multilayer coatings. Modern industrial PVD systems are designed to deposit these types of sophisticated coating architectures. Both arc evaporation and magnetron sputtering and its combinations are suitable to create nano structures. The coating processes to deposit nano structured coatings will be discussed in more detail and it will be shown that the analytical methods for coating development and production control have to be shifted toward a nanostructure compatible level.

9:20am **SE-MoM5 Lubricant-Friendly MoN-Cu Coatings for Extreme Tribological Applications**, ***A. Erdemir***, *O.L. Eryilmaz,* Argonne National Laboratory, *M. Urgen, M.K. Kazmanli*, Istanbul Technical University, Turkey

In this paper, we describe molecular level design and synthesis of a series of nanocomposite coatings providing extreme resistance to wear and scuffing and very low friction in lubricated test environments. The ingredients or chemistry of nanophases in these films were selected strategically so that during lubricated contacts, they can form low-shear and protective boundary films by favorably reacting with some of the additives in formulated oils. Among others, MoN-Cu coatings had the greates beneficial effects in lowering friction and increasing resistance to wear and scuffing. In fact, these films were impossible to scuff even under the maximum loading and sliding conditions that we could establish in our test machines. In this paper, we will present the main characteristics of these nanocomposite coatings and discuss in details the fundamental tribological mechanisms that control their superior friction, wear, and scuffing behaviors under severe sliding conditions.

9:40am **SE-MoM6 Effect of the Microstructure on the Mechanical and Tribological Properties of Cr-Si-N Coatings Prepared by Reactive Sputtering**, *M. Benkahoul, P. Robin, L. Martinu,* ***J.E. Klemberg-Sapieha***, Ecole Polytechnique, Canada

Cr-Si-N thin films were deposited by pulsed DC reactive dual magnetron sputtering with different concentrations of Si. Microstructural evolution and mechanical properties of these thin films were studied using XRD and nanoindentation measurements. Three regions of different Si concentration [Si] were distinguished: For [Si] < 2.3 at.%, the grain size (D) doesn't significantly change with increasing [Si]. For 2.3 < [Si] <7 at.%, D decreases as [Si] increases. At higher [Si], a relatively rapid decrease of D is observed with increasing [Si]. Nanohardness (H) behaviour of these thin films as a function of [Si] is comparable to that observed in the Me-Si-N (Me: Ti, Nb, Zr,…) nanocomposite materials. For [Si] ~2.3 at.%, H is 24 GPa, H3/Er2 ~ 0.24 GPa, and the elastic recovery, We ~ 60%, is comparable with CrN, for which H ~ 18 GPa, H3/Er2 ~ 0.1 GPa, and We ~ 35%. Based on the evolution of the microstructure of these films, solid solution hardening is proposed as the main mechanism to explain the changes observed for [Si] < 2.3 at.% in the Cr-Si-N films, rather than the nanocomposite structure. Subsequently, we systematically studied the deposition of Cr-Si-N films on SS410 steel using a duplex treatment consisting of surface nitriding and deposition of a Cr bond coat. The influence of [Si] on the tribological properties of the Cr-Si-N coatings was found to lead to a reduction of the wear coefficient by a factor of 100 compared to bare SS410 substrate.

10:20am **SE-MoM8 Infrared-Reflecting Thin Film Coatings**, ***A.N. Ranade***, *M.E. Graham, Y.W. Chung*, Northwestern University

The heating of vehicles such as cars and planes is directly dependent on the absorption of solar radiation. Approximately half of the energy that is incident upon vehicles can be attributed to near infrared (IR) radiation of wavelengths in the range of 800-1600 nm. Reflecting instead of absorbing IR radiation would lower cabin temperatures considerably, thereby improving passenger comfort and fuel economy. An inorganic coating that is transparent to visible, absorbing to UV, and reflecting to IR radiation is desired to meet these goals. Doping a TiO_2 matrix with well-dispersed metal atoms produces a film that acts as a plasma with specific electromagnetic properties. By controlling the metal atom concentration, one can tune the wavelength at which electromagnetic radiation is reflected. This paper discusses the properties of TiO_2 films doped with varying metal atom concentrations. The films are made by reactive magnetron sputtering and evaluated by AFM (surface roughness), XRD (structure), and UV-VIS-IR spectroscopy (optical properties).

10:40am **SE-MoM9 Optically Transparent Nanocomposite Thin Films: the System Al-Si-N**, *A. Pelisson, M. Parlinska-Wojtan, P. Schwaller, H.J. Hug*, ***J. Patscheider***, EMPA, Switzerland

Transparent nanostructured coatings of Al-Si-N were deposited by reactive DC magnetron co-sputtering of Al and Si targets in an Ar/N_2 atmosphere at substrate temperatures between 200 and 500°C. The elemental composition was varied from pure AlN to Al-Si-N with 30 at.% of Si. The coatings were characterized by XPS, TEM, XRD, nanoindentation and UV-Visible spectroscopy. X-ray diffraction results suggest that the coatings consist of nanocrystalline h-AlN with substitutionally incorporated silicon for Si concentrations below 13 at%. At Si concentrations exceeding 13 at% the coatings are X-ray amorphous. In contrast to known silicon-containing ternary nitrides and to available thermodynamical data for the Al-Si-N system, this material shows no clear phase segregation during deposition into AlN and SiNx; instead an Al1-xSiNx solid solution is formed that coexists with SiN_x for silicon concentrations above 6 at% Si. XRD and TEM analysis show that the crystalline material consists of elongated grains; the crystallite size decreases from 60 nm to about 10 nm upon addition of silicon. The average optical transparency of 1 micron thick coatings in the visible range of light approaches 100%. The hardness exceeds 30 GPa, with a weak maximum at 8-12 at.% of Si which corresponds to the lowest internal stress in the coatings (= 0.5 GPa). At this composition the elastic strain to failure H/E, or resilience, is increased by 50% by the addition of silicon to AlN.

11:00am **SE-MoM10 Atomistic Processes during Synthesis of Hard Coatings Revealed by STM and LEEM**, ***I. Petrov***, University of Illinois at Urbana-Champaign **INVITED**

Transition-metal nitrides, such as TiN, have a wide variety of applications as hard, wear-resistant coatings, as diffusion barriers, and as scratch-resistant and anti-reflective coatings in optics. Understanding the surface morphological and microstructural evolution of these materials is crucial for improving the performance of devices. Studies of surface step dynamics enable determination of the rate-limiting mechanisms, corresponding surface mass transport parameters, and step energies. However, most models describing these phenomena are limited in application to simple elemental metal and semiconductor surfaces. We summarize recent progress toward elucidating the interplay of surface and bulk diffusion processes on morphological evolution of compound surfaces. Specifically, we analyze the coarsening/decay kinetics of two- and three-dimensional TiN(111) islands and the effect of surface-terminated dislocations on TiN(111) steps. Further, in an attempt to gain better understanding of the origin of TiN-SiNx superhardness, we use in-situ STM and LEED to investigate the atomic-scale structure of the SiNx/TiN interface, of which very little is known. SiNx overlayers were grown onto single-crystal TiN(001) or TiN(111) substrates at temperatures between 700 and 900 ºC. We show both topographic (STM) and diffraction (LEED) evidence that (a) SiNx overlayers on TiN are crystalline with reconstructions including 2x2, c-3x3, and 1x5, depending upon SiNx coverage, surface orientation, and annealing temperature; and (b) TiN grows epitaxially on top of the SiNx layers. Specifically, our results show that for SiNx coverages near 1ML, where maximum TiN-SiNx hardness is attained, the SiNx layer is not amorphous as deposited. Finallly, we will describe a design of a tandem instrument combining a low-energy electron microscope (LEEM) and a negative ion accelerator. This instrument provides video rate imaging of the dynamics of surface microtopography evolution during irradiation by energetic ions, at temperatures up to 1500 K. We will present in-situ real-time atomic-scale studies of energetic epitaxial film growth and etching.

11:40am **SE-MoM12 A Novel Form of Hard Hydrogenated Amorphous Carbon Grown under High Rate Conditions**, ***S.V. Singh***, *M.A. Creatore*, Eindhoven University of Technology, The Netherlands, *R. Groenen, K. van Hege*, NV Bekaert SA, Belgium, *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

A novel form of diamond-like hydrogenated carbon deposited utilizing the expanding thermal remote Ar/C_2H_2 plasma is reported. The plasma is generated in a cascaded arc at subatmospheric pressure in argon. The discharge expands into a low pressure (remote) chamber where acetylene is introduced downstream by means of an injection ring. The downstream plasma is characterised by a low electron temperature which leads to ion driven chemistry and negligible physical effect like ion bombardment (< 2 eV) on the substrate. Distinct from previous works, relatively low argon to acetylene gas flow ratio has been used in this study. Infrared absorption shows a reduced concentration of CH stretching and in addition, it is also evident that the endgroups (sp^2 - CH_2 and sp^3 - CH_3) are absent in the films. Theses films posses relatively low optical band gap and hydrogen content, high refractive index and a nanohardness exceeding 16 GPa. Further characterizations by means of Raman spectroscopy, spectroscopic ellipsometry (SE) and Rutherford back scattering (RBS) indicate that the films are well cross-linked graphite like hydrogenated amorphous carbon. The film properties will be interpreted in view of the specific plasma chemistry taking place in the expanding thermal plasma.

Surface Science

Room: 608 - Session SS1-MoM

Catalysis on Clusters and Nanoparticles

Moderator: M. Mavrikakis, University of Wisconsin - Madison

8:00am **SS1-MoM1 Platinum Nanoparticle Shape and Stabilizing Agent Effects on Catalysis**, ***K.M. Bratlie***, *H. Lee, P. Yang, K. Komvopoulos, G.A. Somorjai*, University of California, Berkeley

Our goal is to understand the behavior of real catalyst systems on a molecular level. To accomplish this task, a model system of capped platinum nanoparticles on a silica substrate is used. The nanoparticles exhibit a narrow size distribution and well defined shape. We were able to monitor two different shapes: cubes, comprised of {100} facets, and cuboctahedra, made of {111} and {100} facets. We were also able to investigate the influence of the capping agent on the catalytic activity of the particles. Kinetic studies of benzene hydrogenation on platinum nanoparticles over a range of temperatures (310 - 400 K) were used to relate nanoparticles to single crystals. In this manner, we uncovered implications for reaction mechanisms nanoparticle surfaces identical to analogous single crystal faces.

8:20am **SS1-MoM2 Catalytic Properties of Pt Nanoparticles on HOPG**, ***J. Nakamura***, *K. Izumi, Y. Iwasaki, T. Kondo*, University of Tsukuba, Japan

Reduction in Pt usage is one of the key requirements for the commercialization of polymer electrolyte fuel cells (PEFCs) for use in everyday life, because of its high price and limited availability, and the difficulty of finding suitable substitutes. We have reported that use of carbon nanotube (CNT) as an electrode material results in high performance with low loading of Pt. That is, the electric power of 12 wt% Pt/CNT was found to be higher than that of 29wt% Pt/carbon black. Moreover, we have observed that RuPt/CNT catalysts show higher tolerance for CO poisoning compared to RuPt/carbon black(CB) catalysts. We have thus found superior performance of CNT as a support material. The CNT used is thicker tubes with diameter of 50-80 nm compared to single wall CNT (0.7-1.5 nm). The diameter of catalyst particles ranges from 2 to 8 nm. The use of thick CNTs in PEFC is very promising because the price is going down recently. Why does CNT show good performance as a support material? There are several physical and chemical reasons. Here, we emphasize the chemical aspect of the interface between catalysts and carbon electrode. That is, difference between CNT and generally used carbon black (CB) is the surface of carbon, at which catalyst particles are attached and electron flows. The surface of thick CNT can be regarded as basal plane of graphite, while the surface of CB is composed of edges of graphene sheets. We thus use a model system of metal catalysts/HOPG (Highly oriented pyrolytic graphite). STM observation shows that Pt particles are attached like two dimension islands on HOPG instead of spherical particles. XPS measurements show that Pt 4f core level is shifted to higher energy compared to bulk Pt. The 2-d Pt particles on HOPG show very high catalytic activity for H2-D2 exchange reaction at high pressures (24 Torr). However, the catalytic activity is reduced by a factor of 30-50 upon heating above 320 K in the presence of hydrogen although no decrease in the amount of Pt is observed by the heating. This is consistent with lower peak temperature shift in TPD of H2 from Pt on HOPG. The change in the catalytic properties of 2-d Pt particles can be ascribed to electronic modification due to a lattice strain of 2-d Pt islands on HOPG. This explains the support effect of carbon supported fuel cell catalysts, that is, Pt/CNT described above.

8:40am **SS1-MoM3 Environmental Effects on Morphology of Oxide Supported Gold Nanoparticles*, S. Shaikhutdinov***, Fritz-Haber Institute, Germany

Metal particles deposited on thin oxide films have been shown to be suitable model systems for studying structure-reactivity relationships of metal catalysts. In this paper, the morphology of Au particles deposited on thin FeO(111) and CeO2(111) films at elevated (up to 10 mbar) pressures of H2, CO, O2 and CO+O2 has been examined using in situ STM at room temperature. The Au particles are found to be fairly stable in oxygen and hydrogen environments. However, in CO+O2 (and CO) atmospheres, the destabilization of Au particles located at the step edges occurs leading to the formation of mobile Au species, which migrate across the oxide surface. General problems encountered with high-pressure STM studies will be also discussed, in particular trace impurities of the gas feedstock may play a big role in system behaviour and data interpretation.

9:00am **SS1-MoM4 The Growth and Characterization of Bimetallic Nanoclusters on Oxide Surfaces: Au-Pt on TiO_2(110)**, ***J.B. Park***, *D.A. Chen*, University of South Carolina

Gold (Au) nanoclusters deposited on TiO2 supports have been shown to be excellent catalysts for various oxidation reactions such as propylene epoxidation and CO oxidation. The size of the nanoclusters is known to be the most critical factor for their unique catalytic activity. However, Au nanoclusters sinter rapidly at elevated temperature, losing their catalytic activity. In this study, we have investigated how the rate of sintering can be controlled by adding Pt to Au nanoclusters since pure Pt nanoclusters are less sintered than pure Au due to stronger metal-metal bonds. As a model system, Pt and Au nanoclusters were deposited on a single crystal TiO2(110) substrate and investigated by STM, XPS, LEIS, and TPD in UHV. When Au is deposited on Pt clusters, Pt nanoclusters act as seeds for Au nucleation. However, for Pt deposition on Au, the Au clusters do not nucleate the growth of bimetallic Au-Pt clusters. The extent of cluster sintering at 1000K decreases with increasing Pt composition within the clusters. Intermixing of Au and Pt occurs readily at room temperature; for bimetallic Au-Pt clusters prepared by depositing Au on Pt, the surface contains a significant fraction of Pt atoms, despite immiscibility of Au and Pt and lower surface free energy of Au.

9:20am **SS1-MoM5 The Fabrication and Reactivity of Anchored Metal Nanoparticles on TiO_2(110)***, **M. Bowker***, Cardiff University, UK**INVITED**

We have investigated the interaction of Pd particles with the TiO2(110) surface in some detail using high temperature STM, XPS and a molecular beam reactor. Upon formation of nanoparticles at low anneal temperatures (<600K), a high adsorption probability of CO is found, much higher than expected from the fraction of the surface covered by Pd. This is due to the influence of a precursor state; this is a weakly-held form of CO on the support, which has a short lifetime at 300K (~ 1 micros), but which can nevertheless find nearby Pd nanoparticles (at which it gets trapped) by surface diffusion, which is extremely efficient. Nonetheless the CO is actually held more weakly on the nanoparticles than on bulk Pd, due, we believe, to modifications of the Pd by the presence of Ti in the surface of the particle. Upon heating to only 700K, the CO is further destabilised on the Pd, such that the sticking probability and uptake become very low; this is NOT due to sintering which is minimal at this temperature. Investigation by XPS shows that Ti has migrated onto the surface of the Pd as the surface was heated. From the chemical shifts this Ti is probably present as surface TiO, with Ti in the 2+ oxidation state. STM shows that, at least for surfaces annealed above 700K, beautiful ordered structures of the surface layer are formed, with large unit cells. The two main structures are a pinwheel and a zig-zag. In this talk I will try to assign the detailed structures of these layers which is proposed to be intermetallic-like, with the two structures being very specific intermetallics with Pd:Ti ratios of 1:1 and 2:1 respectively. This material causes the loss of activity seen for CO adsorption and for catalysis.

10:20am **SS1-MoM8 Enhanced Bonding of Gold Nanoparticles on Oxidized TiO_2(110)**, *S. Wendt, **J. Matthiesen**, D. Matthey, J.G. Wang, R. Schaub, E. Lægsgaard, B. Hammer, F. Besenbacher*, University of Aarhus, Denmark

Finding of distinctive catalytic properties of dispersed gold nanoparticles on oxide supports has stimulated extensive research activities, and a general consensus now exists on several aspects of this system. The size of the gold particles significantly affects the catalytic activity, and the gold clusters must be smaller than 5 nm for high catalytic activity.[1,2] The choice of the oxide support influences the catalytic activity, so there is a strong ‘support effect’ in addition to the ‘size effect’.[1] However, the relation of the adhesion properties of nanosized gold with catalytic activity is still unresolved. We studied the nucleation of gold clusters on TiO_2(110) surfaces in three different oxidation states by high-resolution scanning tunneling microscopy (STM). The three TiO_2(110) supports chosen were (i) reduced having bridging oxygen vacancies, (ii) hydrated having bridging hydroxyl groups, and (iii) oxidized having oxygen ad-atoms.[3] At room temperature gold clusters nucleate homogeneously on the terraces of the reduced and oxidized supports, while on the hydrated TiO_2(110) surface clusters form preferentially at the step edges. From interplay with density functional theory (DFT) calculations, we identified two different gold - TiO_2(110) adhesion mechanisms for the reduced and oxidized supports. The adhesion of gold clusters is strongest on the oxidized support, and the implications of this finding for catalytic applications are discussed.[4]

[1] Meyer, R., Lemire, C., Shaikhutdinov, Sh.K., Freund, H.-J., Gold Bulletin 37 (2004) 72-124.

[2] Valden, M., Lai, X., Luo, K., Guo, Q., Goodman, D.W., Science 281 (1998) 1647-1650.

[3] Wendt, S., Schaub, R., Matthiesen, J., Vestergaard, E.K., Wahlström, E., Rasmussen, M.D., Thostrup, P., Molina, L.M., Lægsgaard, E., Stensgaard, I., Hammer, B., Besenbacher, F., Surf. Sci. 598 (2005) 226-245.

[4] Matthey, D., Wang, J. G., Wendt, S., Matthiesen, J., Schaub, R., Lægsgaard, E., Hammer, B., Besenbacher, F., Science 315 (2007) 1692 - 1696.

10:40am **SS1-MoM9 Tuning the Properties of Gold Atoms and Clusters on MgO by Film Thickness**, ***T. Risse**, M. Sterrer, M. Heyde, N. Nilius,* Fritz-Haber-Institut der MPG, Germany, *G. Pacchioni,* Universita di Milano-Bicocca, Italy, *H.-J. Freund*, Fritz-Haber-Institut der MPG, Germany

The catalytic activity of Au clusters deposited on oxide supports is extensively studied in recent years. There is evidence that the charging of Au particles may play an important role in this respect. In particular, combined theoretical and experimental evidence shows that nucleation of Au clusters at point defects of MgO leads to a charging of the particles and this may be connected with the enhanced catalytic activity in low-temperature CO oxidation. According to theoretical calculations a similar charging is expected for Au deposits on very thin MgO films of a few monolayer.[1,2] In this contribution we present a low-temperature scanning tunneling microscopy investigation on the properties of gold atoms and clusters adsorbed on ultrathin MgO films grown on a Ag(001) single crystal surface. The gold adsorption was studied at 5-10 K using MgO films of different thickness to provide experimental evidence for the theoretically predicted charging of gold atoms and clusters on very thin films. The adsorption of Au on a 3 ML thin MgO film leads to a preferential ordering of Au atoms revealing a repulsive interaction between the Au atoms which is consistent with the expectation for charged atoms. On the contrary Pd atoms which are predicted to be neutral show a statistical nucleation behavior. In addition, it is found that the adsorption sites of Au atoms change when changing the thickness of the MgO film from 8 ML to 3 ML perfectly in line with the theoretical predictions. Whereas Au clusters on bulk MgO or thick films are expected to grow as 3-dimensional islands, their counterparts on thin MgO films are expected to from 2-dimensional islands. Annealing experiments of Au deposited at 5-10 K show that this crossover in dimensionality does exist for Au particles in the thickness range of 3 ML to 8 ML of the MgO films.

[1] G. Pacchioni, L. Giordano, M. Baistrocchi, Phys. Rev. Lett. 94, 226104 (2005).

[2] D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. 97,036106 (2006).

11:00am **SS1-MoM10 Catalytic Dehydration of Alcohols on TiO_2(110) and $(WO_3)_3/TiO_2$(110) Model Catalysts**[1], ***Y.K. Kim***, University of Texas at Austin, *B.D. Kay,* Pacific Northwest National Laboratory, *J.M. White,* University of Texas at Austin, *Z. Dohnálek*, Pacific Northwest National Laboratory

The catalytic dehydration of alcohols on rutile TiO_2(110) and on monodispersed $(WO_3)_3$ clusters on TiO_2(110) was studied using reactive scattering and temperature-programmed desorption (TPD). Two distinct dehydration channels, one at low temperature (LT) and the other at high temperature (HT), are observed on TiO_2(110). The LT and HT channels are shown to be related to reactions on the Ti^{4+} rows and on the vacancies of bridge-bonded oxygen (BBO) rows, respectively. The dehydration rates are shown to be influenced by the inductive and steric effects introduced by the hydrocarbon chains of the reacting alcohols. For the $(WO_3)_3/TiO_2$(110) model catalyst, we find a dramatic increase in catalytic activity compared to bare TiO_2(110). The quantitative correlation between the coverage of $(WO_3)_3$ clusters and the dehydration yield indicates that the W^{6+} Lewis acid sites are involved in the reaction.

[1] The research described in this presentation was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

11:20am **SS1-MoM11 Hot Electron Flow and Chemical Reactivity on Colloid Nanoparticles on Metal-Semiconductor Catalytic Nanodiodes**, ***J.Y. Park***, *J.R. Renzas, B. Hsu, Y. Zhang, H. Lee., P. Yang, G.A. Somorjai*, Lawrence Berkeley National Laboratory and University of California, Berkeley

Atomic or molecular processes in metals can generate flows of hot electrons with kinetic energy of 1-3 eV, and mean free path of about 10 nm. The electron flow is detected as a chemicurrent if the excess electron kinetic energy generated by the exothermic reaction is larger than the effective Schottky barrier formed at the metal-semiconductor interface. Detection of hot electron flows could allow us to understand the role of electronic energy dissipation and charge transport through the metal-semiconductor interface in exothermic metal catalyzed reactions. We fabricated nanoparticle-nanodiode hybrid systems composed of metal (Pt and Rh) nanoparticles (size 3-13 nm), an Au thin film (2 nm thick), and TiO_2. The interface between Au and TiO_2 forms a Schottky barrier with an energy barrier of 1.0 eV. Hot electrons are generated on the surface of the metal nanoparticles, scatter into the Au thin film, and go over the energy barrier between Au and TiO_2. The overall thickness of the metal assembly (nanoparticles and Au thin film) is comparable to the electron mean free path, resulting in the ballistic transport of hot electrons through the metal and into the semiconductor. The chemicurrent and chemical reactivity we measured using nanoparticles with sizes of 3-14 nm, and with various capping agents (citrate (trisodium citrate), PVP (polyvinylpyrrolidone), Ctab (tetradecyltrimethylammonium bromide), hexadecylamine, and hexadecylthiol) during catalytic CO oxidation (at pressures of 100 Torr of O_2 and 40 Torr of CO at 373 ~513 K). We found that chemicurrent and chemical reactivity depend significantly on the choice of capping layer. While nanoparticles with the citrate capping agent exhibit the highest chemical reactivity and chemicurrent, hexadecylamine, and hexadecylthiol capped nanoparticles shows low reactivity and chemicurrent. We will discuss the size dependence of nanoparticles on the chemicurrent yield. The influence of charging of capping layers on the hot electron transport during the catalytic reaction will be also discussed.

11:40am **SS1-MoM12 TiO_2 with Buried Ag Nanoclusters for Photocatalysis**[1], *F. Wang, A.K. Sekharan, B.M. Watson, O. Kizilkaya, P.T. Sprunger,* ***R.L. Kurtz***, Louisiana State University

Many metals readily form nanoclusters on TiO_2 and these clusters can have unusual optical and catalytic properties. The lifetime of these clusters can be limited when exposed to an electrochemical environment, so it can be desirable to bury these metallic clusters in a protective oxide layer. Although the clusters do not participate directly in chemical reactions, optical excitations allow them to provide hot electron-hole pairs to the near surface region to stimulate surface chemistry. We will present a multiple-technique surface study of overcoating Ag nanoclusters on TiO_2(110) with titania using STM, EELS and synchrotron-based resonant photoemission. STM measurements show that Ag readily forms 5-10 nm clusters on TiO_2(110) and EELS measurements show that the bare clusters on TiO_2(110) exhibit a sharp plasmon resonance at 3.7 eV. As the cluster density increases, the underlying substrate bandgap is reduced while the bandgap excitation cross-section increases. These Ag clusters are then buried by coating with a thin layer of Ti that is subsequently oxidized. Within the dielectric medium of the oxide, the plasmon resonance is broadened and red-shifted as shown by EELS. Synchrotron-based resonant photoemission has been used to study the electronic structure of the clusters, both bare and with and the titania overcoat. The valence electronic structure and the origin, whether Ti or Ag-induced, of the bandgap defect states within the titania are identified by tuning over photoemission resonances. The role of these bandgap states in determining the surface optical properties and photochemistry will be discussed.

[1] We would like to acknowledge the support of the LSU CAMD synchrotron light source and the support of NSF through CHE-0615606.

Surface Science

Room: 611 - Session SS2-MoM

Surface Structure, Growth, and Etching of Silicon and Germanium

Moderator: S. Chiang, University of California, Davis

8:00am **SS2-MoM1 Combined Scanning Tunnelling Microscopy and Stress Measurements to Elucidate the Origins of Surface Forces During the Oxidation of Si(111)-7x7**, ***N.T. Kinahan***, *D.E. Meehan,* Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland, *T. Narushima, K. Miki,* National Institutes of Natural Sciences, Japan, *J.J. Boland*, CRANN & Trinity College Dublin, Ireland

The oxidation of silicon surfaces has been widely studied due to its scientific and technological importance. However, despite extensive experimental and theoretical studies, the details of the oxidation reaction are not yet fully understood. It has recently been suggested that surface stress measurements may prove useful in elucidating this and related issues. In the case of adsorption on solid-state surfaces, stress arises primarily from differences in atomic size and electronegativity, in addition to unit cell expansion due to the incorporation of atoms into the substrate. Here, we study the surface stress evolution encountered during oxidation of the Si(111)-7x7 surface using a novel system combining both surface stress measurement and scanning tunnelling microscopy (STM) capabilities.[1,2] The former measurement is based on the displacement of a large silicon cantilever sample, while the latter measurement permits direct observation of the atomic structure of the same cantilever sample. We show that the initial oxidation of the Si(111)-7×7 surface at room temperature involves two compressive stress stages with different growth signatures. The atomic scale origins of the measured surface stress evolution will be discussed and supported via complementary STM data. In particular, we demonstrate that the initial rapid rise in compressive stress is associated with selective oxidation of the faulted-half units of the 7x7 reconstruction.

[1] T. Narushima, N.T. Kinahan, J. J. Boland, Rev. Sci. Instrum. 76 095113 (2005).

[2] T. Narushima, N.T. Kinahan, J. J. Boland, Rev. Sci. Instrum. 78 053903 (2007).

8:20am **SS2-MoM2 Kinetic Monte Carlo Simulation of Oxide Island Formation and Step Pinning during Etching by Oxygen of Vicinal Si(100)**, ***M. Albao,*** National Sun Yat-Sen University, Taiwan, *J.W. Evans,* Iowa State University, *F. Chuang*, National Sun Yat-Sen University, Taiwan

A lattice-gas model was developed incorporating a recently observed oxide island shape transformation from linear to two-dimensional[1] during initial stages of oxidation of Si(001). Kinetic Monte Carlo (KMC) simulations of such a model offers clues as to the nature of the pinning of steps and their subsequent transformation into finger-like structures[2,3] during prolonged etching of vicinal Si(100) by exposure to molecular oxygen. KMC results suggest that the initial linear shape of oxide clusters might allow them to protect slightly wider sections of the steps against erosion than would a similar 2D island of the same number of atoms. This proposal follows from comparison of the width of the "fingers" that subsequently evolved from the pinning by these two cluster types. Thus, the initial shape of the islands as much as their size appears to be key in stabilization and long-term survival of fingers. Additionally, the same model was used to uncover potential mechanisms for boosting oxide cluster nucleation and thus cluster populations at step edges. In turn, this increased concentration of oxide clusters at the steps sets the stage for increased chances of pinning.

[1] H. Togashi, H. Asaoka, T. Yamazaki, M. Suemitsu, Jpn. J. App. Phys. 44 (2005) 1377.

[2] J.V. Seiple and J. Pelz, Phys. Rev. Lett. 73 (1994) 999.

[3] M.A. Albao, D.-J. Liu, M.S. Gordon, and J.W. Evans, Phys. Rev. B 72 (2005) 195420.

8:40am **SS2-MoM3 Etching of Si(100) Surfaces in H_2O**, ***I.T. Clark***, *B.S. Aldinger, A. Gupta, M.A. Hines*, Cornell University

An etchant that produces atomically flat or near-atomically flat Si(100) surfaces has long been sought by the microelectronics industry. While a number of aqueous bases are known to produce atomically flat Si(111) surfaces, a comparable etchant for the commercially important Si(100) surfaces surface has not been demonstrated. We will present the results of a combined chemical and morphological investigation into the etching of Si(100) surfaces by room- temperature deoxygenated water. Over the course of several hours of etching, the surface develops a surprisingly homogeneous 4-fold symmetric cross-hatch motif dominated by orthogonal "stripes" running along {110} directions. Simultaneous spectroscopic investigations demonstrate the development of a microfaceted H-terminated surface, consisting of Si{111}, Si{110} and Si{100} planes. A simple model for the development of highly homogeneous surfaces during H_2O etching will be discussed

9:00am **SS2-MoM4 Super-Saturation Etching on Si(100)-(2x1) via Cl Insertion: A New Reaction Pathway**, ***A. Agrawal***, *R.E. Butera*, *J.H. Weaver*, University of Illinois at Urbana-Champaign

We use scanning tunneling microscopy to show that Cl_2 dosing of Cl-saturated Si(100)-(2x1) at elevated temperature leads to uptake beyond "saturation". The surface then evolves along a new etching pathway that involves insertion of extra Cl, denoted Cl(i), in Si-Si dimer bonds or back-bonds, diffusion of Cl(i) to form the volatile precursor, and pairwise desorption of $SiCl_2$. Insertion is made possible by chemisorption that is mediated by dangling bond sites. Upon dissociation, one Cl atom adsorbs at the dangling bond while the other inserts with ~10% probability. The dangling bonds required for insertion are produced by phonon-activated electron-stimulated desorption of atomic Cl from the surface. These studies establish a novel form of Cl_2 dissociative chemisorption, and this should stimulate further investigations into surface dynamics.

9:20am **SS2-MoM5 The Growth and Evolution of Ag on Ge(111) Studied by LEEM**, ***J.A. Giacomo***, *S. Chiang*, University of California, Davis

The clean Ge(111) surface has a c(2x8) reconstruction at room temperature. When Ag is dosed onto the surface two main structures are found, a low coverage (4x4) and a higher coverage (√3x√3)R30° phase. We have used the real-space imaging capabilities of a low energy electron microscope (LEEM) to investigate the growth, phase transitions, and dynamics of these phases. The (4x4) phase begins to form at temperatures above 200°C and coverages above 0.1ML. LEEM videos show the (4x4) phase grows with a high dependency on surface steps. This dependency on steps has been attributed to the high diffusivity of Ag adatoms along the step edges[1]. The growth of the (4x4) phase also produces faceting of the surface which is shown in the LEEM images as the (4x4) phase grows from the steps. At higher coverages the (4x4) phase transitions into a (√3x√3)R30° phase. LEEM data of the growth of this phase shows little dependence on the steps with the phase propagating over the terraces. This growth pattern is attributed to the higher diffusivity of Ag adatoms across the (4x4) layer[1] reducing the advantage of diffusion along the steps. Near the desorption temperature, we have found an interesting phase transition as domains of (√3x√3)R30° abruptly transform to the lower coverage (4x4) and then to a disordered phase. The disordered phase produces no contrast in the LEEM images but if the condensed phases are allowed to completely disappear and the sample is then immediately cooled the (4x4) and (√3x√3)R30° phases recondense on the surface. This indicates that the Ag has not completely desorbed and is still present on the surface in a disordered phase.

[1] E. Suliga and M. Henzler, Journal of Physics C-Solid State Physics 16, 1543 (1983).

9:40am **SS2-MoM6 Chemical Vapor Deposition of Boron Carbo-nitride as a Passivation Film for Ge Surfaces**, ***P.R. Fitzpatrick***, *J.G. Ekerdt*, The University of Texas at Austin

As electronic device dimensions are scaled down Ge is receiving considerable attention as an alternative to Si. The primary motivation is the higher charge carrier mobility in Ge compared to Si. However, the Ge/GeO_x interface is chemically and electrically unstable. This work investigates the ability of boron carbo-nitride (BCN) films to passivate single crystal Ge surfaces and Ge nanowires. The BCN films are deposited by thermal chemical vapor deposition (CVD) using dimethylamine borane with NH_3 and C_2H_4 coreactants. Adjustments to the gas composition during CVD make it possible to tune the BCN stoichiometric composition, constituent bonding, and dielectric constant. Ion scattering spectroscopy (ISS) and x-ray photoelectron spectroscopy (XPS) were used to determine the minimum thickness of BCN resulting in a continuous film on Si(100) and Ge(100) substrates. Si(100) was chosen to develop the experimental protocol because of its well-documented surface chemistry. To determine film continuity using ISS, the ratio of the post-BCN substrate signal (either Si or Ge) to the predeposition bare substrate signal was plotted as a function of BCN thickness (determined by XPS peak attenuation for Si and spectroscopic ellipsometry for Ge). Due to the high surface sensitivity of ISS, a continuous BCN film should result in complete attenuation of the substrate signal. BCN becomes continuous at ~2.5nm when grown on Si(100) and ~3.5nm when grown on Ge(100). Differences in the BCN/Si and BCN/Ge interface were examined by depth profiling to understand how interface reactions affect film nucleation. A series of ISS scans gradually sputters the BCN, and XPS scans following each ISS scan track the atomic composition of BCN until the Si or Ge substrate is reached. In both cases the film composition at the substrate interface drastically differs from the bulk composition ($BC_{0.7}N_{0.1}$), with N dominating the B and C contributions at the interface. Nitrogen accumulation is much more pronounced on Si. The BCN film at the BCN/Si interface is comprised of ~70% N whereas the film at the BCN/Ge interface is only ~40% N. XPS was used to determine BCN-coated Ge's ability to withstand oxidation by monitoring changes in the Ge 2p and Ge 3d oxidation states with increasing ambient exposure time. A discontinuous 2.0nm BCN film slows, but does not prevent, Ge oxidation. A continuous 3.5nm BCN film shows no oxidation of Ge following 2 weeks ambient exposure.

10:20am **SS2-MoM8 Novel Superstructure of Thin Pb Film on Si(111) Induced by the Interplay of Quantum Well States and Interfacial Adsorbates**, ***A.A. Khajetoorians***, *H. Eisele*, *S.Y. Qin*, *C.-K. Shih*, The University of Texas at Austin

Epitaxial thin Pb films on Si(111) are well known to exhibit pronounced QSE manifested by the phase matching of the Fermi wavelength and the layer thickness, giving rise to bilayer oscillation as well as a re-entrant quantum beats of longer periodicity. Such quantum oscillation phenomena have been observed in preferred film thickness, the location of quantum well states, as well as superconductivity. This work reveals yet another intriguing phenomenon manifested by the QSE: Formation of a novel superstructure resulting from the interplay of the quantum well state of the metal film and the cesium adsorbates at the interface of Si(111) substrate and Pb thin film overlayers. The superstructure consists of a periodicity of about 8 nm, incommensurate with the Si(111) 7x7 periodicity. Moreover, there is a dependence of the actual periodicity and orientation on the film thickness. This work is supported is supported by: IGERT-NSF: DGE-054917; FRG: (DMR-0306239, DMR-0606485), Alexander von Humboldt Foundation.

10:40am **SS2-MoM9 Controlled Selforganization of Atom Vacancies in Monatomic Gallium Layers**, ***P.C. Snijders***, Delft University of Technology, The Netherlands (now at ORNL), *E.J. Moon*, University of Tennessee, Knoxville, *C. Gonzalez*, *J. Ortega*, *F. Flores*, Universidad Autonoma, Madrid, Spain, *H.H. Weitering*, University of Tennessee, Knoxville, and Oak Ridge National Laboratory

Ga adsorption on the Si(112) surface results in the formation of pseudomorphic Ga atom chains. Compressive strain in these atom chains is relieved via creation of adatom vacancies.[1] These vacancies selforganize into meandering vacancy lines (VLs) similar to the well-known nx2 superstructures for Ge on Si(100).[2] We show that the average spacing between these line defects can be experimentally controlled continuously, within limits, by adjusting the chemical potential μ of the Ga adatoms. The small VL spacings in this system result in significant VL correlations that cannot be captured within a mean field analysis of the VLs.[2] We derive a conceptually new lattice model that quantitatively connects Density Functional Theory (DFT) calculations for perfectly ordered structures, with the fluctuating disorder seen in experiment and the experimental control parameter μ for this correlated VL system. Applying this model to statistical data from large scale STM images, we calculate the (repulsive) VL interaction energy and the kink energy. This hybrid approach of lattice modeling and DFT can be applied to other examples of line defects in hetero-epitaxy, especially in cases where correlation effects are significant and a mean field approach is not valid.[3]

[1] C. Gonzalez, P.C. Snijders, J. Ortega, R. Perez, F. Flores, S. Rogge, and H.H. Weitering, Phys. Rev. Lett. 96, 126106 (2004), P.C. Snijders, S. Rogge, C. Gonzalez, R. Perez, J. Ortega, F. Flores, and H.H. Weitering, Phys. Rev. B 72, 125343 (2005).

[2] X. Chen, F. Wu, Z. Zhang, and M.G. Lagally, Phys. Rev. Lett. 73, 850 (1994).

[3] Part of this work (HHW) was supported by the US DOE Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, through Oak Ridge National Laboratory which is managed by UT-Battelle, LLC.

11:00am **SS2-MoM10 Gold Nanowire Formation on Si(110) Studied by SPM**, ***M. Yoshimura***, *M. Tanaka*, *K. Ueda*, Toyota Technological Institute, Japan

Recently, nanostructures such as quantum dots and wires have been focused because of their exotic properties originated from the confinement of electrons, such as Coulomb blockade, charge density waves, spin density waves, etc. Several chain structures have been observed for Au/Si systems such as Au/Si(557).[1] For the Au/Si(110) system, Yamamoto reported a variety of surface phases using reflection high-energy electron diffraction (RHEED),[2] and only one phase, 2×5 structure, has been investigated in real space by scanning tunneling microscopy (STM).[3] In this study, we aim to clarify the relationship between several surface phases of Au/Si(110) by high-resolution STM and atomic force microscopy (AFM). On the basis of high-resolution SPM images, we propose structural models for the phases and discuss the mechanism of nanowire formation. At 0.2-0.3 ML coverage, up-and-down structure of the clean Si(110) surface is destroyed, and 1×2 structure was clearly confirmed by FFT analysis, corresponding to nucleation of the nanowire. It is suggested that (110) facets develop in the Si(110) surface. The density of the nanowires increases with Au coverage to 0.25 ML. The spacing between the wires varies from 5a to 10a (a:unit length along the [-110] direction of Si(110)). At the coverage of 0.30 ML, it becomes constant at 5a, showing 2×5 surface phase. The nanowire consists of double rows with fluctuation character. The detailed atomistic processes of nanowire formation, as well as possible atomic structure models, are discussed.

[1] H. W. Yeom et al., Phys. Rev. B 72, 035323 (2005).

[2] Y. Yamamoto, Surf. Sci. 271, 407 (1992).

[3] J. L. McChesney et al., Phys. Rev. B 72, 035446 (2005).

11:20am **SS2-MoM11 Faceting and Band-Flattening Induced by Sb-Indiffusion into Si(5 5 12)-2x1**, ***H. Li***, *H. Kim, J.M. Seo*, Chonbuk National University, Korea

Initial stages of antimony (Sb) adsorption on the Si(5 5 12)-2x1 surface have been studied by STM/STS in order to understand interfacial reaction between adsorbed Sb atoms and the Si template with one-dimensional (1-D) symmetry. It has been found that there are two distinct steps, Sb indiffusion and preferential adsorption, at the initial Sb adsorption on Si(5 5 12)-2x1 held at 600 C. Initially, deposited Sb atoms (up to 0.15 ML) diffuse into the subsurface and cause indirect Si deposition. As a result a π-bonded Si chain is firstly formed on dimer/adatom row like homoepitaxy, and the surface reconstruction gradually changes from a (5 5 12) terrace to (337) terraces with (113) steps. The band is flattened by 0.2 eV by subsurface doping with indiffused Sb atoms. As soon as the subsurface Sb sites are saturated by indiffused Sb atoms, additionally deposited Sb atoms are preferentially adsorbed along the upper (113)-step edges and form 1-D Sb wires with a spacing of about 10 nm which corresponds to two periodic lengths of the original (5 5 12) surface. Once Sb-adsorption sites, (113) steps, are saturated, deposited Sb atoms cluster for themselves and do not contribute to nanowire fabrication. From the present studies, it has been found that both Sb indiffusion and preferential adsorption stabilize the high-index surface through relieving surface strain by way of either inserting or attaching Sb atoms, but once such surface strain is relieved, the 1-D growth mode also terminates.

11:40am **SS2-MoM12 Surface Reconstructions Induced by Calcium Fluoride Growth on Si(001)**, ***Y. Cui***, *J. Nogami*, University of Toronto, Canada

The growth of Calcium Fluoride (CaF_2) on Silicon has been widely studied since it grows epitaxially on Si with small lattice mismatch (0.6% at room temperature). There is an extensive literature on CaF_2 growth on Si(111) where a natural epitaxial relationship results in flat thin films with low defect density. However, very little work has been reported for CaF_2 on Si(001). It is known that CaF_2 grown on Si(001) forms either compact islands or long ridges in the Stranski-Krastanow mode.[1,2] STM images of the wetting layer show an inhomogeneous row like structure.[3] In this STM study, 2x3 or 2x4 periodicities were identified in the first layer depending on CaF_2 coverage and growth temperature. The LEED pattern shows an unusual combination of spots and streaks with variable line width and intensity. The configuration of the pattern is caused by the alignment of surface unit cells and phase disorder. The nucleation of CaF_2 small areas is also seen and paves a way to further studies on 3D insulator nanowires. Finally the parallels between these results and the ones obtained for growth of CaF_2 on Si(111) is discussed.

[1] Loretto, D.; Ross, F.M.; Lucas, C.A.: Applied Physics Letters, v 68, n 17, 22 April 1996, p 2363-5

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[3] Sumiya, T.; Miura, T.; Fujinuma, H.; Tanaka, S.: Surface Science, v 376, n 1-3, 10 April 1997, p 192-204.

Thin Film

Room: 613/614 - Session TF-MoM

Atomic Layer Deposition and Applications

Moderator: G.N. Parsons, North Carolina State University

8:40am **TF-MoM3 Conformal Polymeric Thin Films via Initiated Chemical Vapor Deposition**, *S.H. Baxamusa, M. Gupta,* ***K.K. Gleason***, Massachusetts Institute of Technology **INVITED**

Conformal surface modification of high aspect ratio micro- and nano-structures is desirable for a range of applications ranging from microelectronics to textiles. In this work, initiated chemical vapor deposition (iCVD) is demonstrated to conformally deposit thin polymer films (<500 nm) at high growth rates (up to 100 nm/min). The iCVD technique is a low energy process (0.01 W/cm^2) that fully retains the pendent functionality in the deposited polymer films, a result that has been demonstrated with more than 40 different vinyl monomers. The iCVD method is particularly valuable for creating ultrathin layers of insoluble polymers. For the process, initiator and monomer vapors simultaneously flow into a vacuum where decomposition of the initiator results in free-radical polymerization of the monomer on the substrate. As iCVD relies on neutral chemistry, directional effects on deposition typically associated with the electric fields in plasma processes are avoided. Step coverage of trenches in silicon substrates by polymeric iCVD coatings will be shown to depend on the ratio of monomer to initiator. A kinetic model highlights the surface-driven nature of iCVD polymerization and that is analogous to free radical polymerization in the bulk phase, albeit on the surface. The iCVD process is often absorption limited and hence cool (~25 ºC) substrates are essential for rapid film growth. From an applications perspective, low substrate temperatures are favorable for the coating of thermal sensitive materials, including paper, plastics, fabrics, and membranes. The iCVD process can be used to functionalize membranes with high aspect ratio (80:1) pores with a hydrophobic polymer coating. X-ray photoelectron microscopy data confirmed the presence of the iCVD coating on the topside and backside of the membranes and electron microprobe analysis confirmed the presence of the coating along the pore wall. Additionally, the iCVD process has been demonstrated conformally to coat carbon nanotube forests and microparticles. Superhydrophobic surfaces (contact angles >175 degrees) result from surface modification of nanostructured substrates by iCVD PTFE and polymerized perfluoroalkyl ethyl methacrylate.

9:20am **TF-MoM5 Nanolaminate Gas Diffusion Barriers on Polymers with Exceptionally Low H_2O Permeabilities**, *A.A. Dameron,* ***S.M. George***, University of Colorado at Boulder, *P.F. Carcia, R.S. McLean*, DuPont Research and Development

Flexible, ultrathin gas diffusion barriers are required for the protection of organic electronics, e.g. organic light emitting diodes (OLEDs) in flexible displays. Existing barriers provide insufficient protection from permeating H_2O and O_2 gases. Our earlier work demonstrated that a low water vapor transmission rate (WVTR) of ~1 × 10^{-3} $g/m^2/day$ could be achieved on polyethylene naphthalate (PEN) and Kapton using Al_2O_3 ALD films with thicknesses of ~25 nm. These H2O transmission rates are not low enough to meet OLED requirements. The Al_2O_3 ALD films also degrade over time with exposure to H_2O vapor. To lower the H_2O transmission rates further and to protect the Al_2O_3 ALD films, we have used additional layers in combination with the ~25 nm Al_2O_3 ALD layer. The additional layers were one layer of silicon nitride with a thickness of >60 nm deposited by plasma-enhanced chemical vapor deposition (PE-CVD) or one layer of SiO_2 with a thickness of ~60 nm deposited using rapid SiO_2 ALD. Both of these additional layers in combination with the ~25 nm Al_2O_3 ALD layer reduced the measured WVTR to ~1 × 10^{-4} $g/m^2/day$. When deposited on top of the Al_2O_3 ALD film, these silicon-containing layers also protect the Al_2O_3 ALD film from H_2O exposure. Nanolaminates of Al_2O_3 ALD and SiO_2 ALD should further reduce the WVTRs. These nanolaminate films are fabricated by alternating the Al_2O_3 ALD and SiO_2 ALD to create 2 bilayers, 3 bilayers or higher numbers of bilayers. Tests of multiple bilayer nanolaminate structures of Al_2O_3 ALD and SiO_2 ALD on Kapton have yielded extremely low WVTRs of 5 × 10^{-5} $g/m^2/day$ using the HTO testing technique. These exceptionally low WVTRs are approaching the range that is necessary for OLED devices in flexible displays.

9:40am **TF-MoM6 Atomic Layer Deposition for Passivation and Corrosion Protection of Metal Substrates**, ***S.I. Sneck***, Beneq, Finland

The unique features of Atomic Layer Deposition; capability to produce highly conformal pin-hole free films on complex structures and excellent adhesion to most surfaces, have been utilized mainly by the semiconductor industry. However, these properties are often highly appreciated by many other industries as well. As an example, silver industry has recently started using ALD to protect silver jewelry from tarnishing. Tarnishing is mostly caused by airborne sulfur compounds forming black silver sulfide on the surface of a silver object. In this application, the most important criteria are invisibility and anti-tarnish properties of the coating. A uniform 10nm thick aluminum oxide layer increases the tarnishing time by two orders of magnitude while being invisible to human eye. The same method can also be applied to other silver products as well as other metals, including copper and copper containing alloys. In addition to passivation of silver and copper based products, more demanding anti-corrosion coatings can be done on stainless steel and other common construction metal parts used in extreme conditions. Relatively low growth rate of ALD compared to other thin film techniques can be compensated with large batch size, since ALD is one of the easiest thin film processes to scale-up. ALD films can also often be much thinner compared to films prepared with other thin film techniques, for example if certain barrier properties are required. This is due to higher film uniformity and fewer pin holes in ALD films. Even though most work with ALD has been done on silicon and glass substrates, metal substrates offer many applications for ALD, since complex shaped parts are often made of metal. By careful selection of coating structure, it is possible to combine anti-corrosion coatings with other functions, including decorative and wear resistant functions.

10:20am **TF-MoM8 Combinatorial Atomic Layer Deposition of Nanolaminates**, ***W.L. Gladfelter***, *T. Moersch, L. Zhong, B. Luo*, University of Minnesota **INVITED**

Nanolaminates of HfO_2 and SiO_2 were prepared using atomic layer deposition methods. Successive exposure of substrates maintained at 120 or 160°C to nitrogen flows containing $Hf(NO_3)_4$ and $(^tBuO)_3SiOH$ led to typical bilayer spacings of 2.1 nm with the majority of this being SiO_2. Combining the $Hf(NO_3)_4/(^tBuO)_3SiOH$ ALD with ALD cycles involving $Hf(NO_3)_4$ and H_2O allowed the systematic variation of the HfO_2 thickness within the nanolaminate structure. This provided an approach towards controlling the dielectric constant of the films. The dielectric constant was modeled by treating the nanolaminate as a stack of capacitors wired in series. The nanolaminate structure inhibited the crystallization of the HfO_2 in post-deposition annealing treatments. As the HfO_2 thickness decreased, the preference for the tetragonal HfO_2 phase increased. Nanolaminates of SiO_2 with compositionally graded mixture of HfO_2 and ZrO_2 were deposited using a combinatorial ALD process. Exposure of repeated cycles of co-dosed alkoxide precursors $Hf(O^tBu)_4$ and $Zr(O^tBu)_4$ with counter-reactant pulses of $Si(O^tBu)_3(OH)$ formed films of uniform thickness (±5%) and uniform silicon oxide concentration. The hafnium and zirconium concentrations exhibited smooth graduation across the film from 18% - 82% (per Hf and Zr metals basis). Self-limiting deposition rates of 1.5 nm/cycle were measured, and a linear relationship of film thickness to number of deposition cycles was observed, both consistent with a true ALD process. Elemental analysis by Rutherford backscattering spectrometry, thickness measurements by ellipsometry, capacitance measurements, electron microscopy, X-ray reflectivity and X-ray diffraction results were used to map the composition and determine the film microstructure. Deposition of mixed films of SrO and HfO_2 were deposited by the related combinatorial chemical vapor deposition process using $Sr(tmhd)_2[HN(CH_2CH_2NMe_2)_2]$, where tmhd = 2,2,6,6-¬tetramethylheptane-3,5-dionato, as the strontium precursor and $Hf(O^tBu)_4$ as the HfO_2 source. XRD showed that films with low Sr concentrations, e.g. < 15% Sr, exhibited a crystalline phase consistent with Sr-stabilized cubic hafnia. Films with higher Sr contents were amorphous. The dielectric constants of the films increased as the proportion of the cubic phase increased. A maximum value of 25 was obtained for the film with a Sr/(Sr + Hf) ratio of 0.07. We will report on our attempts to extend this CVD process to ALD.

11:00am **TF-MoM10 Combinatorial Strategy to Address the Complexities of Surface Chemistry and Multicomponent Materials in Atomic Layer Deposition**, ***L. Henn-Lecordier***, *E. Robertson, P. Banerjee, G.W. Rubloff*, University of Maryland

While atomic layer deposition (ALD) shows unique promise for highly controlled deposition of super-conformal thin films, its perfection and practice are limited by (1) reactant dose (inter)dependencies that reflect deviations from perfect self-limiting reaction and (2) the numerous permutations of stoichiometry that must be investigated to exploit ternary and higher materials systems. We have developed a combinatorial ALD approach to efficiently address these challenges. A wafer-scale (4- OD) substrate-heated ALD mini-reactor delivers reactant gases across the wafer, maintained in a small reactor volume to achieve short cycle times. Downstream mass spectrometry reveals the ALD surface chemistry in real time, enabling direct observation of reaction product generation as a function of dose, as well as direct thickness vs. time determinations during nucleation and growth stages of the ALD process.[1,2] With increasing dose, nominally complete surface saturation conditions are observed. As reactant dose is decreased, incomplete surface coverage is expected and identified, which corresponds to across-wafer depletion conditions in the cross-flow geometry of the mini-reactor. By achieving such depletion, various combinations of reactant dose ratios for binary constituents provide a combinatorial gradient library for ALD process recipe optimization. Results for Al_2O_3 deposited by ALD from TMA and H_2O demonstrate the ability to create linear thickness gradients across the wafer. This combinatorial synthesis is coupled with post-process electrical characterization of MIS capacitors using I-V and C-V measurements automated to assess several hundred devices across the wafer, complemented by wafer maps of thickness and composition. Together these directions reflect an effective strategy for evaluating and optimizing ALD process recipes as well as extending the approach to ternary systems, e.g. Hf aluminates. Work supported in part by MKS Instruments.

[1] "Real-time observation and optimization of tungsten ALD process cycle", W. Lei, L. Henn-Lecordier, M. Anderle, Gary W. Rubloff, M. Barozzi, and M. Bersani, J. Vac. Sci. Technol.B 24 (2), 780-789 (Mar/Apr 2006).

[2] "Real-time sensing and metrology for atomic layer deposition processes and manufacturing", L. Henn-Lecordier, W. Lei, M. Anderle, and G.W. Rubloff, J. Vac. Sci. Technol. B 25 (1), 130-139 (Jan/Feb 2007).

11:20am **TF-MoM11 Physical and Electrical Characteristics of $Zr_xHf_{1-x}O_y$ Films Deposited by Atomic Layer Deposition Method**, ***S. Bang***, *S. Lee, S. Jeon, S. Kwon, W. Jeong, I. Kim, H. Jeon*, Hanyang University, Korea

Zirconium and hafnium-based dielectric materials have been widely studied as a gate oxide for the next generation of CMOS technology due to high dielectric constant, a relatively wide band gap and thermodynamic stability on Si. However, ZrO_2 and HfO_2 films can be crystallized at the temperature below 500°C. For gate dielectrics, an amorphous structure is always preferred to a polycrystalline structure, because a crystalline film can induce high grain boundary leakage current and lead to non-uniformities in k value and in film thickness. Thus, efforts have been made to improve the properties of HfO_2 and ZrO_2 by adding different elements such as Si, Al, N, Ti, and Ta. Addition of Si, Al, or N allows for the increased crystallization temperature of HfO_2 and ZrO_2. However, there is a drawback of a lowered dielectric constant. Although the addition of Ti can increase dielectric constant of HfO_2 and/or ZrO_2 films, it can degrade the leakage current characteristics by decreasing a band offset. The addition of metal elements to improve the quality of high-k oxide film, without reducing dielectric constant and increasing leakage current, is important. ZrO_2 has similar chemical structure to HfO_2 and is completely miscible with HfO_2. Zr addition can yield stability to the higher dielectric constant tetragonal phase. In this study, we deposited $Zr_xHf_{1-x}O_y$ films varying with the content of Zr on Si substrates by adding Zr into HfO_2 film using atomic layer deposition (ALD) process and investigated its physical and electrical characteristics. Auger electron spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) were used to analyze the chemical composition and bonds. AES and RBS data indicated that the composition ratio of $Zr_xHf_{1-x}O_y$ films is varied as the Zr content change in those films. And X-ray diffraction (XRD) was used to analyze the structure properties of $Zr_xHf_{1-x}O_y$ films. The capacitance values of $Zr_xHf_{1-x}O_y$ films showed about 415 ~ 620pF/cm^2 on capacitance-voltage (C-V) measurement. For the analysis of other electrical properties, C-V and current-voltage (I-V) analyses were measured to evaluate the dielectric constant, EOT, and leakage current of $Zr_xHf_{1-x}O_y$ films, etc.

11:40am **TF-MoM12 An ALD Growth Study of ZrO_2 on Si(100)**, ***P.J. Evans***, *G. Traini, J. Murison, M.J.Y. Tayebjee, N. Loh, D.-H. Yu, A.P.J. Stampfl*, Australian Nuclear Science and Technology Organisation, *T.-W. Pi*, National Synchrotron Radiation Research Center, Taiwan

Zirconium and some of its alloys, oxides and nitrides are known for their anti-corrosive and excellent wear resistant character. For this reason the nuclear industry uses Zr-based materials due to their low neutron absorption character, mechanical strength, toughness and ability to withstand harsh environmental conditions such as high temperatures and intense radiation. ZrO_2 has also been singled-out as a candidate material for inert matrix fuels to be used in Generation IV nuclear reactors. The formation of ZrO_2 under different growth conditions leads to variations in electronic properties and crystal structure. Control of growth will enable tuning the electronic and structural properties of this material for specific applications. The current preliminary study investigates the effect of deposition conditions on the electronic and crystal structure of ALD grown ZrO_2 films on silicon, using synchrotron-based high resolution photoemission, TEM, SIMS and glancing angle x-ray diffraction. The precursors used in the deposition were $ZrCl_4$ and H_2O using two growth temperatures of 200°C and 300°C. In addition, ZrO_2 films were subjected to rapid thermal annealing at 600°C to investigate their valence electronic structure on crystallization.

Symposium Plenary Lecture

Room: 6C - Session SP-MoL

Symposium Plenary Lecture

12:00pm **SP-MoL1 NanoSystems Biology and New Technologies for in vitro & in vivo Diagnostics of Cancer**, ***J.R. Heath***, The California Institute of Technology **INVITED**

The emerging world of personalized, preventative, predictive, and participatory (P4) medicine will likely be enabled by the developing field of systems biology. Systems biology and P4 medicine both data driven and, accordingly, both require new tools for making large numbers of measurements rapidly, quantitatively, and at practically zero cost. Microfluidics, chemical, and nanotechnologies will revolutionize our ability to generate comprehensive data sets that span from individual cells to patients, and will allow us to build multiparameter analysis tools (quantitating genes, proteins, and cells) for achieving an informative in vitro disease diagnosis, as well as in vivo molecular imaging probes for spatially localizing specific diseases. However, the requirement that the measurements be done at extremely low cost (information becomes the commodity of value) imposes severe restrictions on these emerging technologies. Using cancer as a theme, I will describe the state-of-the-art in terms of network models of human diseases, and I will describe how those models may be harnessed for information that can impact the clinical care of cancer. I will then describe a suite of multiparameter diagnostics technologies that we are developing in my lab in concert with other groups, with both near and far term applications targeted.

Applied Surface Science

Room: 610 - Session AS-MoA

Quantitative Surface Analysis II. Electron Spectroscopies: (Honoring the contributions of Martin Seah, NPL, and Cedric Powell, NIST)

Moderator: S. Asher, National Renewable Energy Laboratory

2:00pm **AS-MoA1 Cluster Primary Ion Beams Advance the Capability of Bio-Molecule Analysis by SIMS**, ***J.C. Vickerman***, The University of Manchester, UK **INVITED**

The analysis of bio-molecular systems using SIMS with atomic primary ion beams has been bedevilled by three principal limitations - the static limit, the inability to sputter large molecules intact and the very low ionisation probability. The static limit, imposed because of the extensive bombardment induced chemical damage generated by high energy atomic primary ions, limits the amount of material accessible for analysis to 1% of the surface layer, greatly limiting detection sensitivity, the pixel size that can be usefully imaged and eliminating the possibility of molecular depth profiling. Atomic primary ions do not appear to be capable of sputtering intact organic molecules molecular weight much above 500 daltons in significant quantities. This places a major limitation on the value of SIMS in bioanalysis. Finally in common with all desorption mass spectrometries, the ionisation probability of the sputtered species is usually well below 10^{-3}, placing a further limitation on detection sensitivity and the useful minimum pixel size in SIMS imaging. It is clear that making progress into lifting some or all of these limitations would have a dramatic effect on the value of SIMS in bio-analysis. Over the last 10 years the possibility that cluster primary ion beams would lift some of these limitations has been increasingly investigated. The capability of liquid metal ion sources to generate cluster ions such as Au_n^+ and Bi_n^+ has been exploited.[1,2] Gas sources have been used to deliver SF_5^+ and C_{60}^+ ions.[3,4] It has been shown that these ions can greatly increase the yield of higher mass ions by orders of magnitude and enable ions up to ~3000 daltons to be detected. Nevertheless the metal cluster ions still generate significant bombardment induced chemical damage such that the static limit is still necessary.[5] However the larger cluster ions such as C_{60}^+ generate far less bombardment induced chemical damage and for many systems the static limit can be lifted.[5] This greatly increases the potential for high sensitivity analysis, imaging with sub-micron resolution and most significant - molecular depth profiling.[6] This latter development offers the possibility of 3D molecular imaging of bio and organic systems.[7] This paper will review the progress that has been made and will suggest that to fully exploit the benefits of cluster primary ions new approaches to analysis may be required.

[1] N. Davis, D.E. Weibel, P. Blenkinsopp, N. Lockyer, R. Hill, J.C. Vickerman, App. Surf. Sci 203-204 (2003) 223-227

[2] F. Kollmer, App. Surf. Sci 231-232 (2004) 153-158

[3] C.M. Mahoney, S.V. Robertson, G. Gillen, Anal. Chem. 76 (2004) 3199-3207

[4] D.E. Weibel, S. Wong, N.P. Lockyer, P. Blenkinsopp, R. Hill, J.C. Vickerman, Anal. Chem. 75 (2003) 1754-1764

[5] E.Jones, N.P. Lockyer and J.C. Vickerman, Int J, Mass Spectrom., 260 (2007) 146-157

[6] J. Cheng, A. Wucher and N. Winograd, J. Phys. Chem. B 110, 8329-8336 (2006).

[7] J. S. Fletcher, N. P. Lockyer, S. Vaidyanathan, and J. C. Vickerman, Anal. Chem., 79 (2007) 2199-2206

2:40pm **AS-MoA3 Detector Dead-time Effects in the Multivariate Analysis of ToF-SIMS Spectral Images**, ***M.R. Keenan***, Sandia National Laboratories, *V.S. Smentkowski*, General Electric Global Research, *J.A. Ohlhausen*, Sandia National Laboratories

The time-to-digital converters typically employed for ToF-SIMS have a dead-time that is significant with respect to the distribution of times-of-flight characteristic of a given nominal mass. When data are acquired with high mass resolution, it is generally the case that only a single secondary ion can be detected at any given mass per primary ion pulse, regardless of how many ions actually reach the detector. Consequently, the data become non-linear in the sense that the signal intensity is no longer proportional to the local composition. This phenomenon often manifests itself as "saturation," for instance, finding isotope ratios that deviate significantly from generally accepted values. The data non-linearity also poses significant problems for multivariate statistical analysis techniques (MVSA), which fundamentally assume an underlying linear additive model. In these cases, extraneous components are often discovered that simply describe the non-linearity and can ultimately confound chemical interpretation. Dead-time correction procedures have been described, previously, for time-of-flight mass spectrometry. These typically rely upon observing a statistically significant number of ion pulses at each volume element, a situation that is not practical for ToF-SIMS spectral images composed of large numbers of pixels, 3D depth profiles and stage rastering measurements. In this paper, various dead-time effects on ToF-SIMS spectral images will be described. We will also propose a novel data pretreatment protocol that is suitable for use with MVSA. The new method involves a transformation to linearize the data, which is similar to previously published corrections, together with a scaling step to properly account for the non-uniform noise characteristic of dead-time-limited data. The ability of the new protocol to enable the extraction of accurate, meaningful components while excluding noise during MVSA will be illustrated with simple, intuitive examples.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:00pm **AS-MoA4 Quantitative Nanoscale Analysis of Surfaces with Topography using ToF-SIMS**, *J.L.S. Lee*, ***I.S. Gilmore***, *M.P. Seah*, National Physical Laboratory, UK

Surface topography is a crucial issue for the analysis of innovative devices such as microfluidic systems, MEMS devices, fibres, composite materials, sensors, organic electronics and biomedical devices. The strength and durability of these components is critically dependent on their nanoscale surface chemistry and molecular interactions. However, quantitative characterisation of surfaces with topography remains a significant challenge due to the lack of systematic and validated measurement methods.[1] In particular, surface topography can causes many unwanted artefacts in ToF-SIMS spectra and images, including ion shadowing effects caused by distortions in the extraction field, reduced mass resolution caused by the spread in the time of flight of secondary ions, distortions in the images due to the angular differences between the primary ion beam and the analyser with respect to the sample, loss in signal due to the limited angular acceptance of the analyser, and potential problems in charge compensation of insulating samples. This presents enormous technical challenges to process engineers and R&D scientists developing new products and processes. Here, we present a systematic study of the effects of surface topography on SIMS. Experimental data are acquired for model cylinders, fibres and spheres, for both conducting and insulating samples. The results are in good agreement with those obtained using an ion optics simulation program, SIMION,[2] allowing us to understand the effects of surface topography and provide guidance to practical analysts for identifying and reducing topographical effects. In addition, the use of multivariate methods for images with surface topography is investigated using principal component analysis (PCA) and multivariate curve resolution (MCR), extending from our previous work on mixed organic systems on flat surfaces.[3] With careful application and suitable data preprocessing methods, multivariate analysis is shown to improve data interpretation and allows for the rapid processing of high-resolution raw spectral data in SIMS images.

[1] S Rangarajan and B J Tyler, J. Vac. Sci. Technol. A 24(5) (2006) 1730-1736

[2] SIMION version 8.0, Scientific Instrument Services, Inc., 1027 Old York Rd., Ringoes, NJ 08551, USA

[3] J L S Lee, I S Gilmore and M P Seah, submitted.

3:40pm **AS-MoA6 Cluster Primary Ions: Spikes, Sputtering Yields, Secondary Ion Yields and Inter-Relationships for Secondary Molecular Ions for Static SIMS**, ***M.P. Seah***, National Physical Laboratory, UK **INVITED**

A framework is provided to describe the enhanced sputtering yields and secondary ion yields of molecular fragments, from molecules on substrates, achieved when using cluster primary ions. Analysis of published sputtering yield data shows that one particular model of sputtering, that includes spikes, is an excellent quantitative description of the yields for a wide range of monatomic and polyatomic primary ions. Evidence will be shown of the model validity for clusters of up to more than 10 atoms over 3 orders of magnitude in sputtering yield. Using data from one primary ion, within this model, extremely good descriptions of measurements reported with other primary ions is achieved. This theory is then used to evaluate the important molecular ion yield behaviour for static SIMS. This leads to universal dependencies for the de-protonated molecular ion yields, valid for all primary ions, both single atom and cluster, over 5 decades of emission intensity. This formulation permits the prediction of the $(M-H)^-$ secondary ion yield for different, or new, primary ion sources, e.g. Bi_n^+ and C_{60}^+, for the analysis of organic materials. Optimal primary ion sources are predicted and discussed. For analysing materials, raising the molecular secondary ion yield is extremely helpful but it is the ratio of this yield to the disappearance cross section that is critical. Data are evaluated and a description is given to show how this varies with the cluster type to provide a further universal dependence. Optimal analytical conditions are discussed.

4:20pm **AS-MoA8 The 3D Atom Probe Instrument - Introduction to the Technique and Some Applications in Material Science**, ***L. Renaud***, CAMECA, France **INVITED**

The 3D atom probe is a quantitative technique that provides atomic scale 3D element mapping of chemical heterogeneities in sample.[1] The sample has to be prepared in the form of a very sharp tip. Under the effect of high electrical field, the atoms at the surface are evaporated by field effect and projected on a position sensitive detector.[2] This detector allows the localization of the impacts in synchronism with the measurement of the time of flight of the evaporated atoms. At the end of the analysis, it is possible to rebuild in 3D near an atomic scale, the analyzed volume (typically 70nm x 70nm x 200nm), atom by atom. The goal of this presentation is to demonstrate the contribution of the 3D-AP in materials science. For this purpose, we will make first a brief introduction to the technique. Some results obtained with this technique will be shown in order to evaluate the contribution of the instrument in materials science (especially for quantification measurement). In the last part of the presentation, new developments and future applications of the instrument will be discussed and also we will make an insight to the sample preparation issue

[1] D. Blavette et al., Nature 363 (1993) 432 - 434

[2] L. Renaud et al., Nuclear Instruments and Methods in Physics Research Section A: Vo 477, Issues 1-3, 21 January 2002, 150-154

5:00pm **AS-MoA10 Composition of Surfaces: A Comparison of LEIS and ToF-SIMS**, *D. Breitenstein, R. Kersting,* ***B. Hagenhoff***, Tascon GmbH, Germany, *R. ter Veen, H. Brongersma*, Calipso B.V., The Netherlands

Low Energy Ion Scattering (LEIS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) enable the analysis of the atomic and chemical surface composition of vacuum sustainable samples. Applying LEIS, the surface of a sample is hit by noble gas ions (He^+, Ne^+, ...) of low energy (1-5 keV). Elastic collisions with individual surface atoms can cause backscattering of the projectiles. Analyzing the energy of these scattered noble gas ions, and moreover knowing their mass and initial energy, the identity of the atomic collision partner can be calculated. Therefore, LEIS enables the quantitative determination of the elemental composition of the samples‘ outermost monolayer. Ions scattered in deeper layers, loose extra energy along the in- and outgoing trajectories. This is used to obtain non-destructive high-resolution depth profiles (0-10 nm). In ToF-SIMS the surface of the samples is also bombarded with atomic - or even polyatomic - projectiles. In contrast to LEIS the energy (10-25 keV) and the mass (e.g. Bi_3^+: 627 u) of these projectiles is relatively high. The impact of these projectiles leads to a formation of collision cascades in surface near regions resulting in a desorption of particles (electrons, neutral and ionized atoms as well as molecules). The ions can be mass separated and detected in a ToF analyzer providing elemental and molecular information on the first 1-3 surface monolayers. Both techniques provide useful information on the surface composition of solids. However, this information differs for LEIS and ToF-SIMS in several aspects: Firstly, LEIS offers the lower information depth. Whereas ToF-SIMS probes the uppermost three monolayers, LEIS generates information on the outermost monolayer. Secondly, ToF-SIMS offers information on the elemental as well as molecular composition of the surface, whereas with LEIS solely elemental information can be obtained. Furthermore, in terms of quantification, LEIS is superior to ToF-SIMS. Finally, ToF-SIMS allows a laterally resolved probing of the sample down to a resolution of 100 nm whereas in LEIS the lateral resolution is restricted to 0.1-1 mm. This paper compares results of applying LEIS as well as ToF-SIMS to well-defined samples such as Langmuir-Blodgett monolayers but also to analytically relevant samples like nanoparticles. It will highlight the strengths of both techniques and the synergism obtained in applying both methods.

Electronic Materials and Processing

Room: 612 - Session EM+NS-MoA

Semiconductor Nanostructures for Electronics and Optoelectronics I

Moderator: N. Gergel-Hackett, National Institute of Standards and Technology

2:00pm **EM+NS-MoA1 Effect of Organic and Inorganic Capping Agents on Optical Properties of CdS Nanoparticles**, ***N. Hullavarad***, *S. Hullavarad*, University of Alaska Fairbanks

Vast research interest on the synthesis and characterization of II-VI semiconductor nanoparticles for size-dependent optical properties and their potential applications in optoelectronic devices is developed over the few years. A blue shift in the energy is observed due to the quantum confinement effect as the dimensions of nanoparticles approach the Bohr radius of exciton. Size tunable properties of nanoparticles give an opportunity for various photonic applications which might find restrictions because of nonradiative recombinations due to surface defects. Organic and inorganic capping agents are used to stabilize and passivate during the synthesis of nanoparticles in order to overcome these kind of difficulties associated with the nanoparticles. Cadmium sulfide (CdS) is an important II-VI semiconducting material having a direct band gap of 2.42 eV. However, when synthesized chemically through a bottom-up approach by the capping method, the narrow band gap material can be grown with enhanced band gap in the ultraviolet region. In this paper, the synthesis of CdS nanoparticles through a simple, inexpensive and straightforward method will be discussed. The synthesis of CdS nanoparticles using organic and inorganic capping agents by chemical colloidal method will be discussed. The capping agents used are thioglycrol, mercaptoethanol, 1-6 heaxnedithiol and tetraethyl orthosilicate (TEOS) and tetraethyl orthotitaniate (TEOT). It is observed that nature of optical absorption spectra changes depending on the capping agents for CdS nanoparticles synthesized under same parameters. The effect of capping agent on the photoluminescence and UV absorption will be discussed in the light of metal induced defects. The thioglycerol capped CdS nanoparticle sample will be taken as a special case to study the effect of X-ray irradiation.

2:20pm **EM+NS-MoA2 Initial Metallization and Transition Metal Diffusion in ZnO Single Crystals, CVD-Grown Epi-films, and Nanostructures**, *S. Rangan,* ***S. Katalinic***, *R. Gateau, D. Hill, R.A. Bartynski, P. Wu, Y. Lu*, Rutgers University

Transition metal doped ZnO is a promising candidate room temperature dilute magnetic semiconductor for spintronic applications. In previous studies of MOCVD-grown epitaxial ZnO films and nanostructures, either ion-implanted or diffusion doped with Fe or Mn, we have observed that these two metals exhibit significantly different diffusion properties. To explore whether this is an inherent property of ZnO or if it is related to non-ideal aspects of the films or nanostructures, we have studied the initial stages of Mn, Fe, and Cu metallization of the single crystal ZnO(0001)[Zn-terminated] and (11-20) surfaces, as well as MOCVD-grown epitaxial films [for which the (11-20) surface is exposed], using scanning tunneling microscopy and spectroscopy (STM and STS). The subsequent diffusion of these metals into the oxide upon annealing to various temperatures was studied with ion scattering spectroscopy. The as-prepared surface of the epitaxial film shows the same nanoscale morphology as the single crystal (11-20) surface, organized in row-like structures tens of nm in width and 2 - 4 nm in height. While Cu deposition results in well defined islands, all three surfaces exhibit apparent disruption upon Fe deposition, even at room temperature. The surfaces exhibit substantial morphological changes on the nm length scale, with a significant change in terrace widths and a significantly smaller fraction of atomic height steps. Upon annealing, Cu islands become mobile and coarsen, but the underlying ZnO structure is not strongly affected. In contrast, with Fe present on the surface, significant coarsening and roughening of the substrate occurs even at the modest annealing temperature of 200C, and this effect is enhanced upon annealing to 400 C. A comparison of the diffusion of Fe and Mn into the single crystals and the film will be presented. Initial results suggest that uptake of metals into the epi-film is predominantly determined by the properties of the (11-20) surface that terminates the film.

Support for this work from NSF grant 0224166 is gratefully acknowledged.

2:40pm **EM+NS-MoA3 Electron Spin Dynamics in Colloidal ZnO Quantum Dots**, ***K.M. Whitaker***, *D.R. Gamelin*, University of Washington

Conduction band electrons in colloidal ZnO quantum dots have been prepared photochemically. This presentation will describe the use of electron paramagnetic resonance (EPR) spectroscopy to probe the spins of these conduction band electrons. Spectroscopic g-values for 3-7 nm diameter nanocrystals containing single S-shell conduction band electrons have been determined. Room-temperature ensemble spin dephasing times for these electrons were estimated from EPR linewidth analysis. The effects of electron-nuclear hyperfine interactions on T_2^* were investigated systematically by varying the concentration of ^{67}Zn (I = 5/2) ions synthetically. A clear relationship between T_2^* and nuclear spin concentration was observed and will be discussed.

3:00pm **EM+NS-MoA4 Characterization of Ion Beam Deposited Quantum Dots Thin Films from Colloidal Solution**, ***Y. Tani***, *S. Kobayashi*, *H. Kawazoe*, HOYA Corporation, Japan

Distinctly monodispersed core/shell structured semiconductor nanocrystals (NCs) quantum-dots (QDs) prepared by chemical synthetic methods in liquid solutions are fascinating fluorescent materials because of efficient saturated chromatic luminescence. In the consideration of applications to light emitting flat panel displays, ready-synthesized NCs can be expected to be pieces of a light emitting component being deposited on a heterologous large areal polycrystalline or amorphous substrates, in contrast with a restrictive conditioned Stranski-Krastanov mode QDs. However, it has been a daunting challenge to form an organic-free luminescent QD structured film from the wet QDs, which are stably dispersed in an organic solvent or water with hundreds of ligand molecules on their surface. We developed a very low energy NC ion beam deposition technique,[1] which is capable of forming QD ion beam from the colloidal solution to deposit fluorescent thin films without significant organic contamination. In present study fabrications of high efficient luminescent QD structured thin films from CdSe/ZnS colloidal NC source are demonstrated. Semiconductor device requires a compatible technology with the colloidal source and a high-vacuum deposition process for simultaneous pursuit of a preservation of NC configuration and an exclusion of the organics derived from the ligand and solvent. An electrospray technique was employed for a soft ionization process to obtain nanocrystalline ions. From the requirement of a transportation of the ultraheavy ions and a nonequilibrium deposition, a supersonic flow with a speed of 1.1×10^3 m/s was formed with a free jet nozzle arrangement attaching a differential pumping system, which also works as a neutral molecular evacuator. Furthermore, for preventing the depositing films from an exposure with lighter ions such as the ones originated from the organic solvent and surfactant, ion optics including an energy analyzer are applied. Microstructural observations and chemical composition analysis evidenced that the deposited film has a closely packed polycrystalline structure with less organic contamination. Its photoluminescence spectrum reproduces the original distinct single peak spectrum from the colloidally dispersed NCs. The NC ion with kinetic energy of 0.1-0.4 eV/atom provides appropriate energy dissipation for a deposition of NCs.

[1]S. Kobayashi et al Jpn. J. Appl. Phys. 46 (2007) L392.

3:40pm **EM+NS-MoA6 Interdiffusion during Growth of Self-Assembled InAs/InP Quantum Dots by Chemical Beam Epitaxy: A Combined Experimental and Theoretical Study**, ***C. Dion***, *P. Desjardins*, École Polytechnique de Montréal, Canada, *N. Shtinkov*, Université d'Ottawa, Canada, *M.D. Robertson*, Acadia University, Canada, *F. Schiettekatte*, Université de Montréal, Canada, *P.J. Poole*, *S. Raymond*, National Research Council, Canada

The formation of atomically sharp interfaces during the epitaxial growth of heterojunctions is a challenging task since atomic intermixing between the different materials is often unavoidable due to the relatively high growth temperatures involved. This effect has been found to be particularly important during the growth of self-assembled quantum dots (QDs) for which evidence of highly alloyed structures have been reported by several authors for a wide variety of semiconductor systems.[1] In the present work, we investigate intermixing during the growth of self-assembled InAs/InP QDs by chemical beam epitaxy. Using a careful combination of photoluminescence (PL) and transmission electron microscopy (TEM) measurements as well as tight-binding (TB) calculations, we have devised a procedure that enables an unambiguous assignment of QD heights (h_{QD}) and composition to the observed PL transitions. PL spectra from ensembles of QDs are characterized by distinctive peaks which can be attributed to the ground state emission of QD families having the same thickness in terms of an integer number of monolayers (ML).[2] Consequently, QDs electronic transitions are analogous to those of quantum wells and can be analyzed accordingly. TB calculations were performed by assuming (i) InP/$InAs_{1-x}P_x$/InP structures of varying P concentration ([P]) with abrupt interfaces and (ii) InP/InAs/InP structures with P diffusion concentration profiles described by the diffusion length L_D. Both calculation frameworks lead to similar, realistic descriptions of the as-grown material. However, the above procedure yielded two solutions sets of (h_{QD} : [P] or L_D) compatible with experimental results. In order to determine which solution set is the most suitable, they were used as input data in a Bloch-wave simulation of TEM image contrast providing a sequence of contrasts versus h_{QD}. A unique solution set was compatible with observed TEM data, therefore allowing an unambiguous assignment of h_{QD} and [P] to the observed PL transitions. For the samples under investigation, it was concluded that the electronic transitions can be best attributed to a 3 ML-thick wetting layer and 4 to 13 ML-thick QDs with a relatively constant [P] of 10 ± 1 %.

[1] N. Liu, et al., Phys. Rev. Lett. 84, 334 (2000).

[2] S. Raymond, et al., Semicond. Sci. Technol. 18, 385 (2003).

4:00pm **EM+NS-MoA7 Improved Long-Term Thermal Stability of InGaN/GaN Multiple Quantum Well Light-Emitting Diodes using TiB_2- and Ir-based p-Ohmic Contacts**, *L. Stafford*, *L.F. Voss*, *S.J. Pearton*, *H.T. Wang*, ***F. Ren***, University of Florida

InGaN/GaN multiple quantum well light-emitting diodes (MQW-LEDs) are commercially available in a broad range of wavelengths for use in applications such as full color displays, traffic signals, and exterior lighting. There is also interest in shorter wavelength LEDs with AlGaN active regions which can be used in conjunction with down conversion phosphors to produce white light, and hold significant promise for next generation lighting technology. Nevertheless, to compete with fluorescent and other high-efficiency lighting sources, it is essential to drive GaN-based LEDs at very high current densities to maximize light output. One drawback of the high current densities is self-heating of the heterostructure. This can produce either indiffusion of the Ohmic contact elements, leading to an electrical short of the pn junction, or intermixing of the contact scheme, producing very rough surface morphology. One possible way to prevent excessive Ohmic contact degradation is to use a high-melting-point diffusion barrier in the contact stack. TiB_2, with a melting temperature of ~3000°C, reasonable electrical resistivity (28 μΩ.cm) and thermal conductivity (26 $W.m^{-1}.K^{-1}$), and heat of formation comparable to those for silicides or nitrides, shows promise as a diffusion barrier. In this work, we report on the long-term annealing characteristics at 200-350°C of InGaN/GaN MQW-LEDs with TiB_2- and Ir-based p-Ohmic contacts. This high-temperature stress stimulates accelerated aging of GaN-based LEDs and gives an idea of the expected reliability of the Ohmic contacts. By comparison with companion devices with conventional Ni/Au Ohmic contacts fabricated on the same wafer, MQW-LEDs with TiB_2- and Ir-based Ohmic metallization schemes showed superior long-term thermal stability after 45 days at 200°C and 350°C, as judged by the change in turn-on voltage, leakage current, and output power. This is a promising result for applications where high-temperature operation is required.

4:20pm **EM+NS-MoA8 Effects of N Incorporation on the Electronic Properties of GaAsN Alloy Films and Heterostructures**, ***Y. Jin***, *M. Reason*, *H. Cheng*, *R.S. Goldman*, *C. Kurdak*, University of Michigan

(In)GaAsN alloys with a few percent nitrogen have potential applications in infrared laser diodes, high efficiency solar cells, and other electronic devices. However, as-grown materials often exhibit poor photoluminescence efficiencies and electron mobilities substantially lower than those of (In)GaAs. In this work, we investigate the effects of N incorporation on the electronic properties of GaAsN alloy films and heterostructures grown via molecular-beam epitaxy. The total N concentrations and substitutional N fractions were determined by nuclear reaction analysis and Rutherford backscattering spectrometry studies of the bulk-like GaAsN films. Four-terminal magnetoresistance and Hall measurements were performed from 1.6K to room temperature on both bulk and heterostructure films. In GaAsN bulk films, N-composition dependent free carrier concentrations were observed at room temperature, suggesting that N acts as an electron trap. In addition, a strong T dependence of sheet resistivity and electron mobility was observed. This suggests the localization of carriers due to N-induced potential fluctuations in the conduction band, which may be explained in the framework of Anderson localization. Using modulation-doped AlGaAs/GaAs(N) heterostructures, we determine the N-related scattering effects in the GaAs(N) channel, with minimal contributions from ionized impurity scattering from dopants. Low temperature magnetoresistance and Hall measurements of the heterostructures were performed while the carrier densities in channel layer were manipulated via front-gating and illumination. An increase in electron mobility with free carrier density was observed for all heterostructure samples. For control samples (GaAs channel), the mobility depends exponentially on carrier density, i.e., $\mu\sim n^a$, where α is typically 1~1.5, suggesting the dominant scattering mechanism is long-range ionized impurity scattering. For the nitride samples (GaAsN channel), α is 0.2~0.3, and the mobility saturates for $n>1.5\times10^{11}cm^{-2}$, suggesting that N atoms act as short-range neutral scattering centers. The effects of rapid thermal annealing on the substitutional and interstitial N concentrations and the resulting transport properties of GaAsN films will also be discussed.

4:40pm **EM+NS-MoA9 Interface- and Photo-Based Manipulation of Point Defects for Nanoelectronics**, ***Y. Kondratenko***, *R Vaidyanathan, C.T.Z. Kwok, E.G. Seebauer*, University of Illinois, Urbana - Champaign

As electronic devices scale deeper into the nanometer regime, key aspects of device performance become increasingly dominated by point defects within the semiconductor. An obvious example is current flow in silicon nanowire devices, which is heavily influenced by residual point defects. The present work discusses two new mechanisms for controllably manipulating point defect concentrations in semiconductors at the nanoscale, using silicon as a specific example. In the first mechanism, the ability of free surfaces or solid interfaces to annihilate point defects within the solid can be altered by several orders of magnitude through either chemical state modification or mild ion bombardment. The resulting dangling bonds at the surface or interface interact with the defects through direct bond-addition reactions and through electrostatic attraction or repulsion. In the second mechanism, low-level photostimulation to produce excess charge carriers changes the average charge state of certain varieties of point defects, which in turn affects their diffusion rates toward nearby interfaces. Depending on the temperature and time of exposure, diffusion rates can be either enhanced or inhibited. Experiments using arsenic and boron diffusion as markers for defect behavior in silicon are described that demonstrate both mechanisms. Rate-equation-based modeling accurately describes all qualitative and most quantitative aspects of the results.

5:00pm **EM+NS-MoA10 Programmable Memory Devices using Gold Nanoparticles Capped with Alkanethiol of Different Carbon Chain Lengths**, ***P.-Y. Lai***, *J.-S. Chen*, National Cheng Kung University, Taiwan

In recent years, organic nonvolatile memory devices have attracted much attention due to its high potential for fabricating high density, low cost and flexible electronic components. In this work, we have fabricated an organic memory consisting of gold nanoparticles and polystyrene sandwiched between aluminum (Al) electrodes. The gold nanoparticles capped with three different carbon chain lengths of the alkanethiol ligand are prepared by the two-phase arrested growth method. The pristine device, which is initially at a low-conductivity state, exhibits an abrupt increase of current when the device is scanned up to the certain voltage. The high-conductivity state can be returned to the low-conductivity state by applying a positive voltage. The length of the alkanethiol which encapsulates gold nanoparticles affects the distribution of threshold voltage to turn on the memory device. The carbon chain length of alkanethiol varies the electron tunneling ability due to the modification of energy barrier. The results correlate the length of the alkanethiol with switching speed, cyclic write-read-erase-read times, and retention time of memory devices will also be discussed.

In-situ Electron Microscopy Topical Conference

Room: 618 - Session IE-MoA

Dynamics of Nanostructures

Moderator: D.J. Miller, Argonne National Laboratory

2:00pm **IE-MoA1 In-situ Environmental TEM of the Nucleation and Growth of One-Dimensional Nanostructures**, ***S. Takeda***, *H. Yoshida*, Osaka University and CREST-JST, Japan, *Y. Homma*, Tokyo University of Science and CREST-JST, Japan **INVITED**

Solid-gas reaction is a fundamental process of the synthesis of various nanomaterials. For example, carbon nanotubes (CNTs), one of the most promising nanomaterials for future nanotechnology, are grown from metal catalysts in gases containing carbon. In order to apply nanomaterials to future nanodevices, their growth mechanism needs to be better understood at the atomic level. In this respect, transmission electron microscopy (TEM) equipped with an environmental cell (E-cell), which is occasionally called environmental-TEM (ETEM), is one of the best techniques. We have examined the importance of ETEM for the study of the growth mechanism of CNTs via computer simulation of high resolution ETEM images of CNTs under an actual growth condition.[1] Moreover, several pioneer works have revealed various solid-gas reactions by ETEM. In this work, the growth process of CNTs has been actually observed by a newly designed ETEM (FEI Tecnai F20 equipped with E-cell) which has an information limit of nearly 0.15 nm even in 10 mbar N_2 gas. CNTs were grown by catalytic chemical vapor deposition (CVD) of methane, acetylene and so on. The metal catalysts, such as Co and Ni were deposited on a silicon substrate with surface oxide. In our CVD process, the pressure of gases ranges from 1 to 10^3 Pa and the temperature is set at 600 to 800°C. We investigate the growth mechanism and dynamics of CNTs via in situ observations of both catalyst nanoparticles and CNTs. As an example, we have succeeded in the observation of the growth of a short multi-walled CNT (MWNT). During the growth of the MWNT, the shape of the catalyst changes drastically. Before the growth, the shape of the catalyst is a sphere. Then, the shape changes into an elongated shape. At a certain moment, the catalyst lifts off the substrate and contracts to a spherical shape. At the same time, a MWNT grows. The details including other in situ observations of CNT growth will be presented at the meeting.

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2:40pm **IE-MoA3 Observation of Dynamic Nanoscale Processes Using Environmental Scanning Transmission Electron Microscope**, ***R. Sharma***, Arizona State University **INVITED**

The world of nanomaterials has become the ‘real world’ for most of the applications in the area of nanotechnology. As post-synthesis handling of materials at a nanoscale is not practical, nanomaterials often need to be synthesized directly as part of a device or circuit. This demand posted by nanotechnology has led to the modifications in the design of transmission electron microscopes that permit us to perform in situ synthesis and characterization simultaneously. In situ observations of the synthesis process are used to understand and evaluate the effect of synthesis conditions (starting material (reactants), temperature and pressure) on the morphology, structure and chemistry of the product. Moreover, functioning (e.g. activity of a catalyst) of many nanosystems changes during operation. The effect of operating condition (time, temperature, and the ambient) can be elucidated by atomic scale in situ observation. Such in situ observations can be used to optimize the synthesis conditions for nanomaterials with desired structure and properties and improve the functioning of nano systems. Environmental scanning transmission electron microscope (ESTEM) permits us to observe gas-solid interactions at elevated temperatures in gaseous environment. A modern ESTEM, equipped with a field-emission gun (FEG), energy filter or electron energy loss spectrometer, scanning transmission electron microscopy (STEM) coils, and bright and dark field detectors, is a versatile tool for understanding chemical processes at nanometer level. Its applications range from in situ characterization of reaction steps such as oxidation-reduction or corrosion, to in situ synthesis of nanomaterials such as quantum dots, carbon nanotubes or Si nanowires. Examples including synthesis and characterization (e.g. CNT, Si nanowires) and structural modifications during functioning of nanomaterials (catalyst) will be used elucidate the applications of the ESTEM. Future applications and improvements in the instrument design will be discussed.

3:40pm **IE-MoA6 Using Real Time Electron Microscopy to Understand Nucleation and Growth in Semiconducting Nanowires and Carbon Nanotubes**, ***E.A. Stach***, *B.-J. Kim, S.-M. Kim, D.M. Zakharov*, Purdue University, *F.M. Ross, J. Tersoff*, IBM T.J. Watson Research Center, *S. Kodambaka*, UCLA, *M.C. Reuter, K. Reuter*, IBM T.J. Watson Research Center, *B. Maruyama, M. Pender*, Wright Patterson Air Force Research Laboratory **INVITED**

Semiconducting nanowires and carbon nanotubes are two of the primary 'new' materials of interest in the field of nanotechnology, This is because their small dimensions and unusual structures allow for new technologies to be established that exploit their unique electronic properties. We have been focused on understanding the mechanisms and kinetics associated with their nucleation and growth, in an attempt to provide a scientific framework for controlling their structure. Through the use of in-situ chemical vapor deposition in both ultra-high vacuum and at elevated pressures, we can observe the mechanisms of nucleation and quantitatively characterize the kinetics of these processes. In the case of vapor-liquid-solid silicon nanowire growth, we have found that the dissociative desorption of disilane is the rate limiting step. Additionally, after nucleation, we find that the nuclei undergo a rapid growth in size, driven by the supersaturation of silicon in the host gold-silicon liquid alloy drop. We will present a theoretical framework to describe this behavior which balances the roles of supersaturation, pressure and interface energies and show how this can be used to find the kinetic liquidus line in the AuSi phase diagram. In the case of carbon nanotube growth, we utilize a unique catalyst approach wherein the catalysts are firmly embedded in a silicon dioxide support film, so as to permit high resolution images of their surface structure at the onset of nanotube growth via the alcohol catalytic chemical vapor deposition process. We will report quantitiative measurements of catalyst coarsening, and discuss how this process plays a controlling role in nanotube nucleation and subequent growth. In each case, we will emphasize the power of the in-situ approach for providing quantiative data for discovering unique information regarding fundamental growth processes.

4:20pm **IE-MoA8 In-situ Probing and Manipulation of Dynamical Processes on the Nanoscale using Combined Scanning Tunneling and Transmission Electron Microscopy*, E. Olsson***, Chalmers University of Technology, Sweden **INVITED**

Properties on all scales are influenced and sometimes dominated by the atomic arrangement at individual defects and interfaces. Both scanning tunneling and transmission electron microscopy can be used to extract information about the structure of materials with high spatial resolution. The techniques are complementary where the scanning tunneling microscope (STM) allows us to image surfaces and perform spectroscopy on the nano- and subnanoscale. However, it is not possible to image and measure simultaneously. In addition, the images contain information about the surface while processes below the surface are not directly accessible. We have developed a combined STM and transmission electron microscopy (TEM) to enable the recording of dynamical processes on the nanoscale and direct correlation between local atomic structure and properties.[1] This talk will address experiments on carbon nanotubes including electromigration and a nanopipette function.[2] Another example concerns gold nanoparticles and the effect of laser irradiation on individual particles as well as ensembles of particles. An intense nanosecond laser pulse can cause melting, evaporation and diffusion which induce changes in particle size distribution, morphology, structural and properties.[3] Nanostructures are inherently small and often electron transparent without specimen preparation. However, it may be necessary to develop methods to extract the individual nanostructures or to manipulate and follow the changes of individual nanoparticles during dynamical processes. A combined focused ion beam workstation and scanning electron microscope with an in-situ manipulator provides the ability to reach into nanostructures and enables reproducible techniques of local extraction and identification.[3,4]

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5:00pm **IE-MoA10 High-Resolution In-Situ Electron Microscopy Studies of Aqueous Samples*, N. de Jonge,*** Oak Ridge National Laboratory*, D.B. Peckys,* University of Tennessee, Knoxville*, G.M. Veith,* Oak Ridge National Laboratory*, S. Mick,* Protochips Inc.*, D.W. Piston,* Vanderbilt University*, S.J. Pennycook,* Oak Ridge National Laboratory, *D.C. Joy*, University of Tennessee, Knoxville

One of the main challenges of our time is the in-situ study of the molecular machinery of life in order to gain a fundamental understanding of how cells function at a molecular level. This challenge requires ways of imaging live cells. Recently, time-resolved confocal laser microscopy has been used to image protein function in living cells,[1] but this method's spatial resolution is on the order of the wavelength of light. Several new super-resolution techniques provide a high spatial resolution, but not temporal resolution.[2] We have begun applying electron microscopy (EM) to image cells in a liquid environment at atmospheric pressures. EM has sub-nanometer resolution and typically exhibits fast image acquisition. Others developed liquid enclosures for high-resolution imaging with transmission electron microscopy (TEM).[3] But, TEM imaging is sensitivite to materials with low atomic numbers, resulting in a strong background signal from the liquid and a low resolution for relevant volumes of liquid needed to image whole cells. Here, we present results from our new liquid scanning transmission electron microscopy (STEM) technique. STEM is insensitive to low z materials facilitating imaging through thicker samples. The liquid and the sample are enclosed between two ultra-thin windows of silicon nitride that are essentially electron transparent. Nanometer resolution and dynamic motion of gold nanoparticles enclosed in an aqueous environment will be reported. In addition we will present liquid STEM data from the high-resolution imaging of Ecoli bacteria labeled with quantum dots. Liquid STEM presents a new alternative to optical methods for time-resolved studies of intact Eukaryotic cells and bacteria. We are grateful to T. McKnight, R. Dona, G. Kremers, T.L. Harvey, C. Chisholm and P. Herrell. Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725.

[1] J. Lippincott-Schwartz, E. Snapp, A. Kenworthy, Nature Reviews 2, 444 (2001).

[2] V. Westphal, S. W. Hell, Phys. Rev. Lett. 94, 143903 (2005).

[3] M. J. Williamson, R. M. Tromp, P. M. Vereecken, R. Hull, F. M. Ross, Nature Materials 2, 532 (2003).

The Industrial Physics Forum 2007: The Energy Challenge

Room: 602/603 - Session IPF-MoA

Nuclear Energy

Moderator: J. Hobbs, American Institute of Physics

2:00pm **IPF-MoA1 Status of Fusion Power*, R.J. Hawryluk***, Princeton Plasma Physics Laboratory **INVITED**

Fusion is an attractive long-term form of nuclear energy. Experiments on magnetically confined plasmas in the 1990's demonstrated not only the ability to confine plasmas with the temperatures required for a fusion reactor but also produced significant fusion power (up to 10.7 MW in the Tokamak Fusion Test Reactor and 16.1 MW in the Joint European Undertaking for <1sec) using deuterium-tritium fuels. This major step, together with results from a worldwide research effort, has provided confidence in the design of the International Thermonuclear Experimental Reactor (ITER) to produce 500MW (thermal) of fusion power for 400 sec. ITER is an international experiment whose partners are the European Union, India, Japan, the People's Republic of China, the Republic of Korea, the Russian Federation and United States. ITER aims to demonstrate the scientific and technical feasibility of fusion power and will be constructed in Cadarache, France. For the first time, the fusion reactions will provide the majority of the heating for the plasma with an energy gain >10. The design of ITER has identified important scientific and technology issues, which are currently being addressed in facilities around the world. However for a fusion demonstration power plant, further progress on the underlying science and technology is required to achieve ~2500 MW (thermal) continuously with a gain >25 in a device whose size is comparable to ITER. This requires addressing issues associated with plasma boundary due to the higher power and plasma stability due to the need to sustain even higher pressure plasmas at the magnetic field of ITER. Furthermore, efficient continuous operation requires minimizing the external power for controlling the plasma. Experiments on the three main approaches to magnetically confining a plasma, the advanced tokamak, the spherical tokamak, and the stellerator, in parallel with the design and construction of ITER, are exploring innovative solutions required for a demonstration power plant. The advanced tokamak relies on active instability control and a combination of external current drive to increase the fusion power and achieve continuous operation. The spherical tokamak achieves higher fusion power at a given size and magnetic field by decreasing the ratio of the plasma major radius to minor radius. The stellarator is passively stable and does not require external power to drive the plasma current continuously. This research is supported by the U.S. Department of Energy under Contract Number DE-AC02-76CH03073.

2:40pm **IPF-MoA3 The Role of High Temperature Gas Reactors in the Future Development of Nuclear Power*, E.M. Campbell***, *F. Venneri, A.S. Shenoy, C.J. Hamilton*, General Atomics **INVITED**

Given the increased worldwide demand for energy, the desire for energy security and the need to reduce anthropenic influence on the earth's climate, it appears certain that there will be a significant increase in the role of nuclear power. While the early expansion of nuclear power will be dominated by light water reactors with modern safety features and improved economics, advanced Generation IV reactors such as high temperature gas reactors will become increasingly important following the demonstration of commercial scale prototypes in the next decade. High temperature gas reactors have many attractive features arising from the use of inert helium gas as a coolant, graphite as a moderator and fuel encapsulated in a robust TRISO ceramic coating. These features enable the reactors to be passively safe — they employ no safety features with an emergency core coolant reservoir — while not sacrificing attractive economics, and at the same time producing output temperatures in excess of 900ºC. Such temperatures allow for flexibility in siting (even in regions with little or no water availability), and the efficient production of electricity as well as numerous process heat applications such as the large scale production of hydrogen and economic desalination. These latter applications which to date have not used a "nuclear heat source" will become increasingly important in the future and are made possible only by these Generation IV reactors. The fuel form in these reactors enables a wide range of fission fuels to be deployed including uranium, thorium, and actinides including those from spent fuel, allows for extremely deep burn, and provides increased barriers for proliferation. In this presentation the role of gas reactors in an expanding nuclear market will be discussed. Their unique features will be presented including passive safety, economics, modularity, fuel and siting flexibility, applications and symbiosis with other reactors such as fast sodium reactors. An attractive scenario for the large scale deployment of these reactors which addresses fuel availability and waste will also be included.

*Work supported by General Atomics internal funding.

3:40pm **IPF-MoA6 Sustainable Nuclear Energy Production and Nuclear Waste Management**, ***M. Peters***, Argonne National Laboratory **INVITED**

The world energy demand is increasing at a rapid pace. In order to satisfy the demand and protect the environment for future generations, future energy sources must evolve from the current dominance of fossil fuels to a more balanced, sustainable approach to energy production. The future approach must be based on abundant, clean, and economical energy sources. Therefore, because of the growing worldwide demand for energy and need to minimize greenhouse gas emissions, there is a vital and urgent need to establish safe, clean, and secure energy sources for the future. Nuclear energy is already a reliable, abundant, and carbon-free source of electricity for the U.S. and the world. In addition to future electricity production, nuclear energy could be a critical resource for “fueling” the transportation sector (e.g., process heat for hydrogen and synthetic fuels production; electricity for plug-in hybrid and electric vehicles) and for desalinated water. Nuclear energy must experience significant growth to achieve the goals of our future energy system. The most significant technical challenge that must be addressed to allow the necessary expansion is safe, secure, and sustainable nuclear waste management. The nuclear fuel cycle is a key concept when discussing a sustainable future for nuclear energy. The nuclear fuel cycle is a cradle-to-grave concept starting from uranium mining to fuel fabrication to energy production to nuclear waste management. At first order, there are two approaches to the nuclear fuel cycle. An open (or once-through) fuel cycle, as currently planned by the United States, involves treating spent nuclear fuel (SNF) as waste with ultimate disposition in a geologic repository. In contrast, a closed (or recycle) fuel cycle, as currently planned by other countries (e.g., France, Russia, Japan), involves treating SNF as a resource whereby separations and recycling of transuranics (TRU’s) in reactors work with geologic disposal. Open fuel cycles require multiple geologic repositories whereas closed fuel cycles can reduce the volume and toxicity of waste, conserve uranium resources, and provide additional energy. Nuclear waste management and lack of a closed fuel cycle are principal impediments to the future viability of the nuclear energy option. In the advanced, closed fuel cycles that are currently being developed in France, Russia, Japan, the United States, China, and India, SNF would be sent to a reprocessing plant where its major constituents are separated into several streams: a TRU stream, to be recycled, and several other streams, including a “clean” uranium waste stream (note that this uranium could be recycled as part of future nuclear fuels), and waste streams containing the fission products. The TRU’s are fabricated as fresh nuclear fuel, to be irradiated again in a fission reactor, ideally a fast-neutron system. Approximately 30% of the TRU’s are fissioned each time the fuel is irradiated in a low conversion-ratio fast reactor. The remaining 70% stay in the cycle until they are fully fissioned. Even a closed fuel cycle requires a geologic repository to dispose of long-lived fission products and potentially very small amounts of TRU’s, the latter being from minor separations process losses. The volume and toxicity of waste requiring geologic disposal is reduced significantly in a closed fuel cycle; however, the doses from the encased radionuclides still require long-term isolation in durable waste forms in geologic repositories. Engineering and technology development will improve the reliability and cost effectiveness of nuclear energy and closed fuel cycle approaches. However, the rapid expansion of nuclear energy technologies required to satisfy the needs of the future will require breakthroughs that will only be possible through a coupling of applied and basic science and engineering. In particular, advanced modeling and simulation tools and approaches integrated with engineering and facilities design will be the avenue for using basic science insights to further the prospects for sustainable nuclear energy and nuclear waste management.

4:20pm **IPF-MoA8 Nuclear Energy Policy**, ***D. Hill***, Idaho National Laboratory **INVITED**

The U.S., through the National Energy Policy and the landmark legislation, Energy Policy Act of 2005, has adopted policies that support a diverse clean energy portfolio, including expanded use of nuclear energy. The nuclear industry is pursuing the business and licensing cases for building at current count, more than thirty new plants over the next decade. Government is sharing the risk that first movers of these new plants will face by cost-sharing the license preparation effort, by sponsoring production tax credits for the first 6,000 MW of new nuclear generating capacity, and through loan guarantees for the low emissions technologies. Additionally, last year, the Bush Administration proposed the Global Nuclear Energy Partnership, a multinational initiative that focuses on developing the technologies and infrastructure that will be needed to support anticipated global expansion of nuclear energy. A key element, advanced recycling of spent nuclear fuel, would address the waste burden associated with the once-through fuel cycle that relies extensively on surface storage and eventually, deep geologic disposal of spent nuclear fuel. Recycling would recover and reuse materials contained in spent fuel by separating them from the waste products without producing plutonium. This paper examines nuclear energy policy in the U.S., outlook for nuclear energy in the U.S. and the world, reasons to move toward a closed fuel cycle and U.S. and international progress on development of advanced fuel cycle technology.

Marine Biofouling Topical Conference

Room: 609 - Session MB+BI-MoA

Control of Marine Bioadhesion

Moderator: G.P. Lopez, University of New Mexico

2:00pm **MB+BI-MoA1 Engineered Polymer Coatings for Foul-Release Applications**, ***J. Genzer***, *A.E. Özçam*, *K. Efimenko*, North Carolina State University **INVITED**

Marine biofouling is a serious and complex problem resulting in losses of operating efficiency of ships. Current coating technologies derived from copper- and tin-based compounds are being banned because of detrimental effects on marine environment. Hence there is need for developing efficient marine coatings that would possess no ecological concern. In addition to various chemical approaches, surface topography has also been shown to be important for mechanical defense against biofouling. For instance, Hoipkemeier-Wilson and coworkers reported that topographically corrugated surfaces are capable of reducing biofouling. The degree to which fouling was reduced was found to depend on the dimensions of the geometrical protrusions as well as the chemistry of the surfaces. Because biofouling includes a very diverse range of various species, whose sizes span several orders of magnitude, one single topographical pattern will not likely perform as an effective antifouling surface. Rather, surface corrugations having multiple length scales acting in parallel should be used in designing effective antifouling surfaces. We have developed a method leading to substrate comprising hierarchically wrinkled (H-wrinkled) topographies. These specimens were prepared by first uniaxially stretching poly(dimethylsiloxane) films, exposing them to ultraviolet/ozone (UVO) radiation for extended periods of time (30-60 minutes), and releasing the strain. After the strain was removed from the specimens the surface skin buckled perpendicularly to the direction of the strain. A detailed analysis of the buckled surface uncovered the presence of hierarchical buckling patterns; buckles with smaller wavelengths (and amplitude) rested parallel to and within larger buckles, forming a nested structure. At least 5 distinct buckle generations (G) were detected with their wavelengths ranging from tens of nanometers to a fraction of a millimeter. The method for producing coatings with H-wrinkled topographies may represent a convenient platform for designing foul-release surfaces. Our recent sea water immersion experiments involving testing over an extended time period indicated that these coating are far superior to flat coatings. We will discuss how the H-wrinkle topographies can be applied to make coatings from just about any type of material and offer methodologies for preparing amphiphilic foul-release coatings from commercially available materials. While more work still needs to be done, the initial observations suggest that the H-wrinkled coatings may represent a new and promising platform for fabricating efficient foul-release marine coatings.

2:40pm **MB+BI-MoA3 Nanoscopically-resolved Amphiphilic Surface Features as Non-toxic, Treacherous Terrain to Inhibit Marine Biofouling**, ***K.L. Wooley***, Washington University in Saint Louis **INVITED**

This presentation will detail amphiphilic nanostructured material systems, constructed from a general methodology that involves the kinetic, in situ crosslinking of thermodynamically-driven phase segregated states of polymer assemblies. Macroscopic crosslinked networks composed of amphiphilic nanodomains presented on the surface and dispersed throughout the material are obtained by crosslinking of the assemblies in bulk samples. Of particular interest for these materials are the complex surface topographies and morphologies that allow for the materials to exhibit antifouling characteristics. The crosslinked macroscopic networks have been focused upon compositions that include hyperbranched fluoropolymers and linear poly(ethylene glycol)s, although the compositional profiles are being expanded. The domains or channels that are present throughout the samples offer interesting opportunities for the packaging and release of guest molecules. The nanoscale dimensions and large interfacial surface areas provide for high loading capacities within uniform host environments, but then also promote the release of these guests at significantly reduced temperatures. The uptake and release of guests from hydrophobic vs. hydrophilic, of varying compositions, structures, and sizes, will be discussed. Most recently, unique mechanical properties have also been observed, and these data will also be presented.

3:40pm **MB+BI-MoA6 Basic Surface Properties and Their Influence on the Adhesion of Marine Organisms**, ***A. Rosenhahn***, University of Heidelberg, Germany **INVITED**

The prevention of biofouling is a major challenge for all man made objects which are in long term contact with seawater. In order to systematically develop non toxic coatings, a fundamental understanding of basic surface properties that inhibit or encourage settlement of marine inhabitants is required. Together with biological partner groups within the EU IP AMBIO[1] we investigate the influence of surface properties such as wetting, charge or morphology on the adhesion and on the removal properties for different marine organisms. To tune wetting and chemical surface properties, self assembly is used as highly versatile technique. For preparation of well defined micro- and nanomorphologies, different lithography and multilayer approaches are used. The interaction of different marine inhabitants with these surfaces will be discussed and compared to general protein resistive properties. Although one main focus of this work is inhibition of settlement, also release properties are tested as important measure of adhesion strength. Apart from established ways of evaluating anti fouling properties, we use digital in-line holography as new tool to study and compare the exploration of different surfaces by swimming marine organisms.[2] Following the original idea of D. Gabor,[3] coherent scattering of radiation can be used to record scattering patterns which contain three dimensional information about investigated objects due to the presence of a reference wave. Holography therefore allows the investigation of three dimensional processes e.g. by tracking particles in real time with sub¬micrometer resolution.[4] We use this novel technique to visualize and analyze the motion and exploration behavior of swimming marine organisms towards surfaces with systematically changing properties. The goal of these three dimensional tracking experiments is to gain a more detailed understanding about surface sensing and the early attachment stages of marine organisms.

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4:20pm **MB+BI-MoA8 Bioresponse to Engineered Topographies**, ***A.B. Brennan***, University of Florida **INVITED**

This study examines hierarchical combinations in polymers that have been used to produce engineered surfaces, which elicit micro-topographical and chemical cues in biological systems. Nature provides complex chemical forms of polymers that are manipulated through both conformational and configurational forms to yield specific functions. Our recent studies have been focused on the design of polymeric surfaces that can be used as models in the study of biological adhesion mechanisms. The recent expansion of bioengineering has increased our need for better models of cellular adhesion and chemical manipulation of surfaces. A process commonly referred to as contact guidance has been shown to modulate cell shape and function in a variety of cell types. Control of endothelial cell (EC) shape using micropatterned chemical substrates is shown in numerous studies by influencing cell adhesion to proteins, which selectively adsorb to the chemical micropatterns. This presentation will focus on the polymer structures that we have been developing for a topographically modified surface with a range of surface energies and bulk modulus values developed through nanostructural modifications on larger microstructures. In this model, we have been able to study the interactions of the biological-induced factors with the polymer chemistry.

5:00pm **MB+BI-MoA10 Development of Environmentally Benign and Durable Nonfouling Marine Coatings**, ***S. Jiang***, University of Washington

Biofouling on ship hulls and other marine surfaces has become a global environmental and economic issue. Traditionally, the best antifouling coating is TBT (tributyltin)-based paint. Due to increased environmental concern, TBT antifouling coatings have been restricted. Non-toxic, fouling-release coatings based on silicone or fluorinated compounds are under development. These coatings are only effective on vessels moving at high speeds. Currently, we are developing environmentally benign, durable, and cost-effective nonfouling coatings, to which marine microorganisms can not attach, as the next-generation marine coatings. In this work, zwitterionic-based materials will be shown to be effective against various marine microorganisms in laboratory and field tests. We have demonstrated for the first time that poly(sulfobetaine methacrylate) [p(SBMA)] and poly(carboxybetaine methacrylate) [p(CBMA)] based materials and coatings are superlow biofouling. In addition, we have explored various approaches to apply p(SBMA) or p(CBMA) materials onto surfaces and developed several noncoatings for marine applications. Laboratory tests confirmed the excellent performance of sulfobetaine (SB)-based coatings against marine microorganisms (Ulva spores and barnacle cypris larvae). Recently, we developed SB-based paints and spray-coated them onto surfaces covered with an epoxy primer. Initial field tests of these panels clearly demonstrated that our coatings effectively deferred the settlement of hard foulants. Because of their excellent stability and high effectiveness at preventing microorganisms from adhering to surfaces, SB and carboxybetaine-based materials are excellent candidates for marine coatings. The objective of our work is to create products that will effectively defer biofouling under static conditions over a long period of time.

MEMS and NEMS

Room: 615 - Session MN-MoA

Materials Processing, Characterization and Fab Aspects

Moderator: B. Ilic, Cornell University

2:00pm **MN-MoA1 Electromechanical Resonators from Graphene Sheets**, ***P.L. McEuen***, Cornell University **INVITED**

We fabricate nanoelectromechanical systems from single and multilayer graphene sheets by mechanically exfoliating graphite over trenches in SiO2. Vibrations with fundamental resonant frequencies in the MHz range are actuated either optically or electrically and detected optically by interferometry. The thinnest resonator consists of a single suspended layer of atoms and represents the ultimate limit of two dimensional nanoelectromechanical systems. The high Young's modulus (E = 1 TPa), extremely low mass (single layer of atoms), and large surface area make these resonators ideally suited for use as mass, force, and charge sensors. We will discuss recent work on nanochambers sealed with graphene membranes. The pressure of the gas inside the nanochamber determines the pressure and damping of the graphene resonator.

2:40pm **MN-MoA3 Determination of the Density, Viscosity and Activation Energy of Small Liquid Volumes using Microcantilevers**, ***G. Hähner**, N. McLoughlin, S.L. Lee*, University of St Andrews, Scotland, UK

The density and the viscosity are important parameters for the understanding and tailoring of many processes taking place in liquids. Their determination is generally performed with macroscopic liquid amounts and in separate measurements. In recent years some approaches have been proposed to determine these properties simultaneously. The majority of the methods applied still requires macroscopic liquid volumes and is based on macroscopic techniques. With the growing interest in microfluidic applications, however, alternative approaches for the determination of liquid properties on the microscale are desirable. We present a method for determining the viscosity and density of small liquid volumes (microliters) simultaneously from the resonance spectra of both magnetically driven as well as thermally excited microcantilevers.[1] Parameters characteristic of the resonance behavior of the system were extracted from resonance spectra recorded in a liquid of known density and viscosity. Subsequently, these parameters were used to determine the properties of further samples. In addition, temperature dependent spectra were exploited to extract the activation energy of viscous flow. The procedure we present is fast and reliable and requires no calibration of the cantilever force constant or specific knowledge of the cantilever geometry. Based around existing AFM technology the approach we propose can be easily adapted to suit a variety of microfluidic applications.

[1] N. McLoughlin, S. L. Lee, G. Hähner Appl. Phys. Lett. 89, 184106 (2006).

3:00pm **MN-MoA4 A Micromachined Ultrasound Transducer for Noncontact Nondestructive Evaluation**, *X. Wang, Y. Fan, **W.-C. Tian**, H. Kwon, S. Kennerly, G. Claydon, A. May*, General Electric Co.

We report a capacitive micromachined ultrasound transducer (CMUT) for air-coupled, noncontact, nondestructive evaluation (NDE) applications. Air-coupled ultrasound is an attractive inspection technique for materials or structures that are not suitable for contact or immersion ultrasound inspections, such as the honeycomb composites used in aircraft structures. In the past CMUTs have been extensively studied for water-coupled, immersion applications.[1] In principle, CMUTs have better acoustic impedance match with air compared with piezoelectric ultrasound transducers. This makes them ideally suited for air-coupled NDE. However, they are not widely used in air inspection due to large air attenuation of acoustic power. To overcome this problem, CMUTs' transduction efficiency must be improved. We have successfully developed a large gap air-coupled CMUT. The device has a 1MHz operation frequency and can function both as ultrasound transmitter and receiver. The CMUT structure employs a large gap and a specially patterned SiO2 layer to provide large acoustic output while avoiding dielectric charging. A wafer-bonding process was used in fabrication.[2-4] In this process, a Si substrate was first etched to create cavities and oxidized. The SiO2 on the cavity floor was patterned to form pillar structures, which prevented arcing and charging in actuation. An SOI wafer was then bonded to the substrate wafer followed by handle wafer removal and metallization steps to complete the device. In our tests, CMUTs with patterned SiO2 insulation layers showed consistent operation over time. In comparison, control devices with un-patterned blanket SiO2 layers suffered from unsynchronized cell vibrations and fast signal decay due to dielectric charging. Acoustic though-transmission tests with paired CMUTs showed a loop gain of -51dB. As a comparison, a pair of state-of-the-art commercial air-coupled ultrasound transducers showed a -65 dB loop gain, 14 dB lower than the CMUTs reported here. This clearly indicates that improvement of air-coupled CMUTs is achievable and can lead to wide use of CMUTs for air inspections.

[1] X. Jin, et al., J. Microelectromech. Syst., 8, 100 (1999).

[2] Y. Huang, et al., J. Microelectromech. Syst., 12,128 (2003).

[3] Y. Huang, et al., IEEE T. Ultrason. Ferr., 52, 578 (2005).

[4] W-C. Tian, et al., US Patent Publication #2006/0004289 (2006).

3:40pm **MN-MoA6 Design, Synthesis, and Fabrication of a Biomolecular Nanovalve**, ***H. Li***, *L.E. Ocola, O. Auciello, M.A. Firestone*, Argonne National Laboratory

A device containing microfluidic and nanofluidic channels was designed and fabricated to study on the performance of a bio-nanovalve controlled by polarization of ferroelectric substrate. The microfluid channel consisting of 200 (W) x 200 (H) µm and 35 (W) x 200 (H) µm straight channels, micro-nozzles, and micro-diffusers, was designed to provide high driving pressure and low mass flow rate for fluid flow in the nanochannel. A recently developed lead-zirconium-titanate (PZT) substrate integrated with nano-electrodes was coated on the bottom of nanochannels to control the nanovalve made of biological molecules. By observing the fluid mixing behavior variation in nanofluid channels of 200 (W) x 200 (H) nm before and after the polarization of PZT substrate, the function of the bio-nanovalve would be demonstrated. The biovalve will prove useful for many applicatons including lab-on-a-chip and release-on-demand drug delivery systems. This device can also be used to study the basic science of fluid flow and heat transfer at the nanoscale with the purpose of improvement of flow and heat transfer efficiency in nanoscale devices.

4:00pm **MN-MoA7 XeF_2 Etching of Si and SiO_2 for MEMS Manufacturing**, ***J.-F. Veyan***, *Y.J. Chabal*, Rutgers, The State University of New Jersey, *M.Y. Yan, E. Gusev, A.L. Londergan*, Qualcomm

XeF_2 is used for etching a number of materials during MEMS fabrication, such as silicon,[1] and metals. Its strong reactivity with silicon and metals leads to rather violent reactions that make it difficult to characterize with typical surface science techniques under typical manufacturing conditions (XeF_2 pressure in a few Torr range). The fundamental reactions involved under these conditions are therefore harder to understand than typical elementary surface reactions in ultra-high vacuum conditions. It is therefore important to investigate etching mechanisms under such conditions. This work focuses on the characterization of gas phase, surface species, and substrate surfaces during XeF_2 etching using in-situ infrared absorption spectroscopy (IRAS) for both silicon and silicon oxide surfaces under typical etching conditions. To that end, a compact reactor has been constructed out of non-reactive materials (e.g. stainless steel, aluminum, Teflon and Kalrez o-rings), with the capability to perform IR spectroscopy. Despite these precautions, IRAS is critical to detect the presence and role of fluorinated contaminants (from reaction with molecules adsorbed on the walls) and the presence of products.[2] Thus, while XeF_2 induces a strongly exothermal reaction with Si, producing large amounts of SiF_4 gas (with a characteristic IR signature), and the incorporation of SiF, SiF_2 and SiF_3 in the subsurface region (~30Å deep) as previously observed in UHV studies, the presence of H_2O and HF gas, and CF_x and othe r adsorbed impurities can also be observed, pointing to side reactions on the walls despite thorough baking. XeF_2 etching of SiO_2 is much weaker and thereby harder to study. IRAS studies confirm that amorphous SiO_2 is etched at the rate of ~2-3Å/cycle at room temperature, where a cycle consists of 2Torr in 427cm^3 (i.e. ~ 3.10^{19} XeF_2 molecules). Although SiF_4 gas is also detected, it is not possible to exclude the potential etching of Si due to scratches. In contrast, no measurable SiF_4 gas is observed when crystal quartz is placed in contact with XeF_2, indicating that quartz does not etch. Preliminary data indicate that SiO_2 etching is highly dependent on the substrate temperature. Based on IRAS data, this talk will discuss various etching mechanisms and optimization of etching conditions for both Si and SiO_2.

[1] Harold.F Winter and I.C. Plumb J. Vac. Sci. Tech. B 9(1) 197 (1990)

[2] J. I. Steinfeld, Chem. Rev., 89, 1291, (1989)

4:20pm **MN-MoA8 Advances in Magnetometry through Miniaturization**, ***A.S. Edelstein***, *J. Burnette, G.A. Fischer,* U.S. Army Research Laboratory, *S.F. Cheng,* U.S. Naval Research Laboratory, *E.R. Nowak*, University of Delaware **INVITED**

Recent innovations will lead to magnetic sensors that are smaller, more sensitive and/or cost less than current magnetometers. Examples of this are the chip scale atomic magnetometer, magnetic tunnel junctions with MgO barriers, and a device for minimizing the effect of 1/f noise, the MEMS flux concentrator. In the chip scale atomic magnetometer researchers have been able to fabricate the light source, optics, heater, optical cell, and photodiode detector in a stack that passes through a silicon wafer. There are limits on decreasing the size of the cell, because collisions with the cell walls limit the spin lifetime. A search is underway for materials to be used as cell liners that have a smaller effect on the spin lifetime. Theoretical and subsequent experimental work led to the observation of magnetoresistance values of 400% at room temperature in magnetic tunnel junctions with MgO barriers. The large magnetoresistance occurs because electrons in the majority band can tunnel more easily through the MgO barrier than electrons in the minority band. The MEMS flux concentrator has the potential to increase the sensitivity of magnetic sensors at low frequencies by orders of magnitude. The MEMS flux concentrator does this by shifting the operating frequency to higher frequencies where 1/f noise is unimportant. The shift occurs because the motion of flux concentrators on MEMS flaps modulates the field at kHz frequencies at the position of the sensor. The concept and development of the MEMS flux concentrator will be presented.

5:00pm **MN-MoA10 Fabrication of Stationary Micro-Optical Shutter Based on Semiconductor-To-Metallic Phase Transition of W-doped VO2 Active Layer Driven by an External Voltage**, ***M. Soltani***, *M. Chaker,* INRS-Energie, Matériaux et Télécommunications, Canada, *E. Haddad, R. Kruzelecky,* MPB Communications Inc., *J. Margot,* Université de Montréal, Canada, *P. Laou, S. Paradis*, Defence R and D Canada-Valcartier

At a transition temperature of T_t = 68 °C, thermochromic vanadium dioxide (VO_2) smart coatings undergo a reversible semiconductor-to-metallic phase transition (SMT). This phase transition is accompanied by an important modification of the electrical resistivity and optical properties in the infrared region. The T_t can be controlled by doping the coating with donorlike or acceptor like centers. In addition, the SMT of VO_2 can be controlled by external parameters such as temperature, pressure, photo-carrier injection into a VO_2 heterostructure, and an electric field. VO_2 smart coatings are thus excellent materials for various switching applications. Recently, we have successfully fabricated micro-optical switch device based on semiconducting and transmitting (on) state to the metallic and reflecting (off) state of W(1.4 at. %)-doped VO_2 operating at λ = 1.55 µm and driven by an external voltage.[1] This device exhibited an extinction ratio (on/off) as high as 28 dB. In addition, the electro-transmittance switching modulation of the device was demonstrated at 1.55 µm by controlling the SMT with superposition of a dc and ac switching voltages. In this paper, we present our recent results on the mico-fabrication and characterization of stationary optical shutter device based on transmittance switching (on/off) of W-doped VO_2 active layer. This shutter consists on 16 smart micro-slit arrays, which can be controlled individually by an external voltage (either a dc or ac switching voltage). This control allows to perform any desirable on-off combination of the micro-optical slits. The starting W-doped VO_2/Al_2O_3 was synthesized by reactive pulsed laser deposition. The micro-slit arrays were patterned by photolithography and plasma etching, whereas Au/NiCr electrical contacts were integrated on the top of the micro-slit by means of the lift-off process. The response of the device was investigated at 1.55 µm by controlling individually the transmittance switching of the active slits by an external voltage. The results show clearly that this device can be used as stationary Hadamard shutter to increase the sensitivity of infrared spectrometer.

[1] M. Soltani, M. Chaker, E. Haddad, R. V. Kruzelecky, and J. Margot, J. Vac. Sci. Technol. A 25(4), Jul/Aug (2007).

Nanometer-scale Science and Technology

Room: 616 - Session NS-MoA

Nanoscale Assembly and Manipulation II

Moderator: H. Schift, Paul Scherrer Institute, Switzerland, H. Wolf, IBM Research GmbH, Zurich Research Laboratory

2:40pm **NS-MoA3 Controlled Manipulation of Self-Organized Ni (II)-Octaethylporphyrin Molecules Deposited from Solution on HOPG with a Scanning Tunneling Microscope***, **L. Scudiero**, K.W. Hipps*, Washington State University

We have investigated the controlled manipulation of self-assembled NiOEP molecules adsorbed from a benzene solution onto a freshly cleaved high ordered pyrolytic graphite surface using the scanning tunneling microscope (STM) under ambient conditions. STM images acquired before and after scans of different patterns at a high current setpoint value reveal the creation of molecule free regions. In these cleared regions STM images reveal a 2D HOPG lattice with atomic spacing of 2.5 Å and a pattern depth of about 1.2 Å which is a typical STM height value for a monolayer NiOEP film on graphite. These molecule free regions are created by the transfer of NiOEP molecules from the surface to the tip when the STM is operated at very high current setpoint (tunneling resistance of about 120 MΩ or less). Once the molecules are picked up by the tip they then diffuse along the wire as confirmed by the absence of molecular build-ups around the patterned areas of the STM images. Furthermore, once the molecular film is damaged the size of the uncovered area keeps on growing larger with subsequent scans. In the case of square scans performed at high current setpoint values the freshly created regions exhibit straight edges with directions that are dictated by the lattice vectors of the underlying graphite substrate.

3:00pm **NS-MoA4 Manipulation and Electrical Characterisation of Carbon Nanotubes by using Nanomanipulators in the SEM System***, **M. Passacantando**, F. Bussolotti, V. Grossi, S. Santucci, L. Lozzi*, University of L'Aquila - Italy

The results of in situ manipulation and electrical transport characterisation of individual MWCNT grown on nickel tip by using a piezoelectric nanomanipulation system operating in a SEM chamber have been reported. The growth of MWCNT directly on nickel wire by chemical vapour deposition technique ensures a good electrical contact with the catalyst substrate. Using the electron beam induced welding a fully characterization of electronic properties of several MWCNT has been explored without the usual postprocessing methods which may alter, in principle the intrinsic properties of the CNT. Thanks to the high mechanical and electrical stability ensured by the electron beam welding procedure a detailed study of the CNT electrical transport properties modification under CNT buckling has been performed. The crucial role played by the structural defects in determining an irreversibility of a long MWCNT IV characteristic under mechanical stress has been clearly evidenced. Finally, by a proper sequence of CNT/tip welding and movement the potentiality in creating ohmic junction between two nanotubes has been demonstrated opening the route to a systematic investigation of one of the most fundamental aspect of the CNT physics.

3:40pm **NS-MoA6 Automatic Manipulation of Nanoparticles with a Software-Compensated AFM***, B. Mokaberi, D.J. Arbuckle, J. Yun, **A.A.G. Requicha***, University of Southern California

Manipulation of nanoparticles by pushing them with the tip of an Atomic Force Microscope (AFM) has been under development for over a decade, and is now routinely performed in several laboratories around the world. However, AFM nanomanipulation of small particles with sizes on the order of 10 nm has been until now a time-consuming and labor-intensive process. Automation has remained a desirable but elusive goal, primarily because of the spatial uncertainties associated with the positioning mechanisms of the AFM and with the manipulation process itself. Extensive user intervention has been required, resulting in very low throughput and severely limiting the complexity of structures that could be built with a reasonable amount of time and labor. This talk describes an automatic system for building patterns of nanoparticles by AFM manipulation. A planner determines the paths required to convert an initial, random distribution of particles on a surface into a desired pattern. The planner generates a sequence of motion commands for positioning the tip and pushing the particles. The commands are executed through software that compensates for thermal drift, creep and hysteresis. Experimental results show that the system can build in minutes a pattern that would take an experienced user several hours to construct interactively.

4:00pm **NS-MoA7 Directed Assembly of Metal Contacts to Silicon Nanowires using Electrodeposition***, **S. Ingole**, P. Aella,* Arizona State University*, S.J. Hearne,* Sandia National Laboratories*, S.T. Picraux*, Los Alamos National Laboratory

A technique based on electrodeposition for electrically contacting semiconductor nanowires (NWs) is presented. In the majority of exploratory studies electron-beam lithography has been utilized for establishing the metal-nanowire contacts. While useful for laboratory investigation this technique requires a post nanowire-assembly photolithography step and is too slow for large scale assembly. Thus new techniques are needed that are easy to integrate, low cost and involve minimum additional time for integration of nanowires onto device platforms. In the present work we report a process based on electrodeposition for establishing metal contacts to silicon nanowires (SiNWs). In this technique nanowires are first aligned between pairs of planar metal electrodes using dielectrophoresis. These electrodes have been predefined on top of an oxidized silicon substrate using photolithography. After the alignment, the ends of SiNW are resting on top of the metal electrodes and held in place by the Van der Waals attraction with the electrodes. In order to achieve good electrical contacts, metal has to be conformally deposited encapsulating the ends of these nanowires. In the present work this has been achieved via electrodeposition where prefabricated metal electrodes act as selective sites for deposition of metal. As the deposition proceeds the ends of nanowire become encapsulated by the electrodeposited metal. This avoids post NW-assembly photolithography, reducing the associated processing complexity. Metal doesn't deposit on the SiNW surfaces because of the native oxide present around them. We have demonstrated this process using electrodeposited Ni on electrically doped Si nanowires. Good coverage and control for nanowires aligned between Au/Cr pre-defined electrodes has been achieved and post-electroplating annealing resulted in specific contact resistivities $\sim 10^{-6}$ Ohm-cm^{2}. Although native oxide is useful for avoiding metal plating on the surface of NW, it acts as barrier for metal-SiNW reaction during annealing of such contacts. Also Au is not a desirable metal for devices. Therefore we have explored the use of other electrode array metals such as Ni/Ti to replace Au as well as to assist in reducing the native oxide during annealing for good metal-SiNW contacts. The results are promising for development of a general self-assembly technique for the integration of nanostructures on device platforms.

4:20pm **NS-MoA8 Multi-Island Single-Electron Transistors Made by Lithographic Contacting of Gold-Nanocrystal Chains***, **D.N. Weiss***, Washington Technology Center*, X. Brokmann, L.E. Calvet,* CNRS, France*, M.A. Kastner, M.G. Bawendi*, Massachusetts Institute of Technology

We demonstrate a fabrication scheme that bridges the dimensional gap between lithographic dimensions and nanocrystal sizes. The method involves lithographic contacting of previously self-assembled, alkanethiol-coated nanocrystal chains. Because one nanocrystal is incorporated into the edge of the larger electrode, all of the important tunnel junctions are defined by self-assembly rather than lithography. This method allows the fabrication of one-dimensional island arrays, similar to those used for metrology, with predictable electronic characteristics. Specifically, we show that the electronic behavior of a double-island device can be fully explained using the standard theory of Coulomb blockade, with very few adjustable parameters.

4:40pm **NS-MoA9 Dip Pen Nanolithography using NanoInk's NSCRIPTOR System: Nanolithography and Nanoscale Assembly Using Biological and Metal Inks***, **E.R. Tevaarwerk**, M. Parpia, N.A. Amro, S. Rozhok, J. Haaheim, F. Villagran, T. Renner, M. Nelson, J. Fragala, T. Levesque*, NanoInk

Precision nanoscale deposition of biological, organic, and inorganic materials is a fundamental need in nanoscience research. Relative to other nanopatterning techniques, dip-pen nanolithography-DPN is a direct-write technique maintaining high resolution (30 nm line widths, 50 nm pitches), and among sub-50 nm techniques, DPN is the only one that can directly deposit molecules under ambient conditions. A wide variety of biological, organic and inorganic materials can be deposited. We will discuss the development of a silver nanoparticle based ink for the writing of conductive metal traces, as well as recent developments in "Just Add DNA" inks for DNA nanopatterning for the making of DNA nanoarrays. We demonstrate results of DPN patterning with these two inks using NanoInk's one dimensional probe arrays, and microfluidic ink delivery tools. We discuss the implications of these results and tools in furthering the application of dip-pen nanolithography as a large scale, multi-ink patterning tool, including recent developments for massively parallel patterning using the two-dimensional nanoprint array (2DnPA).

Plasmonics Topical Conference

Room: 619 - Session PL-MoA

Plasmon Dynamics and Magnetoplasmonics

Moderator: J.P. Long, Naval Research Laboratory

2:00pm **PL-MoA1 Nanoplasmonics under Coherent Control*, M.I. Stockman***, Georgia State University **INVITED**

Surface plasmon (SP) modes of metal nanostructures can and do localize at the nanoscale in the regions much smaller than the excitation radiation wavelength. Their minimum localization size is limited by the smallest features of the nanostructures and limits of the macroscopic electrodynamics. In practical terms, SPs can localize within just a few nanometers. Local optical fields in a plasmonic nanostructure form nano-sized hot spots where the SPs are localized. In many cases, such a hot spot is a superposition of several or many SP modes. Exciting such a nanoplasmonic system with an optical field that is a coherent superposition of different frequencies, one can impart different phases on the excited SP modes. Due to the interference of these SPs, the intensity of the corresponding hot spot can be changed: the constructive interference leads to the enhanced local fields, and the destructive one to their suppression at any given hot spot. This is a principle of the coherent control of nanoplasmonic energy concentration at the nanoscale proposed theoretically in our paper.[1] The coherent control can be implemented by both continuous-wave excitation and ultrashort pulses that can be considered as a coherent superposition of wide band of harmonics. Since this publication, this coherent control at the nanoscale has been both significantly developed theoretically.[2] and observed experimentally.[3] In this talk, we review the existing knowledge on the ultrafast coherent control of nanoscale optical energy localization in surface plasmonics. We also discuss the latest theoretical ideas including the time-reversal coherent control,[4] carrier-envelope phase effect,[5] and the spatio-temporal coherent control.[6]

[1] M. I. Stockman, S. V. Faleev, and D. J. Bergman, Coherent Control of Femtosecond Energy Localization in Nanosystems, Phys. Rev. Lett. 88, 67402 (2002)

[2] See, e.g., M. I. Stockman, D. J. Bergman, and T. Kobayashi, Coherent Control of Nanoscale Localization of Ultrafast Optical Excitation in Nanosystems, Phys. Rev. B 69, 054202-10 (2004); T. Brixner, F. J. G. d. Abajo, J. Schneider, and W. Pfeiffer, Nanoscopic Ultrafast Space-Time-Resolved Spectroscopy, Phys. Rev. Lett. 95, 093901-1-4 (2005); M. Sukharev and T. Seideman, Phase and Polarization Control as a Route to Plasmonic Nanodevices, Nano Lett. 6, 715-719 (2006)

[3] A. Kubo, K. Onda, H. Petek, Z. Sun, Y. S. Jung, and H. K. Kim, Femtosecond Imaging of Surface Plasmon Dynamics in a Nanostructured Silver Film, Nano Lett. 5, 1123-1127 (2005); M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, F. J. G. d. Abajo, W. Pfeiffer, M. Rohmer, C. Spindler, and F. Steeb, Adaptive Subwavelength Control of Nano-Optical Fields, Nature 446, 301-304 (2007)

[4] X. Li and M. I. Stockman, Time-Reversal Coherent Control in Nanoplasmonics, arXiv:0705.0553 (2007); Phys. Rev. Lett. (Submitted)

[5] M. I. Stockman and P. Hewageegana, Absolute Phase Effect in Ultrafast Optical Responses of Metal Nanostructures, Appl. Phys. A (2007) (In Print)

[6] M. Durach, A. Rusina, K. Nelson, and M. I. Stockman, Toward Full Spatio-Temporal Control on the Nanoscale, arXiv:0705.0725 (2007)

2:40pm **PL-MoA3 Metal Colloids Nano-Antenna for Local Linear and Nonlinear Optical Response*, P. Guyot-Sionnest,*** *M. Liu*, University of Chicago **INVITED**

The optical absorption and scattering of metal colloids is strongly shape dependent due to collective Plasmon resonances. Such particles are attractive for future optical integration. In particular, very large local electric field can also be achieved, both inside and outside the metal particles, providing means to locally enhance the linear and nonlinear optical response of the colloids and their environment. Of primary interest are structures in which one plasmon mode dominates the spectral response. These are typically elongated structures which exhibit the narrowest spectral response and large field enhancements. An example of such structure is an elongated bipyramid shape recently synthesized for Au colloids. For small particles in the dipole limit, the limiting linewidth of a Plasmon is due to dissipation inherent to the metal and to additional effects of the surface. In this context I will describe Au/Ag core/shell systems. Finally, achieving large nonlinear optical response, so that fast optical switching can be made at the single particle level is an ongoing challenge and initial results on Au nanorods will be presented.

3:40pm **PL-MoA6 Ultrafast Microscopy of Surface Plasmon Dynamics in Silver Films*, H. Petek***, University of Pittsburgh **INVITED**

We study the dynamics of localized surface plasmons and propagating surface plasmon polaritons in nanostructured Ag films on femtosecond temporal and nanometer spatial scale by means of interferometric time-resolved two-photon photoelectron emission microscopy (ITR-PEEM). Identical, phase correlated pump-probe pulses excite two-photon photoemission mediated by surface plasmon excitation in silver films; the resulting electron emission is imaged with electron optics. The combination of laser excitation an electron imaging provides <10 fs temporal and 50 nm spatial resolution. We record movies of surface plasmon propagation, dispersion, dephasing, interference and focusing in nanolithographically patterned metal films. The ITR-PEEM method provides a revolutionary advance in ultrafast electron microscopy for visualizing and controlling electromagnetic fields and ultrafast processes on the nano-femto scale.[1,2].

[1] A. Kubo, K. Onda, H. Petek, Z. Sun, Y.-S. Jung, and H.-K. Kim, Nano Letters 5, 1123 (2005).

[2] A. Kubo, N. Pontius, and H. Petek, Nano Lett. 7, 470 (2007).

4:20pm **PL-MoA8 Ultrafast Studies of Gold, Nickel, and Palladium Nanorods*, J.C. Owrutsky,*** *A.D. Berry,* Naval Research Laboratory, *G.M. Sando*, Malvern Instruments

Steady state and ultrafast transient absorption studies have been carried out for gold, nickel, and palladium high-aspect ratio nanorods. For each metal, nanorods were fabricated by electrochemical deposition into ~6 µm thick polycarbonate templates using two nominal pore diameters (10 nm and 30 nm, resulting in nanorod diameters of about 40 and 60 nm, respectively). Static spectra of the nanorods for each metal reveal a mid infrared longitudinal surface plasmon resonance (SPR) band as well as a transverse SPR band in the visible for the gold and larger diameter nickel and palladium nanorods. This demonstrates that high aspect ratio nanorods of transition metals have mid infrared SPR bands. Time resolved studies were performed on the gold and nickel nanorods with subpicosecond resolution, 400 nm excitation, and a wide range of probe wavelengths from the visible to the mid-IR as well as using infrared excitation (near 2000 cm^{-1}) and probing at 800 nm. The dynamics observed for both diameters of gold and nickel nanorods include transients due to electron - phonon coupling and impulsively excited coherent acoustic breathing mode oscillations, which are similar to those previously reported for spherical and smaller rod-shaped gold nanoparticles. The results demonstrate that the dynamics of high aspect ratio metal nanorods resemble those for smaller nanoparticles.

4:40pm **PL-MoA9 Magnetoplasmonic Effects in Au/Co/Au Nanodisks*, G. Armelles***, Instituto de Microelectrónica de Madrid (IMM-CNM-CSIC), Spain*, J.B. González-Diaz, A. Garcia-Martin, R. Asenjo, J.M. Garcia-Martin, A. Cebollada,* IMM-CNM-CSIC, Spain*, B. Sepulveda, Y. Alaverdyan, M. Käll,* Chalmers University of Technology, Sweden*, L.l. Balcells*, ICMAB-CSIC, Spain

Noble metal-Ferromagnetic metal nanodisks exhibiting simultaneously localized surface plasmon resonances and magneto-optical (MO) activity were prepared from continuous Au/Co/Au films by colloidal lithography. Up to now, such phenomena have been only observed in continuous films made of Au/Co/Au trilayers. This system exhibits simultaneously well defined propagating surface plasmon resonaces and MO activity,[1] and have been the basis to develop new high sensitive biosensors.[2] However, a nanostructured system exhibiting localized surface plasmon resonances (LSPR) has two main advantages: i) the strong localization of the electromagnetic field around the nanostructures suggests a noticeable enhancement in the MO properties; ii) the spatial localization of electromagnetic fields associated with these resonances would make such a system a promising candidate for the development of high spatial specificity magneto-plasmonic sensing devices. Even though complex onion-like nanoparticles made of noble metals and ferromagnets that exhibit LSPR have been obtained using different chemical methods,[3] no MO activity has been reported in any of them. In this work we show for the first time that such active nanostructures exhibiting optical and MO properties can actually be obtained. The nanodisks (60-110nm diameter) were prepared by colloidal lithography from Au/Co/Au films grown onto glass by sputtering. The absorption spectra of the samples exhibit a peak around 2 eV that can be associated to the LSPR of the nanodisks. As we increase the disk diameter the energy position of the peak shifts towards lower energies. The MO activity was determined measuring the Polar Kerr rotation and ellipticity spectra. These spectra present a well defined structure in the same energy region than that of the absorption peak. Moreover, an enhancement of the MO activity is also observed. The results will be explained with the help of theoretical simulations made with a scattering matrix formalism that takes into account the MO activity.

[1] C.Herman et al. Phyts. Rev. Lett 73,3584(1994)

[2] B. Sepúlveda et al. Oppt Lett.31,1085 (2006)

[3] Z.Ban et al J. Mater. Chem 15, 4660 (2005); J. Zhang et al. J. Phys. Chem B 110, 7122 (2006); S. Mandal et al J. Mater. Chem 17 , 372 (2007); N. S. Sobal et al. Nano Letters 2, 621 (2002).

5:00pm **PL-MoA10 Magnetoplasmonic Activity in Systems with Interacting Localized and Extended Surface Plasmon Modes***, A. Garcia-Martin, J.B. Gonzalez-Diaz,* ***A. Cebollada****, J.M. García-Martin, G. Armelles,* IMM-CNM-CSIC, Spain*, M.U. González, G. Badenes, R. Quidant*, ICFO, Spain

In the last years, plasmonics has consolidated as a powerful approach to obtain photonic devices with novel capabilities. To get this progress forward, important efforts are dedicated to developing active and/or externally controlled systems. Magnetic fields can influence the propagation of surface plasmon polaritons (SPP),[1] so the mixing of magnetic and plasmonic materials seems a promising approach for obtaining these externally controlled systems. Up to now, multilayers of noble and magnetic metals have been analyzed and they have shown to present both plasmonic and magneto-optic (MO) effects. Moreover, the MO effect is enhanced in the presence of an excited plasmon in the system.[2] In this work, we present the study of the MO and plasmonic activity in structures exhibiting both SPP and localized surface plasmons (LSP). The samples consist on a continuous Au/Co/Au trilayer deposited on glass by sputtering, covered with a dielectric spacer of SiO2 on top of which an array of Au nanodiscs (100 nm in diameter) have been fabricated by electron beam lithography. This system presents two kinds of surface plasmon resonances: The Au nanoparticles sustain LSP, and the trilayer/silica interface SPP, which can be excited by means of the Au nanoparticles grating. By controlling the parameters of the nanoparticles array, the relative positions of the two plasmon resonances of the system can be engineered.[3] The trilayer also presents MO properties due to the presence of the Co layer. The MO properties of the system have been analyzed measuring the polar Kerr rotation and ellipticity spectra. The trilayer/nanoparticles system shows a different spectrum from that of the trilayer alone. In particular, an increase of the MO signal in the trilayer/nanoparticle spectra appears at the spectral position of the LSP. This increase depends on the coupling strength between the LSP and the SPP, which can be controlled by the periodicity of the array and the thickness of the dielectric spacer. These results open the door to the design of active magnetoplasmonic devices based on interacting localized and propagative surface plasmon modes.

[1] B. Sepúlveda, L. M. Lechuga and G. Armelles, J. Lightwave Technol. 24, 945-955 (2006).

[2] C. Hermann et al., Phys. Rev. B 64, 235422 (2001).

[3] J. Cesario, R. Quidant, G. Badenes and S. Enoch, Opt. Lett. 30, 3404 (2005).

Plasma Science and Technology

Room: 607 - Session PS-MoA

Plasma Processing for High k, III-V and Smart Materials

Moderator: L. Stafford, University of Houston

2:00pm **PS-MoA1 Activation Energies for HfO_2 and Si Etching in BCl_3 Plasmas, and Boron Cleaning from Si in H_2 Plasmas**, ***C. Wang***, *V.M. Donnelly*, University of Houston

We have investigated plasma etching of a high dielectric constant material, HfO_2, as well as poly-Si in BCl_3 plasmas. Etching rates of HfO_2 and poly-Si were studied as a function of substrate temperature (T_s) and plasma source power, and activation energies for HfO_2 and poly-Si etching were measured at several powers. There is only a slight increase in the etching rate of HfO_2 and poly-Si with increasing temperature. Activation energies range from 0.2 to 0.9 kcal/mole for HfO_2 and 0.8 to 1.8 kcal/mole for Si, with no obvious dependence on source powers over the range studied (20 to 200 W). These low activation energies suggest an etching mechanism in which product removal is limited by chemical sputtering of the chemisorbed layer on the surface and higher T_s modestly increases the reaction rate during the ion "thermal" spikes. H_2 plasma cleaning of the thin B-containing layer remaining after BCl_3 plasma etching of HfO_2 on Si was also studied. Previously, we have reported that B can be cleaned from Si in dilute H_2/Ar (1% H_2) plasmas in 20 s at room temperature, provided the reactor chamber was cleaned in pure H_2 plasmas first with sample absent. Here we present a study of boron cleaning in dilute H_2/Ar plasmas at elevated substrate temperatures, using x-ray photoelectron spectroscopy to measure B removal rates for individual BCl_xO_y moities. We have found that the B cleaning rate is faster at higher T_s. An activation energy of 2.7 kcal/mole was obtained for total B removal in a 1% H_2/Ar plasma. Conversely, the Si etching rate under these conditions displayed little if any dependence on substrate temperature; the activation energy was between 0.2 and -0.6 kcal/mole. Therefore, it is advantageous to remove B at higher T_s to minimize Si removal. For example, at T_s = 235 °C, ~90% of B is cleaned from Si in less than 10 s, while <10 Å of Si is removed in this period. Moreover, it was found that etching of Si stops and a Si-oxide layer forms if oxygen is present in the H_2 plasma (e.g. from erosion of silica components in the reactor). Consequently, still higher selectivities of B removal with respect to Si are possible under conditions where a small amount of oxygen is present in the H_2/Ar plasma.

2:20pm **PS-MoA2 Analyses of Deposition/Etching Regimes during Selective Etching of HfO_2 on Silicon in BCl_3 Plasmas: Impact of Chamber Walls**, ***E. Sungauer***, ST Microelectronics, France, *X. Mellhaoui, E. Pargon*, LTM/CNRS, France, *Th. Lill*, Applied Materials Inc., *O. Joubert*, LTM/CNRS, France

With the continuous scaling down of CMOS devices to ensure higher speed and density, the thickness of the SiO_2 gate dielectric is expected to be reduced down to 1nm for the 45 and 32nm technological nodes. This thickness reduction brings some serious issues such as increased gate leakage current and reduced oxide reliability. Therefore, high-k metal oxides, and more particularly HfO_2 have been considered as alternative materials to provide substantially thicker dielectric layers for reduced leakage current and increased gate capacitance. The present work focuses on the understanding of HfO_2, SiO_2 and Si etching mechanisms in BCl_3 based plasmas. BCl_3 seems to be a promising gas providing high etch selectivity between HfO_2 and Si substrates. The 200mm wafers are etched in an industrial ICP reactor, and then transferred under vacuum into an X-ray Photoelectron Spectroscopy (XPS) analysis chamber to investigate surface modifications induced by plasma exposure. XPS experiments help us in understanding the mechanism driving the etch selectivity between HfO_2 and Si-containing substrates. The role of Boron is fundamental since Boron by reacting with Silicon and forming Si-B bonds favour the growth of BCl_x polymer on Silicon surfaces slowing down Silicon etching. On the other hand, on HfO_2 surfaces Boron is directly involved in the etching by helping the formation of volatile BOCl etch products. The ionic bombardment plays also a key role since it controls the BCl deposition rate. The ion energy threshold which controls the transition between etching and deposition is lower on HfO_2 than on Si and SiO_2 wafers, implying that infinite etch selectivity between HfO_2 and Silicon can be obtained if the ion energy is well adjusted. In-situ kinetic ellipsometric measurements were also carried out on HfO_2, SiO_2 and Si substrates to monitor in real time the etching/deposition transition during BCl_3 plasma exposure. These experiments have revealed that the etch or deposition rate is linear with time only after a transient regime of about 10s and that during the10 first seconds, HfO_2, Silicon and SiO_2 show very different kinetic behaviors. We also observed that reactor wall conditioning plays a key role in controlling BCl_x deposition on the wafer and that infinite selectivity can be obtained by coating the reactor walls with carbon layer prior etching in BCl_3.

2:40pm **PS-MoA3 Optical Emission Study of an Inductively Coupled Cl_2/H_2 Plasma during InP Etching of Micro-nanostructures used for Photonic Applications**, ***L. Gatilova***, *S. Bouchoule, S. Guilet*, Laboratoire de Photonique et de Nanostructures (LPN)-CNRS, France, *P. Chabert*, Laboratoire de Physique et de Technologie de Plasmas (LPTP)-CNRS, France

Cl2/H2-based chemistry has proven to be very efficient for highly anisotropic ICP etching of InP-based heterostructures used in photonic devices. It was shown recently that the Cl2/H2 ratio is a key parameter to control the sidewall profile. At low pressure (0.5mT-1mT), the onset of anisotropic regime occurs at H2 = 35-45%, where the evolution of the etch rate with H2 percentage shows a maximum. A possible explanation, proposed in literature, is the decrease of the reactive atoms and ions (Cl, Cl+) because of the by-products (i.e. HCl) formation. However, deeper understanding of InP etching mechanism requires more detailed investigations. We have used OES combined with electron and positive ion density measurements, during the etching of InP ridge structures, to obtain insight into the etch mechanism of InP in Cl2/H2 ICP plasma. The pressure was 0.5 mT, the ICP power was 800W, the DC bias voltage was –150 V, the total gas flow was kept constant at 28 sccm, and the H2 concentration is varied from 0 to 100%. The main emission lines recorded during the etching process were Cl (725.7 and 754.7nm), H (656.3nm), In (325.6, 410.2, 451.1nm), InCl (350nm), PH (340nm). In order to estimate the relative atom concentrations, 10% of argon was added in the initial gas mixture. The etch rate and the In-line intensity have roughly the same behavior versus Cl2/H2 ratio, which can be divided into three regions. For H2 concentration between 0-25% (corresponding to strongly undercut profiles), the etch rate rapidly decreases with %H2 increase, so as the positive ion current and the reactive species concentration – the Cl density falls down continuously when H2 increase from 0 to 100%. For H2 concentration greater than 60%, the etch rate also decreases down to very low values < 100nm/min and the etched surface becomes grassy. Despite the H2 concentration increases, the concentration of H atoms decreases, probably due to the decrease in the electron density. For intermediate H2 concentration (the second region which lies between 35% and 45%), corresponding to the highly anisotropic region, the etch rate remains constant. This intermediate region corresponds to a maximum in H concentration. The etch rate could thus be the result of a balanced effect between the Cl density decrease and the H density increase, with a change in etching mechanisms of P-atoms; for high H density P-atoms leave the InP surface by PHx formation, as suggested by the increase of PH-line intensity.

3:00pm **PS-MoA4 Dry Etching of $Ge_2Sb_2Te_5$ for Phase Change Memory Applications: Characterization and Design of Low Damage Process**, ***P. Petruzza***, STMicroelectronics Italy

In order to realize highly integrated PRAM involving $Ge_2Sb_2Te_5$ (GST) thin films,[1] the etching process must be developed. Until now, there were several work devoted to the investigations of etching properties of GST films using fluorine and chlorine based plasma chemistries.[2] Unfortunately, the relationships between plasma parameters and damage of GST thin films remained out of attention. We investigated the etching behaviours of GST in terms of etching process parameters such as pressure, gas, temperature, gas flux directionality in closely bound up with film stack of GST and subsequent problems such as voiding, poisoning of GST ad decreased mechanical strength. Etching of chalcogenide alloy may result in chemical and structural modification of the sidewall and surface residues. GST reactive ion etching plasmas have been studied by measuring etch rate and composition using XRF spectroscopy, etch profile, surface - chemical aspects and bulk morphology by employing TEM/SEM. Etching experiments were performed in a low pressure inductively coupled plasma reactor supplied with 13.56 MHz rf powers. GST thin films were prepared on SIN substrate. Damage and degradation of GST has been investigated by down stream plasma treatments after GST etching definition. SEM cross section analysis shows that the sidewalls of GST are eroded after ashing process. The thickness of damaged thin layer depends of etching chemistry and of other process parameters such as temperature. In the present work it's explained the results obtained with this method for different etching gas chemistry of chalcogenide alloy. The experiments results show that Cl_2 etching process have induced a composition change of the alloy and thick erosion in sidewalls of GST film patterns. Unlike Cl_2, fluorine chemistry avoids GST erosion. In order to perform manufacturability phase change memory: using the obtained results, a etching process by Cl_2 free chemistry with suitable process parameters has been provided.

[1] F. Pellizer, A Pirovano, et all., Proc. Symposiumon VSI technology, june 2004, pg 18-19.

[2] Sung-Min Yoon et al., Japanese Journal of Applied Phisics, Vol. 44, No 27, 2005, pp L 869-L 872 .

3:40pm **PS-MoA6 John A. Thornton Memorial Award Lecture - Etching of SiC, GaN and ZnO for Wide Bandgap Semiconductor Device Applications**, ***S.J. Pearton****, *L.F. Voss*, *W.T. Lim*, University of Florida, *R.J. Shul*, Sandia National Laboratories **INVITED**

A review will be given of dry etching of three technologically important wide bandgap semiconductors, namely GaN,SiC and ZnO. Dry etching of GaN is needed for mesa formation on electronic and photonic devices and for through-wafer vias on power devices. Generally chlorine-based plasma chemistries are used, with etch rates in the range of a few thousand angstroms per minute to almost one micron per minute. A typical issue is the preferential loss of nitrogen from the near-surface region, leading to the presence of an n-type surface layer after etching. This can be used to advantage in improving contact resistance of n-type Ohmic contacts. For SiC, the main chemistries are based on fluorine and changes to the surface electrical properties are less of an issue. For ZnO, the low volatility of all Zn etch products leads to low etch rates at room temperature and changing to iodine or bromine chemistries does not improve the removal rates. Examples will be given of device etching processes for all three materials systems.

4:20pm **PS-MoA8 Comparative Study of ECR and ICP Plasma Etching of High-k Dielectric HfO_2 Films with BCl_3-Containing Gas Chemistries**, ***D. Hamada***, *K. Nakamura*, *Y. Ueda*, *M. Yoshida*, *K. Eriguchi*, *K. Ono*, Kyoto University, Japan

Etching of high-k materials is indispensable for their removal in integrating them into device fabrication. Moreover, the high-k etching is required for chamber cleaning of the deposition apparatuses in mass production. This paper presents a comparative study of the etching of high-k HfO_2 films in electron cyclotron resonance (ECR) plasma and inductively coupled plasma (ICP) reactors with BCl_3-containing chemistries, where emphasis is placed on a better understanding on the etching mechanisms concerned. The ECR reactor had a configuration of divergent magnetic fields, and the discharge was established by 2.45-GHz microwave powers of 600 W. The ICP reactor had a three-turn planar coil, and the discharge was established by 13.56 MHz rf powers of 300 W. Feedstock gases were BCl_3, Cl_2, O_2, and Ar at total pressures of 2-20 mTorr with a total flow rate of 40 sccm. The significant differences between ECR and ICP plasmas are: the etching of HfO_2 without rf biasing was obtained in ECR BCl_3-containing plasmas, while was not obtained in ICP; moreover, the etch selectivity HfO_2/Si was >> 1 with no bias in ECR, while was < 1 with bias in ICP. In ECR, the HfO_2 etch rate was increased in order of BCl_3, BCl_3/O_2, BCl_3/Cl_2, and $BCl_3/Cl_2/O_2$; typically, the HfO_2 etch rate in BCl_3/Cl_2 was ~100 nm/min at ~60% Cl_2 with a selectivity of ~10 over Si, and a high selectivity >50 was obtained at 40-50% Cl_2 with a HfO_2 etch rate of ~50 nm/min. The Langmuir probe measurements indicated that in ECR, the difference between the plasma and floating potentials was of the order of 10 V, which is lower than the threshold ion energy ~26 eV known for the HfO_2 etching in BCl_3 plasmas. In contrast, the HfO_2 etching in ICP occurred with additional rf biasing, where the threshold energy was estimated to be ~ 30 eV from the difference between the plasma potential and dc self-bias voltage; the etch rate increased with increasing rf bias power, being ~50 nm/min with a HfO_2/Si selectivity of ~0.5 at an ion energy of ~100 eV in BCl_3/Cl_2. The gas-phase and surface chemistries responsible for the HfO_2 etching is discussed based on several plasmas and surface diagnostics including OES, QMS, LIF, FTIR, and XPS, to achieve higher etch rate and selectivity under conditions of low ion energies and/or less ions.

4:40pm **PS-MoA9 Investigation of Surface Reactions for Chlorine-Based Plasma Etching of Nitrided Hafnium Silicates**, *R.M. Martin*, University of California at Los Angeles, *B. Xia*, *A. Misra*, Air Liquide, ***J.P. Chang***, University of California at Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium-based oxides, for sub-45nm CMOS devices. Nitrided hafnium silicates (HfSiON) are promising since they combine the high dielectric constant and improved interface state density of hafnium silicates with the beneficial properties of silicon oxynitrides. In this work, chlorine-based chemistries are used in an electron cyclotron resonance high density plasma reactor to etch Hf-rich and Si-rich nitrided hafnium silicates, with 0 to 15 at.% of nitrogen. The plasma density, electron temperature, and gas phase species are characterized by a Langmuir probe, optical emission spectroscopy, and quadrupole mass spectrometry. The etching of SiO_2 and HfO_2 was first studied in Cl_2 and BCl_3 plasmas, to allow for studies of the etching of HfSiON with well controlled and varying compositions of Si and N in HfO_2. The etch rates of nitrided hafnium silicates were found to increase with the square root of ion energy, and the etching rate of films increased with increasing nitrogen incorporation as well as SiO_2 percentage in the film. The surface chlorination was enhanced with increasing ion energy, ranging from 1 to 4 at.% of chlorine on the etched surfaces, demonstrating that the etching reaction is limited by the momentum transfer from the ions to the film surface. The measured etching threshold energies were higher than that of pure HfO_2, suggesting that Si and N incorporation modifies film structure/density. In addition, nitrogen was detected removed in the form of SiN_2Cl_x, and more nitrogen remains on the surface of the Hf-rich films than the Si-rich films. This suggests that the removal of N is related to its bonding within the film. Hafnium and silicon were removed as $HfCl_x$, $SiCl_x$, and SiO_2Cl_x, and increased with ion energy. A generalized phenomenological model will be presented to describe the effect of SiO_2 and N incorporation on the etching behavior of HfO_2.

5:00pm **PS-MoA10 Plasma Source-Dependent Charging Damage Polarities in the Performance Degradation of MOSFETs with Hf-based High-k Gate Dielectrics**, ***M. Kamei***, *K. Eriguchi*, *H. Fukumoto*, *K. Ono*, Kyoto University, Japan

We report that the polarities of charging damage in n- and p-ch MOSFETs with Hf-based high-k gate stack ($HfAlOx/SiO_2$) depends on plasma sources, in contrast to those with conventional SiO_2. In order to investigate the charging polarity in MOSFETs with the high-k gate stack (high-k) and those with SiO_2 (SiO_2), the gate leakage current, drain current - gate voltage, and capacitance - voltage measurements were conducted for at least 12 difference devices with different device sizes (antenna ratio) to evaluate the deviation. The electrical thicknesses by capacitance-voltage measurements are ~2.7 and ~7.4 nm for high-k and SiO_2, respectively, while both devices have approximately the same physical thickness of 7 nm. ECR with the bias power of 200 W under two plasma conditions, Ar- and Cl-based gas mixtures, were utilized to induce the charging damage. The Langmuir probe and bias voltage measurements were carried out for correlating the electrical data to plasma parameters to understand the mechanisms. For Ar-plasma, high-k gate stacks were identified to suffer from negative charge trapping for both n- and p-MOSFETs, while SiO_2, from positive charge trapping for pMOSFET. For Cl-plasma on the other, positive charge trapping was observed for n- and p-MOSFETs with high-k, in contrast to Ar-plasma. The observed unique features in high-k were attributed to the difference in the measured ion currents and electron densities between Ar and Cl plasmas as well as the effects of device polarities (n-/p-ch) and asymmetric energy band structures of high-k gate stacks on the stress configurations during plasma exposures. It is suggested that Ar- and Cl-plasmas exhibit different current sources (positive, negative, or bi-directional current sources) in response to device structures, in particular with high-k subject to charge trapping. In addition to the experimental result that high-k devices are more susceptible to plasma charging damage compared to SiO_2 devices, it can be concluded that the observed plasma source-dependent charging polarity for high-k devices, in

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* John A. Thornton Memorial Award Winner

particular pMOS, should be considered in future device design rules and plasma process designs.

Advanced Surface Engineering

Room: 617 - Session SE+PS-MoA

Pulsed Plasmas in Surface Engineering

Moderator: J. Patscheider, EMPA, Switzerland

2:00pm **SE+PS-MoA1 Modulated Pulse Power Deposition of Nanometer-Scale Multilayered Coatings**, *R. Chistyakov, B. Abraham,* Zond, Inc./Zpulser, LLC, ***W.D. Sproul***, Reactive Sputtering, Inc., *J.J. Moore, J. Lin*, Colorado School of Mines

Modulated pulse power (MPP) sputtering is a variation of high power pulse magnetron sputtering that overcomes the rate loss issue through modulation of the pulse shape, intensity, and duration. In MPP, the pulse shape and duration and plasma perturbations directly affect the degree of ionization of the sputtered material. In this study, the MPP plasma generator was controlled by a special electronic device that allowed the generation of two different plasma discharges within the same deposition cycle. Nanometer scale layers of material deposited under the two different plasma condition were alternately deposited, and the thickness and structure of each nanolayer was controlled by varying the output voltage pulse shape of the MPP plasma generator. Films of carbon and reactively deposited titanium nitride and chromium nitride were sputtered, and the film structure, orientation, and mechanical properties were analyzed and measured. These variations in the plasma conditions directly affect the film properties, and results of the film property measurements will be presented.

2:20pm **SE+PS-MoA2 Reactive High Power Impulse Magnetron Sputter Deposition of Alumina**, *E. Wallin, S. Swedin, M. Lattemann,* ***U. Helmersson***, Linköping University, Sweden

Alumina, Al_2O_3, is one of the technologically most important ceramic materials. Due to the existence of a variety of different polymorphs, it finds use in a wide range of applications. In the present work, alumina thin films have been deposited using high power impulse magnetron sputtering (HIPIMS) of an Al target in Ar/O_2 gas mixtures. HIPIMS is a new and promising technique for ionized physical vapor deposition (I-PVD), in which a high degree of ionization of the deposition flux as well as an inherently high energy of the depositing species can be achieved at relatively low average power, by applying high power pulses with a low duty factor (typically around 1 %) to a conventional sputtering target (see, e.g., Helmersson et al., Thin Solid Films 513, 1 (2006)). Stoichiometric alumina films could be grown in a stable and essentially arc free process at rates which are high compared to the deposition rate for pure Al metal and comparable to, or even higher than, what can be achieved with traditional DC deposition methods. A model qualitatively describing and giving explanations for this behavior of the reactive process will be presented. The resulting films were investigated by x-ray diffraction, as well as scanning and transmission electron microscopy. Films deposited directly onto Si substrates at a substrate temperature of 400 °C were found to have a microstructure consisting of small, equiaxed grains with a diameter of the order of 10 nm, and with γ-alumina as the only detectable crystalline polymorph. The results demonstrate the potential of depositing dielectric films at relatively high rates using HIPIMS. In addition, HIPIMS deposition of such films opens the possibility of utilizing the ionized deposition flux to improve the film quality and affect the structure of the coatings, also at reduced substrate temperatures.

2:40pm **SE+PS-MoA3 Effect of Sub-Surface Reactions on the Growth of Nano-Structured Functional Thin Films Deposited under Energetic Ion Bombardment**, *A. Amassian, M. Dudek, P. Jedrzejowski, R. Vernhes, O. Zabeida, P. Desjardins, J.E. Klemberg-Sapieha,* ***L. Martinu***, Ecole Polytechnique, Canada **INVITED**

Recent advances in science and technology stimulate the development of new coating materials, surface and interface engineering processes and thin film systems that provide an ever increasing performance in numerous areas ranging from optical and optoelectronic to aerospace, automotive, biomedical, microelectronic, and other applications. Many successful solutions in these particular fields have been identified when using ion-assisted deposition of thin films and thin film systems with tailored functional characteristics including the complex refractive index, the mechanical properties such as stress, hardness, friction coefficient and wear, the electrical conductivity, the gas and vapour permeation, and many others. In this context, we have recently investigated ion-surface interactions in a plasma environment (biased-controlled PECVD and PVD) using a methodology combining in situ real-time spectroscopic ellipsometry (RTSE), dynamic Monte-Carlo simulations, and different complementary methods such as ERD, HRTEM, SEM, AFM and others. These have the capability to detect and simulate subplantation-related processes, such as sub-surface structural and compositional modifications, and interface broadening, on time and depth scales relevant to functional coatings deposition. The ion-induced effects result in (i) rapid structural (<< 1 s) and compositional (< 2 s) changes as deep as ?10 nm below film or substrate surfaces, as well as (ii) significant ion mixing and interface broadening, and (iii) relocation of a large proportion of deposited atoms below the growth surface. Specifically, following a description of the principal physical processes, we will show examples when the above-mentioned methodology helped to enhance our understanding of the film growth and interface evolution for numerous single and multilayer functional coatings comprising TiO2, SiO2, Si3N4, ITO and the nanocomposite superhard TiN/SiN and TiCN/SiCN systems. We will also discuss the ion-controlled growth mechanisms in the context of new deposition approaches such as plasma pulsing.

3:40pm **SE+PS-MoA6 Microstructure Evolution in High Power Magnetron Sputter Deposited Titanium Nitride**, ***M. Lattemann***, *D. Jädernäs, U. Helmersson*, Linköping University, Sweden

Transition metal (TM) nitrides are well known for their remarkable physical properties including high hardness and mechanical strength, chemical inertness, high temperature stability, low resistivity, and good optical properties. As a result they have become of high technological and scientific importance and are used in a wide range of applications. NaCl δ-TiN has received by far the most attention and is therefore often used as a model system. In this work, TiN thin films were deposited onto MgO(100) and MgO(111) substrates in an Ar/N_2 atmosphere using high power impulse magnetron sputtering (HIPIMS). HIPIMS has earlier been proven to produce a highly ionized metal flux exhibiting a broad ion energy distribution with energies up to 100 eV advancing surface processes. It was shown that these ion energies are sufficient to produce fully dense films even at ambient temperature. However, the high amount of metal species with an energy around 1 eV promote the formation of underdense grain boundaries as the energy only allows the ions to interact with the nearest neighbor sites by single hop events. At ambient temperature and grounded substrate, the TiN thin films show a columnar structure with almost random orientation of the crystals as a result of combination of arriving species with high and low mobility as well as highly energetic ions creating defects and nucleation sites. The window for epitaxial growth of TiN for a variety of different process parameters was investigated. E.g. a more monoenergetic ion energy distribution can be achieved by tailoring the substrate bias and process conditions. In addition to the metal ion energy and substrate temperature, also the effect of assisting gas ion irradiation was investigated both during the pulse and in between the pulses, where no deposition occurred. In this way, the onset and breakdown of structure relation towards polycrystalline morphology can be monitored. The resulting structure of the TiN thin films was investigated by x-ray diffraction and high resolution transmission electron microscopy.

4:00pm **SE+PS-MoA7 High Power Impulse Magnetron Sputtering (HIPIMS): Scaling Up to the Industrial Level**, ***G. Greczynski***, *J. Bohlmark*, Chemfilt Ionsputtering AB, Sweden

High Power Pulsed Magnetron Sputtering (HIPIMS or HPPMS) is a novel magnetron sputtering technique that draws increasing interest due to the ability to form the droplet-free films out of highly ionized vapor of the target material. Invented by Kouznetsov in 1999 (US patent US6296742) HIPIMS has gone the long way and is nowadays entering the stage of commercial applications. The focus of the work presented here is the basic parameter study performed on the industrial system equipped with HIPIMS power supply capable of delivering up to 10 kW average power in MW pulses. The target material used is Ti/Al and Ti. Purely metallic films, as well as, reactively sputtered TiAlN and TiN films were grown. The deposition rate and film quality were studied as a function of the energy per pulse (up to 20J), pulsing frequency (up to 500Hz), working gas pressure and the substrate bias. The degree of ionization, that was simultaneously monitored with optical emission, reached 90% under optimum conditions. Results are compared to the films produced with the state-of-the-art industrial DC coater. It is apparent from this study that the technique can be successfully used in the industrial applications.

4:20pm **SE+PS-MoA8 Mechanisms of Adhesion Enhancement by High Power Impulse Magnetron Sputtering**, ***A.P. Ehiasarian***, Sheffield Hallam University, UK **INVITED**

Adhesion to steel and carbide substrates is one of the primary factors determining coating performance under environmental attack such as wear in cutting and automotive engine operations, errosion-corrosion, and high temperature oxidation. Technologies that improve adhesion aim to sputter-clean the substrate by high energy ion bombardment with energy >500 eV. These energies are sufficient for ions to be implanted into the bulk of the substrate to a depth of several monolayers (1-3 nm). Therefore the chemical composition of the bombarding flux can have a strong influence on the structure of the coating-substrate interface. Technologies that use gas ion bombardment typically incorporate Ar as interstitial or at vacancy sites generated in the steel or carbide lattice by the high energy of irradiation. The inert nature of Ar means that it does not form bonds with the surrounding atoms and thus greatly disturbs atomic ordering and increases stress. In the case of high power impulse magnetron sputtering (HIPIMS) plasmas operating at peak current of 2 Acm^{-2}, the ion bombardment flux contains high fractions of metal ions. For HIPIMS of Cr and Ti, the ratio $Ar^{1+} : Me^{1+} = 1 : 1$ was observed with energy-resolved mass spectroscopy, whilst the metal ion-to-neutral ratio was $Me^{1+} : Me^0 = 1 : 1$ as determined from atomic absorption spectroscopy. Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) analysis of 304 stainless steel bombarded at 600 V by HIPIMS of Cr showed a layer of implanted Cr ions with depth of 5-8 nm, resulting from ballistic implantation as confirmed with TriDyn simulations. High-resolution TEM revealed that this region is highly crystalline with low defect density, probably due to the substitutional incorporation of Cr ions in the steel lattice. Incorporation and retention of Cr is improved by irradiation- and temperature- enhanced diffusion. As a result of the crystalline interface, the coating nucleated in local epitaxial growth mode which was maintained over several microns in lateral direction. A number of susbtrate-coating combinations demonstrated such epitaxy, for example for steel substrates: CrAlN, CrN, VN, TiAlN, and for γ-TiAl substrates - CrAlN, and CrN. This resulted in significant improvements to the adhesion and performance in wear and cutting of Ti and Al tests.

5:00pm **SE+PS-MoA10 Deposition Rate of High Power Pulsed Magnetron Sputtered Cu**, ***J. Emmerlich****, S. Mráz, R. Snyders, K. Jiang, J.M. Schneider*, RWTH Aachen University, Germany

In high power pulsed magnetron sputtering (HPPMS), several kW target power are dissipated during µs pulses resulting in a high degree of ionization of the sputtering gas as well as the sputtered target material.[1] A major drawback of this deposition process is reported to be the low deposition rate compared to d.c. magnetron sputtering (dcMS). Self-sputtering, due to a metal-ion dominated plasma later in the pulse, and plasma conductivity may play a large role in the deposition rate loss. However, the high target potential (up to ~2kV) applied during HPPMS influences the sputtering yield induced by both, the sputtering gas and the target ions (self-sputtering). The effect of the energy dependent sputtering yield on the deposition rate is discussed for Cu. Using transport-of-ions-in-matter (TRIM) software, we simulated the sputtering yield for a Cu target bombarded with energetic Ar^+ and Cu^+ ions for dcMS and HPPMS target potentials. The results show that the deposition rate of HPPMS compared to dcMS based on an energy dependent sputtering yield is in the range of 77% to 43%.

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Surface Science

Room: 608 - Session SS1-MoA

Water-Surface Interactions

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

2:00pm **SS1-MoA1 Water Adsorption on Ruthenium (0001) Pre-covered with Atomic Oxygen Studied by Scanning Tunneling Microscopy**, ***T.K. Shimizu****, A. Mugarza,* Lawrence Berkeley National Laboratory*, P. Cabrera-Sanfelix,* Donostia International Physics Center, Spain*, D.S. Portal,* Unidad de Física de Materiales, Centro Mixto CSIC-UPV, Spain*, A. Arnau,* Departamento de Física de Materiales UPV/EHU, Spain*, D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory

The adsorption of water on a Ru(0001) surface pre-covered with atomic oxygen forming a (2x2) structure was studied using low temperature scanning tunneling microscopy (STM). Below 0.25 ML, water adsorbs molecularly on top Ru sites within the (2x2) superstructure and forms two hydrogen bonds with pre-adsorbed O atoms. Because of the additional H-bonding, the water molecules are more strongly bound than those on the bare Ru metal. Water dissociation is completely blocked on the (2x2)-O/Ru surface and annealing results only in molecular desorption in the temperature range of 140-230 K. This is in contrast to the water adsorption on Ru with smaller pre-coverage of oxygen. These results will be discussed in light of current models relating water binding to the hydrophillicity and hydrophobicity of the underlying metal surfaces.

2:20pm **SS1-MoA2 Vibrational Study of Individual Water Dimers on Pt(111) using Scanning Tunneling Microscope**, ***K. Motobayashi,*** RIKEN, The University of Tokyo, Japan*, C. Matsumoto,* Gakushuin University, Japan*, Y. Kim,* RIKEN, Japan*, M. Kawai*, RIKEN, The University of Tokyo, Japan

The adsorption and diffusion of water molecules on metal surfaces play an important role in various fields of surface science, such as electrochemistry, heterogeneous catalysis, corrosion, and so on. Although the adsorption structure of water on a variety of metal surfaces at low coverage has been extensively investigated with various techniques, still unclear is the microscopic feature of adsorbed isolated water molecules. On the other hand, Vibrational spectroscopy methods have been used as powerful tools to get information of bond specific interactions, but in spite of that, the spatial resolution and sensitivity of conventional methods are not sufficient to detect vibrational signals from individual water monomers and dimers. To solve these problems, we investigated and report microscopic and vibrational study of adsorption behaviors of individual water molecules, especially water dimers, on Pt (111) by use of the scanning tunneling microscopy (STM) at 4.7 K. The Pt (111) single crystal surface was dosed with a small amount of water molecules (< 0.01 ML) at a temperature lower than 20 K. This temperature is low enough to prevent water molecules from thermal processes, such as diffusion, desorption and chemical reaction, on the surface, so that one can easily observe isolated water monomers and without forming large clusters. A water dimer appears as a flower like protrusion in the STM images, while a water monomer as a single protrusion as shown in Figure 1. It can be explained as one of the water molecules in a dimer rotating around the other. Indeed, we have succeeded in forming a dimer by manipulating two monomers with an STM tip, and also breaking a dimer into two monomers by inducing pulse bias. We obtained vibrational information by analyzing diffusion behavior of individual water dimers using STM, which method is so called "Action spectroscopy". The result of this measurement provides us not only the information of bond specific interaction but also the detailed features of adsorption structure. We found a kind of hydrogen bonding between one water molecule and Pt surface atoms in adsorption structure of a dimer.

2:40pm **SS1-MoA3 Dissociation of Water on Modified Transition Metal Surfaces**, ***G. Held***, University of Reading, UK **INVITED**

Water dissociation on surfaces of late transition metals has been a topic of intense discussion in the last few years.[1-4] It is remarkable in this context that different members of the Pt group, which normally show very similar chemical behavior, cause water to react in very different ways. This could be caused by small differences in the surface lattices, affecting the (mis)match with ice-like water layers, or by electronic differences, affecting the balance between inter-molecular hydrogen bonds and water-substrate bonds. Atomic or molecular coadsorbates are convenient means of modifying both types of bonds and were used in a systematic study to address this question. We compare the reactivity of water on clean and O-modified Pd{111}, Ir{111}, Pt{111} and Ru{0001} using LEED, TPD, high resolution XPS and NEXAFS. All four surfaces have the same surface symmetry and very similar lattice constants. Except for Ru{0001}, no dissociation is observed on the clean surfaces, even after prolonged irradiation with X-rays. Small amounts of oxygen, however, cause water to dissociate, whereas high coverages (> 0.25ML) tend to leave water intact with more stable surface bonds than for the clean surfaces.[5] The exception here is Pt{111}, where water dissociates for all oxygen coverages up to saturation. Molecular co-adsorbates, such as CO and methanol tend to inhibit water dissociation. Possible geometrical effects were investigated using Pt{111}, {110} and {531}, these surfaces represent a series with increasing atomic roughness and coordination numbers decreasing from 9 to 6. We could not find any increased reactivity of low-coordinated Pt atoms with respect to the dissociation of water only an increase in the water-substrate bond strength. Small amounts of oxygen promote water dissociation on all three surfaces; a high coverage (exceeding half the saturation coverage) prevents dissociation on Pt{531} and Pt{110}, but not on Pt{111}. These results indicate that dissociation of water on Pt group surfaces depends more sensitively on electronic modifications, as induced by oxygen coadsorption, than on the surface geometry.

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[2] P.J. Feibelman, Science 295 (2002) 58.

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[4] K. Andersson, et al. PRL 93 (2004) 196101.

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3:40pm **SS1-MoA6 Crystallization of Thin Amorphous Solid Water Films on Ru(0001) and on CO-precovered Ru(0001)**, ***T. Kondo,*** RIKEN and University of Tsukuba, Japan, *H.S. Kato,* RIKEN, Japan, *M. Bonn,* AMOLF, FOM, The Netherlands, *M. Kawai*, RIKEN and University of Tokyo, Japan

The deposition and the isothermal crystallization kinetics of thin amorphous solid water (ASW) films on both Ru(0001) and CO-precovered Ru(0001) have been investigated in real time by simultaneously employing helium atom scattering, infrared reflection absorption spectroscopy and isothermal temperature-programmed desorption. The modification of the Ru(0001) surface by the pre-adsorption of CO has been found to affect the deposition feature of water layers at the water coverage below ~5 ML: whereas an ordered first layer structure of water is formed on both the bare surface and the surface pre-adsorbed with 0.33 ML CO, a disordered structure is formed when 0.65 ML CO is pre-adsorbed. During ASW deposition, the interaction between water and the substrate depends critically on the amount of pre-adsorbed CO. However, the mechanism and kinetics of the crystallization of ~50 layers thick ASW film were found to be independent of the amount of pre-adsorbed CO. We demonstrate that crystallization occurs through random nucleation events in the bulk of the material, followed by homogeneous growth, for solid water on both substrates with an apparent activation energy of 650 ± 25 meV. The morphological change accompanying the formation of 3D grains of crystalline ice results in the exposure of the water monolayer just above the substrate to the vacuum. Remarkably enough, the appearance of this first water layer occurs already during the crystallization process, on both substrates.

4:00pm **SS1-MoA7 Growth, Structure, and Dynamics of Nanoscale Water Films on Various Substrates**, ***B.D. Kay,*** *G.A. Kimmel, N.G. Petrik, Z. Dohnalek, R.S. Smith*, Pacific Northwest National Laboratory

The growth of amorphous solid water and crystalline ice films on various substrates (Pt(111), Pd(111), C(0001) and FeO(111)) is investigated using temperature programmed desorption, rare gas physisorption, specular helium scattering, and infrared spectroscopy. At low temperatures water forms an amorphous film that wets all substrates studied. Heating the amorphous film, or growth at higher temperatures, results in the formation of crystalline ice. Concomitant with crystallization, the water films form non-wetting three dimensional crystallites on either the bare substrate or a substrate covered by only a single monolayer of water. The experimental results and their implications concerning hydrophobicity and the wetting-dewetting transition will be presented.

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Science Division. The experiment and calculations were performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle.

4:20pm **SS1-MoA8 The H/D Exchange in Water at Surfaces of Ice and on Cu(100) Studied by Infrared Vibrational Spectroscopy and DFT Calculations**, ***P. Uvdal,*** *J. Blomquist*, Lund University, Sweden

Proton transfer in water through the reaction $H_2O + D_2O \rightarrow 2HDO$ is one of many intriguing properties of water. We have studied the exchange in water at ice surfaces and on a Cu(100) surface using infrared vibrational spectroscopy. Intact molecules of H_2O and D_2O are observed up on adsorption at 84 K and no H/D exchange is observed in H_2O/D_2O mixtures . By monitoring the O-H (3695 cm^{-1}) and O-D (2730 cm^{-1}) stretches assigned to none-hydrogen bonded water molecules at the surface of the ice we have followed the H/D exchange in the temperature region 84 - 145 K. A clear isotope effect is observed in 4/1 mixtures of H_2O/D_2O or D_2O/H_2O. The majority isotope governs the exchange efficiency. The exchange is completed at 140 K resulting in at total scrambling of the isotopes. The vibrational data is interpreted with the aide of DFT calculations of small water complexes.

4:40pm **SS1-MoA9 Hydrogen Bonding, H/D Exchange and Molecular Mobility in Thin Water Films on TiO_2(110)**, ***G.A. Kimmel,*** *N.G. Petrik*, Pacific Northwest National Laboratory

We use the electron-stimulated desorption (ESD) of water from films of D_2O, $H_2{}^{16}O$ and $H_2{}^{18}O$ to investigate hydrogen bonding, H/D exchange and molecular mixing in water films on TiO_2 (110) for coverages ≤ 2 ML. By depositing water on the Ti^{4+} adsorption sites (H_2O_{Ti}) at 190 K using one water isotope and water on the bridge bonded oxygen sites (H_2O_{BBO}) at T ≤ 70 K using a different isotope, films with no appreciable mixing of the isotopes between the layers can be prepared. When H_2O_{BBO} is deposited at T > 70 K, partial or complete mixing of the layers occurs depending on the temperature and time. H/D exchange between the first and second water layers occurs at ~15 K lower temperatures than $H_2{}^{16}O/H_2{}^{18}O$ exchange. Isothermal experiments demonstrate that the mixing occurs with a distribution of activation energies centered on 0.29 ± 0.07 eV (0.26 ± 0.07 eV) for $H_2{}^{16}O/H_2{}^{18}O$ (H/D) exchange. While these distributions of activation energies are relatively narrow, they have a profound affect on the kinetics. The results demonstrate that H_2O_{BBO} is hydrogen bonded to H_2O_{Ti}. Since the lateral distance (0.325 nm) for atop adsorption at these sites is too large for hydrogen bonding, one (or both) of the adsorbates must be laterally displaced toward the other in agreement with theoretical predictions.

5:00pm **SS1-MoA10 Vicinal and Interfacial Water Structure of Non-Fouling Poly(ethylene glycol) and Sulphobetaine Self Assembled Monolayers**, ***M.J. Stein,*** *B.D. Ratner*, University of Washington

Poly(ethylene glycol) (PEG) and sulphobetaine (SB) are currently used in the formation of non-fouling surfaces. As yet, an understanding of the water phase effects in the vicinal realm of these surfaces and their impact on protein resistance remains imperfect. In this work, we present analysis of mixed self-assembled monolayers (SAMs) with either the PEG or SB functionality and the impact of hydration on both monolayer and vicinal water structure using multiple surface analytical techniques. The degree of protein resistance in the SAMs was modified through successive addition of diluent hydrophobic thiols to achieve a broader spectrum of protein resistant surfaces as measured through radio-labeled protein adsorption. The hydrophilic diluents yielded lower amounts of protein adsorption overall for both PEG and SB surfaces. However, the overall trends in protein adsorption differed for the two non-fouling thiols. SB yielded lowest adsorbed fg, alb, and lys when assembled in a 50:50V concentration with 11-mercaptoundecan-1-ol; whereas, pure PEG SAMs yielded the lowest levels of adsorbed protein. The packing density and chemical composition of the SAMs were examined by XPS, as well as ToF-SIMS. The orientation of the SB head groups was confirmed through angular XPS revealing a nearly horizontal head group. This contradicted ellipsometric thickness measurements. PEG data showed no similar contradictions. The terminal hydrophilicity of the groups was characterized through contact angle measurements and followed protein adsorption trends. Unpolarized infrared spectroscopy (FTIR) showed that the stretching frequencies, $vCH_{2,asym}$ and $vCH_{2,sym}$, of the ultra-nonfouling SB and PEG SAMs decreased and approached 2918 and 2850 cm^{-1}, indicative of a crystalline phase, when hydrated. To study hydration effects, each SAM was exposed to a series of timed D_2O soaks. Band shapes of the composite ν_{OH} band of H_2O obtained were fitted to individual peak components and a ratio of the component band areas from the 3400 and 3200 cm^{-1} regions was utilized to cross-compare samples. A single linear trend between the water peak ratio minima and protein adsorption was obtained for both the PEG and SB SAMs with lower ratios corresponding to higher levels of protein resistance. Using this method, FTIR has been used for the first time to demonstrate a correlation between strongly-bound water structure and protein adsorption.

Surface Science

Room: 611 - Session SS2-MoA

Electronic and Vibrational Structure

Moderator: M. Trenary, University of Illinois at Chicago

2:00pm **SS2-MoA1 Action Spectroscopy of Single Adsorbate Motions**, ***H. Ueba***, The University of Toyama, Japan **INVITED**

I will discuss an idea of action spectroscopy for a single molecule motion induced by vibrational excitation with a scanning tunneling microscope (STM).[1] A simple formula describing the energy transfer from the vibrational mode excited by tunneling electrons to a reaction coordinate mode through anharmonic coupling to overcome the activation barrier[2,3] is combined with the inelastic tunneling current calculated using the non-equilibrium Keldysh Green's function method. This enables the reaction rate to be calculated as a function of the bias voltage, and is applied to CO hopping on Pd (110)[2] and CCH rotation on Cu(001).[4] I propose that the second-derivative of the reaction rate with respect to the bias voltage gives the density of states of the vibrational mode excited by tunneling electrons,[4] which can not be directly observed with inelastic tunneling spectroscopy because of the negative contribution of the elastic current to the total current, and when a molecule motion is induced by the vibrational excitation.

[1] H. Ueba, B.N.J. Persson, Phys. Rev. B 75, 041403(R) (2007).

[2] T. Komeda et al., Science 255, 2055 (2002).

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2:40pm **SS2-MoA3 Action Spectroscopy of Vibrationally Excited Molecules by Inelastically Tunneled Electrons**, ***Y. Kim***, RIKEN, Japan

The excitation of molecular vibration by means of the inelastically tunneled electrons from the tip of a scanning tunneling microscope (STM) can lead to various dynamical processes at surfaces.[1-5] The vibrational spectrum of a single molecule provides useful information not only for the chemical identification of the molecule but also for investigating how molecular vibration can couple with the relevant dynamical processes. Inelastic electron tunneling spectroscopy with the STM (STM-IETS) has been mainly used for obtaining vibrational spectrum of individual molecules. STM-IETS detects the vibrational modes of a single molecule by measuring the total conductance change resulting from both elastic and inelastic electron tunneling.[2,3] However, the STM-IETS is not applicable to some molecules showing mobile character when they are vibrationally excited by inelastically tunneled electrons during measurement. The response of vibrationally mediated molecular motion to applied bias voltage, namely an "action spectrum", can reveal vibrational modes that are not visible in STM-IETS, because the molecular motion is induced via only inelastic tunneling.[3,5] Thus, the action spectrum would be a candidate for detecting which vibrational mode is actually excited and associated with molecular motions. Here, I discuss the usefulness and selection rules of the two types of single molecule vibrational spectroscopic methods by considering the action spectroscopy as an alternative vibrational spectroscopic method for the STM-IETS through the study of vibrationally mediated molecular motions with a low-temperature STM.

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3:00pm **SS2-MoA4 "Walking" Molecules and their Dynamics and Energetics**, *K.L. Wong, G. Pawin, D.H. Kim,* ***L. Bartels***, University of California, Riverside

Thiol groups, despite being proposed as rigid linker for many molecular electronics applications, anchor aromatic molecules to metal surfaces in a fashion that permits rapid rearrangement of the molecule on the substrate even at temperatures as low as 60K. The aromatic ring of individual benzenethiol molecules experiences a rotation barrier around the substrate linker of ca. 120 meV; even diffusion of the sulfur anchor on the substrate has a barrier of only ca. 150 meV.[1] Placement of two thiol groups in a molecule (9,10-dithionanthracene, DTA) does not increase the diffusion barrier. Rather it renders the moleculeâ?Ts diffusion behaviour on Cu(111) anisotropic, i.e. following a single line on the otherwise threefold symmetric substrate.[2] Density functional theory calculations show, that this behaviour originates from sequential occupation of optimal adsites by each of the two substrate linkers, strikingly resembling bipedal locomotion ("walking"). The resultant linear (uniaxial) motion on the surface can be used for transport of "cargo" molecules across a surface[3] as well as for the exploration of fundamental concepts of chemistry.

[1] K.L. Wong et al., Appl. Phys. Lett. 88, 183106 (2006)

[2] K.-Y. Kwon et al., Phys. Rev. Lett. 95, 166101 (2005)

[3] K.L. Wong et al., Science 315, 1391 (2007)

3:40pm **SS2-MoA6 Feedback-Controlled Single Molecule Surface Chemistry**, ***N.L. Yoder,*** *J.S. Fakonas, M.C. Hersam*, Northwestern University

In the past 25 years, the scanning tunneling microscope (STM) has enabled the detailed study of the chemistry and physics of single molecules on surfaces. Electron-driven processes (including desorption and dissociation) are especially advantageous because they offer the possibility of rapidly exciting a molecule far from equilibrium with exceptional spatial localization of the excitation.[1] Attaining precise control over the electron dose requires a method for both detecting the desired events and rapidly terminating the flow of electrons to prevent overdosing. A significant advance in this area was Feedback Controlled Lithography (FCL),[2] which involved the creation of isolated reactive sites on H:Si(100) through the controlled desorption of hydrogen. Since reaction products could also be susceptible to electrons, the ability to both detect a molecular conformational change and immediately terminate the flow of electrons is fundamentally relevant to the study of single-molecule processes. In this study, we apply this technique to the investigation of the byproducts of cyclopentene desorption[3] from clean Si(100). Experiments were performed using a cryogenic ultra-high vacuum (UHV) STM operating at 8 K and 80 K. At low temperatures, cyclopentene molecules are controllably desorbed, and a feedback loop is utilized to detect the desorption event and halt electron flow. At the desorption conditions of –4 V and 2 nA, the desorption reaction alternately results in three distinct surface features: a clean silicon dimer (55 %), a half-dimer dark feature (30 %), and fully darkened silicon dimer (15 %). Additionally, the radial and angular distributions of the byproduct binding sites were also measured. The desorption products were often observed at significant distances from the initial desorption site, with some features as far as 3 dimer rows (~23 Å) away. The dark desorption products are attributed to hydrogen-passivated silicon atoms resulting from the dissociation of a cyclopentene C-H bond and the subsequent bonding of the ejected hydrogen with the reactive silicon surface. Finally, tunneling electrons from the STM tip were used to induce hopping and desorption of hydrogen from the partially passivated silicon dimers.

[1] A. J. Mayne et al., Chemical Reviews 106, 4355 (2006).

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4:00pm **SS2-MoA7 Isotope-Specific Deposition of Vibrationally Excited Molecules**, ***D.R. Killelea,*** *V.L. Campbell, N.S. Shuman, A.L. Utz*, Tufts University

Direct IR excitation of gas-phase reagents offers a potential means of isotope selective chemical vapor deposition (CVD). A narrow bandwidth IR laser selectively excites a vibrational mode in a single isotopomer of methane. These vibrationally excited molecules are significantly more reactive, enhancing their rate of deposition. Here we present results showing control of the carbon isotopic ratio of surface adsorbates by IR excitation of methane. We recombinatively desorb the methyl fragment deposited on a Ni(111) surface after methane dissociatively adsorbs on the surface. We are able to quantify the yield of both carbon-13 and carbon-12 using a mass spectrometer to measure $^{13}\mathrm{CH}_4$ and $^{12}\mathrm{CH}_4$ desorbing from the surface. Using a methane molecular beam with the natural abundance of carbon-13 and carbon-12, we are able to achieve an eight-fold enhancement in carbon-13 deposition by exciting less than 0.1% of the methane molecules in the molecular beam.

4:20pm **SS2-MoA8 Ion Effects on the Liquid-Vapor Interface of a Non-Aqueous Solution**, ***M.J. Krisch,*** *J.C. Hemminger,* University of California, Irvine, *S. Baldelli*, University of Houston

We find that electrolytes modify the liquid-vapor interface of a non-aqueous solution. A variety of recent studies have observed ion-dependent changes in the surface structure of aqueous electrolyte solutions. In this project, we examine the influence of the solvent by probing the surface structure of non-aqueous electrolyte solutions. Our experiments use surface-specific sum frequency vibrational spectroscopy to obtain information about the liquid-vapor interface. We examine a series of alkali halides in ethylene glycol in which the identity of the anion is varied systematically. The spectra show that the addition of salt modifies solution surfaces to a degree that follows the polarizability of the anion in solution, particularly as seen through changes in the OH bonding stretch. Results are compared to surface tension measurements of the same solutions.

4:40pm **SS2-MoA9 Transport Limitations in Tunneling Spectroscopy of Pentacene on SiC**, ***S. Gaan,*** *R. Duca, R. Feenstra*, Carnegie Mellon University

Pentacene (Pn) is a promising material for organic field effect transistors because of its relatively high mobility and its tendency to form ordered structures. In this work we have used scanning tunneling microscopy (STM) and spectroscopy (STS) to probe the electronic properties of Pn thin films. The substrates were hydrogen-etched SiC, oxidized by exposure to 4000 L of molecular oxygen at 700°C. The Pn was deposited from a crucible by vacuum sublimation, with the sample at room temperature. On a large scale, the Pn films display a layered morphology with dendritic edges, consistent with prior results.[1] Within each layer, the molecules form ordered arrangements; it is on these regions that STS was performed. We obtain a HOMO-LUMO gap of about 2 eV.[2] Effects of degradation of Pn molecules were seen in the spectra, producing smearing of the band edges. Using the STM, with various tip-sample separations, widely different currents were injected into the sample in order to probe transport of the charge carriers. The tunnel current was found to saturate at positive bias for all tip sample separations, thus revealing a spreading resistance type of effect in Pn films. In other words, a quasi Fermi level exists in the sample and varies as a function of distance from the apex of the probe tip. In order to determine current saturation at negative bias, we examined the dependence of the current on tip-sample separation, at constant voltage. Significant deviation from ideal vacuum tunneling was observed, which also indicates transport limited tunnel current. To explain the observed transport limitation in the tunnel current we propose a simple two resistor model, one resistor for the vacuum and one for the sample, with the assumption that the sample resistance is constant. With different injection levels and voltages we obtain reasonable fits to the data. Using this model we are able to deduce resistivities of the sample for both filled and empty states, $3.3\text{x}10^2$ and $2\text{x}10^4$ Ω cm, respectively. Work is underway to interpret these results in terms of possible transport mechanisms in our Pn thin films.

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[2] Repp et. al., Phys. Rev. Lett., 94, 026803 (2005).

5:00pm **SS2-MoA10 Intrinsic Accumulation Layer Quantum Well States and Anomalous Valence Band Dispersion in Indium Nitride**, ***K.E. Smith***, *L. Colakerol, T. Learmonth, P.A. Glans, L.F.J. Piper,* Boston University*, A. Fedorov,* Lawrence Berkeley National Laboratory*, T.D. Veal, C.F. McConville,* University of Warwick, UK*, S. Healy, E.P. O'Reilly,* University College Cork, Ireland*, T.C. Chen, T.D. Moustakas*, Boston University

The valence and conduction band electronic structure in InN thin films has been measured using high resolution Angle Resolved Photoemission Spectroscopy (ARPES). InN exhibits an accumulation layer near the film surface, and our ARPES measurements reveal that the conduction band electrons in the accumulation layer exist in intrinsic quantum well states.[1] We also used ARPES to measure the Fermi surface of these quantum well states, as well as their constant binding energy contours below the Fermi level. The energy of the Fermi level, and the size of the Fermi surface for these quantum well states could be controlled by varying the method of surface preparation. Furthermore, a minimum is observed in the dispersion of the top of the valence band, with the highest measured valence band having an electron-like dispersion at the Brillouin zone center, which is unexpected in the context of earlier measurements and calculations. Valence band holes see a quantum barrier near the surface, and a theoretical analysis using a k.p approach of the influence of this barrier indicates that the anomalous dispersion is most likely due to a negative crystal field splitting in InN, contrary to previous expectations. This work was supported in part by the DOE under RF-06-PRD-001 (subcontract from University of Nevada, Las Vegas), by the NSF under grant number DMR-0311792, and by Science Foundation Ireland. The ALS is supported by the DOE, Materials Sciences Division under contract no. DE-AC03-76SF00098.

[1] 1. L. Colakerol, T.D. Veal, H.-K. Jeong, L. Plukinski, A. DeMasi, S. Wang, Y. Zhang, L.F.J. Piper, P.H. Jefferson, A. Fedorov, T.C. Chen, T. D. Moustakas, C.F. McConville, and K.E. Smith, Phys. Rev. Lett. 97, 237601 (2006).

Thin Film

Room: 613/614 - Session TF-MoA

Emerging Topics in Atomic Layer Deposition

Moderator: S.M. George, University of Colorado at Boulder

2:00pm **TF-MoA1 Atomic Layers in Nano(bio)technology**, ***M. Knez***, *L. Zhang, S.-M. Lee,* Max-Planck-Institute of Microstructure Physics, Germany*, A.J. Patil, S. Mann,* University of Bristol, UK*, K. Nielsch, U. Gösele*, Max-Planck-Institute of Microstructure Physics, Germany**INVITED**

In nanotechnology biological systems play an increasingly important role, since some of the naturally occurring biological macromolecules show perfect order on the nanoscale. The perfection of the natural organization of molecules is, in particular for the nanotechnology, often a target for imitation, but can almost never be obtained in a similar quality. An alternative way to obtain nano- or microstructures in close similarity to natural ones is their structural replication from inorganic materials or the modification of the chemical or physical properties of such systems by attachment of inorganic materials. Some of the methods applied recently rely on wet-chemistry which frequently leads to non-uniformity or bad quality of the attached materials. The ALD is one method-of-choice for performing such replication and modification experiments, since it offers the unique possibility to cover biological structures with inorganic films as thin as few Angstroms or nanometers. In this way a number of novel nanostructures with interesting properties can be synthesized, however, limited with the deposition processes which can be performed at temperatures below the stability limit of the biological or organic molecular units.

2:40pm **TF-MoA3 Al_2O_3 and W/Al_2O_3 Atomic Layer Deposition on Quantities of Multiwalled Carbon Nanotubes**, ***A.S. Cavanagh***, *C.A. Wilson, S.M. George*, University of Colorado at Boulder

Atomic layer deposition (ALD) can be employed to coat individual single-walled (SW) and multi-walled (MW) carbon nanotubes (CNTs). We have performed Al_2O_3 and W/Al_2O_3 ALD on quantities of multiwalled carbon nanotubes (MWCNTs) in a rotary reactor designed for ALD on high surface area nanoparticles. Al_2O_3 ALD was performed using trimethylaluminum (TMA) and H_2O. W ALD was performed using WF_6 and Si_2H_6. Al_2O_3 ALD on MWCNTs yielded nanospheres that grew with the number of trimethylaluminum and H_2O reaction cycles. Al_2O_3 ALD is believed to nucleate only at defect sites on the surface because the graphene surface of MWCNTs is unreactive. The NO_2/TMA nucleation procedure developed by Farmer and Gordon [Nano Letters 6, 699 (2006)] for ALD on SWCNTs was used to obtain very conformal Al_2O_3 ALD films on gram quantities of MWCNTs. The Al_2O_3 ALD films grew linearly with the number of TMA/H_2O reaction cycles. This Al_2O_3 ALD film is not covalently attached to the MWCNTs. Evidence for only a physisorption interaction was provided by ALD-coated MWCNTs where the Al_2O_3 ALD coating had broken to yield "ALD macaroni on a CNT string". W ALD also grew on the conformal Al_2O_3 ALD coating to create W/Al_2O_3 bilayers. X-ray photoelectron spectroscopy indicated that the surface of the metallic W was oxidized to form WO_3 upon exposure to atmosphere. The W ALD oxidization should be avoided by passivation with Al_2O_3 ALD. Calculations show that a metallic W ALD coating significantly enhances the CNT conductivity.

3:00pm **TF-MoA4 Molecular Layer Deposition of Alkyl-Aromatic Polyamide Films**, ***Q. Peng***, *R.M. VanGundy, G.K. Hyde, S.M. Stewart, G.N. Parsons*, North Carolina State University

Organic thin film materials with well controlled microstructure have significant applications in organic light-emitting devices, organic thin film transistors, organic photovoltaic cells, quantum devices, molecular electronics, biomaterial interfaces, and others. Molecular layer deposition (MLD) is a binary self-limited deposition process to form uniform and conformal polymer thin films with well controlled microstructure. We have recently investigated vapor-phase polymer MLD using (1, 4 butane diamine) and aromatic (terephthaloyl dichloride) polyamide. 1, 4 butane diamine and terephthaloyl dichloride were evaporated at room temperature and 70°C respectively. Growth on a variety of surfaces, including Au, Si-OH, Si-H, methyl-terminated Si, and amino-terminated Si, was investigated, with substrate temperature controlled between 70 and 150°C. An in-situ quartz crystal balance was used to monitor the adsorption and desorption behavior of the monomers. Generally, the deposition rate decreased as the reaction temperature increased. At 85°C, the thickness of the polyamide film measured using ellipsometry as a function of the number of deposition cycles results in a growth rate of 0.2 nm/cycle. Transmission infrared spectroscopy verified the characteristic polyamide peaks in the films. Contact angle measurements were carried out after each monomer dosing cycle resulting in expected changes in the surface energy with each half-cycle. The thermal stability, chemical inertness and capacitance properties of the deposited polymer thin film were also characterized. Results give insight into process requirements to achieve well controlled molecular layer deposition of organic films that include aromatic elements.

3:40pm **TF-MoA6 Fabrication of Hybrid Inorganic/Organic Multilayers Using Atomic and Molecular Layer Deposition**, ***D. Seghete***, *S.M. George*, University of Colorado at Boulder

Inorganic/organic multilayers occur in the nacreous layer of the mollusk shell and are among the strongest structures in nature. These "brick and mortar" composites are known for their high elasticity, toughness, and hardness. In this study, we report the fabrication of alternating inorganic and organic multilayers consisting of inorganic alumina (Al_2O_3) or tungsten (W) in combination with organic alucone polymer. Al_2O_3 atomic layer deposition (ALD) is performed using trimethylaluminum (TMA) and H_2O as the reactants. W ALD is accomplished using WF_6 and Si_2H_6 as the reactants. The organic alucone layer is grown using molecular layer deposition (MLD) with TMA and ethylene glycol as the reactants. The growth of the inorganic/organic multilayers was investigated using in situ quartz crystal microbalance studies. The nucleation of the inorganic Al_2O_3 or W ALD was explored on the alucone layer. The nucleation of the organic alucone MLD was also examined on the Al_2O_3 and W layers. The nucleation behavior provides information about the bonding between the inorganic and organic layers. The adhesion between the inorganic and organic layers is important for the mechanical properties of these multilayer structures. The structure and stability of the inorganic/organic multilayers were also explored using x-ray reflectivity measurements. Future mechanical property studies are planned using a nanoindenter.

4:00pm **TF-MoA7 Optimization of ALD Conformality in Ultra-High Aspect Ratio Nanopores Formed in Anodic Aluminum Oxide Templates**, ***E. Robertson***, *I. Perez, L. Henn-Lecordier, S.J. Son, S.B. Lee, G.W. Rubloff*, University of Maryland

The very high conformality for thin film deposition in high aspect ratio structures is a major driver for broad use and adoption of atomic layer deposition (ALD) processes. ALD is particularly promising for applications coupled to anodic aluminum oxide (AAO) membranes, in which cylindrical nanopores with uniform dimensions (15-300nm dia) and spacing are formed by self-assembly during anodization. In turn these structures form templates useful for creating energy and display devices within the AAO template, or released nanotube or nanowire systems after AAO dissolution, e.g. for nanoparticle-based targeted drug delivery. We have created high-K dielectric nanotubes by HfO_2 ALD in AAO templates to investigate the relationship between ALD process parameters and the conformality of the ALD films in the nanopores as a function of nanopore dimensions and aspect ratios. SEM was used to measure pore diameters (40-80nm) before and after the ALD deposition. The HfO_2 nanotubes were then released by dissolution of the AAO template and examined via TEM imaging of the nanotubes on standard grids. TEM profiles showed HfO_2 nanotubes with lengths 1-2 microns (determined by the AAO template) and having wall thicknesses in the range 3-10 nm which vary with position along the depth of the original AAO nanopores. The AAO templates are attractive both for the applications above and for the ease with which they generate very high aspect ratio nanopores to study ALD conformality, while the nanotube release through AAO template dissolution provides a very simple means to achieve TEM analysis of ALD conformality. These advantages are particularly striking in comparison to requirements for more conventional high aspect ratio devices such as DRAM trench structures, where challenging lithography, dry etching, etc. must be combined with difficult cross-sectional TEM sample preparation to understand and optimize ultrathin conformal device layers.

4:20pm **TF-MoA8 Molecular Layer Deposition of Alucone Polymer Films Using Trimethylaluminum and Various Glycols**, ***A.A. Dameron***, *S.D. Davidson, B.B. Burton, J.A. McCormick, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Conformal polymeric films can be grown by a sequential, self-limiting surface chemistry process known as molecular layer deposition (MLD) that is very similar to atomic layer deposition (ALD). The MLD reactants are typically monomers for step-wise condensation polymerization and can yield completely organic or organic-inorganic alloys. Our earlier work has demonstrated polyamide growth using diamines and diacid chlorides. Alucone MLD is performed using trimethylaluminum (TMA) and various glycols as the reactants. When the glycol is ethylene glycol (EG), the alucone is poly(aluminum ethylene glycol), $[Al\text{-}(OCH_2CH_2O)_x]_n$. Alucone films have been fabricated on silicon substrates at temperatures ranging from 85 °C to 175 °C. In situ quartz crystal microbalance and ex situ x-ray reflectivity experiments have confirmed linear growth of the alucone film versus number of TMA/EG reaction cycles at all temperatures. The MLD growth rates decreased at higher temperatures. Growth rates were 4 Å per cycle at 85 °C and 1.7 Å per cycle at 135 °C. In situ and ex situ Fourier transform infrared spectroscopy (FTIR) have also been used to monitor the surface reactions during alucone growth. Experiments with other glycols, such as benzene-1,4-diol (hydroquinone), demonstrate the general applicability of the alucone MLD surface chemistry to fabricate organic-inorganic films with tunable functionality.

4:40pm **TF-MoA9 Film Properties and In-Situ Optical Analysis of TiO_2 Layers Synthesized by Remote Plasma ALD**, ***W. Keuning***, *J.L. Van Hemmen, O. Muraza, E. Rebrov, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

TiO_2 is a widely studied material due to its optical and photocatalytic properties and its hydrophilic nature after prolonged UV exposure. When synthesized by atomic layer deposition (ALD) the TiO_2 can be deposited with ultimate growth control with a high conformality on demanding topologies and even at room temperature when e.g. using a plasma based process. We report on the deposition of TiO_2 films using remote plasma ALD with titanium (IV) isopropoxide as precursor and O_2 plasma as oxidant. Stochiometric TiO_2 films with carbon and hydrogen levels below the detection limit of Rutherford backscattering/elastic recoil detection (< 2 at.%) have been deposited within the temperature range of 25°C to 300°C. Depending on the ALD conditions and film thickness amorphous films turn anatase for temperatures higher than 200°C as revealed by X-ray diffraction. It is demonstrated that this change in crystal phase can also be observed by spectroscopic ellipsometry revealing an increase in growth rate per cycle (from typically 0.45 Å/cycle to 0.7 Å/cycle) and change in bandgap (from 3.4 eV to 3.7 eV) when the TiO_2 becomes anatase. An accompanying change in surface topology is clearly observed by atomic force microscopy. The hydrophilicity of low temperature TiO_2 films is studied by contact angle measurements for adhesion purposes revealing that the amorphous films are super-hydrophilic after UV exposure.

Applied Surface Science

Room: 610 - Session AS+BI+NS-TuM

Surface Analysis and Related Methods for Biological Materials

Moderator: J. Soares, University of Illinois at Urbana-Champaign

8:00am **AS+BI+NS-TuM1 Nano-bio Chemical Image of Single Cells and Tissues for Bio-medical Applications**, ***D.W. Moon**, T.G. Lee, J.Y. Lee*, Korea Research Institute of Standards and Science **INVITED**

Biochemical imaging of cells and tissues is a basic infra-technology in various bio-medical applications. Instead of conventional labeling methodology for biomolecular imaging with fluorescent dyes, label-free single cell and tissue biochemical imaging methodologies such as a nonlinear optical technique, coherent anti-Stokes Raman scattering (CARS) and an ion beam sputtering analysis technique, Secondary Ion Mass Spectrometry (SIMS) using cluster ion beams were developed. They were used to measure in a complementary manner 2D or 3D biochemical images of various cells and tissues such as Hella cells, adipogenic stem cells, fat liver tissues, cancer tissues, and skin tissues. Preliminary results will be discussed on the following issues. 1) Interactions of fibroblasts with native and denatured collagen thin films were studied with CARS and SIMS. It was extended to study the interactions of fibroblasts with 500 nm nano-fibers and 5 µm micro-fiber made of 40% poly (glycolic acid) (PGA) and 60% collagen. 2) Photoaging effects of skin by UV radiation were studied with SIMS, which showed significant changes in the biochemical imaging of amino acids representing collagen fibers and lipid molecules. 3) It was shown that SIMS imaging of colon cancer tissues has some potential to develop personalized cancer therapy with new drugs. Finally, the present status and future prospects of nano-bio technology based on laser, mass spectrometry, and nanoprobe for biochemical imaging of single cells and tissues at KRISS will be discussed for practical applications in bio, medical, and pharmaceutical researches.

8:40am **AS+BI+NS-TuM3 SIMS Imaging of Polymer Membranes and Single Cells**, ***G. Jiang**, R. Michel, D.J. Responte, L. Mayorga, K. Greenland, T.N. Davis, T.A. Horbett, D.G. Castner*, University of Washington

The ability to obtain 3-D images of drug distributions in polymers can provide information about drug loading and release profiles. Likewise 3-D images of biological species (lipids, proteins, sugars, etc.) in cells can provide information about the distribution of those species within the cell. With the advent of C_{60} cluster ion beam sources, it is now possible to use time-of-flight secondary ion mass spectrometry (ToF-SIMS) to examine these important biological problems. This study used a dual beam approach (C_{60}^+ for sputtering and Bi_1^+ or Bi_3^+ for analysis) to generate 3-D images from drug (dipyridamole) loaded polyurethane (PEU) films cast onto glass and single cells (yeast and monocytes) adsorbed onto porous polycarbonate (PC) membranes. 3-D images were successfully obtained from all samples. For PEU films without the drug, the intensity of organic fragment ions from the PEU remained constant until the PEU/glass interface was reached, then decreased as the intensity of fragments from the glass increased. In the initial stages of sputter profiling drug loaded PEU films, the intensity of the drug peaks decreased while the intensity of the PEU fragments increased. Then intensities from both components remained relatively constant until the PEU/glass interface was reached. Molecular ions from the drug were readily detected throughout the entire PEU film. ToF-SIMS 2-D and 3-D images of single yeast (size ~ 5 microns) and monocyte (size ~ 10 microns) cells were obtained for cells adsorbed onto the surface of the PC membrane and within the pores of the PC membrane. Fragments from biological species from these cells (e.g., phospholipid at m/z = 184) could be detected in the ToF-SIMS images. These results indicate the possibility of 3-D chemical state mapping of single cells and other biomedical samples with the spatial resolution of a few microns.

9:00am **AS+BI+NS-TuM4 Surface Energy Control Within Copolymer Libraries Synthesised as Micro Arrays for Biological Screening**, *M. Taylor, A.J. Urquhart,* The University of Nottingham, UK*, D.G. Anderson, R. Langer,* Massachusetts Institute of Technology*, M.C. Davies, **M.R. Alexander***, The University of Nottingham, UK

There is currently much interest in polymer microarrays in the field of high-throughput materials development.[1,2] Although combinatorial material synthesis is relatively advanced, methods for characterising the surface chemical properties of such libraries are less well developed. We report on methods to characterise the surface chemistry and surface energy of 480 polymers on a microarray formed using on-slide copolymer synthesis. We used X-ray Photoelectron Spectrometry and Time of Flight Secondary Ion Mass Spectrometry to provide surface chemical information from each spot. Water and diiodomethane contact angle measurements were made from individually dosed picolitre volume droplets to estimate surface energy of each copolymer formulation.[3] Such arrays provide extra challenges for characterisation due to the large sample numbers, small sample size and increased data volume. Here, we will focus on the correlations determined between the monomer structures and the surface energy. The information XPS and SIMS can provide on the actual surface chemistry is presented and contrasted to the bulk surface chemistry. We highlight the ability to tune the surface energy using certain polymerised monomer combinations by varying their relative concentrations. This has great utility in controlling the biological response to polymer surfaces.

[1] J. A. Hubbell, Nature Biotechnology 2004, 22, 828.

[2] D. G. Anderson, S. Levenberg, R. Langer, Nature Biotechnology 2004, 22, 863.

[3] Taylor, M.; Urquhart, A. J.; Zelzer, M.; Davies, M. C.; Alexander, M. R., Picolitre water contact angle measurement on polymers. Langmuir Letters (2007, in press).

9:20am **AS+BI+NS-TuM5 Surface Characteristics of Listeria Monocytogenes Mutants with Variable Pathogenicity Levels***, **N.I. Abu-Lail**, B.-J. Park*, Washington State University

Despite being an important food-borne pathogen, L. monocytogenes in fact comprises a diversity of strains with varying virulence. Whilst many strains of L. monocytogenes have pathogenic potential and can result in disease and mortality, others have limited capability of establishing infections and relatively avirulent. Although very important, the question of how the composition of the bacterial surface and the properties of bacteria vary between strains that have different level of virulence at the molecular level needs to be answered. To answer this question, interaction forces between five different L. monocytogenes mutants that vary in their virulence and a model surface of silicon nitride were investigated using atomic force microscopy (AFM). Adhesion measurements between the strongest Listeria mutant and silicon nitride reveled that although both surface polysaccharides and surface proteins contributed significantly to the total adhesion, polysaccharides contribution (1.0 ± 0.2 nN) was larger than that of proteins' contribution(0.38 ± 0.1 nN). Adhesion forces were also dependent on the pH value of the solution, temperature, and media type. Experiments on intermediate virulence mutants and avirulent mutants are currently ongoing. Successful completion of these experiments will improve our understanding of the main molecular differences between virulent and avirulent strains of L. monocytogenes. Such findings would be very important, because it will allow for the first time and at a molecular level, to define a criteria that can distinguish virulent L. monocytogenes' strains from avirulent ones and therefore reduce unnecessary recalls of food products and help in preventing disease outbreaks.

9:40am **AS+BI+NS-TuM6 First Observation of Charge reduction and Desorption Kinetics of Multiply Protonated Peptides Soft Landed onto Self-assembled Monolayer Surfaces***, **O. Hadjar**, J.H. Futrell, J. Laskin*, Pacific Northwest National Laboratory

Soft-landing (SL) of hyperthermal ions onto semiconductive surfaces is a promising approach for highly-selective preparation of novel substrates using a beam of mass-selected ions. In addition, controlled deposition of complex ions onto surfaces presents a new approach for obtaining molecular level understanding of interactions of large molecules and ions with a variety of substrates relevant for biology and catalysis research. In this work we present a first study of the kinetics of charge reduction and desorption of peptide ions soft-landed onto a fluorinated self-assembled monolayer (FSAM) surface at hyperthermal energy (40 eV). An in situ 8 keV Cs^+ secondary ion mass spectrometry (SIMS) in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer is used. Doubly protonated peptide ions are produced by electrospray ionization, mass-selected and transferred to the surface. The experiment allows the Cs^+ beam to merge with the peptide ion beam on the surface facilitating real time soft landing process monitoring. The surface is regularly probed using SIMS during and after ion soft-landing. All peptide-related peaks in SIMS spectra show a gradual increase during the soft-landing. Rapid decay of the $[M+2H]^{2+}$ signal accompanied by increase of the $[M+H]^{+}$ signal is observed after soft-landing is stopped. The $[M+H]^{+}$ signal maximizes 2-3 hours after the end of the soft-landing and shows a relatively slow time decay at longer delay times. Several peptide fragments followed a very different kinetics behavior showing very slow, almost linear decay after soft-landing. We attribute this time signature to fragments that originate from neutral peptide molecules on the surface. Other peptide fragments show a mixed behavior suggesting that they are formed from different charge states of the soft-landed peptide ions. Our results demonstrate for the first time that various peptide-related peaks follow very different kinetics, signatures for doubly protonated, singly protonated and neutral peptides retained on the surface. The experimental results are in excellent agreement with a simple kinetic model that takes into account charge reduction and desorption of different species from the surface. The kinetic modeling allowed us to obtain for the first time desorption and charge exchange rate constants for different peptide species on the surface.

10:40am **AS+BI+NS-TuM9 Ultra Fast Mid Infrared Spectroscopic Imaging for Biomedical Applications**, ***J. Phillips***, *H. Amrania, J. Plumridge, M. Frogley*, Imperial College London, UK

We discuss the potential biomedical applications for a unique infrared spectroscopic micro-imaging system. A table top tuneable solid state laser has been coupled to a commercial infrared microscope to create a unique mid-IR imaging tool. By integrating with a modified high resolution infrared camera that has previously only been available to the military market, we have constructed a broadband imaging system capable of performing diffraction limited spatially resolved spectroscopy of biological specimens. The narrow line-width of the laser allows us to take spectra at a resolution of 20cm-1. A polymer film sample with a micron scale structure has also been imaged in reflective mode to resolve details down to 8 microns in size. We also discuss results from spectrally imaging cancerous cervical tissue samples. The high peak power of the laser (10MW) offers signal to noise levels previously unobtainable with stand-alone laboratory based commercial instruments. This coupled with a short pulse duration will for the first time enable time resolved imaging at a 100psec resolution.

11:00am **AS+BI+NS-TuM10 X-ray Spectromicroscopy and Ion Spectroscopy to Evaluate a Blend of Poly(L)lactic Acid and Fluorine End-capped Poly(L)lactic Acid**, ***D. Wells***, *J.A. Gardella*, University at Buffalo

Blending polymers is a versatile method for tuning the physical and chemical characteristics of a material such as strength, thermal stability, optical properties, and degradation rates. As the field of nanomaterials continues to grow it is essential to be able to evaluate the microstructure of polymeric materials as well as to characterize the chemistry that occurs at the interfaces of blended polymer films. Two techniques capable of such analysis are scanning transmission X-ray microscopy (STXM) and imaging time of flight secondary ion mass spectrometry (ToF-SIMS). STXM is a spectromicroscopy technique, that is, it combines both imaging and chemical spectral information. Recent advancements in cluster primary ion sources for ToF-SIMS have extended the range of its applications. The system of primary interest in this work is a blend of poly(L)lactic acid (PLLA) with fluorine end-capped poly(L)lactic acid (F-PLLA). This material has potential as a drug delivery device whose degradation could be controlled by changing the ratio of hydrophobic F-PLLA to hydrophilic PLLA. It is known that the fluorine containing component will preferentially surface segregate.[1] By reducing the concentration of F-PLLA we predict that we can create lateral surface segregation as well as vertical segregation. Both STXM and ToF-SIMS generate images containing chemical information and are useful to evaluate lateral phase segregation. Our intent is to use these two techniques as the primary means to evaluate the effects of changing the ratio of F-PLLA to that of pure PLLA.

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[1] Won-Ki Lee, I. L., Joseph A. Gardella Jr., Synthesis and Surface Properties of Fluorocarbon End-Capped Biodegradable Polyesters. Macromolecules 2001, 34, (9), 3000-3006.

11:20am **AS+BI+NS-TuM11 Influence of Molecular Environment on ToF-SIMS Detection of Bio-Active Molecules on Self-Assembled Monolayers**, ***Z. Zhu***, Pacific Northwest National Laboratory

Bio-active molecules can be immobilized on solid substrates to form a monolayer or sub-monolayer. Because interactions between bio-active molecules are typically special, this structure is very useful in bio-recognition. So far, it has been widely used in bio-analysis or disease diagnosis. Alkanethiol self-assembled monolayer (SAM) on Au substrate is one type of commonly used solid substrate due to its versatile surface properties. During the last decade, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has proven one of the most convenient techniques to detect sub-monolayer of organic molecules on alkanethiol SAMs. We have earlier described the possibility of quantitative detection of peptide molecules on COOH-terminated SAMs. However, we found that molecular environment greatly affect the signal intensity. For example, Au+ signal from -S(CH2)2(CF2)9CF3 film is much stronger than Au+ signal from S(CH2)11CO2H film. Therefore, quantitative comparison of the density of bio-active molecules on different SAMs by ToF-SIMS is difficult unless effect of molecular environment can be quantitatively considered. In this work, a number of bio-active molecules were deposited on -S(CH2)11CH3, -S(CH2)10OH, -S(CH2)10CO2H, and -S(CH2)2(CF2)9CF3 films with similar density, and ToF-SIMS measurements were made. Two major factors are found to affect SIMS signal intensity. Firstly, electron-attraction organic functional groups are found to enhance positive ion signals but depress negative ion signals. For example, positive ion signals are enhanced on -S(CH2)2(CF2)9CF3 film but negative ion signals are depressed. In addition, active H-atoms such as those from COOH groups are able to enhance signal of positive molecular ions since they are normally protonated.

11:40am **AS+BI+NS-TuM12 Advances in Organic Depth Profiling Using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) under Optimized Ion Beam Conditions**, ***H.-G. Cramer***, *T. Grehl*, ION-TOF GmbH, Germany, *N. Havercroft*, ION-TOF USA Inc., *F. Kollmer, R. Moellers*, ***E. Niehuis***, *D. Rading*, ION-TOF GmbH, Germany

Depth profiling of inorganic materials has been one of the most important applications of SIMS in general, and more recently also of TOF-SIMS. In contrast, depth profiling of organic materials has always suffered from the fact that high-mass molecular information, to a large extent, is rapidly lost under high-dose sputtering conditions. With the advent of cluster ion beams, however, more and more examples of successful organic depth profiling have been presented, such as C_{60} profiling of PMMA, PLA, etc. On the other hand, it also became obvious that the projectiles and conditions commonly used were not successful for profiling of every organic material analyzed. In this paper we used the so-called dual beam mode of depth profiling to start a systematic investigation of organic depth profiling with a TOF-SIMS instrument. Similar to the case of inorganic profiling, we found the dual beam mode beneficial because sample erosion and the sample analysis are decoupled and can be independently optimized. We applied different primary projectiles, such as C_{60}, Bi_n cluster ions, O_2 and Cs with a wide range of impact energies to a variety of organic specimens. The results will be discussed with respect to the specificity of the detected ions, their yields, the damaged and removed sample volume per primary ion, and classical figures of merit such as depth resolution.

12:00pm **AS+BI+NS-TuM13 Fragment Free Mass Spectrometry for Bio-Molecular Surfaces with Size Selected Cluster SIMS**, ***J. Matsuo***, *S. Ninomiya, K. Ichiki, Y. Nakata, T. Aoki, T. Seki*, Kyoto University, Japan

Polyatomic and cluster ions have been utilized for bio-molecular analysis as the primary ion beam for SIMS. Enhancement of sputtering and secondary ion yields, and the capability for depth profiling of bio-materials have been reported for cluster ions, and are due to the effects of multiple collisions and high-density energy deposition of such ions on solid surfaces. In bio-molecular analysis, not only molecular ions, but also fragment ('daughter') ions are usually observed in the mass spectra, and this makes interpretation of the spectrum difficult. Therefore, reducing fragment ions is very important especially for practical applications. These phenomena strongly depend on cluster size, which is a unique parameter, and one of the fundamental questions is what size of cluster ion is most appropriate for bio-SIMS. To date there have been very few studies on the effect of size on secondary ion emission from bio-molecules. We have examined the size dependence of the secondary ion emission from amino acid, sugar and small peptide films with large cluster ion (N>100) by using the double deflection technique. When the total energy of the cluster ion is fixed, the secondary ion emission (SI) yield of molecular ions increases with size due to the non-linear effect. However, when the cluster size is too large, the SI yield is gradually diminished, because the energy per atom becomes too low to emit secondary ions. The maximum molecular SI yield from amino acid film was obtained for Ar clusters with the size of a few hundred at the energy of 20keV. The ratio of fragment ions to molecular ions was also measured as a function of cluster size. The ratio decreases quite rapidly with increasing the cluster size. When the cluster size was larger than 1000, very few fragment ions were observed in the mass spectrum. In this case, each incident Ar atom has kinetic energy of a few eV, which is comparable to the bonding energy of peptides. Ultra-low energy SIMS can be realized by using large cluster ions. The size effect in secondary ion emission and damage cross-section will be discussed.

Biomaterial Interfaces

Room: 609 - Session BI-TuM

Proteins at Interfaces

Moderator: D.G. Castner, University of Washington

8:00am **BI-TuM1 Inter-Domain Structural Flexibility and Biological Activity of Pro-Matrix Metalloproteinase-9 Revealed by Single-Molecule AFM Imaging**, *G. Rosenblum, **S.R. Cohen**, J. Frenkel,* Weizmann Institute of Science, Israel, *N. Slack,* Veeco Metrology Division, Santa Barbara, *I. Sagi*, Weizmann Institute of Science, Israel

The multi-domain enzyme pro-matrix metaloproteinase-9 (pro-MMP-9) is recognized as playing a key role in tumor biology, autoimmune diseases, and vascular pathology. This enzyme cannot be crystallized and hence the only structural information available is of the two isolated terminal domains. Until now, structure of the vital linker domain that connects these terminal domains was unknown. A lack of reliable means to bind the protein to the surface has plagued previous structural characterization by high-resolution AFM imaging. In order to obtain high-quality AFM images of the small protein, novel amine-modified surfaces were employed to immobilize the protein during the extensive rinsing required for removing features due to buffer salts. AFM images presented in this work provide the first definitive confirmation of the multi-domain structure, wherein two terminal domains are connected by a linker segment. Parallel analysis of a mutant lacking the linker showed a less extant shape. Statistical analysis of the AFM images revealed differences in both heights and lengths between the native and mutant proteins, and provided evidence that the linker imparts significant conformational freedom to the molecule, which is likely important in its biological functioning. Biological functioning was further probed, by examining interaction of the enzyme with collagen. Molecular modeling based on the SAXS data provides complementary supporting data.

8:20am **BI-TuM2 Sum Frequency Generation Vibrational Spectroscopic Studies in the C-H, O-H, N-H, and Amide I Regions of Model Peptides at Solid-Liquid Interfaces**, ***R.L. York**, G. Holinga, W.K. Browne, C. Hahn,* Univ. of California, Berkeley and LBNL, *D.R. Guyer,* LaserVision, Inc., *K.R. McCrea, R.S. Ward,* The Polymer Technology Group, *G.A. Somorjai*, Univ. of California, Berkeley and LBNL

We have developed a library of small, model peptides and have examined their interfacial structure at model hydrophobic and hydrophilic surfaces using surface-specific sum frequency generation vibrational spectroscopy (SFG). A fourteen amino acid peptide containing hydrophobic leucine (L) and hydrophilic lysine (K) residues was synthesized and characterized. This amphiphilic α-helical peptide has sequence Ac-LKKLLKLLKKLLKL-NH2 (LK14). SFG spectra in the C-H, O-H, and N-H region reveal that at a hydrophobic deuterated polystyrene surface, methyl groups from the hydrophobic leucine residues are ordered at the interface, while the hydrophilic lysine residues adopt a random orientation (presumably due to lack of interaction with the surface). When adsorbed onto a hydrophilic silica surface, the SFG spectra reveal a completely different molecular orientation: the methyl groups now appear to have a random orientation, and the N-H groups of the lysine side chains and/or peptide backbone are now ordered. A study of the influence of the ionic strength of the solution on the structure of LK14 revealed the following results: the LK14 peptide was α-helical in solution at high ionic strength but random coil at low ionic strength. Furthermore, leucine side chain ordering on hydrophobic surfaces was not perturbed by ionic strength changes, but N-H ordering on hydrophilic surfaces had a strong dependence on ionic strength. More recently, we have developed a new optical parametric amplifier (OPA) utilizing lithium thioindate (LIS) to study the Amide I mode of the peptide backbone. LIS provides high IR energy (~175 µJ at 1500 cm-1, ~375 µJ at 2000 cm-1), a high damage threshold, and good beam quality. The high energy output of LIS allows for the study of interfacial peptide structure without having to use a total internal reflection geometry. Using this new OPA, we have seen evidence for α-helical peptide structure at both hydrophobic and hydrophilic surfaces (at high ionic strengths). Additionally, there appears to be evidence for α-helical structure of the LK14 peptide at hydrophobic surfaces in low ionic strength solutions. We are currently examining lysine homopeptides, collagen-like peptides, new experimental geometries, more biologically relevant surfaces (such as HEMA and polymers with Surface Modifying Endgroups) and molecular dynamics simulations of peptides at interfaces to aid interpretation of experimental data.

8:40am **BI-TuM3 Thin Hydrogel Layers on Biomedical Polymers - Biological Responses and Effects on Protein Adsorption Studied by Mass Spectrometry**, ***D.L. Elbert***, Washington University **INVITED**

Medical devices used in contact with blood often contain features that are on the order of microns, (e.g. the struts on stents). Application of thin polymeric coatings on stents is feasible for the release of antiproliferative agents. However, the use of hydrogel coatings in this application is limited by a number of factors. Thin hydrogel coatings may be difficult to apply on complex geometries. The large volume of water in the hydrogel also limits the amount of drug that can be delivered from the coating. To address the first issue, we previously synthesized a copolymer of polylysine and polyethylene glycol (PLL-g-PEG) that self-assembles on negatively charged surfaces. We demonstrated that very thin yet stable layers of water-soluble polymer reduce biological responses, both in vitro and in vivo. We followed these experiments with investigations into the uses of layer-by-layer strategies, however, practical utility of these films is limited by time-prohibitive methods of fabrication, and the formed films may be too thin for drug delivery. We have addressed these shortcomings in two ways. Rather than delivering drugs directly, we are incorporating an enzyme into hydrogels. The enzyme produces a biologically active molecule (sphingosine 1-phosphate) from a precursor already present in blood (sphingosine). This molecule causes endothelial cell chemotaxis and inhibits smooth muscle cell migration. Additionally, we are producing multilayer films from nanogels that are formed by crosslinking PEG-vinylsulfone with albumin (average particle sizes 40 - 80 nm). Even a single layer of the nanogels covalently-reacted with RFGD-modified PET greatly reduces cell adhesion. Finally, in characterizing protein adsorption on thin hydrogel films, it is important to know not only the amount of adsorbed protein but also the conformations adopted by the adsorbed proteins. To study this, we have developed a proteomics-based strategy to detect differences in the exposure of lysine residues following adsorption. Our studies demonstrated an increased accessibility of lysine residues in fibrinogen adsorbed from low concentration solutions, which correlated well with the increase in the spread area of fibrinogen as measured at the same solution concentrations by OWLS. Overall, tremendous challenges and opportunities exist for producing thin surface coatings that resist non-specific biological adhesion and deliver drugs to control the biological response.

9:20am **BI-TuM5 Development of a Molecular Modeling Program Specifically Designed for the Simulation of Protein Adsorption to Biomaterials Surfaces**, ***R.A. Latour**, P. Biswas,* Clemson University, *B.R. Brooks,* Laboratory of Computational Biology - NIH, *S.J. Stuart*, Clemson University

Although it is well understood that cellular responses to biomaterial surfaces and substrates for tissue engineering and regenerative medicine are primarily governed by the bioactive state of adsorbed proteins, very little is known regarding the molecular-level events involved in these processes. Without this understanding, surface design can only be approached by trial and error. Molecular simulation provides a means to overcome this problem by providing an approach to directly investigate protein-surface interactions at the molecular level. Molecular simulation methods have already been successfully developed and widely applied for the study of protein folding and for drug design. However, these methods are not suitable for protein-surface interactions studies as it involves solid-liquid multiphase interactions which must be addressed specifically. Also, force-fields specifically designed for solid or liquid phase are not easily transferable. We are therefore working to develop capabilities within the CHARMM molecular simulation program to specifically adapt it for the simulation of protein adsorption processes to biomaterials surfaces. In particular, capabilities are being developed to control the solid phase, the solution phase, and the interactions between them with three separate force fields, thus enabling the molecular behavior of each phase of the system to be accurately represented. While force field parameters for proteins in solution and various solid materials have previously been developed and validated, parameters for the interactions between proteins in solution and functional groups presented by a solid surface have not. As an integral part of this program, we are therefore also generating experimental data on peptide-surface interactions for a wide range of amino acid residues and polymer-like functional groups for the design and validation of an interfacial force field for use in the developed program. In this presentation, we will describe the modifications in the CHARMM code and results exhibiting the usefulness of this hybrid force field approach for the simulation of peptide and protein interactions with a solid surface. Once fully developed, this approach holds promise to provide the biomaterials field with an exciting new tool to proactively design biomaterials surfaces to direct cellular response by controlling the bioactive state of adsorbed proteins with broad application in biomedical engineering and bionanotechnology.

9:40am **BI-TuM6 Switching the Force between a Hydrophobic Probe and Self-Assembled Monolayers on Gold by Changing the Ionic Strength**, ***N. Bonnet***, *D. O'Hagan, G. Hähner*, University of St Andrews, Scotland, UK

Alkanethiol based self-assembled monolayers (SAMs) have seen an ever increasing interest since they were first introduced more than two decades ago. Part of their attraction is due to the ease of their preparation in combination with the great flexibility they offer to create concentrated planes of functionality by modification of the surfactant molecules. One prominent example are oligo(ethylene glycol) (OEG)-terminated alkanethiol SAMs. They have been shown to resist the non-specific adsorption of some proteins and hence are of significant interest in the life sciences and related areas. Inspired by their protein repelling properties several studies were carried out to determine the underlying mechanisms and the interactions involved. The forces measured with a hydrophobic probe (attraction or repulsion) on these films were found to correlate with the protein adsorption properties (adsorption or resistance to adsorption). The forces indicated the existence of an electrical double layer, suggesting that an electrostatic component is involved. This was confirmed by theoretical calculations. We report on surfactant films based on OEG modified alkanethiol SAMs that can switch between an attractive and a repulsive force with hydrophobic probes depending on the ionic conditions of the environment. The ionic strength is an external parameter that can be easily controlled. The films are interesting for the reversible immobilization of hydrophobic (nano)particles and in colloidal chemistry. Similar surfactants might become important in bio-related fields and in connection with biosensors since they have the potential to adsorb/immobilize proteins reversibly if the switch can be tailored to occur in an ionic range that is compatible with proteins.

10:40am **BI-TuM9 When Good Cholesterol Goes Bad: Proteins at the Water:Lipid Interface**, ***J.W. Heinecke***, University of Washington **INVITED**

Apolipoproteins are amphipathic alpha helical proteins that play a key role in lipid transport in biological systems. HDL - the good form of blood cholesterol that protects against heart disease - is a complex of apolipoprotein A-I (apoA-I), free cholesterol, phospholipids and neutral lipids. Posttranslational oxidative modifications of apoA-I have been proposed to play a pathogenic role in atherosclerosis. Quantifying oxidized amino acids in atherosclerotic tissue proteins by isotope dilution gas chromatography mass spectrometry (GC-MS) has been used to assess oxidative stress in vivo and to investigate the biochemical pathways that contribute to inflammatory disease. These studies have identified myeloperoxidase, a heme protein secreted by activated phagocytes, as one important pathway for oxidizing HDL in the human artery wall. Electrospray ionization tandem mass spectrometry (ESI-MS/MS) coupled with liquid chromatography is rapidly emerging as a powerful technique for pinpointing sites of amino acid oxidation within apolipoproteins. Oxidants generated by myeloperoxidase lead to the site specific oxidation of apoA-I, and these posttranslational modifications are associated with major impacts on the biological function of the proteins. We have recently used 2-dimensional liquid chromatography ESI-MS/MS to test the hypothesis that proteins implicated in inflammation might be enriched in the HDL of subjects with coronary artery disease (CAD). Our observations suggest that HDL carries a unique cargo of proteins in CAD subjects and that certain of these proteins might make previously unsuspected contributions to the anti-inflammatory properties of HDL.

11:20am **BI-TuM11 In situ Quartz Crystal Microbalance Studies of Multi-Layer Glucagon Fibrillation at the Solid-Liquid Interface**, ***M.B. Hovgaard***, *M. Dong,* University of Aarhus, Denmark, *D.E. Otzen,* University of Aalborg, Denmark, *F. Besenbacher*, University of Aarhus, Denmark

The ability of certain polypeptides to form amyloid aggregates and their subsequent deposition at plague sites has been associated with multiple protein folding disorders.[1] As in vivo conditions associated with amyloid fibrillation are often dictated by surface and lipid membrane phenomena, the study of amyloid fibrillation at the solid-liquid interface represents an important and physiologically relevant approach to the study of amyloid fibrillogenesis. We have used Quartz Crystal Microbalance with Dissipation (QCM-D) to monitor the changes in layer surface mass density and viscoelastic properties accompanying multi-layer amyloid deposition in situ for the first time. By means of Atomic Force Microscope (AFM) imaging, an unequivocal correlation is established between the interfacial nucleation and growth of glucagon fibrils[2] and the QCM-D response. The combination of the two techniques allows us to study the temporal evolution of the interfacial fibrillation process. We have modelled the QCM-D data using an extension to the Kelvin-Voigt viscoelastic model. Three phases were observed in the fibrillation process: I) A rigid multilayer of glucagon monomers forms and slowly rearranges; II) This multilayer subsequently evolves into a dramatically more viscoelastic layer, containing a polymorphic network of micrometer long fibrils growing from multiple nucleation sites; III) The fibrillar formation effectively stops, due to the depletion of bulk phase monomers, although the process can be continued without a lag phase by subsequent addition of fresh monomers. The robustness of the QCM-D technique, consolidated by complementary AFM studies, should make it possible to combine different components thought to be involved in the plaque formation process and thus build up realistic models of amyloid plaque formation in vitro.

[1] Frokjaer, S. and D.E. Otzen, Protein drug stability: A formulation challange, Nat Rev Drug Discov. 4, 298-306 (2005).

[2] M. Dong, M. B. Hovgaard, S. Xu, D. E Otzen, and F. Besenbacher, AFM Study of Glucagon Fibrillation Via Oligomeric Structures Resulting in Interwoven Fibrils. Nanotech. 17, 4003-4009 (2006).

11:40am **BI-TuM12 Modulating the Orientation and Conformation of Bone Osteopontin and Bone Sialoprotein for Osteoblast Adhesion**, ***M.T. Bernards***, *S. Jiang*, University of Washington

Bone tissue is primarily composed of hydroxyapatite (HAP), which accounts for 70-90% of the mass of bone. The remaining 10-30% is composed of protein, of which ~90% has been shown to be collagenous. During natural bone formation cells first lay down a collagenous matrix composed of primarily type 1 collagen. After this collagen network is formed, proteins bind to the matrix and then the matrix is mineralized to form bone. While a number of proteins have been located within bone, only osteopontin (OPN) and bone sialoprotein (BSP) have been localized in the matrix ahead of the mineralization front. Additionally, both of these proteins have been found to be enriched at bone-implant interfaces. These two proteins are hypothesized to play an important role in cellular adhesion at these interfaces. This work details efforts to understand the roles of OPN and BSP in cellular binding to engineered systems mimicking the collagen and mineralized interfaces of bone. In the first part of this work, we compared the cell binding abilities of OPN and BSP when specifically bound to collagen. Both of these proteins have been shown to have a specific binding interaction with collagen and this was confirmed through the development of radiolabeled adsorption isotherms for each of the proteins. These isotherms were used to determine adsorption parameters that resulted in identical amounts of adsorbed protein, to directly compare the cell binding properties of these two proteins when specifically bound to collagen. The results indicate that OPN promotes a greater amount of cell binding to a collagen interface than BSP. The second part of this work compared the cell binding abilities of OPN and BSP when they are specifically bound to HAP, mimicking mineralized bone interfaces. HAP was formed from a simulated body fluid and characterized by scanning electron microscopy, energy dispersive x-ray spectroscopy, and electron spectroscopy for chemical analysis. Both OPN and BSP have been shown to have a specific HAP binding domain and this was confirmed through the development of radiolabeled adsorption isotherms. The cellular adhesion to HAP was then compared with identical amounts of adsorbed proteins. The results of this work indicate that BSP has a more favorable orientation/conformation for cellular adhesion as compared to OPN. However, this influence on cell binding is eliminated when the surface roughness of the underlying HAP substrate becomes too great.

12:00pm **BI-TuM13 Characterization of ECM Protein Production in Spatially Cultured Hippocampal Neurons on Micro-Patterned Surfaces in Serum-Free Conditions**, ***M. Ramalingam***, *S. Kootala, N. Bhargava, M. Stancescu, M. Hirsh-Kuchma, M. Klimov, P. Molnar, J.J. Hickman*, University of Central Florida

Spatial positioning of neurons on patterned surfaces and characterization of their functional synaptic connectivity and specific extra-cellular matrix (ECM) protein productivity is of great importance for the fabrication of neuron-based biosensors and in developmental cell biology. We have determined that a combination of traditional biological analysis techniques, such as SDS-PAGE and PT-PCR, and surface analytical techniques, such as X-ray Photoelectron Spectroscopy (XPS) and SIMS, is a good approach for ECM analysis. Here, we report on ECM deposition on patterns of hippocampal neurons on surfaces composed of self-assembled monolayers (SAMs) of two different organic compounds, trimethoxysilylpropl-diethylenetriamine (DETA) and tridecafluoro-1,1,2,2,-tetrahydroctyl-1-tricholorsilane (13F) as well as unpatterned controls, in a serum-free culture condition. The patterns were characterized by XPS, contact angle goniometry, electroless metallization and surface profilometry to confirm their surface composition, wettability and topography. Immunostaining of cultured neurons for synapsin I and microtubule-associated proteins (MAP-2) confirmed the pre- and post-synaptic formation. The electrophysiological study of neurons cultured for 14 days further confirmed the functional synaptic connectivity. The deposition and composition of ECM proteins were determined by immunocytochemistry, confocal laser spectroscopy and reverse transcriptase –polymerase chain reaction (RT-PCR), and it was found that the neurons produce laminin, collagen, fibronectin and vitronectin at differing amounts depending on the conditions. We have quantified the amounts of these proteins using Western Blot and SIMS spectroscopy. The overall results indicate that the neurons cultured on patterns secrete ECM proteins in a differential fashion and these data will have significant implications in engineering functional neuronal systems and hybrid devices.

Electronic Materials and Processing

Room: 612 - Session EM-TuM

Molecular Electronics

Moderator: I. Hill, Dalhousie University

8:00am **EM-TuM1 Dynamics of Molecular Switch Molecules Imaged by Alternating Current Scanning Tunneling Microscopy**, ***A.M. Moore***, *P.S. Weiss*, The Pennsylvania State University

We have studied oligo(phenylene-ethylene) (OPE) molecules as candidates for molecular electronic switches. We previously determined the switching mechanism to rely on hybridization changes between the substrate and molecule. Here, we have determined which molecules will be more or less active in our samples using a custom-built alternating current scanning tunneling microscope (ACSTM). The polarizabilities of the OPE molecules are observed using the ACSTM magnitude signal. The stability of the ACSTM magnitude correlates to the stability of the switches in our samples. From this, we can determine which molecules are more likely to exhibit motion and/or switching events and which molecules will remain stable in our images.

8:20am **EM-TuM2 Probing the Polarization and Dielectric Function of Molecules with Higher-Harmonic Demodulation in s-NSOM**, *M.P. Nikiforov*, University of Pennsylvania, *S. Schneider*, Dresden University of Technology, Germany, ***T.-H. Park***, University of Pennsylvania, *U. Zerwek, C. Loppacher, L. Eng*, Dresden University of Technology, Germany, *M.J. Therien, D.A. Bonnell*, University of Pennsylvania

In recent years a family of scanning probe microscopy (SPM) techniques has been evolved basing on applying multiple modulations to samples and tips and accessing optical higher-order harmonics. Scanning surface potential microscopy (SSPM or KPFM) based on noncontact atomic force microscopy (nc-AFM) is the first and most basic of the implementations exploiting multiple modulations. SSPM allows the analysis of local work functions on metallic samples and of surface charge distributions on insulators. In addition to the electric modulation, nc-AFM can be extended to optical investigations with the potential to access dielectric functions at surfaces. Of these scanning optical microscopes, so-called scattering near field optical microscopy (S-NSOM) offers the best opportunity for high spatial resolution. In s-NSOM a sharp probe tip is positioned near a surface and illuminated with optical radiation. The electric field is highly enhanced underneath the tip which acts as an optical antenna. Is a sample placed close to the tip, the local dielectric constant of the sample is probed by the tip and may be detected in the far-field scattered light. The strongly nonlinear distance dependence of the near-field may be used to separate its contribution from background signals by so-called higher-harmonic demodulation. In the present study the properties of porphyrin monolayers deposited on highly oriented pyrolytic graphite (HOPG) by evaporation in vacuum are probed. The molecular structure of the monolayer is known from nc-AFM. The polarization dependence of light scattering on the optically active molecules (porphyrin) was measured at four harmonics of the tip oscillation frequency. The contrast differences in the higher harmonics related to the dielectric properties of the molecules is compared with an analytical description of the signal transfer function. The limits in quantifying dielectric function and spatial resolution will be discussed as will the potential to probe dielectric function at the molecular level in the future.

8:40am **EM-TuM3 Electronic and Vibronic Spectroscopy of Molecular Junctions**, ***J.G. Kushmerick***, NIST **INVITED**

Transition voltage spectroscopy and inelastic electron tunneling spectroscopy are used to explore charge transport in molecular junctions. Our recent work has shown that a mechanistic transition occurs from direct tunneling to field emission in molecular junctions. The magnitude of the voltage required to enact this transition is molecule-specific, and thus constitutes a form of spectroscopy. We demonstrate that the transition voltage of a conjugated molecule depends directly on the manner in which the conjugation path is extended. Furthermore using inelastic electron tunneling spectroscopy to measure the vibronic structure of non-equilibrium molecular transport, aided by a quantitative interpretation scheme based on non-equilibrium Greens function/density functional theory methods, we are able to characterize the actual pathways that the electrons traverse when moving through a molecule in a molecular transport junction.

9:20am **EM-TuM5 Real-time Conductivity Analysis through Single-Molecule Electrical Junctions**, ***J.-S. Na***, *J. Ayres, K.L. Chandra, C.B. Gorman, G.N. Parsons*, North Carolina State University

We have recently developed a molecular electronic characterization test-bed that utilizes a symmetric pair of gold nanoparticles, 40 nm in diameter, joined together by a single or small group of conjugated oligomeric phenylene ethynylene (OPE) molecules. These nanoparticle/molecule/nanoparticle structures are subsequently assembled between nanoscale test electrodes to enable current through the molecule to be characterized. At low voltage (< ±1.5 V) the observed current is consistent with common non-resonant tunneling (i.e., I vs V is independent of temperature between 80 and 300 K). This molecular analysis approach is unique because it enables the stability of the molecular conductance to be observed and characterized over extended periods (several weeks so far) after fabrication. Conductance through single molecule junctions was monitored in real-time during several process sequences, including dielectrophoretic directed self assembly and post-assembly modification. Assembly faults are directly detected in real-time when non-ideal assembly conditions result in molecular junction failure and nanoparticle fusion in the junction. Real-time conductivity measured through the junction was sensitive to ambient conditions, and changes persisted over several days of exposure. Atomic layer deposition of Al_2O_3 was used to encapsulate and isolate the molecular junctions, and the effect of the deposition process sequence on current through the junction was evaluated in real-time. Results indicate that the current measured during atomic layer deposition is sensitive to the chemical oxidation and reduction reactions proceeding in the 1-2 nanometer confined region between assembled nanoparticles.

9:40am **EM-TuM6 Electronic Transport through Redox-Active Organic Molecules in Nanogap Molecular Junctions**, ***A.K. Mahapatro***, *J. Ying, B. Muralidharan, S. Datta, T. Ren, D.B. Janes*, Purdue University

Electronic properties of various organic molecules have been studied for potential nanoelectronics and sensor applications. Studies of redox active molecules can allow investigation of the energy-band alignments of the molecular levels with respect to the contact Fermi levels and studies of molecules in specific charge states. A recently developed technique to efficiently fabricate stable nanogap molecular junctions (NMJs)[1] are used in this study for room-temperature electrical measurements through single/few molecule systems. Electronic properties of redox active molecules Oligo(phynilene ethylene), OPE and trans-$Ru_2(ap)_4(C{=}CC_6H_4S\text{-})_2$, where $(ap)_4$ is 2-anilinopyridinate, are studied by localizing the molecules in the NMJs. The current-voltage characteristics of the OPE devices exhibit switching behavior at a threshold voltage between 1.6 V and 3.0 V. The di-ruthenium devices exhibit a negative differential resistance region, corresponding to an irreversible current peak at a bias voltage of ~ 0.3-0.4 V, followed by a conductance peak at higher bias. A theoretical model using sequential tunneling Coulomb blockade model[2] explains the current peak in terms of a blocking transport level that cannot be emptied easily, causing the conducting level to float out of the bias window as a result of Coulomb repulsion. Assuming equal capacitive coupling at both the metal-molecule contacts,[3] the observed conductance peak positions at ±0.25 ±0.05 V and ±1.05 ±0.15 V correspond to molecular level energies of E_{HOMO} = 5.23 eV and E_{LUMO} = 4.6 eV for the di-ruthenium molecule. These values are in close agreement with the molecular level energies estimated from the measured oxidation and reduction peaks in cyclic voltammetry.[4] The current study demonstrates that devices employing redox active molecules, in which the molecular levels are close to the metal Fermi level, allow resonant tunneling and could provide suitable structures for memory or chemical sensing applications.

[1] A. K. Mahapatro, S. Ghosh, and D. B. Janes, IEEE Trans. Nanotech., 5, 232 (2006).

[2] B. Muralidharan and S. Datta, Preprint, arXiv:cond-mat/0702161 (2007).

[3] S. Datta, W. Tian, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, Phys. Rev. Lett. 79, 2530 (1997).

[4] T. Ren et. al., J. Organ. Chem., 690, 4734 (2005).

10:40am **EM-TuM9 Electron Transport through Silicon-Based Molecular Electronic Devices: Effects of Molecular Chainlength and Molecular Dipole**, ***N. Gergel-Hackett***, *L.J. Richter, C.D. Zangmeister, C.A. Hacker, C.A. Richter*, National Institute of Standards and Technology

It is important for the advancement of the field of molecular electronics to develop an improved understanding the electron transport through molecular junctions, specifically silicon-based junctions that may enable the integration of molecular devices with traditional semiconducting technologies. In this work we examine the effects of molecular length and dipole on the electrical behavior of a metal-molecule-silicon, planar, enclosed devices. Devices with alkanethiol molecules of different lengths, with semi-fluorinated and non-fluorinated molecules, and with differently doped silicon were characterized to systematically understand the energetics of the metal-molecule-silicon junction and how the electron transport through the device is affected. We characterized devices with monolayers of various chainlengths of alkanethiols and observed the device current to decrease with increased molecular length. This inverse dependence on chainlength has been widely observed from metal-molecule-metal devices, but is an important characterization metric for silicon-based devices. However, we observed a different dependence of the current density on the chainlength than has been observed for metal-molecule-metal junctions. We attribute this difference in dependence to the Schottky barrier between top metal and bottom silicon contact in the metal-molecule-silicon devices that is not present in metal-molecule-metal devices. This will be explained in greater detail. We also compare the electrical characteristics of alkanethiol molecules with those of semi-fluorinated alkanethiols. The molecular dipole is dramatically different for semi-fluorinated alkanethiols than for non-fluorinated alkanethiols, and we observed current-voltage characteristics that depend on the fluorination. In order to confirm that the differences in current observed were due to the molecular dipoles shifting the Schottky contact barrier, we characterized devices with differently doped substrates. The relative effects of the molecular dipoles on the different starting Schottky contact barriers are used to develop an energetic model of the junction and the effects of surface dipoles. The observed changes in electrical behaviors as a result of changes in the chainlength and dipole of the molecular monolayer help us to understand the electrical transport through these devices and to verify that the energetic behavior of the devices has a molecular dependence.

11:00am **EM-TuM10 Characterization of Aryl Monolayers on Silicon for Molecular Electronics Applications**, ***A. Scott***, *D.B. Janes*, Purdue University

Recently there has been a significant amount of interest in developing molecular electronics to miniaturize and enhance functionality of integrated circuits. Molecular electronic devices with silicon contacts are of particular interest due to the relevance of silicon as an electronic material and the ability to engineer the substrate properties through doping. Molecular layers have been grafted to <111> silicon by electrochemical reduction of para-substituted aryl-diazonium salts for use in silicon-based molecular electronics. These molecular layers were characterized using atomic force microscopy, ellipsometry, x-ray photoemission spectroscopy, infrared spectroscopy, and contact angle measurements. It was found that the surface characteristics were dependent both on monolayer headgroup chemistry and substrate doping. Consequences for the application of these molecular layers to electronic devices on silicon were examined. Hydrogen-terminated silicon samples were prepared by etching cleaned silicon in deoxygenated ammonium fluoride. Various doping densities of silicon were used and it was determined that oxide-free surfaces could be realized on all of them using this method, however the doping affected the surface topology. Lightly doped samples exhibited atomically flat surfaces with well-defined step edges corresponding to individual planes of silicon atoms, whereas heavily doped samples maintained a low surface roughness, but had no defined structure. Molecular layers were prepared on hydrogen-terminated silicon by electrochemical reduction of various commercially available para-substituted aryl-diazonium salts in acidic aqueous solution.[1] Chemical characterization of the surfaces indicates that the substituent plays an important role in monolayer quality. Nitro-substituted species exhibited chemical instability and significant oxidation of the silicon substrate. Other molecular layers showed more ideal monolayer characteristics. These findings can be correlated with observations about electronic transport in gold-molecule-silicon devices.[2]

[1] P. Allongue, C. H. de Villenueve, J. Pinson, F. Ozanam, J. N. Chazalviel, and X. Wallart, Electrochim. Acta 43, 2791 (1998).

[2] A. Scott, C. Risko, M. A. Ratner, D. B. Janes, Appl. Phys. Let., to be published.

11:20am **EM-TuM11 Nanoscale Electrical and Structural Characterization of Gold/Monolayer/Silicon Junctions**, ***W. Li***, *M.A. Kuikka, H.Z. Yu, K.L. Kavanagh*, Simon Fraser University, Canada

The effect of molecular modification of metal-Si diode junctions has been investigated by electrical and structural measurements at both the macroscale and the nanoscale. Molecular junctions prepared with carbon-silicon bonded, n-alkyl monolayers and thermally evaporated gold contacts yield identical barrier heights and ideality factors irrespective of the alkyl chain length and end-group of the molecular layer. Nanoscale electrical and structural measurements, using ballistic emission electron microscopy (BEEM), and transmission electron microscopy (TEM), indicate laterally uniform penetration of deposited gold atoms into the junctions except for thiol-terminated monolayers where BEEM transmission is laterally non-uniform and TEM shows a continuous interfacial layer. In all cases, average BEEM transmission is reduced by the presence of a molecular layer with the largest effects also observed for the thiol terminated system.

11:40am **EM-TuM12 New Methods for Metal Deposition on Self-Assembled Monolayers: Towards Molecular Electronic Circuitry**, *P. Lu*, ***A.V. Walker***, Washington University in St. Louis

We have investigated the deposition of metals on alkanethiolate self-assembled monolayers (SAMs) adsorbed on Au using chemical vapor deposition (CVD) and electroless deposition. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. Chemical vapor deposition (CVD) is a widely employed technique for the deposition of metals on semiconductor substrates. CVD has not been widely employed to deposit films on organic materials because high temperatures (Tsubstrate > 200 °C) are often required that are not compatible with most organic thin films. However, by exploiting the chemical reactivity of functional groups at the SAM surface it is possible to deposit thin metallic films at room temperature. We demonstrate this method using trimethyl aluminum (TMA). TMA reacts at room temperature with a -COOH terminated SAM to form an Al overlayer, whereas TMA does not react with a -CH_3 terminated SAM. We have also investigated the mechanism of electroless deposition of copper on functionalized SAMs using a copper sulphate/formaldehyde reaction. Copper is deposited on -CH_3 and -COOH terminated SAMs but not on -OH terminated SAMs. For -CH_3 and -COOH SAMs, the deposited Cu is weakly stabilized at the SAM/vacuum interface and so slowly penetrates through the SAMs to the Au/S interface. Further, Cu does not deposit on -OH terminated SAMs because the formaldehyde reacts with the -OH terminal groups rather than reducing the copper.

12:00pm **EM-TuM13 Contact Properties in Molecular Electronics: The Effect of Molecular Orientation on Potential at Organic- Metal Interfaces**, ***M.P. Nikiforov***, University of Pennsylvania, *U. Zerwek, C. Loppacher*, Dresden University of Technology, Germany, *T.-H. Park, M.J. Therein*, University of Pennsylvania, *L. Eng*, Dresden University of Technology, Germany, *D.A. Bonnell*, University of Pennsylvania

Developments in molecular electronics over the last 5 years emphasize that the contact between molecules and electric contacts often define the behavior of the device. Controlling the structure and consequent properties of these junctions is of paramount importance. To date, it has not been possible to probe the relation between molecular structure and properties at the nm scale. The combination of molecular structure and local property measurement is demonstrated here. Vapor deposition of TET - H2 - TET porphyrin on HOPG results in islands that self assemble into 2 structures; one with the molecules oriented perpendicular to the film, one with a parallel orientation. The molecular structures are determined by nc-AFM. Variations in surface potential determined by Kelvin Force Microscopy (Scanning Surface Potential Microscopy) are correlated with the orientation of the porphyrin monolayers. The difference between the potential of the two structures is about 50mV. The difference in work function with orientation reflects a difference in the coupling between the molecule and the substrate. Perpendicular porphyrin does not alter the work function implying the absence of reaction and self assembly is dominated by van der Walls interactions. The decrease in work function with parallel orientation is indicative of a substrate-molecule interaction. The mechanism of this interaction will be discussed in terms of atomic orbitals. This is a direct measure of the effect of molecular orientation on the electronic properties of the junction.

The Industrial Physics Forum 2007: The Energy Challenge

Room: 602/603 - Session IPF-TuM

Energy for Low Carbon Input

Moderator: J. Hobbs, American Institute of Physics

8:00am **IPF-TuM1 The Prospects for Low-Cost Photovoltaic Electricity**, ***D.E. Carlson***, BP Solar **INVITED**

In the last decade the photovoltaic (PV) industry has grown at an annual rate of about 35%. While PV modules made in the 1960s sold for hundreds of dollars per Watt, prices are now in the range of $3-$4 per Watt, and this corresponds to levelized electricity costs of about 20-25 cents/kWh for large commercial systems. Silicon technology has dominated the industry since its inception and about 91% of all solar cells sold in 2006 were based on crystalline silicon. However, there are a number of other technologies under development involving materials such as amorphous silicon, microcrystalline silicon, cadmium telluride, copper-indium-gallium-diselenide, gallium arsenide (and related compounds), dye-sensitized titanium oxide, nanocomposite materials and organic molecules and polymers. The U.S. Department of Energy has set a goal of attaining levelized electricity costs of 6 to 8 cents/kWh for commercial PV systems as part of the Solar America Initiative, and this will require not only a reduction in the cost of the PV modules, but also in the cost of inverters, support structures, wiring and installation. Continued improvements in solar cell conversion efficiency will help to reduce costs. While the efficiency of crystalline silicon PV modules is generally in the range of 12 to 15% today, the module conversion efficiency should increase to about 17 to 20% by 2015. In the laboratory efficiencies as high as 24.7% have been demonstrated for single crystal silicon solar cells. The efficiencies associated with other PV technologies also continues to improve, and thin film copper-indium-gallium-diselenide solar cells have been fabricated with conversion efficiencies as high as 19.5% in the laboratory. Efficiencies as high as 40.7% have been demonstrated for a triple-junction cell operating under concentrated sunlight. There are also a number of new potentially disruptive PV technologies that could lead to significantly higher efficiencies in the next few decades, and new types of solar cells may be developed using novel multijunction structures, intermediate-band semiconductors, multiple-carrier generation, collection of hot carriers, etc. that could lead to conversion efficiencies in excess of 50%. If the growth rate of the last several years continues, then PV module prices could fall below $1 per Watt by 2030, and PV could be supply about 10% of the world's electricity in the 2030-2035 timeframe.

8:40am **IPF-TuM3 Constraining Carbon to Confront Climate Change**, ***R. Bierbaum***, University of Michigan **INVITED**

Article 2 of the Framework Convention on Climate Change calls for stabilizing concentrations of greenhouse gases in the atmosphere at levels that prevent *dangerous anthropogenic interference with the climate system* and in a time frame to *allow ecosystems to adapt naturally to climate change*. Increasingly, expert assessments are calling for limiting the global average temperature increase to 2-2.5oC above pre-industrial levels and atmospheric concentrations below 550 ppm CO2-equivalent to meet these goals. Given that the earth is already committed to 1.4oC today and emissions are growing rapidly, domestic and international policy responses must be immediate, significant and sustained. The size of this task and the potential roles of various technologies and policies to achieve these goals will be described. A roadmap to confront climate change will need to include the following elements: accelerating the implementation of win-win solutions; developing a new global framework for mitigation; identifying strategies to adapt to ongoing and future changes in climate; creating and rebuilding cities to be climate resilient; increasing investments and cooperation in energy technology innovation; and forging partnerships across governments, corporations, the financial community and private organizations.

9:20am **IPF-TuM5 Offshore Sustainable Electricity Supply Systems: The POSEIDON Vision*, D. de Jager***, Econcern B.V., The Netherlands **INVITED**

Seas and oceans cover over 70% of the earth's surface. They already play a crucial role in the global energy supply: a considerable part of our oil and natural gas is extracted off shore, and will be in the future. But at sea, also large potentials of renewable energy sources can be harvested, like wind, wave, tidal and osmotic energy. By offering space, abundant energy resources, and the opportunity for geological sequestration of carbon dioxide, the seas offer a huge opportunity to meet the world's growing energy demand in a sustainable way. The POSEIDON vision is a seaway to harvest these energy resources and to create a sustainable electricity supply system. The heart of the concept is the construction of an off shore electricity transmission grid. This grid connects major onshore demand regions with each other, and with off shore fossil and renewable electricity production and storage technologies. In combination with geological sequestration of carbon dioxide (including enhanced oil or gas recovery), a carbon free electricity supply could be attained. The POSEIDON vision emphasizes the importance of an integrated system approach. Production, conversion and transformation, transmission and distribution, storage and final energy demand are not separate elements, but must be considered from a system perspective. Also changes over time should be taken into account. POSEDION builds on current infrastructure, ensures access to sources, balances load and demand, and enables the incorporation of new emerging off shore technologies. By combining these technologies and marine resources, the seas offer the opportunities to build a truly sustainable energy system: cheap, reliable and sustainable. POSEIDON is an initiative of Econcern, the sustainable energy solution provider. Europe is seen as an excellent region to prove the concept. The North Sea region will be discussed as an example, as well as the key technologies that are expected to form the basis of this concept: off shore wind and wave energy, high-voltage electricity transmission technologies, and zero emission power plants. Developing POSEIDON-like systems asks for venturous project developers and other companies, inventive policy and decision makers, and creative researchers. They all can contribute to building this new, truly sustainable perspective.

10:40am **IPF-TuM9 Science & Technology Barriers to Economic Ethanol Biorefineries**, ***M. Himmel***, NREL **INVITED**

Lignocellulosic biomass has long been recognized as a potential low-cost source of mixed sugars for fermentation to fuel ethanol. Several technologies have been developed over the past 80 years that allow this conversion process to occur, often in wartime context, yet the clear objective now is to make this process cost competitive in today's markets. Replacing 30% of U.S. 2004 finished motor gasoline demand (or about 60 billion gallons) with ethanol by 2030 will require a significant increase in ethanol production over today's corn starch-based industry. This process is technically feasible for corn stover and wheat straw today using biochemical conversion technology that includes pretreatment, enzymatic hydrolysis, and fermentation. However, the process remains fundamentally inefficient and is therefore risky to commercialize. Cellulosic ethanol production via biochemical conversion can provide fuel at prices commensurate with historical gasoline prices (<$1.00/gallon) only by taking full advantage of critical scientific breakthroughs in feedstock production and biomass conversion science. Indeed, in order to ensure a successful transition from existing to 2030 technologies, investing in knowledge-based solutions to critical barriers is essential.

11:20am **IPF-TuM11 Carbon Sequestration to Mitigate Climate Change - A Geological Perspective*, R.C. Burruss***, US Geological Survey **INVITED**

The fraction of global carbon emissions that must be eliminated to impact climate change is huge, about 70% of present emissions over many years (100's to 1000's of gigatonnes of CO_2) to stabilize atmospheric CO_2 at about 500 ppm. Such reductions require all means of carbon management, including geological and biological sequestration; shift from fossil fuel to renewable biomass; electricity from solar, wind, and nuclear power; and improved efficiency of generation and use. The IPCC Special Report on Carbon Capture and Storage (2005) estimates that storage of CO_2 in geological formations (geological sequestration) could eliminate about 50% of emissions. The potential role of enhanced carbon storage in biomass and soils (biological sequestration) is difficult to evaluate due to the complex dynamics of greenhouse gases in the global biosphere. Geological sequestration involves injection of supercritical CO_2 into porous and permeable rock formations at depths of 1 to 3 km beneath low permeability seals. Storage formations include oil and gas reservoirs, saline aquifers, coal beds, and organic-rich shale. Over 30 years of experience with CO_2 injection in oil fields for enhanced oil recovery demonstrate that injection and storage of CO_2 is possible with existing technology. Geological sequestration projects currently deployed in Norway, Canada, and Algeria, collectively store 3 megatonnes (MT) CO_2/year. For perspective, a 1000 MW coal-fired power plant emits about 4 MT CO_2/yr and the largest CO_2 separation plant captures 4 MT CO_2/yr. Clearly, CO_2 capture and storage to eliminate a significant fraction of atmospheric emissions will require deployment of new energy systems at an enormous scale. Although the basic principles of geological sequestration are well known and reservoir engineering for CO_2 injection is understood, significant research remains. A particular concern is identification of storage sites with adequate capacity for commercial projects (CO_2 storage from a 1000 MW power plant for 50 years requires a volume equivalent to a 2-3 billion barrel oil field). Other concerns include detailed knowledge of the integrity of sealing formations, and the rates of reaction of CO_2 with dissolved components in formation water, host rocks, and organic matter. This information is needed to assess the permanence of CO_2 storage and the potential environmental impacts of leakage.

MEMS and NEMS

Room: 615 - Session MN-TuM

Integration and Packaging in MEMS/NEMS

Moderator: E. Gousev, Qualcomm MEMS Technologies

8:00am **MN-TuM1 Wafer Level Integration of Ultrananocrystalline Diamond (UNCD) Film with CMOS Devices for Monolithically Integrated Diamond MEMS/NEMS-CMOS Systems**, ***A.V. Sumant***, *O. Auciello,* Argonne National Lab, *H.C. Yuan, Z. Ma,* Univ. of Wisconsin-Madison, *B. Kabius,* Argonne National Lab, *V. Adiga, R.W. Carpick,* Univ. of Pennsylvania, *D.C. Mancini*, Argonne National Lab

Most devices for MEMS are currently based on silicon because of the available surface micromachining technology. The average mechanical and tribological properties of Si, however, are not suitable for many high-performance devices for current MEMS and future NEMS, such as resonators and switches which involve mechanical motion and intermittent contact. Other materials, such as SiC and AlN, have shown some promises due to better mechanical, chemical, and tribological properties compared to silicon. SiC thin films are grown at temperatures above 600°C and therefore incompatible with the CMOS thermal budget. Ultrananocrystalline diamond (UNCD), a novel material developed in thin film form at Argonne, exhibits exceptional mechanical, electrical, chemical, and tribological properties that make it excellent for high-performance MEMS/NEMS. Most importantly, UNCD is the only diamond film that can be grown at 400 °C, and retain properties comparable to that of single crystal diamond. In order to exploit excellent properties of UNCD to develop next generation of devices for MEMS and NEMS, however, such devices have to be integrated with CMOS at the wafer level, which will require a materials integration strategy and detailed understanding of degradation mechanism of CMOS upon integration. This paper discusses integration of UNCD with CMOS devices at wafer level (200 mm), which will open new avenues for building CMOS-driven devices for MEMS/NEMS based on UNCD. UNCD films were grown successfully on individual Si-based CMOS chips and on 200 mm CMOS wafers at 400 °C in a plasma-deposition system using microwave-plasma-enhanced chemical vapor deposition with Ar-rich/CH4 gas mixture. The CMOS devices were characterized before and after UNCD deposition. All devices were performing to specifications with acceptable degradation after UNCD deposition and processing. A threshold voltage degradation in the range of 0.08-0.44V and transconductance degradation in the range of 1.5-17% were observed. We also report the on cross-section TEM and RBS studies of the UNCD/CMOS interface and discuss the possible mechanisms responsible for the degradation of CMOS performance.

This work was supported by DARPA under contract MIPR06-W238 and US Department of Energy, BES-Materials Sciences, under contract DE-AC02-06CH11357.

8:20am **MN-TuM2 Optical Excitation of Higher Flexural and Torsional Modes of Nanoelectromechanical Oscillators**, ***B. Ilic,*** Cornell University, *S. Krylov,* Tel Aviv University, Israel, *M. Kondratovich, H.G. Craighead*, Cornell University

Excitation of biologically functional micro and nanomechanical structures using optical fields is a recently emerging arena of research that couples the fields of optics, fluidics, electronics and mechanics with potential of generating novel chemical and biological sensors. We present experimental and theoretical elucidation of optical excitation of higher order flexural and torsional modes in resonant nanoelectromechanical systems (NEMS). The modulated optical fields were coupled directly into the NEMS device layer causing amplified mechanical vibrations. Dynamic detection of vibrational characteristics of nanomechanical resonators, fabricated from low-stress silicon nitride and mono-crystalline silicon thin film layers, was accomplished using optical interferrometry. As a model system, 200nm and 250nm thick single crystal silicon cantilevers with dissimilar lengths and widths ranging from 6 to 12µm and 500nm to 1µm, respectively, were fabricated using surface micromachining techniques. We have analyzed the actuation mechanism using finite element modeling, and we found that the dominant actuation mechanism in close proximity of the clamped end was primarily thermal. In contrast, mechanical traveling waves are attributed as possible excitation mechanisms in the far-field regime. Higher order modes of slender cantilevers, calculated using linear Euler-Bernoulli beam model, differed significantly from the measured values. Three dimensional finite element analysis incorporating shear, rotational inertia, deplanation and non-ideal boundary conditions due to the structural undercut, are shown to adequately describe the dynamics of the nanomechanical structures. The quality factor of a particular in-plane harmonic was consistently higher than the transverse mode. The increased dissipation of the out of plane mode was attributed to material and acoustic loss mechanisms.

8:40am **MN-TuM3 Ultrasensitive, Magnet-tipped Cantilevers for Magnetic Resonance Force Microscopy**, ***S.A. Hickman***, *S.R. Garner,* Cornell University, *L.E. Harrell,* United States Military Academy, *B.I. Penkov, S. Kuehn, J.A. Marohn*, Cornell University

Magnetic resonance force microscopy (MRFM) is a technique that may one day allow us to acquire magnetic resonance images of a single molecule - an extremely exciting prospect. To date we have demonstrated a sensitivity of ~10^5 proton spins. Achieving the attonewton force sensitivity necessary to image single proton spins requires custom-fabricating cantilevers with extreme aspect ratios and mitigating sample-induced dissipation. In MRFM the force exerted on the cantilever, per spin, is proportional to the field gradient from the cantilever's magnetic tip. Achieving single proton sensitivity therefore also requires dramatically reducing magnet size. Unfortunately, all MRFM tips produced to date have been made by manually affixing magnets one-at-a-time to a cantilever. Even if the tips are ion-beam milled, it is difficult to see how they can be made small enough to detect a single proton. We have developed an electron-beam-lithography process for batch fabricating nanoscale tip magnets overhanging the leading edge of ultrasensitive silicon cantilevers. As proof of concept, we will present a 50-nm wide overhanging cobalt magnet fabricated by a process involving electron beam lithography and anisotropic KOH etching, as well as cantilevers with 50-600 nm wide, non-overhanging magnets. Our current goal is to integrate the separate processes of cantilever fabrication and magnet fabrication. With our designed cantilever, we expect a sensitivity of better than 10^3 protons. Even through the process integration challenges are daunting, our successes so far indicate that batch fabricating cantilevers capable of detecting single proton magnetic resonance may indeed be feasible.

9:00am **MN-TuM4 Fabrication of Reliable Through-Silicon via (TSV) Interconnects for 3D Stacking**, ***I.U. Abhulimen***, *A. Kamto, Y. Liu, S. Burkett, L. Schaper*, University of Arkansas

The formation of through-silicon vias (TSVs) provides vertical interconnects that can be used in 3D stacking technology. A sloped via sidewall is essential for conformal coverage in subsequent deposition steps that provide insulation (SiO_2), barrier (TaN) and metal seed (Cu) layers. In this paper, varying via sidewall angles (82^o - 90^o) are investigated which allow variable degrees of conformal lining of the insulation, barrier and seed layers. The critical thickness of these lining layers that enable conformal coverage of the via sidewall is also investigated. Via insulation is deposited by plasma enhanced chemical vapor deposition (PECVD), while barrier and Cu metal seed layers are deposited by sputtering. A modified Bosch process using a deep reactive ion etch (DRIE) time multiplexing tool is used to create the different via profiles on 125 mm diameter silicon wafers. The cross-sectional view of via lining materials (SiO_2, TaN, and Cu) are examined with both an optical microscope and an environmental scanning electron microscope (ESEM). The via profile is examined using the ESEM. Furthermore, for a fixed via sidewall angle, variable aspect ratios are examined to determine the via profile that can be conformally lined and filled by Cu electroplating without any voids. The aspect ratios of the vias under study are 3, 4, 5, 6, and 8. Electrical performance and via integrity of the TSV process is also reported. Test structures are created during TSV processing that allow for a thorough study of interconnect reliability. This includes tests for via chain continuity, single via resistance, and via isolation.

9:20am **MN-TuM5 Micro and Nano Electro-Mechanical Systems: Technology for Engineering Metamorphosis**, ***A. Lal***, DARPA **INVITED**

The core of MEMS technology is the capability to form chip-integrated micro beams, cantilevers, and plates. DARPA has mined MEMS technology since the early 1990s in an effort to provide increased performance and functionality to integrated circuits. MEMS allows one to use reduced mass for increased resonance frequencies in micro-resonators; craft long and thin high aspect ratio structures for high thermal resistances; and generate huge surface-to-volume ratios for increased interaction with the environment. MEMS technology changes systems so rapidly that there is less of an evolution, and more of a metamorphosis; gradual growth is replaced by complete transformation. This is especially true in the last decade of MEMS, where integration over multiple MEMS devices is finally making the Systems part of MEMS closer to reality. This talk will describe scaling issues in realizing MEMS systems with a particular emphasis on micropackaging, new materials, and design principles on reliability of MEMS and NEMS subcomponents. The successful realization of the chip-scale atomic clock, which is a multiphysics microsystem, will be described in the context of MEMS thermal isolation.

10:40am **MN-TuM9 Self-Packaged Micro Fluorescence Detection Systems**, ***S.S. Kim***, *E. Saeedi,* University of Washington, *D.R. Meldrum,* Arizona State University, *B.A. Parviz*, University of Washington

We present a self-packaging micro-fluorescence biosensor chip which assembles fully functional separately fabricated micro-components onto a common substrate. The essential components of the fluorescence based sensor are: 1) an excitation light source, and 2) a means to detect fluorescence emission. AlGaAs LEDs and silicon pn-junction photosensors are self-assembled onto a glass template to meet these requirements. The micro-components range in size from 100 to 300 microns and were specifically designed to optimize and aid in the self-assembly process. The powder-like collection of micro-components are suspended in a liquid and flowed onto a glass substrate. They self-assemble into their receptor site locations through gravity, shape recognition, and capillary forces, resulting in an array of individually addressable fluorescence detection units. Self-assembly provides a number key advantages over traditional packaging and fabrication approaches. First and foremost, it allows us to integrate micron-scale heterogeneous materials together onto a common substrate. This gives us a unique ability to have all the essential components of a fluorescence detection system on chip, without the need for an external scanner device or benchtop system. Second, the self-assembly process is parallel in nature and benefits from economies of scale. Large arrays of devices can be packaged at the same time. We have demonstrated the packaging of a 10K element array onto a plastic substrate. Thousands of individually addressable fluorescence detection units are possible allowing for data acquisition of a large number of samples simultaneously without being limited by the field of view of the optics. Third, self-assembly gives us the ability to use low cost substrates such as glass and plastics. Only small amounts of semiconductor materials are used where they are needed, reducing the total amount used for each device. This has the potential to drive down the overall cost per device low enough to make them disposable, opening new doors to biosensing applicaitons which require a fluorescence detection platform which is both portable and disposable. Potential applications include point-of-care diagnostics, bioterrorism, food/industrial testing, HIV/STD testing in developing countries, and so on. The benefits of mature fluorescence based assays could be realized on a portable and disposable chip-level platform using this approach to device packaging.

11:00am **MN-TuM10 Bi-Directional Transport of Ultra-Low Volume Droplets Using Capacitive Sensing**, ***P. Dykstra***, *X.Z. Fan, M. Mischiati, L.A. Mosher, N.P. Siwak, R. Ghodssi*, University of Maryland

MEMS cantilever sensors are utilized to detect trace quantities of specific agents in liquid. One of the most common methods to deliver the fluid is by flooding the cantilever's surroundings, but this often leads to stiction-related failures due to surface tension. We present a bi-directional microfluidic device for analyte delivery to MEMS sensors. Our device can deliver a picoliter-sized droplet to the cantilever sensor and then retract the droplet without wetting the entire sensor, thus eliminating this problem. The most commonly used drop-on-demand technology through a nozzle, exploited for inkjet printing and for the selective deposition of polymers, is based on the release of an entire droplet over the target. Our design proposes to eject only enough to reach the target area, without breaking the droplet from the bulk of the liquid. This allows the droplet to be retracted by reversing the flow, thus achieving bi-directional transport of ultra low volumes of liquid. Droplet control is facilitated by position-sensing from a capacitive sensor. As the droplet lowers, a change in capacitance is measured by a sensor electrode located below the nozzle. Our microfluidic system, consisting of packaging, micronozzle, and microsensor wafers, was fabricated using conventional MEMS techniques. The through-etched micronozzle was diced and aligned to the microsensor wafer using peg-in-hole (SU-8 pegs in etched silicon holes) assembly. This precisely aligns the nozzle over a gold electrode on the sensor wafer. Capacitance is measured between the nozzle die itself and the gold electrode using an Agilent CV meter. The liquid is administered using a syringe pump at a constant flow rate. Our initial results show that the capacitance slowly rises as the droplet is formed. A significant change in capacitance occurs when the droplet makes contact with the microsensor. A complete analysis of droplet formation measurements, by way of capacitive sensing, will be presented. Transport will be characterized to enable the integration of our device with any MEMS sensor.

11:20am **MN-TuM11 Microfluidic Transport Control Using Remotely Powered Semiconductor Diodes**, ***D.N. Petsev,*** University of New Mexico, *S.T. Chang, O.D. Velev,* North Carolina State University, *V.N. Paunov*, University of Hull, UK

The precise control of fluid transport in microchannels is of paramount importance for the successful design and operation of fluidic devices. We have recently demonstrated[1] that using miniature diodes embedded in the walls of fluidic microchannels in combination with AC field is a very simple and convenient tool to manipulate the flows in microchannels. Our focus is on two particular problems briefly described below Mixing. Due to the low Reynolds number of microflows, mixing of components is a real challenge. Due to the laminar character of the flow different solution tend to flow side by side and the only way for solutes to cross the streamlines is by diffusion. Using properly (anti-parallel) oriented diodes, placed alongside the channel walls, allows generating a vortex fluid motion by simply turning on a properly connected Alternate Current (AC) field source. Such vortex dramatically improves the mixing in the microfluidic device. Another advantage of this approach is that such diode mixer can easily be turned on and off through the AC field power source. Separation. Using parallel oriented diodes and a combination of AC and Direct Current (DC) fields in a loop-shaped channel allows complete decoupling of the fluid electroosmosis from the analyte electrophoresis. Balancing the electrophoretic and convective forces on the different analytes allows for a very easy and efficient separation. The parallel oriented pair of diodes, powered by the applied AC field, acts as a miniature pump and drives the fluid in a circulatory motion in the loop shaped channel. Any charged analytes, however, will not migrate in the AC field. Applying DC field to the fluidic device will not drive the fluid motion because this particular design (closed symmetric loop) cancels the electroosmotic driving force. Hence, combining the two fields (AC and DC) allows decoupling of the fluid flow from the particle electrophoretic migration.

[1] S. T. Chang, V. N. Paunov, D. N. Petsev and O. D. Velev, "Self-Propelling Microdevices and Microfluidic Pumps Based on Remoutely Powered Miniature Semiconductor Diodes, Nature Materials, 6 (2007) p. 235.

11:40am **MN-TuM12 Towards Feedback Control with Integrated Position Sensing in Micromachines**, ***M.I. Beyaz***, *N. Ghalichechian, A. Modafe, R. Ghodssi*, University of Maryland

Micromachines require closed loop systems to facilitate synchronization and yield maximum performance. However, little effort has been spent on implementing feedback control in these devices. We present for the first time the design, fabrication and testing of an integrated feedback control system for a synchronous electrostatic micromotor. This system aims to synchronize the mechanical motion and the electrical excitation to improve stability and performance. The micromotor is composed of a stator and a movable slider supported on microball bearings. Interdigitated photodiodes are located on the stator to detect the position of the slider moving relative to the stator electrodes. Through holes, created by deep reactive ion etching, are aligned with the poles on the slider. This allows light, provided from the top, to reach the photodiodes on the stator. The design is such that the optical sensing of slider position is achieved by simultaneous alignment of pole-electrode and hole-photodiode pairs, causing an increase in photodiode current. The change in current is sensed and the appropriate voltages are applied to stator electrodes by a feedback circuit. The designed photodiodes have been implemented on n-type 20 Ω-cm silicon wafers. The fabrication consists of etching the native oxide on the wafer, aluminum sputtering and wet etching. Prior to the integration of the photodiodes with the micromotor, a test setup was built to verify the feasibility of the feedback system. In this setup the stator, on which only the photodiodes are fabricated, is fixed to an oscillating platform driven sinusoidally at 5 Hz at an amplitude of 1.6 mm. The slider is kept stationary and a light source is provided from the top. Resulting photodiode current depends on how much light it receives through the holes. The motion of the stator is monitored by the photodiode response that is in the form of a triangular wave. Each peak on the waveform corresponds to a complete alignment between the photodiode and a hole on the slider. Using this peak detection, the instantaneous platform speed is calculated showing good agreement with the applied sinusoidal motion with an R^2 value of 0.925. This work verifies the feasibility of the feedback system for the given micromotor to achieve higher speeds and to stand varying load conditions. Detailed fabrication steps and experimental results of the micromotor with the control system will be presented.

12:00pm **MN-TuM13 An Adaptive Feedback Control Circuit for Resonator Sensors**, ***X.Z. Fan***, *N.P. Siwak, R. Ghodssi*, University of Maryland

Integration of smart electronics with MEMS sensors will enable systems to be versatile, compact, and portable. MEMS resonator sensors are powerful tools for the detection of target analytes due to the high sensitivity of resonant frequency to absorbed mass. We present an adaptive feedback control circuit to detect and trace the resonant frequency of MEMS resonator sensors. The purpose of our feedback circuit is its integration with a fully developed III-V optical resonator system for chemical and biological sensors, facilitating testing and data acquisition. Feedback circuits with similar functions, such as self-excitation systems, have been reported before in literature. These systems, however, require phase and amplitude compensation stages that require separate designs for each resonator measured. Our feedback circuit utilizes a hill climbing algorithm which is valid for any resonator sensor that exhibits any range of resonant frequency, thus broadening the applicability of the circuit. The hill climbing algorithm sweeps the driving frequency searching for maximum cantilever response. The algorithm is implemented using a four-stage CMOS circuit consisting of an amplitude detector, a differentiator, a digital logic circuit, and a voltage controlled oscillator (VCO). The feedback circuit receives the displacement output of the resonator and supplies the actuation signal to the resonator from the VCO output. Utilizing the hill climbing algorithm, the resonator is driven at its resonant frequency. By monitoring the VCO input voltage, the resonant frequency with respect to time can be measured. We have confirmed the adaptability of the design of the circuit with initial testing results. The results have demonstrated that the maximum amplitude of an input signal can be detected with input frequencies ranging from 100 KHz to 500 KHz. This range is only limited by the frequency response of the CMOS components. A delay of 3 ms was observed between the input and output signal of the circuit, which is acceptable due to a significantly larger sensor time constant. We will present the test results of the combined circuit with indium phosphide MEMS cantilever sensors. The flexibility of the circuit and its improved capabilities over conventional measurement circuits will be demonstrated.

Nanometer-scale Science and Technology

Room: 616 - Session NS-TuM

Imaging of Nanostructures

Moderator: N.P. Economou, Carl Zeiss SMT, S. Hasegawa, University of Tokyo, Japan

8:00am **NS-TuM1 Atomic-Scale Studies of Complex Oxide Interfaces Using Aberration-Corrected Z-Contrast Imaging and EELS**, ***R.F. Klie***, *G. Yang*, University of Illinois - Chicago **INVITED**

Interfaces in complex oxide materials have been an enduring theme in materials physics, where the interplay of the reduced dimensionality, proximity effects, as well as surface relaxation, reconstruction and segregation creates interfacial states that are distinct from their bulk counterparts. It has long been recognized that the perovskite oxides provide a unique opportunity to bring materials with diverse and even mutually exclusive properties into intimate contact, thereby creating interfaces with excellent structural and chemical compatibility that potentially can be implemented in novel electronic devices. In recent years, novel techniques have been developed in analytical scanning transmission electron microscopy (STEM) that can be used to directly study the atomic-scale structure-property relationships of interfaces in complex oxides, both at room and LN_2 temperature. In particular, by using aberration-corrected Z-contrast imaging and electron energy-loss spectroscopy (EELS), the structure, composition and bonding can all be characterized directly with a spatial and energy resolution that cannot be achieved by any other technique. Here, we will demonstrate that the combination of aberration-corrected Z-contrast imaging and EELS can be used to analyze a wide range of properties in complex oxide materials, such as CMRs, high-k dielectrics and high-temperature superconductors. In particular, I will concentrate on my recent discovery of the cooperative doping-effect in the high-T_c superconductor $YBa_2Cu_3O_{7-x}$ (YBCO), where the presence of grain boundaries causes a significant reduction in the critical current density (J_c). I will explain the atomic-level origin of the improved J_c across grain boundaries in Ca-doping YBCO, and propose a number of potential dopants to further improve the materials properties.[1] Further, I will discuss the effects of oxygen vacancy segregation on the dielectric property of ultra-thin $SrTiO_3$ on GaAs(001)[2] and conclude with our recent discovery that the Co-ion spin-state in Co-based perovskite oxides can be directly measured by EELS.

[1] Klie, R.F., J.P. Buban, M. Varela, A. Franceschetti, C. Jooss, Y. Zhu, N.D. Browning, S.T. Pantelides, and S.J. Pennycook, Nature, 2005. 435(7041): p. 475-478.

[2] Klie, R.F., Y. Zhu, E.I. Altman, and Y. Liang, Applied Physics Letters, 2005. 87(14).

8:40am **NS-TuM3 In-situ Observation of Active Electronic Devices using Electrically Biased TEM Holder**, ***D.S. Ko***, *S.D. Kim*, Seoul National University, Republic of Korea, *X.S. Li, K.S. Park, Y.K. Kim,* Samsung Advanced Institute of Technology, Republic of Korea, *C.G. Park,* National Center for Nanomaterials and Technology, Republic of Korea, *Y.W. Kim*, Seoul National University, Republic of Korea

In-situ transmission electron microscopy (TEM) became one of the major fields in physics and materials science as the advanced technologies were adopted to observe real-time changes of microstructures in a confined space of TEM.[1,2,3] We developed an in-situ TEM holder to investigate the live operation of electronic devices and we present step-by-step manufacturing procedures of nano-manipulator-electrical signal holder applied to investigate the transport of matters in Light Emitting Diode (LED) and Phase-changing Random Access Memory (PRAM). The TEM sample of active electron device was prepared by focused ion beam followed by plasma etching as reported earlier[4] to remove the Ga-contamination at the surface. The removal of surface layer with Ga was essential to remove a leakage path of current. As-FIB-prepared LED sample showed illumination only after the plasma etching process. In order to make electrical contact to the samples of electronically active device, tungsten tip was fabricated using electro-chemical polishing technique in 10% NaOH. The tip fabricated was small enough to locate the contact pad with 30-40 nm in apex diameter. The apex radius of commercially available tungsten tip was too big for probing to make electrical contact to the target device. Tungsten probe was mounted on the 4-mm diameter, quadrant piezo tube, which was linked to micrometer for the coarse movement. In-situ observation of intermixing and materials transport in commercially available GaN LED and phase-changing of calcogenide material in PRAM device, is investigated and the recorded.

[1] C.M. Grimaud and O. Lourie, In Situ Electrical Probing by TEM-STM: instrumentation and applications for nanocharacterization, Microsc. Microanal. 10(suppl 2), 1112 (2004)

[2] T. Kizuka et al, Metal-Insulator Transition in Stable One-Dimensional Arrangements of Single gold Atoms, Jpn. J. Appl. Phys. 40 L170 (2001)

[3] D. Golberg, et al, In situ electrical probing and bias-mediated manipulation of dielectric nanotubes in a high-resolution transmission electron microscope, Appl. Phys. Lett. 88 123101 (2006)

[4] D.S. Ko, et al, Effective removal of Ga residue from focused ion beam using a plasma cleaner, Ultramicroscopy 107, 368 (2007).

9:00am **NS-TuM4 Measuring Atomic Size Objects on Electrically Insulating Surfaces in Ultrahigh Vacuum**, ***S.C. Fain***, *N. Ruzycki, J. Morales, T.C. Lovejoy, E.N. Yitamben, M.A. Olmstead, F.S. Ohuchi*, University of Washington

Frequency modulation non-contact atomic force microscopy (ncAFM) provides a way to measure atomic size objects on electrically insulating surfaces in ultrahigh vacuum. Computer simulations indicate that the apparent height of clusters one atomic layer high is much less than the actual height when the lateral extent of the cluster is much less than the tip radius.[1] For example the apparent height of a 1.4 nm diameter, one-atomic-layer-high cluster of 19 atoms on a flat surface is expected to be 12% of its actual height when imaged by a typical probe tip of 20 nm radius. The apparent height of the cluster is predicted to be much closer to the real height as the cluster height increases. We have performed measurements on semiconducting surfaces with various cluster sizes by both ncAFM and scanning tunneling microscopy (STM) using various probe tips. Evidence in qualitative agreement with the computer simulations has been obtained for clusters on a surface with Cr co-deposited with Ga_2Se_3 on Si(100):(2x1)As. We acknowledge support from NSF NER-0508216, NSF DMR-0605601, and an IGERT Traineeship to TCL from NSF and NCI grant DGE-0504573.

[1] S. C. Fain, Jr., C. A. Polwarth, S. L. Tait, C. T. Campbell, and R. H. French, Nanotechnology 17, S121-127 (2006).

9:20am **NS-TuM5 Ambient Dynamic Mode AFM Non-contact Operating Regime Determination**, ***C.C. Wang***, *B. Liu, B. Leung, Y. Uritsky*, Applied Materials Inc.

Dynamic mode AFM, which uses a cantilever vibrating near its natural mechanical frequency, is the most popular AFM imaging method in the ambient. As AFM tip approaches the sample, it enters the non-contact regime first due to attractive force interactions and, as tip continues to descend, it starts to contact surface intermittently.[1] During tip descend, the vibration amplitude continuous to decrease. Therefore, using a feedback loop that maintains a constant amplitude set-point during AFM imaging, the AFM can be operated in either non-contact mode or intermittent contact mode and the set-point of former is higher than that of the latter. Non-contact mode is desirable, because it affords higher spatial resolution and longer tip life.[2] Hence, accurate determination of the non-contact amplitude operating range is needed. A unique characteristic of phase signal of cantilever is that, in non-contact regime, phase changes monotonically with tip-to-sample distance, but as soon as tip makes intermittent contact with sample, the phase signal abrupt jumps in the other direction.[1] Therefore, non-contact regime can be determined by approaching tip to surface in open-loop condition, monitoring the amplitude and phase signals at the same time and determining the amplitude corresponding to phase reversal point. However, this popular method causes tip and sample damage and inaccurate non-contact regime determination. A new method is reported here. In this method, the tip approach is stopped at the start of non-contact interaction regime and the feedback loop is turned on; the tip descend is then resumed by lowering the amplitude set-point continuously and at the same time monitoring the phase signal; as soon as the phase signal makes a sudden discontinuous reversal, the intermittent contact mode is reached. By recording the amplitude set-point at the onset of intermittent contact, the non-contact regime can be determined more precisely. It is shown that this range depends on tip material, sample material and the cantilever initial vibration amplitude. Therefore, this method can be used to image sample surface properties and to optimize non-contact operating parameters.

[1] R. Garcia and A. S. Paulo, Phys. Rev. B 60, 4961 (1999)

[2] C. Wang et al., Proceedings: the 2005 International Conference on Characterization and Metrology for ULSI Technology, 194 (2005).

9:40am **NS-TuM6 Atomic Resolution AFM with a Purely Electrical QPlus Sensor**, ***B. Uder***, *M. Maier, A. Bettac, A. Feltz*, Omicron NanoTechnology, Germany

In contrast to conventional optical detection AFM, self-sensing or purely electrical detection schemes have not yet been established as reliable and routine techniques for atomic resolution under UHV conditions. The QPlus sensor however, has successfully been used for LT STM with 5 K operation and is now intruduced for variable temperature operation with the VT STM. The QPlus sensor employs a quartz tuning fork for force detection in non-contact AFM operation mode. One prong of the tuning fork is fixed while the SPM probe tip is mounted to the second prong. It thus acts as a quartz lever transforming it's oscillation into an electrical signal as a result of the piezo-electric effect. The feedback signal is based on frequency shift originating from tip-sample force interaction. A dedicated pre-amplification technique ensures distance control based on the vibrational signal. The main motivation for the QPlus sensor is to improve AFM resolution for short range forces by the high spring constant of the sensor (approx. 1800 N/m, cantilever typ. a few ten N/m) and small oscillation amplitudes in the range of 1nm or below (cantilever typ. 10 nm), which more precisely match the range of the involved (chemical) forces. Optimal image performance was achieved using conventionally wet-chemically etched tungsten tips, glued onto the tuning fork. This allows for highest performance in simultaneous or alternative STM/STS operation. Measurements on Si(111) 7x7 show that tunnelling current and vibrational signal are clearly separated. In addition, benchmark measurements on NaCl with a typical corrugation of approx. 10pm prove that resolution on insulation samples is competitive to best cantilever based AFM results.

10:40am **NS-TuM9 Imaging Performance Variations in Organic Solar Cells with Time-Resolved Electrostatic Force Microscopy and Photocurrent-sensitive Atomic Force Microscopy**, ***D.S. Ginger***, University of Washington **INVITED**

We study organic/organic and organic/inorganic interfaces in polymer solar cells using time-resolved Electrostatic Force Microscopy (trEFM), and photoconductive Atomic Force Microscopy (pcAFM). These techniques allow us to measure charge generation, collection, and trapping with sub-100 nm resolution so we can correlate variations in performance directly with variations in local film morphology. This talk will describe our trEFM and pcAFM studies of polymer/polymer and polymer/fullerene solar cells. In model blends of polyfluorenes we present surprising evidence that the majority of the collected photocurrent arises away from the visible domain interfaces. In polymer/fullerene cells we show that even the best devices exhibit a distribution of local quantum efficiencies and fill factors that vary on two characteristic length scales. First, we observe performance variations over tens of nanometers that we associate with vertical connectivity of the fullerene domains. Second, in these same devices we observe performance variations over several hundred nanometer length scales (much larger than the characteristic polymer or fullerene domain sizes). We explore the possibility that these larger-scale performance variations are associated with the interface between the polymer blend and the underlying indium tin oxide contact.

11:20am **NS-TuM11 Investigation of Charge Trapping in GaN Films using Scanning Kelvin Probe Microscopy and Conductive Atomic Force Microscopy**, *J.C. Moore, M.A. Reshchikov, J. Xie, H. Morkoc,* ***A.A. Baski***, Virginia Commonwealth University

A new combination of conducting atomic force microscopy (CAFM) and scanning Kelvin probe microscopy (SKPM) was used to study localized charge trapping for MBE-grown GaN films. Charge was injected into the near-surface region of a GaN film by scanning local regions using CAFM with a reverse bias applied to the sample. Time-resolved local surface potential measurements were then obtained using SKPM after charge injection, where an induced band bending caused by charging of surface/interface states was observed. In dark environments and for applied CAFM biases greater than 10 V, the density of charged states ($2x10^{12}$ cm^{-2}) doubled immediately after scanning as compared to unscanned regions. This increase in charged states resulted in an increase of surface band bending of ~3 eV that dissipated quasi-exponentially with time. Induced band bending greater than 0.5 eV was still observed up to 4 hr after charge injection, indicating that charge trapping is relatively stable in a dark environment. Initial values for band bending depend on the applied CAFM bias during injection, where nominal band bending (<0.5 eV) occurs for biases less than 8 V and a saturation value of ~3 eV occurs at biases greater than 10 V. A phenomenological model was used to model the CAFM charge injection via a tunneling mechanism, where electrons travel from the tip through a thin surface gallium oxide barrier and become trapped at the oxide/GaN interface. Saturation occurs due to the existence of a finite density of chargeable interface states. After charging occurs via CAFM, the decrease in induced band bending with time was found to be consistent with a thermionic model of charge transfer from the interface to the bulk. As expected, charged interface states could be rapidly neutralized (<1 s) via photovoltage caused by illumination with UV light. Funding provided by NSF and AFOSR.

11:40am **NS-TuM12 Sinc or Sine? The Band Excitation Method and Energy Dissipation Measurements by SPM**, ***S. Jesse***, *S.V. Kalinin*, Oak Ridge National Laboratory

Mapping energy transformation pathways and energy dissipation on the nanometer scale and understanding the role of local structure on dissipative behavior is a grand challenge for nanoscale imaging in areas ranging from electronics and information technologies to efficient energy production and use. To date, dissipation measurements are invariably based on either phase and amplitude detection in constant frequency mode, or as amplitude detection in frequency-tracking mode. Sampling of a single frequency in the Fourier domain of the system allows only two out of three parameters (amplitude, resonance, and Q) to be determined independently. The analysis in both cases implicitly assumes that amplitude is inversely proportional to the Q-factor and is not applicable when the driving force is position dependent, as is the case for virtually all SPM measurements. Here, we developed and implemented a new approach for SPM detection based on the excitation and detection of a signal having a finite amplitude over a selected region in the Fourier domain. The detected signal is Fourier transformed and fitted by appropriate model. This data acquisition scheme substitutes standard lock-in or PLL detection. This band excitation (BE) SPM allows very rapid acquisition of the full frequency response at each point in an image and in particular enables the direct measurement of energy dissipation through the determination of the Q-factor of the cantilever-sample system. This band excitation method allows acquisition of the local spectral response at a ~10ms/pixel rate, compatible with fast imaging. We demonstrate this technique with electromechanical imaging, the investigation of dissipative defects in magnetic force microscopy, and force-distance spectroscopy. The BE method thus represents a new paradigm in SPM, beyond traditional single-frequency excitation and is applicable as an extension to many existing SPM techniques. Research was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

12:00pm **NS-TuM13 Electromechanical Imaging, Polarization Switching, and Intermittent-Contact PFM in a Liquid Environment**, ***B.J. Rodriguez***, *S. Jesse, A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Electromechanical activity is a universal feature of molecular and biological systems, ranging from piezoelectricity in calcified tissues to voltage-controlled ion channels and the functionality of cardiac miocytes and cells for auditory signal transduction. Here, we study the mechanisms of electromechanical imaging by Piezoresponse Force Microscopy (PFM) in liquid environments using model ferroelectric systems. The effects of the conductive properties of the liquid on the localization of the dc electric field are studied from the polarization patterns created by the voltage pulses applied to the tip. Under ambient conditions, the biased tip establishes a highly-localized electric field that decays rapidly with distance from the tip-surface junction, resulting in small, well-defined domains. For solvents with intermediate conductivities, the electric field is localized, but the characteristic length scale is significantly larger than the tip size and is mediated by pulse length via the mobile ion diffusion length. The switching in this case results in the formation of irregular fractal domains. In conductive solvents, the solution is uniformly biased, resulting in a homogeneous electric field across the film thickness and partial or complete uniform switching. Notably, high resolution imaging is possible even in polar solvents because of the high excitation frequencies, minimization of the diffusion paths, and high localization of the strain that transmit predominantly through the mechanical (rather than electrical) contact. The same screening effect in solution enables a mechanically modulated approach for intermittent-contact PFM in solution. In air, this mode is dominated by electrostatic forces, which are screened in solution, allowing the electromechanical signal to dominate. These results elucidate a strategy for high resolution imaging of electromechanical activity in biological and molecular systems in liquid environments.

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Understanding Biointerphases and Magnetism with Neutrons Topical Conference

Room: 618 - Session NT-TuM

Applications to Biological Materials and Soft Matter

Moderator: M. Lösche, Carnegie Mellon University

8:00am **NT-TuM1 Cold and Thermal Neutrons: Suitable Probes for Biomaterials*, J. Katsaras***, National Research Council of Canada **INVITED**

Neutrons are electrically neutral, subatomic elementary particles whose existence had been postulated by Ernest Rutherford and discovered by James Chadwick in 1932. With the exception of hydrogen, neutrons are found in all atomic nuclei, and free neutrons are unstable with a mean lifetime of ~ 900 s. Thermal and cold neutrons, used for the study of materials ranging from engineering to biomedical applications, are typically produced by reactor- or accelerator-based sources and are the result of interacting with a given temperature moderator (e.g., graphite, water, liquid deuterium). Compared to thermal neutrons, cold neutrons possess 5 - 20 times longer wavelengths and are preferred for the study of biological materials with inherently large unit cells. Unlike x-rays, neutrons interact strongly with nuclei and the strength of their interactions varies dramatically and non-monotonically from element-to-element across the periodic table. This statement applies equally to isotopes of the same element and has been used to great advantage by biologists and polymer scientists who typically study materials rich in hydrogen. The classic example is the isotopic substitution of ^{1}H for ^{2}H (deuterium), where one can accentuate, or nullify, the scattering from particular parts of a macromolecular complex by selective deuteration. Recently, we have used a number of neutron scattering techniques to study for example, the location of cholesterol in polyunsaturated fatty acid membranes (discovered that cholesterol can reside in unexpected places within the membrane!) and the distribution of water in aligned, self-assembled lipopolysaccharide bilayers isolated from the Gram-negative bacterium, Pseudomonas aeruginosa. These results provide insights as to how molecules penetrate and assemble in biologically relevant membranes, and will be the topic of discussion. Web Site: http://neutron.nrc-cnrc.gc.ca/people/katsaras/index.html.

8:40am **NT-TuM3 Small Angle Neutron Scattering Studies of the Counterion Effects on the Molecular Conformation and Structure of Charged G4 PAMAM Dendrimers in Aqueous Solutions*, W.-R. Chen***, Oak Ridge National Laboratory **INVITED**

The structural properties of generation 4 (G4) poly(amidoamine) starburst dendrimers (PAMAM) with an ethylenediamine (EDA) central core in solutions have been studied by small angle neutron scattering (SANS). Upon the addition of , SANS patterns show pronounced inter-particle correlation peaks due to the strong repulsion introduced by the protonation of the amino groups of the dendrimers. By solving the Ornstein-Zernike integral equation (OZ) with hypernetted chain closure (HNC), the dendrimer-dendrimer structure factor is determined and used to fit the experimental data, where is the magnitude of the scattering wave vector Q. Quantitative information such as the effective charge per dendrimer and the radius of gyration, R_G, at different pD values is obtained. The results show that only changes by about 4 % when the pD value varies from 10.25 to 4.97, and significant counterion association/condensation occurs, strongly mediating the inter-dendrimer interaction. The influence of interplay between counterions and molecular protonation of dendrimers imposes a strong effect on the dendrimer conformation and effective interaction. Although the change of is very small, careful analyses of the high data and fitting parameters indicate a possible internal structure change of a dendrimer when the amino groups are progressively charged.

9:20am **NT-TuM5 Neutron Reflection Study of Peptides and Proteins at Interfaces*, J.R. Lu***, *X.B. Zhao, F. Pan, M. Yaseen*, University of Manchester, UK **INVITED**

Neutron reflection has been deployed to study the adsorption of short designed peptides and proteins at the solid/water interface, focusing on the determination of the structure of the interfacial layer. The effects of surface hydrophobicity, the size and stability of globular proteins and the solution environmental conditions on the structure and composition of the adsorbed protein layers are examined and key features highlighted. The advantegeous features of neutron reflection are described.

10:40am **NT-TuM9 Neutron Reflectivity and Scattering for Studying Biomolecules at Interfaces*, T. Nylander***, Lund University, Sweden **INVITED**

Neutrons are relatively more harmless to matter than X-rays and therefore they are particularly usefull to study biological material. Hydrogen scatters neutron very well and further more the scattering from hydrogen and deuterium is very different. Selective deuteration of one component and contrast matching of the aqueous solvent makes it possible to study one component at a time as the other can be made invisible. The potential of neutron scattering/reflectivity measurements will be discussed for two systems, lipid self-assembly and DNA compaction. There is an increasing demand for methods to study processes at the lipid-aqueous interface as the importance of lipids and lipid self-assembly structures as regulators for biological activity as well as for vehicles for drug delivery. Spreading of vesicles on surfaces are quite an established method to forming bilayers on hydrophilic surface, and spreading can be affected by the surface properties as well as properties that affect the stability of the vesicles. The full potential of non-lamellar liquid crystalline nano particles (LCPN) has only recently been realized, as improved methods and new lipid combinations have been introduced for producing biocompatible and structurally well-defined nano-particle dispersions of different phase structures. These include bicontinuous cubic, reverse hexagonal, and reverse cubic phases. Directly relevant for drug delivery systems is the fusion of these LCPN with a (model) membrane. Again numerous studies has been conducted on vesicle fusion, but very few on the interaction between non-lamellar LCNP and membranes. The compositional changes in the lipid bilayer will be monitored by neutron reflectivity using selective deuteration of the lipids and proper contrast matching. This has given us information on structural changes when the LCNP interacts with a surface and a bilayer. Our results show that interaction between the LCPN lipid components with the acyl chains of the bilayer, consistent with the formation of a mixed bilayer. As we observed a diffraction peak at high q after a certain time, we concluded that the interaction eventually lead to formation of multilayers on the surface. We are today fascinated of the supra-molecular structures formed by DNA packing in the cell nucleus and we are trying to understand to what extent packing regulates transcription/translation. The long-term objective of our work is to design a module for DNA packaging, where the packing and thereby the transcription can be switched on and off. This module would be a transcription competent synthetic analogue of a real cell nucleus. We are therefore study the relation between structure of the aggregate (using dynamic light scattering, small angle x-ray and neutron scattering, cryo-TEM), the degree of compaction (using fluorescence) and transcription/translation (using biochemical assays, including RNAse and luciferase production). It has been shown that DNA can be compacted by cationic lipids both in bulk and at interfaces. By using neutron scattering of DNA coated particles we have shown that the aggregate formed by CTAB when interacting with DNA is elongated and of the same structure on the surface as on the bulk.

11:20am **NT-TuM11 Roles of Carbohydrates in Fine Adjustment of Biological Interfaces*, M. Tanaka***, University of Heidelberg, Germany **INVITED**

In nature, cell-cell and cell-tissue contacts are madiated by various biopolymers based on carbohydrates. This paper describes some of our recent studies that physically model the active roles of carbohydrates in fine-adjustment of contacts at biological interfaces by specular and off-specular neutron scattering at defined relative humidity as well as in bulk water. The planar planar geometry of the biomembrane models containing oligo- and polysaccharides enable one to identify the in-plane and out-of-plane momentum transfers at various angles quantitatively, which can be used to determine the influence of carbohydrates on structural and mechanical properties of membranes.

Plasmonics Topical Conference

Room: 619 - Session PL+BI-TuM

Plasmon-mediated Sensing and Biosensing

Moderator: J.C. Owrutsky, Naval Research Laboratory

8:00am **PL+BI-TuM1 Combining Surface Plasmons, Enzyme Chemistry and Nanoparticles for Ultrasensitive Biosensing*, R.M. Corn***, *H.J. Lee, A.W. Wark*, University of California-Irvine **INVITED**

Surface bioaffinity biosensors have become invaluable biotechnological tools for the rapid, multiplexed detection of biomolecules. In the last decade, a number of surface-sensitive spectroscopic techniques based on changes in the local optical index of refraction near an interface upon adsorption have emerged as attractive alternatives to traditional fluorescence-based detection methods for surface bioaffinity biosensing. For example, we have successfully applied surface plasmon resonance imaging (SPRI) to measure the bioaffinity adsorption of DNA, RNA, antibodies, proteins and biomarkers. In this talk we will describe our recent efforts to create the next generation of ultrasensitive biosensors which use a combination of (i) surface enzyme chemistry and (ii) nanoparticle surface incorporation. For example, SPRI, DNA microarrays, nanoparticles and poly(A) RNA polymerase can be used together for ultrasensitive microRNA profiling measurements at femtomolar concentrations. In addition, we will also describe a new optical technique, nanoparticle-enhanced diffraction gratings (NEDG), that can be used to create novel ultrasensitive biosensors.

8:40am **PL+BI-TuM3 Polarization-Dependent Surface Enhanced Raman Scattering from Silver Nanoparticle Arrays**, ***W. Luo***, *P. Chu, D.L. Mills, R.M. Penner, J.C. Hemminger*, University of California, Irvine

One specially promising method to design Surface Enhanced Raman Scattering (SERS) substrates is to fabricate silver nanoparticle arrays with nanoscale gaps that can carry strong and localized surface plasmon resonances. Studies have revealed that dramatic SERS phenomena require interparticle spacings to be around 10 nm or less which is hard to achieve with current fabrication technologies. We present the straightforward fabrication of ordered spherical silver nanoparticle arrays with gaps less than 10 nm on Highly Oriented Pyrolytic Graphite (HOPG). Physical Vapor Deposition (PVD) of silver on HOPG under controlled experimental conditions results in the self-assembly of rows of silver nanoparticles. Straight rows of particles are obtained that extend over distances as large as 100 microns. Arrays of rows of particles are parallel over similar distances. Since these 2-dimentional particle arrays are organized over 100's of microns they are easily addressed in conventional optical experiments. Using thiophenol adsorbed on the silver particles as probe molecules, highly polarization-dependent enhanced Raman scattering has been observed form these particle arrays. When light is polarized along the axis of the nanoparticle arrays, the enhanced Raman spectra are much stronger than when light is polarized perpendicular to the axis of the nanoparticle arrays. Theoretical calculations of the electromagnetic response of the interacting nanoparticles to a light field will also be presented. Ongoing research with these arrays includes a number of different studies. Among these is the use of the particle arrays as a collection of "nano-electrodes". For example, electrodeposition of semiconductors on the silver nano-arrays has been accomplished with the subsequent observation of enhanced photoluminescence.

9:00am **PL+BI-TuM4 Nanoplasmonic Sensing of Surface and Bulk Modifications of Metallic Nanoparticles using Localized Surface Plasmon Resonances: Studies of Hydrogen Uptake in Supported Pd Nanoparticles and Oxidation of Al Nanoparticles**, ***I. Zorić***, *C. Langhammer, E. Larsson, B. Kasemo*, Chalmers University of Technology, Sweden

We propose a novel nanoplasmonic sensing scheme for optical, real time, monitoring of property changes in metal nanoparticles. The property changes can be both bulk and/or surface changes induced e.g. by interaction with the surrounding medium. To sense these changes we use the localized surface plasmon resonance (LSPR) of the nanoparticle as signal transducer for remote optical readout. The high sensitivity of the LSPR (i.e. plasmon energy and extinction cross-section) to electronic, structural and shape changes, taking place in the nanoparticle, makes the latter an extremely sensitive and non-invasive probe for studies of surface and bulk changes in nanoparticles. Furthermore, since the LSPR seem to be a rather universal feature for nano-confined metallic systems the proposed sensing method is quite universal. The supported metallic nanodisks were fabricated by the hole-mask colloidal lithography method relying on electrostatically self-assembled polystyrene beads as evaporation masks. The method is suitable for fabrication of large-areas covered by nanostructures allowing for easy spectroscopic studies. The proposed sensing scheme was used to study: a) metal hydride formation in nanometer sized Pd disks exposed to hydrogen atmosphere and b) oxidation of Al nanodisks. In both cases we have quantified the optical repsonse by complementing the optical studies with gravimetric studies (QCM-D). In the latter case the same processes were studied by monitoring the frequency and dissipation shifts when Pd or Al nanoparticles, prepared on the of the quartz crystal microbalance electrode, were exposed to the hydrogen and oxidizing environment respectively. In addition, AFM and SEM studies were used to characterize the morphological changes induced during the process of interest. Te most important results include: a) hydrogen pressure-composition isotherms covering the solid solution (α) phase, the coexistence region of the α and hydride (β) phases, and finally the pure hydride phase at large hydrogen pressure. Similarities and differences to the corresponding isotherms for 2D continuous Pt films are also presented. b) Al nanoparticle oxidation kinetics in water shows an initially fast oxide growth followed by a transport limited slower kinetics accompanied by oxide shell cracking. We also show how extension of this sensing approach from nanoparticles to thin films can be made by using LSPR of the 100nm diameter holes made in continuous films.

9:20am **PL+BI-TuM5 Surface Modification of Metallic Nanoparticles for Plasmonics Applications: Potential, Challenges and Advances in the Field**, ***V.H. Perez-Luna***, Illinois Institute of Technology **INVITED**

Nanoparticles of noble metals such as gold and silver exhibit size and shape dependent optical properties that are sensitive to changes in the dielectric environment and degree of aggregation. These properties arise from collective oscillations of plasmons excited by incident light. For metals such as gold and silver resonant excitation of particle plasmons can be tuned to occur in a wide region of the visible and near infrared spectrum by proper manipulation of size and morphology. In addition to their interesting optical properties, excitation of particle plasmons by light give rise to enhanced electric fields in the vicinity of nanoparticles. The enhanced electric fields hold enormous potential for biosensing applications using Surface Enhanced Raman Scattering and Surface Enhanced Emission of Fluorescence. Despite this potential, some applications remain largely unexploited due to inherent morphological instability of anisotropic metallic nanoparticles, irreversible aggregation, and difficult surface modification when templating surfactants such as hexadecyltrimethyl ammonium bromide are used to synthesize anisotropic nanoparticles. Surface modification can overcome these obstacles but has not received sufficient attention. This presentation will focus on understanding displacement reactions at the surface of nanorods and model crystalline gold surfaces; the effect ofsurface modification in overcoming morphological instability; and potential applications in biosensing. Specific applications presented involve the combination polymers and nanoparticles for detection; creation of environmentally sensitive nanostructured surfaces; and photostability of fluorophores in the vicinity of metallic nanorods. New opportunities and future challenges will be discussed.

10:40am **PL+BI-TuM9 Environmental Sensitivities of Localized Surface Plasmon Resonances of Immobilized Nanoparticles: Substrate Modulation of Generic Bulk Phase Results**, *M.M. Miller, S. Chen, A. Chilkoti*, ***A.A. Lazarides***, Duke University

The plasmon bands of metal nanoparticles are known to be sensitive to the refractive index of the environment. The magnitude of the sensitivities vary widely for resonances supported by particles of various shape, size, and composition. Through spectral simulation, however, it has been shown that the resonant frequency of particles suspended in a medium have sensitivities to refractive index of the medium that are determined with high accuracy by the plasmon frequency and the dielectric properties of the particle and medium, when the particle is composed of a single component and of modest phase volume.[1],[2] Immobilized particles, in contrast, display sensitivities to the exchangeable component of their media that are reduced relative to those of suspended particles and expected to be dependent upon the nature and localization of the mode and its interaction with the substrate. Here, we report measurements and simulations of the refractive index sensitivities of a family of gold nanorods immobilized on glass, and a comparison of the immobilized particle sensitivities with the generic sensitivities of plasmons supported by suspended particles. The refractive index sensitivities of the immobilized rods are found to be well predicted by a band location dependent sensitivity function reduced from the generic solution phase sensitivity function by a constant scale factor derived from comparison of simulation and theory. The applicability of the result to immobilized particles of other shapes, sizes, and compositions will be discussed within the framework of sensitivity theory.

[1] Miller, M. M.; Lazarides, A. A. "Sensitivity of Metal Nanoparticle Surface Plasmon Resonance to the Dielectric Environment" J. Phys. Chem. B 2005, 109, 21556-21565

[2] Miller, M. M.; Lazarides, A. A. "Sensitivity of Metal Nanoparticle Plasmon Resonance Band Position to the Dielectric Environment as Observed in Scattering" J. Opt. A: Pure Appl. Opt. 2006, 8, S239-S249.

11:00am **PL+BI-TuM10 Controlled Plasmonic Coupling in Reconfigurable Nanoparticle Assemblies**, ***D.S. Sebba***, *T.H. LaBean, A.A. Lazarides*, Duke University

Metal nanoparticles (MNPs) support localized surface plasmon resonances that are sensitive to particle shape, size, composition, and the presence of other polarizable particles and materials. Advances in MNP synthesis and surface chemistry have yielded biomolecule nanoparticle conjugates that interact specifically with oligonucleotides, peptides, and proteins. The specific recognition properties of these components have been exploited in responsive plasmonic systems with formats that range from amorphous solution phase particle networks to immobilized colloidal monolayers and individually responsive particles. For molecular detection applications, various formats have various advantages, with single particle sensors generally offering ease of control and multi-particle systems offering strong plasmon modulation. Here, we report plasmon modulation in pre-formed, few particle assemblies linked by reconfigurable DNA nanostructures. The investigation is motivated by the potential of reconfigurable few particle assemblies to provide control of plasmon coupling in a format that displays high responsiveness per molecule. In the coupled system upon which we report, DNA nanostructures tether satellite MNPs to a core MNP. The DNA nanostructures use duplex DNA to control interparticle separation and are responsive to target strands that modulate interparticle helix length. The reconfigurable assemblies are characterized in two states, using dynamic light scattering and transmission electron microscopy to monitor structure and scattering spectroscopy to monitor plasmonic properties. A two state structural model is tested by comparison of spectroscopic data with spectra calculated for structures defined by core/satellite stoichiometry from TEM and interparticle separations from measurements in DNA-linked networks. Thermodynamic properties derived from melting transition data collected from the reconfigurable DNA linker ex-situ are reported and reviewed as a source of insight into DNA nanostructure control of system stability.

11:20am **PL+BI-TuM11 Metal Films with Arrays of Tiny Holes: Infrared Plasmonic Scaffolding for Spectroscopy**, ***J.V. Coe***, *K.R. Rodriguez, S. Teeters-Kennedy, H. Tian, J.M. Heer*, The Ohio State University **INVITED**

The surface plasmon (SP) mediated, extraordinary transmission of metal arrays of subwavelength holes has been moved into the infrared (IR) region in order to overlap with the traditional range of molecular vibrations. SP-enhanced IR absorption spectra are recorded (using standard FTIR instrumentation) of metal-supported self-assembled alkanethiol monolayers, phospholipid bilayers, gramicidin (an antibiotic peptide) and cholesterol in phospholipid bilayers, as well as hexadecane thin films. The interaction of a SP resonance and a vibrational excited state has been examined by tuning a SP resonance (both by film thickness and angle of the mesh) through the primary rocking vibration of the hexadecane molecule producing vibrational band intensity changes, peak shifts, and lineshape changes. The nature of the enhancements will be discussed.

12:00pm **PL+BI-TuM13 Photo-Recognition and Control of a Small Number of Moleclues at Metal Nano-Gap Arrayed on Solid Surface**, ***K. Murakoshi***, Hokkaido University, Japan

Detection, recognition, and control of single molecules are a common theme in recent advanced technologies. It has been demonstrated that the surface-enhanced Raman scattering (SERS) phenomenon can drastically increase the scattering cross section, which is comparable to that of fluorescence at high quantum yield. Although the importance of single-molecule SERS (SM-SERS) has been well recognized from the early stage of its discovery, there are only a few examples supporting the observation of SM-SERS. In the present study, well-ordered, periodic metal nano-dot dimer arrays were prepared. The gap distance between two metal dots was optimized to show intense SERS in an aqueous solution. The system was also applied to control the adsorption of target molecules. In-situ Raman spectroscopic measurements with 785 nm excitation were carried out in aqueous solution using metal nano-gap array. Intense Raman signals were observed when the metal dimer structure was optimized. The SERS activity was dependent upon on the structure of the metal dimer with a distinct gap distance, suggesting that the intense SERS originates from the gap part of the dimer. Characteristic time-dependent spectral changes were observed both in Stokes and anti-Stokes region. In the system of Au dots array, relatively stable SERS signals was observed even under relatively strong photo-irradiation. Possibility of the molecular manipulation by electromagnetic filed will be discussed based on the characteristic behavior of SERS signals observed under relatively strong photo-irradiation.

Plasma Science and Technology

Room: 606 - Session PS1+TF-TuM

Plasma Enhanced Atomic Layer Deposition and Plasma Deposition

Moderator: S. Agarwal, Colorado School of Mines

8:00am **PS1+TF-TuM1 Characteristics for HfO_2 Gate Dielectrics Deposited by Remote Plasma ALD Method**, *S. Kim*, ***H. Jeon***, Hanyang University, South Korea **INVITED**

Many high-k dielectric materials have been studied extensively to replace current gate dielectric materials such as SiO_2 and SiO_xN_y. Among the high-k dielectric materials, Hf-oxide is considered to be one of best choices for 45 nm technology and beyond. However, most of high-k oxides such as HfO_2, ZrO_2, Ta_2O_3, and TiO_2 are transition metal oxides with the ionic nature and have poor interface quality and poor thermal stability with Si substrate. In addition, they exhibits high oxide traps and interface state densities, and large amount of oxygen vacancies, and are easily crystallized compared to SiO_2. To overcome these drawbacks of high-k oxides, the technologies for growing high quality high-k oxides and improving the interface properties between high-k oxide and Si substrate are required. In this study, we chose HfO_2 as high-k gate dielectrics and atomic layer deposition (ALD) as a deposition method. Among many deposition methods, ALD method is studied by many researchers because of its thin film deposition superiority. In our lab we applied both direct plasma ALD (DPALD) and remote plasma ALD (RPALD) methods to grow HfO_2 thin films on Si substrates. These two different plasma methods exhibited the different thicknesses of silicate interlayer. We believe this interlayer is critical for the degradation of high-k dielectric materials. To investigate these interlayers we grew several different buffer layers before HfO_2 growth. These buffer layers were formed by remote plasma oxidation (RPO) and nitridation (RPN) on Si substrates to monitor this interlayer, to suppress the initial formation of Hf silicate or interlayer and to improve the interlayer quality. The buffer layers were thin SiO_2, SiO_xN_y, Al_2O_3, nitrided Al silicate and nitrided Hf silicate layers. The HfO_2 films with buffer layers suppressed silicate formation or growth of an interlayer more effectively than those without buffer layers. The HfO_2 films with buffer layers also showed lower effective oxide thickness (EOT), lower effective fixed oxide charge density ($Q_{f,eff.}$), and lower leakage current density compared to those without buffer layers. The physical and electrical properties of HfO_2 with buffer layers will be presented and discussed depending on the various buffer layers.

8:40am **PS1+TF-TuM3 Pulsed Plasma-Enhanced Pulsed CVD of Y_2O_3 in MIM Capacitors**, ***C, Vallee***, *M. Kahn, E. Gourvest, M. Bonvalot, O. Joubert*, CNRS, France

The development of integrated metal-insulator-metal (MIM) capacitors for advanced analog and rf circuits aims at achieving development of capacitors with higher capacitance density, low leakage current, and good voltage linearity. High k materials are thus integrated and evaluated as MIM dielectrics. Moreover, system-on-chip (SOC) applications also require a deposition process with a low thermal budget which can be carried out with a plasma deposition process. In the past, we have shown interesting results on MIM capacitors based on Y_2O_3 materials deposited by a low temperature process, namely pulsed liquid injection MOCVD assisted or not by a capacitive RF plasma. With the plasma, depositions have been achieved at temperatures as low as 300°C, and for this reason, good results have been obtained with TiN as bottom electrode. Without plasma, the deposition takes place at 450°C and a non desirable TiO_x interface is formed, which degrades the MIM electrical properties. In this study, we compare Y_2O_3 MIM capacitors deposited on $WSi_{2.3}$ substrates when assisting the pulsed CVD process by a pulsed RF plasma instead of a continuous plasma. With $WSi_{2.3}$ substrates, the interfacial layer is SiO_2-like, which can be beneficial to the MIM electrical properties in terms of linearity behavior. The plasma is pulsed either in phase or out of phase with the pulsed liquid injection of precursors. Moreover, depending on the plasma pulse width and frequency, the plasma can play a role in precursor dissociation and CVD post-deposition in-situ annealing treatment. The electrical behavior C(V) and I(V) of the obtained structures will be presented and discussed in terms of capacitance density, capacitance linearity and leakage currents. They will be correlated to chemical analysis results (XPS and FUV-SE), with special attention devoted to carbon content as well as metal/oxide interface investigations. C(V) curves suggest the presence of positive charges in the oxide, some of which are mobile, when the plasma is continuously applied. In this study, we will show the impact of exposure time of the dielectric to the plasma on the amount of trapped positive charges in the oxide affecting the MIM linearity properties. Moreover, the nature and thickness of the interfacial dielectric layer originate from both oxygen and solvent which can be limited by pulsing the plasma.

9:00am **PS1+TF-TuM4 Engineering Plasma-Enhanced Chemical Vapor Deposition to Deliver Self-Limiting Deposition of Metal Oxide Thin Films**, ***M.T. Seman***, *S. Agarwal,* Colorado School of Mines, *J.J. Robbins,* CMD Research, LLC, *C.A. Wolden*, Colorado School of Mines

In this presentation we describe how conventional plasma-enhanced chemical vapor deposition (PECVD) may be engineered to deliver self-limiting deposition of metal oxides using pulsed power modulation. Self-limiting growth is assured when no deposition occurs during continuous operation with either the plasma on or the plasma off. The requirements that must be met to achieve this behavior are described. The pulsed PECVD technique has the potential to combine the digital control over thickness and composition provided by atomic layer deposition with the high throughput and low temperature capability offered by PECVD. To date the process has been demonstrated for both tantalum[1] and aluminum oxides,[2] and in this paper we focus on the process-property relationships in the former system. Tantalum oxide films were deposited by pulsed PECVD using continuous delivery of oxygen and penta-ethoxy tantalum (PET, $Ta(OC_2H_5)_5$) in a capacitively-coupled reactor. Deposited films were characterized by spectroscopic ellipsometry, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and dielectric performance. The deposition rate per pulse may be readily adjusted over a broad range (1- 10 Å/pulse) using variables such as the PET concentration and the plasma off time. With these variables fixed digital control over film thickness is demonstrated. The process is insensitive to substrate temperature, with a constant deposition rate observed from 90 to 350 °C. Films contain impurities due to carbon and hydroxyl groups, however these signals attenuate as the rate is reduced and are not detectable by FTIR for rates < 3 Å/pulse. Films deposited under these conditions at 190 ºC displayed a high dielectric constant ($\kappa \sim 25$) while maintaining leakage current densities below 1 $\mu A/cm^2$ out to a field strength of 1 MV/cm.

[1] M. Seman, J. J. Robbins, S. Agarwal, and C. A. Wolden, Appl. Phys. Lett. 90, 131504 (2007).

[2] S. Szymanski, M. T. Seman, and C. A. Wolden, Surf. Coat. Technol. in press (2007).

9:20am **PS1+TF-TuM5 Peter Mark Memorial Award Lecture - Plasma-assisted Atomic Layer Deposition: Applications, Opportunities, and Mechanisms**, ***W.M.M. Kessels****, Eindhoven University of Technology, The Netherlands **INVITED**

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with submonolayer growth control. Recently, the extension of the technique with plasma processes is actively being researched. These so-called plasma-assisted ALD processes can provide several potential advantages over thermal ALD for selected applications such as an enhanced growth rate, improved material properties, and lower deposition temperature (down to room temperature). In this contribution, different plasma-assisted ALD configurations such as direct plasma, remote plasma and radical enhanced ALD will be discussed and an overview will be presented of oxide and nitride materials (Al_2O_3, HfO_2, TiO_2, TiN, TaN, etc.) deposited. In particular, remote plasma ALD processes based on halide and metalorganic precursors and plasmas of H_2, N_2, O_2, NH_3 and combinations thereof will be described and the resulting material properties will be presented for wide substrate temperature ranges. The versatility of the plasma-assisted ALD process will be illustrated by several applications ranging from the semiconductor industry (capacitor stacks) to emerging applications in the field of 3D-integration in microelectronics (Cu diffusion barriers), photovoltaics (Si surface passivation), energy storage (Li diffusion barriers) and flexible electronics (ultrahigh moisture barrier coatings). Generic insight into the plasma-assisted ALD surface reactions will be presented from mechanistic studies carried out by a variety of in situ techniques: spectroscopic ellipsometry for monitoring film thickness and film properties (including electrical resistivity and crystal phases), transmission infrared spectroscopy to probe reactive surface groups, quartz crystal microbalance measurements to measure surface mass uptake, and mass spectrometry and optical emission spectroscopy to detect reaction products. On the basis of the results, the paradigms for plasma-assisted ALD are reviewed and differences with thermal ALD processes are discussed.

10:40am **PS1+TF-TuM9 Silicon Based Coatings by Means of Glow and Townsend Dielectric Barrier Discharges**, ***F. Massines***, CNRS PROMES, France, *N. Gherardi*, LAPLACE CNRS-UPS-INP, France **INVITED**

The development of a PECVD process working at atmospheric pressure and allowing an easy on-line treatment of silicon wafer, glass plate or polymer film is a challenge of great interest. The successful solution will avoid batch treatments and significantly reduce the cost of the coating. The main questions to be solved are how to get a well controlled thin film in terms of chemical composition, structure and thickness? and how to get a high growth rate? Previous to the process development, the main difficulties concern the plasma homogeneity, the gas injection over large dimensions, the control of the atmosphere in the plasma area while the substrate is moving and the efficiency of the transfer of the reactive species to the surface taking into account the very low diffusion of the neutral radicals at atmospheric pressure. In case of two dimensional materials like, dielectric barrier discharge (DBD) appears like the more suitable discharge: it is cold, robust and not disturbed by the movement of the substrate. As example DBD generate the plasma of corona treaters useful for surface activation. However, making a thin film coating having well controlled and uniform properties is more delicate. Homogeneous DBD (HDBD) is a solution to reach that goal. Conditions to get such a HDBD are now widely known and easy to up-scale in one direction allowing to get a uniform plasma band of several meters in the direction perpendicular to that of the substrate movement. This solution is in competition with remote plasmas but knowing that the quenching of excited state drastically increases with the pressure, and as far as the substrate can be moved inside the discharge without inducing perturbation, remote plasma has to be avoid. At atmospheric pressure, the reactive gases leading to the coating formation are diluted in a main gas, which is usually helium, argon or nitrogen. The main gas determines the discharge regime and then the energetic species created during the plasma development. In nitrogen, the HDBD is a Townsend discharge while in noble gases the HDBD is a glow one. In this presentation results concerning SiOx coatings obtained from SiH4 or hexamethyldisiloxane mixed with N2O and diluted in N2 will be compared. The coating thickness, the refractive index and the chemical composition as a function of the gas residence time will be discussed and correlated to the main growth mechanism.

11:20am **PS1+TF-TuM11 Film Microstructure Control and Characterization of Ion Bombardment- Aided Remote Plasma Deposition of Silicon Dioxide Films**, ***M.A. Creatore***, *N.M. Terlinden*, *M.C.M. van de Sanden*, Eindhoven University of Technology, the Netherlands

The control on thin film growth and microstructure in plasma deposition is a challenging issue. For example, in the case of an inorganic layer on an organic substrate (e.g., SiO_2 on polymers), the organic/ inorganic interphase affects the bulk inorganic properties, such as adhesion and moisture permeation barrier performance. Within this framework, ion bombardment-aided remote plasma deposition of SiO_2 layers, deposited from a hexamethyldisiloxane/O_2 chemistry, is carried out: the purpose is to engineer an interphase allowing the growth of dense, yet adhesive barrier films. This control is achieved by coupling the use of ion bombardment with a graded growth flux, obtained by a gradient (e.g. a decrease) in the hexamethyldisiloxane flow rate during film growth. At constant substrate bias voltage, i.e. constant ion energy, this gradient allows to tune the ion-to-growth flux ratio and the film densification. Initially, an adhesive porous layer is deposited, gradually shifting towards a highly dense barrier layer, due to the increase in the ion-to-growth flux ratio. The role of ion bombardment on the film microstructure is investigated by means of ellipsometric porosimetry, which monitors the refractive index (n) change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity and the pore volume distribution can be extracted. In the absence of ion bombardment porous (n= 1.35-1.38) layers are characterized by an isotherm shape mimicking the structure of disordered mesoporous films (pore diameter in the range of 2-50 nm), i.e. a very broad distribution in pore size and shape, resulting in 20% porosity. A progressive increase in substrate bias voltage leads towards film densification (n=1.46) and induces a change in the isotherm: the adsorption/desorption process becomes reversible since unrestricted ethanol multilayer adsorption occurs on the non- porous surface. When a mild ion bombardment (ion energy of 20 eV) is accompanied by an increasing ion-to-growth flux ratio, both the isotherm and the hysteresis behavior exhibit the transition from meso- to microporosity (pore diameter less than 2 nm). The implications in terms of porosity determination in barrier layers deposited on polymeric substrates will be also addressed.

11:40am **PS1+TF-TuM12 Self-Limiting Growth of Aluminum Oxide by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, ***S.F. Szymanski***, *M.T. Seman*, *D. Richards*, *C.A. Wolden*, Colorado School of Mines

In this presentation we describe the self-limiting deposition (~ Å/pulse) of aluminum oxide by pulsed plasma-enhanced chemical vapor deposition (PECVD). In this process the trimethyl aluminum (TMA, $Al(CH_3)_3$) and oxygen are mixed and delivered simultaneously in a remote PECVD configuration. Deposited films were characterized by spectroscopic ellipsometry, Fourier transform infrared spectroscopy, and dielectric performance. In addition, the plasma and gas-phase chemistry in this system were characterized using optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS), respectively. The chemistry and deposition kinetics were quantified as a function of TMA concentration, plasma power, substrate temperature, and pulse parameters. The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TMA concentration and pulse duration, the depositing rate may be readily adjusted over a broad range (1 - 10 Å/pulse). The deposition rate also decreases with plasma power, and OES is used to highlight the role of atomic oxygen in this process. The chemistry was quantified under steady-state operation using the QMS. It is shown that O_2 and TMA are unreactive with the plasma off. In contrast, TMA is completely consumed during plasma operation.

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* Peter Mark Memorial Award Winner

Combustion of the TMA precursor is complete, yielding a mixture of CO, CO_2, H_2O, and H_2. Transient experiments show how TMA adsorbed on the walls of the chamber can impact both deposition rate and quality. The deposition rate was found to be independent of temperature for $T_s > 100$ °C. At lower temperatures the deposition rate per pulse increased, but film quality was degraded. Using a combination of ex situ film characterization and in situ diagnostics it is suggested that this behavior may be attributed to thermal chemistry occurring between TMA supplied during the off step with H_2O produced during the plasma on step. This reaction adversely effects film quality, but its effects are mitigated when the both reactor walls and substrate are maintained at temperatures > 100 °C.

12:00pm **PS1+TF-TuM13 Correlation of Surface Reactivity and Gas Phase Properties of CN Active Species in the Plasma Deposition of Carbon Nitride**, ***J. Stillahn***, Colorado State University, *D. Liu*, Dalian Nationalities University, China, *E.R. Fisher*, Colorado State University

Amorphous carbon nitride materials have generated interest due to their potential for commercial applications. One of the possible precursors in the plasma enhanced chemical vapor deposition (PE-CVD) of carbon nitride is the CN radical, but its role in the deposition process is still unclear. In an effort to clarify the processes taking place during film formation, carbon nitride deposition systems have been studied in rf inductively coupled plasmas by utilizing acetonitrile (CH_3CN) as a film precursor to allow direct generation of CN active species. The imaging of radicals interacting with surfaces (IRIS) technique has been utilized in our lab to provide a measure of the surface reactivity of the CN radical, R(CN), in these systems. Preliminary results indicate that CN radicals formed in acetonitrile plasmas react with near unit probability during deposition of a-CN_x:H films. Results from IRIS studies using other CN precursors will also be discussed. Characterization of gas phase species in these deposition systems has also been performed using spectroscopic and mass spectrometric (MS) methods. MS measurements are consistent with the direct formation of CN active species, and mass spectra are dominated by ions formed by the loss of CN from the parent molecule. Measurement of the relative number density of gas phase CN radicals by laser-induced fluorescence (LIF) spectroscopy indicates that increases in CN radical production due to increases in the pressure of the precursor gas or applied rf power give way to plateau behavior at higher values for both pressure and power. LIF measurements of the rotational temperature of CN radicals yield values near 320 K, suggesting that the rotational energy of CN radicals is re-distributed to maintain near-equilibrium conditions in the plasma. These data, along with film formation and characterization studies, will be discussed with respect to the information that they provide about the deposition process and their implications for continuing work in this area.

Plasma Science and Technology

Room: 607 - Session PS2-TuM

Advanced Gate Etch

Moderator: T. Kropewnicki, Freescale Semiconductor

8:00am **PS2-TuM1 Reaction Mechanisms in Patterning Hafnium Aluminate High-k Thin Films**, ***R.M. Martin****, University of California at Los Angeles, *H.-O. Blom*, Uppsala University, Sweden, *J.P. Chang*, University of California at Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium-based oxides, for sub-45nm CMOS devices. Hafnium aluminates ($Hf_{1-x}Al_xO_y$) have arisen as a promising material for gate oxide replacement due to their high dielectric constant, bandgap, and recrystallization temperature. Hafnium aluminates with the Al_2O_3 content varying from 0 to 100% were synthesized to study the effect of alumina addition to hafnia. An electron cyclotron resonance high density plasma reactor was used in this work to study the etching of hafnium aluminates in chlorine-based chemistries. The plasma density, electron temperature, and gas phase reactive species were characterized by a Langmuir probe, optical emission spectroscopy, and quadrupole mass spectrometry (QMS). $Hf_{1-x}Al_xO_y$ films were etched in Cl_2 and BCl_3 plasmas and the etch rate scaled linearly with the square root of ion energy at high ion energies (> 50 eV), however the etch rate in BCl_3 was 1.5 to 2 times that in Cl_2. The faster etch rate in BCl_3 was attributed to a change in the dominant ion from Cl_2^+ to BCl_2^+ as determined by QMS. At low ion energies, (< 50 eV), a physical-sputtering-like process was observed in Cl_2 while deposition was observed in BCl_3. The dominant metal-containing etch products were $HfCl_x$ and $AlCl_x$ in Cl_2 plasma and $HfCl_x$, $HfBOCl_4$, $AlCl_x$, and Al_2Cl_x in BCl_3 plasmas, and increased with ion energy. Oxygen was detected removed in the form of ClO in Cl_2 and $(BOCl)_3$ in BCl_3 plasmas. The etching threshold energy can be tuned by about 2 eV by changing the film composition, making it possible to design a composiiton near the interface to maximize the etching selectivity with respect to silicon. Chlorine was measured on the surface of all etched films (0-3 at. %) as well as boron (~7 at. %) for the BCl_3-etched films. The surface chlorination was enhanced with increasing ion energy, demonstrating that the etching reaction is limited by the momentum transfer from the ions to the film surface. Finally, a generalized phenomenological model will be presented to elucidate the effect of Al_2O_3 addition on modifying the etching characteristics of HfO_2.

8:20am **PS2-TuM2 Tungsten and Tungsten Nitride Etch Characterization for sub 45nm Metal Gate**, ***T. Morel***, STMicroelectronics France, *S. Barnola*, CEA-LETI France, *O. Joubert*, CNRS/LTM France

Continuing downscaling of structures involved in advanced CMOS devices brings new complexity in plasma etching processes. The introduction of new materials, (metal gates, high-k dielectrics) to avoid the poly depletion effect and to minimize the equivalent oxide thickness, requires new dry etch approaches. Innovation proposed here is the use of thin MOCVD tungsten or tungsten nitride layers (10nm) to achieve PMOS devices on 300mm wafers. In this work, we characterized both metal layers by angle resolved X-ray Photoelectron Spectroscopy (XPS) and X-Ray Reflectometry (XRR). It is found that W and WN layer present differences in terms of oxygen and carbon concentration and density. To get a better understanding of interfaces between the different layers of a complete gate stack (Poly-Si / TiN / WN or W / high-k), Secondary Ion Mass Spectroscopy (SIMS) and XPS depth profiling were performed. The characterization of as-deposited and integrated tungsten alloy revealed variations between both metals that involved two different strategies to achieve good profile in patterned metal gate electrode. Concerning the process development, etch rates of W and WN were carried out in chlorine and fluorine based chemistries on a 300mm ICP tool with in-situ optical emission spectroscopy and in-situ interferometer. With the support of ion mass spectroscopy and quasi in-situ XPS, etch mechanisms of tungsten alloy were identified. Finally, the integration of W and WN etch into a multiple steps process for sub 45nm metal gates were investigated. Cl_2-O_2 and Cl_2-O_2 with additional fluorine are the proposed solutions to control, respectively, the profile of tungsten nitride and tungsten, without damaging the passivation on the Poly-Si sidewalls.

8:40am **PS2-TuM3 Nitride Spacers Dry Etching for sub-20nm HfO2 - Metal Gate on Fully Depleted SOI**, ***C. Arvet***, STMicroelec., FR, *J. Chiaroni, V. Loup*, CEA-Léti/Minatec, FR, *P. Besson*, STMicroelec., FR, *P. Brianceau*, CEA-Léti/Minatec, FR, *M.P. Clement*, STMicroelec., FR, *V. Delaye, L. Tosti, C. Buj*, CEA-Léti/Minatec, FR, *O. Louveau*, STMicroelec., FR, *E. Vermande, M. Heitzmann, S. Barnola*, CEA-Léti/Minatec, FR, *R. Blanc*, STMicroelec., FR

Fully Depleted Silicon on Insulator is one of the most promising MOS transistors fabrication technologies to address low power and high speed applications challenges. Due to the very thin channel silicon thickness, selective epitaxial growth is mandatory to raise source and drain areas. So in addition to there classical uses as sidewall for ion implantation, spacers play a major role to avoid leakage current between metal gate and raised source and drain. On this way new constraints appear for nitride spacer dry etching. An accurate control of etch polymers is mandatory to allow a good performance of the next step, while a very high selectivity to thin silicon, silicon dioxide and HfO2 materials is required to avoid any silicon surface damage or HfO2 modification. Indeed, typical HfO2 thickness is less than 3 nm, thin silicon film is 10 nm or less while silicon dioxide hard mask on top of the gate must not be impacted. Moreover, two different approaches can be used for gate stack building. In the "spacer first approach", the nitride layer is deposited over the HfO2 material then spacers are etched, while in the "spacer last approach", the HfO2 is etched before nitride layer deposit. This affects the requirements for spacer etch, resulting in two different dry etch processes. These processes were developed in a DPS2 (Decoupled Plasma Source) Applied Material reactor either with a CH2F2 based chemistry or a CF4/HBr based chemistry. Etch rates, selectivities and non uniformities were optimized by adjusting gas ratio, source and bias RF power. SEM Cross sections, SEM-CD and TEM demonstrate good spacers profile and metal gate coverage. A 1.5 nm range spacer size control has also been reached, although spacer size adjustment by use of the overetch step seems to be limited. Plasma impact and selectivity to HfO2 and Silicon were measured by ellipsometry and XPS analysis. Results show no consumptions for HfO2 and less than 1.5 nm for silicon. A CFx polymer deposition allows high selectivities and no HfO2 modification. Post nitride

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* PSTD Coburn-Winters Student Award Finalist

dry etch XPS and particle measurement show also that HF wet chemistry is required to fully achieve High-K removal and optimize next integration steps. From these experiments, robust processes were developed. Electrical test of sub-20nm HfO2 and TiN Metal Gate on Fully Depleted SOI will be presented with the two integration schemes. This work has been carried out within the frame of Léti/Minatec-Crolles2 alliance program.

9:00am **PS2-TuM4 XPS Sidewall Analyses of Poly Si/TiN/HfO$_2$ Gate Stack Etched with Chlorine and Fluorocarbon Based Chemistries**, ***O. Luere***, Freescale Semiconductors, France, *L. Vallier, E. Pargon,* LTM-CNRS, France, *L. Thorsten*, Applied Materials

Patterning sub-40 nm metal gates on high k dielectrics is one of the biggest challenges for the fabrication of next generation devices. The metal gate etching step is, indeed, difficult: it must be highly anisotropic to maintain a tight CD control ($\leq$ 2 nm) and must not damage the underlying high k material. In this work, we have investigated and compared the impact of the etching of the TiN layer in a Poly Si/TiN/HfO$_2$ gate stack using Cl$_2$/HBr and SF$_6$/CH$_2$F$_2$ based chemistries. The experimental work has been performed on a 200 mm etch platform connected, under vacuum, to an x-ray photoelectron spectroscopy surface analysis system. In order to better understand the etching mechanisms, we have used a technique based on X-ray photoelectron spectroscopy (XPS) to analyse the passivation layer deposited on the sidewalls of the patterns during the Polysilicon etching step and investigate its modification during the TiN etching step. We also used SEM pictures to analyse the gate profiles and determine the thickness of the passivation layer. The etching of polysilicon with a Cl$_2$/HBr based chemistry requires the introduction of O$_2$ in the plasma in order to form a SiOClBr layer which protects the polysilicon sidewalls. On the contrary, the etching of TiN must be O$_2$ free to prevent the metal oxidation. The absence of oxygen in the plasma gas phase during TiN etching can potentially lead to a modification of the passivation layer formed on the Polysilicon sidewalls. Nevertheless, We have shown that, using appropriate plasma conditions, the SiOClBr layer deposited on the chamber walls during Polysilicon etching is eroded during the TiN etch step, leading to an increase of the passivation layer thickness on the Polysilicon sidewalls. Same analyses using a SF$_6$/CH$_2$F$_2$ based chemistry will also be presented.

9:20am **PS2-TuM5 Reactive Ion Etching of Ru Compounds Modified by Ion Implant**, ***C. Park***, *B.S. Ju, S.C. Song, M. Cruz,* SEMATECH, *B.H. Lee, R. Jammy*, IBM

One of the technical hurdles for implementing high-k / metal gate in advanced CMOS is high threshold voltage (V$_{th}$) in p-MOSFETs. Recently, it was shown that the V$_{th}$ of p-MOSFETs can be lowered by using Ru compounds as a metal gate on HfSiO high-k dielectric. Gate etch requires good local and global etch uniformity across the wafer without damaging the underlying gate dielectric. Unlike Ru or RuO$_2$ films, Ru compounds have high etch resistance with conventional etch chemistries, which imposes a significant technical challenge on gate stack patterning. It is possible to etch Ru compounds by applying higher than normal bias power. A high bias power etch, however, poses the high risk of forming either a micro-trench or footing on the pattern sidewall and causing a rough patterned sidewall as well as punch-through of the gate dielectric. It was demonstrated that ion implant could modify the bond structure of Ru compounds, so that they could be etched in a highly controlled manner with O$_2$/Cl$_2$ plasma. Optimum implant condition, which enables plasma etch of the Ru compounds, was found by splitting of implant energy and dose conditions. The effects of the ion implant on film thickness, bonding of Ru compounds, and knock-on of Ru compounds and gate dielectric into silicon substrate were also studied.

9:40am **PS2-TuM6 Plasma Etching Processes for Aggressively Scaled Gate Features**, ***N.C.M. Fuller***, *M.A. Guillorn, Y. Zhang, W.S. Graham, E.M. Sikorski*, IBM TJ Watson Research Center

Scaling of device dimensions for 32nm and beyond technology nodes demands process, integration and tooling innovations to meet feature profile, line edge roughness (LER) and line width roughness (LWR) requirements. To these ends multi masking schemes have been employed to attempt to enable scaled devices and reduce LER/LWR constraints. Further, we have utilized various process conditions to increase the mechanical integrity of patterning materials in such multi masking schemes patterned with mixed electron beam and optical lithography. This methodology has enabled 20nm gates on a 60nm pitch with 0.5-1.0nm improvement in post lithography LER/LWR and 100% physical yield. These and other results will be presented and discussed.

10:40am **PS2-TuM9 Investigation of 45nm Silicon Gate Etching Process Variability Contributors**, ***L. Babaud,*** Freescale Semiconductor, France, *P. Gouraud,* STMicroelectronics, *O. Joubert, E. Pargon*, CNRS/LTM, France

In a semiconductor world more and more aggressive in term of device performance and market cost, the control of critical dimension for 45 nm poly gate and beyond appears as a big challenge. Indeed as conventional photolithography is not able to define the novel design targets, other strategies as the double patterning on complex stack are developed. But the introduction of such complex process will induce additional sources of dimension variability and so alter the final functionality of the device. In this way, the research of the variability contributors from lot to lot, wafer to wafer, site to site will be the keys of an understood and controlled process. Some new parameters such as Line Edge Roughness (LER) will have to be considered. This presentation will focus on profile and dimension variability studies of the different steps of a gate stack process integrating a Hard Mask. Moreover we will investigate the impact of the 300 mm industrial ICP chamber walls conditioning strategies on the gate morphology. Chemical topography analyses by X-Ray Photoelectron Spectroscopy (XPS) will be performed to correlate the morphological results with passivation layer composition, deposited during the silicon etch process.

11:00am **PS2-TuM10 Control of SiO$_2$/Si Interface States during Plasma Etching Processes**, ***Y. Ishikawa***, *Y. Ichihashi,* Tohoku University, Japan, *S. Yamasaki,* National Institute of Advanced Industrial Science and Technology, Japan, *S. Samukawa*, Tohoku University, Japan

Plasma processes are indispensable in the fabrication of MOS LSI devices. During plasma processes, however, serious problems can occur, such as charge-build up damage and UV photon irradiation damage. In particular, UV irradiation from the plasma causes drastic degradation of sub-50nm MOS LSI device characteristics, because the penetration depth of UV photons into dielectric films is more than 10nm. We have previously reported that UV photons from plasma effectively generate E' centers (Si dangling bond in SiO2 film) in SiO2 films. However, the relationship between UV irradiation from plasma and interface states' (Pb centers, Si dangling bond at SiO2/Si interface) densities must be basically understood during the plasma process, because the generation of interface states directly degrades the electronic properties of MOS LSI devices. We focus on SiO2/Si interface state density trends during conventional continuous wave (CW) plasma and pulse-time-modulated (TM) plasma etching processes. In order to evaluate the generation of interface state density, 5nm thick thermally grown SiO2 films were formed on Si substrates. The SiO2 films were then irradiated using Ar inductively coupled plasma. After that, we evaluated the Pb centers using electron spin resonance spectroscopy. Before the plasma irradiation, the density of the Pb centers was less than 1×10^{10} cm^{-2} spins. After the Ar CW plasma irradiation, and without any substrate RF bias power, Pb centers drastically increased. That is, the Pb centers increased drastically even after irradiation using conventional Ar CW plasma and elimination of ion bombardment. We also investigated the dependence of ion bombardment energy on the density of Pb centers in conventional CW plasma. However, even when 100W of RF power was applied during the plasma process, the ESR spectrum did not change. This result indicates that Pb centers are mainly generated by irradiation with UV photons during plasma processes. Therefore, we investigated the effects of TM plasma on eliminating Pb centers. During the TM plasma irradiation, the UV photon irradiation was drastically reduced during the plasma's "off" period. After the TM plasma irradiation, the Pb centers densities reduced dramatically to less than 1×10^{10} cm^{-2} spins, compared to those observed after CW plasma irradiation. We found that TM plasma was the most promising candidate for the elimination of Pb centers during the plasma etching processes.

11:20am **PS2-TuM11 Plasma Etching in the Era of Intensive Integration Innovation**, ***Th. Lill***, Applied Materials, Inc. **INVITED**

Driven by relentless pursuit of Moor's law, plasma etching advances at a rate never before seen in the history of this IC processing technology. New challenges are posed by several significant co-emerging trends: 1. Pattern fidelity requirements within wafer and lot reach sub nanometer, i.e. atomic resolution. 2. Plasma Etching is now an integral part of pattern generation (resist trim, double pattering, multilayer resist schemes). 3. Aspect ratios increase almost inverse proportional to the nominal line width for any given technology node reaching 100:1 for capacitor silicon etches and 40:1 for capacitor dielectric etches. 4. The number of potential new material candidates and their possible combinations in future stacks is exploding. At a first glance these challenges are well known and represent just another incremental tightening of known requirements. In this paper, we will show that these trends lead to three new paradigms in plasma etching: divergence of plasma etch applications, convergence the required process space to cover these applications and the need for precision chamber matching. We will discuss the consequences for plasma etch engineers and show examples for how Applied Materials Etch is responding to these new paradigms today to provide productive solutions for whatever device and integration engineers hold in store for the plasma etch community.

12:00pm **PS2-TuM13 The Effect of Oxygen Addition in a Chlorine Plasma during Shallow Trench Isolation Etch**, ***C.C. Hsu***, *J.P. Chang*, University of California at Los Angeles

Shallow trench isolation has been widely used to electrically isolate adjacent transistors. The mixtures of chlorine and oxygen have been one of the most commonly used chemistries for the shallow trench isolation etching process. In this work, an electron cyclotron resonance high density plasma is used to study the effect of oxygen addition in a chlorine plasma during the etching of silicon. To quantitatively assess the effect of oxygen addition, the plasma density and the electron temperature were characterized by using a Langmuir probe. The plasma species, including the etching by-products, were studied using the quadrupole mass spectrometry and the optical emission spectroscopy. The silicon etching rate was measured in-situ by using laser interferometry. Scanning electron microscopy was used to observe the topography change of the etched blanket films. The silicon etching rates were found to increase with the square root of the ion energy with a 9 eV threshold energy, suggesting the etching reaction is limited by the momentum transfer from the ions to the surface. With a relatively small amount of oxygen addition to the chlorine plasma, the etching rate remained approximately constant while the by-product identity and its distribution changed significantly. The dominant ionic etching by-products in chlorine plasmas were $SiCl^+$ and $SiCl_3^+$, but changed to $SiCl^+$, $SiOCl_2^+$, and $SiCl_3^+$ with the oxygen addition. The roughness of the etched surface increased significantly with oxygen addition. The significant changes of the by-products distribution and the etched surface topography suggest that the etching mechanism changes with the oxygen addition to the chlorine plasmas.

Advanced Surface Engineering

Room: 617 - Session SE-TuM

Glancing Angle Deposition

Moderator: D. Gall, Rensselaer Polytechnic Institute

8:00am **SE-TuM1 Temperature Effect on the Glancing Angle Deposition of Si Nanostructures**, ***C. Patzig***, *B. Rauschenbach*, Leibniz Institute of Surface Modification, Leipzig, Germany

It is well-known that combining a glancing angle deposition (GLAD) process with suitable substrate rotation offers the ability to grow nanostructures with various shapes, including spirals, screws or vertical posts. When depositing on bare substrates, different growth phenomena are often encountered: Starting of as single fibers at the substrate, adjacent structures will merge together at a certain stage of growth. Also, dying out of structures due to a competitive growth of neighboured structures, and a broadening of the structures diameter with increasing structure height is often observed. However, for most applications, well-aligned, non-merged structures with comparable diameters are needed. Therefore, it is important to understand the influence of the deposition parameters on the nano-scaled structures in order to be able to control their growth. Here, the effect of the substrate temperature T_S on the growth of different Si nanostructures is studied. An ion-beam induced GLAD process was used to grow Si nanostructures at different substrate rotational velocities and at different substrate temperatures T_S ranging from room temperature (RT) up to 360°C, while all other deposition parameters where held constant. Due to the different rotational velocities, spirals, screws and vertical posts could be deposited. Analyzing the structures by means of scanning electron microscopy , it is found that T_S strongly influences the morphology of the grown structures. For the spirals and the screws, T_S effects the critical structure height h_{crit} at which the single fibers start merging together. From RT to T_S = 300°C, h_{crit} is increased with increasing T_S from h_{crit}(RT) = 150nm to h_{crit}(300°C) = 350nm (for the spiral structures), thus giving the possibility to grow spirals consisting of single fibers without merging together over a larger thickness range. However, it was found that increasing the temperature over T_S = 300°C results in a sudden drop of the critical height h_{crit} (360°C) = 130nm. Moreover, the total structure height was found to be dependent on T_S as well, indicating a change of the film density. For the posts, it was found that T_S influences the total number of posts and the inter-post-distance as well as the total structure height , showing a change of the film density as found for the spirals and screws.

8:20am **SE-TuM2 Gold Nanorod Arrays for Surface Enhanced Raman Scattering Imaging of Micro-objects**, ***M. Suzuki***, *K. Nakajima*, *K. Kimura*, Kyoto University, Japan, *T. Fukuoka*, JST Kyoto Pref. CREATE, Japan, *Y. Mori*, Doshisha University, Japan

Recently, we have demonstrated the direct formation of Au nanorods with a quasi-parallel major axis on a template layer of SiO_2 having a strongly anisotropic surface morphology. Those Au nanorods show excellent surface enhanced Raman scattering (SERS) properties.[1] Since the number density of nanorods is considerably high, we tried to apply our nanorod arrays to SERS imaging of micro-objects. Template layers of SiO_2 were prepared by the serial bideposition technique (SBD) on a glass substrate. During the SBD, the deposition angle measured from the surface normal was fixed at an angle of 79°, while the azimuthal angle was changed rapidly by 180° with each deposition of a 10-nm-thick layer. After repeating 30 cycles of the serial bideposition, Au was evaporated at a deposition angle of 73° onto the fabricated template layer. Owing to the self-shadowing, Au nanorods aligned in such a way where their major axes are parallel with each other. On the Au nanorod arrays, surface-modified polystyrene (PS) beads (5 µm in diameter), which have pyridyldithio group on their surface, were distributed. Raman spectra were measured by scanning the laser (λ=785 nm) with 1 µm step in a 40x40 µm^2 region. Raman peaks those originate from pyridyldithio group were detected only at the points where the PS beads and Au nanorods coexist. By assigning the Raman intensity levels to colors, SERS images were obtained. The PS beads were successfully resolved. Therefore, Au nanorod arrays are useful for the imaging of micro-objects such as cells and dusts without any labeling by other chemicals.

[1] M. Suzuki, K. Nakajima, K. Kimura, T. Fukuoka, and Y. Mori, Analytical Sciences (2007) in press.

8:40am **SE-TuM3 Applications of Porous Thin Films Fabricated by Glancing Angle Deposition**, ***M.J. Brett***, University of Alberta, Canada **INVITED**

Considerable efforts have been made by a number of research groups to advance the Glancing Angle Deposition (GLAD) technique in order to achieve precisely engineered and porous thin film structures. Carefully controlled substrate motion and glancing incidence evaporative flux enable fabrication of regular and random arrays of metals, semiconductors and insulators in architectural shapes such as posts, chevrons and helices. After a brief overview of the GLAD process and some advanced fabrication algorithms, this presentation will highlight some recent advances in applications of these coatings, in particular their use in sensor devices. Porous nanostructures of insulator materials have been deposited over planarized interdigitated electrodes and demonstrate fast (100 ms) response in conjunction with capacitive detection. Optical filters have been fabricated with the GLAD process to produce spectral hole or narrow bandpass characteristics ideal for optical detection through shift of the transmission peak. These filters have also been chemically functionalized to alter their sensitivity. Ag nanostructures will be presented that utilize surface plasmon resonance absorption for optically based sensing of biochemical compounds. For these and other applications, GLAD provides the advantages of broad material choice and precise control of microstructure shape and degree of porosity.

9:20am **SE-TuM5 Periodic Nanostructures by Glancing Angle Deposition**, ***C.M. Zhou***, *D. Gall*, Rensselaer Polytechnic Institute

Periodic Ta nanopillar arrays were grown by glancing angle deposition onto patterned substrates. Both the effects of pattern size and surface diffusion on morphological evolution were studied by varying the pattern length-scale and by growing at temperatures T_s ranging form 200 to 900 ºC. The surface patterning experiments show a direct scaling, indicating that the overall nanopillar morphologies are determined by geometric shadowing and are for T_s = 20 ºC independent of material parameters such as the characteristic length-scale for surface diffusion. However, at high growth temperatures, the increased adatom diffusion length causes Ta nanopillars to grow in a competitive growth mode, which in turn results in the breakdown of the regular array morphology. Glancing angle deposition has also been extended to fabricate novel Ta/Si two component nanostructures onto self-assembled close-packed silica nanosphere arrays. The two component nanostructures are shaped into zigzags or nanopillars by adjusting the deposition angle and/or the substrate rotation. By manipulating the sequence of the deposition, that is, by sequential or simultaneous deposition from two sources, complex nanostructures are formed where the two components are stacked vertically, laterally, or in a checker board arrangement. Scanning electron microscopy, back scattered imaging, and transmission electron microscopy provide clear compositional and microstructural contrast and show sharp vertical and horizontal interfaces.

9:40am **SE-TuM6 Electrically Actuated Alq_3 Nanospring Arrays**, ***G.D. Dice**, M.J. Brett, D. Wang, J.M. Buriak*, University of Alberta, Canada

We report the fabrication and characterization of an electrically variable Fabry-Perot interferometer constructed from a nanospring array placed between partially reflective mirrors. Electrostatic compression of the nanosprings provides peak transmission wavelength control. Previous work studied the compression of SiO_2 nanosprings,[1] and individual Si nanospring actuation through electric current applied via a contact mode atomic force microscope (AFM).[2] High quality nanostructures have recently been created using the organic material tris (8-hydroxyquinoline) aluminum (Alq_3), which has a significantly smaller Young's modulus than inorganic films.[3] Glancing Angle Deposition (GLAD) is a single step physical vapour deposition (PVD) technique utilizing an oblique deposition angle to create porous thin film helical structures.[1] Our device is constructed from three films deposited on a conductive indium tin oxide electrode. A 25 nm thick aluminum film forms both a partially reflective mirror and one parallel capacitor plate. A two turn helical Alq_3 nanospring film (300 nm pitch)is then deposited via GLAD PVD. A patterned 25 nm thick layer of aluminum forms the final mirror layer and top capacitor plate. Spring compression as a function of applied voltage was measured through a conducting contact mode AFM. The measured compression varies from 0 nm at 0 V, to ~ 1.2 nm at 6 V. We calculate the Young's modulus of the deposited Alq_3 to be ~ 0.93 GPa. A shift in the peak transmission wavelength from 582.4 nm to 580.8 nm was measured utilizing a fiber-coupled white light source and spectrometer as the applied voltage was raised from 0 V to 10 V. This 1.6 nm wavelength shift corresponds to a physical spring compression of 1.73 nm for the nanospring structure which has an effective refractive index of 1.42.

[1] M. W. Seto, K. Robbie, D. Vick, and M. J. Brett, "Mechanical response of thin films with helical microstructure," J. Vac. Sci. Techol. B, vol. 17, pp. 2172-2177, Sep. 1999.

[2] J. P. Singh, D. L. Liu. D. X. Ye, R. C. Picu, T. M. Lu, and G. C. Wang, "Metal-coated Si springs: Nanoelectromechanical actuators," Appl. Phys. Lett, vol. 84, pp. 3657-3659, Apr. 2004.

[3] P. C. P. Hrudey, K. L. Westra, and M. J. Brett, "Highly ordered organic Alq3 chiral luminescent thin films fabricated by glancing-angle deposition,"Adv. Mater., vol. 18, pp. 224-228, Jan. 2006.

10:40am **SE-TuM9 Effect of Thermal Oxidation and Annealing on the Structure and Morphology of Glancing Angle Deposited TiO_x Films**, ***W.J. Kiether**, C.R. Guarnieri, H.T. Nagle*, North Carolina State University

The typical Glancing Angle Deposited (GLAD) structure is an isolated, self-similar construct on a nanometer scale. Therefore, each structure can react to external influences independently of the other structures, as a separate, albeit similar system. This small scale system independence allows the nanostructures to exhibit different material characteristics than conventional thin films. As with other nanoscale structures, the large surface-volume ratio enhances surface effects, but the isolated GLAD structures are also effectively pinned on the substrate suppressing cross-structure grain growth and other microstructure propogation phenomena. Therefore, they provide an excellent surface engineering template to investigate the effects of annealing and thermal oxidation on thin film structure and morphology. Oxidation of titanium, with the existence of the metastable anatase and stable rutile polymorphs within the titania system, is significantly influenced by the microstructure obtained by GLAD films. Simple GLAD structures (pillars and chevrons) were deposited using reactive e-beam evaporation with a titanium source at various partial pressures of oxygen and argon. Additional process variables included deposition rate, flux angle of incidence, rotation speed, and substrate. Post deposition anneals were conducted in oxidizing, inert, and reducing atmospheres from 150-1200 °C. XRD patterns and SEM images served as the primary forms of film characterization. The combination of reactive evaporation at higher oxygen partial pressures and lower temperature anneals formed films with the highest percentage of the anatase phase. Depositions at lower oxygen partial pressures yielded films with a higher percentage of the rutile phase, which supports the role of oxygen vacancies as nucleation centers for the anatase to rutile transformation. Higher temperature annealing produced rutile films as expected from the thermodynamics of the titanium dioxode system, however the thermal stability of anatase phase structures was significantly enhanced by the GLAD microstructure. The titanium films also exhibit highly ordered crystallographic textures dependent on the flux angle of incidence for both ss-deposited films and after subsequent thermal oxidation. Finally, SEM images provide an interesting perspective on the dynamics of oxidation, grain growth, and sintering for a surface reaction dominated oxidation process.

11:00am **SE-TuM10 Glancing Angle Deposition of Organic Molecules**, ***M.D. Fleischauer**, G.D. Dice, S. Tsoi*, University of Alberta, Canada, *B. Szeto, M.J. Brett*, University of Alberta / NRC National Institute for Nanotechnology, Canada

Glancing Angle Deposition (GLAD) has developed in to a widely-used nanostructuring technique because of the wide range of possible structures and material choices. Efforts to understand the fundamental mechanisms central to GLAD, including self-shadowing and limited surface diffusion, have largely focused on metals and oxides. Hrudey et al.[1] recently demonstrated that the GLAD technique can also be used for organometallics such as the luminescent material tris (8-hydroxyquinoline) aluminum (Alq_3). Unlike their inorganic counterparts, GLAD-fabricated Alq_3 nanostructures are smooth, show a self-ordered periodicity, and do not broaden or bifurcate. A solid wetting layer was also observed to form below the Alq_3 structures whose thickness varies with deposition conditions. Alq_3 molecules differ from metal atoms in that they are larger (1 nm dia.), heavier (ca. 460 a.m.u.), approximately planar, and possess an electronic quadrupole moment. A better understanding of how these properties lead to wetting layer formation, self-ordering, and smooth feature morphology, as a function of deposition conditions, is critical to the future realization of GLAD-nanostructured optical and optoelectronic organic devices. Here, we will present our investigations of the growth of Alq_3 nanostructures during GLAD. Methods to control film morphology (including wetting layer thickness) via deposition conditions and substrate preparation will be presented. Special attention will be paid to the initial stages of Alq_3 film growth during GLAD, especially compared to initial growth mechanisms observed at normal incidence by Brinkmann et al.,[2,3] with an eye towards predicting the behaviour of other organic and organometallic materials in the glancing angle regime.

[1] P.C.P. Hrudey, K.L. Westra, and M.J. Brett, Adv. Mater. 18, 224 (2006).

[2] M. Brinkmann, S. Graff, and F. Biscarini, Phys. Rev. B 66, 165430 (2002).

[3] M. Brinkmann, F. Biscarini, C. Taliani, I. Aiello, and M. Ghedini, Phys. Rev. B, 61, R16339 (2000).

11:20am **SE-TuM11 Scaling Behavior of the Surface Roughness of Platinum Films Grown by Oblique Angle Deposition**, *A. Dolatshahi-Pirouz, M.B. Hovgaard*, University of Aarhus, Denmark, *K. Rechendorff*, Ecole Polytechnique Federale de Lausanne, Switzerland, ***M. Foss**, F. Besenbacher*, University of Aarhus, Denmark

Recently there has been an increasing focus on the growth of thin films and nanostructures with rough surface morphologies on the nanometer length scale for applications in biotechnology, cell/tissue engineering, and catalysis, since the surface morphologies and the absolute value of the surface roughness on the nanometer scale may influence the performance in these areas. In this work, thin platinum films were grown by e-gun evaporation with oblique angle of incidence between the deposition flux and the substrate in order to generate surfaces with well controlled rough morphologies. Atomic force microscopy (AFM) was used to determine the root-mean square (rms) value, w, of the surface roughness. From the scaling behavior of w for the thin platinum films, we observe that while the roughness exponent α remains unchanged, the growth exponent β changes from 0.49 ± 0.04 to 0.26 ± 0.01 as the deposition angle approaches grazing incidence. The change in the growth exponent β indicates that the kinetics of the film growth is influenced by both surface diffusion and shadowing effects under oblique incidence deposition.

11:40am **SE-TuM12 Tailoring the Wettability of Vertically Aligned Si Nanorod Arrays by Glancing Angle Deposition**, ***J.G. Fan**, A. Collins, Y.P. Zhao*, University of Georgia

We report a facile method to tailor the wettability of vertically aligned Si nanorod arrays by glancing angle deposition. As-prepared Si nanorod array surface is hydrophilic, while after coating a fluorocarbon layer, it becomes hydrophobic. For vertically aligned nanorod arrays, when increasing the nanorod height from tens of nanometers to several microns, the as-prepared samples become more hydrophilic while fluorocarbon coated samples become more hydrophobic. A wetting transition from a rough surface to a composite surface is observed at the same critical nanorod height (~ 150 nm for deposition angle of 86°) for both hydrophilic and hydrophobic surfaces. This critical height decreases when increasing the sample deposition angle, i.e., reducing the surface coverage of the nanorods. With a deposition angle of 88°, both superhydrophilic (contact angle = 0) and superhydrophobic (contact angle = 170°, and contact angle hysteresis < 10°) surfaces are obtained. For tilted nanorod arrays, strong anisotropic wetting behavior is observed in the plane formed by the vapor incident direction and the substrate normal. After hydrophobization, the difference between the left and right (nanorod tilting direction) contact angles of a water droplet could be as large as 30°. Such a droplet is able to move along the nanorod tilting direction under external disturbances. This tilting nanorod array provides a new morphological manipulation method for liquid delivery in microfluidic or nanofluidic devices.

12:00pm **SE-TuM13 Chemical Modification of Nanocomposite Si-SiOx Films Obtained by Oblique Deposition**, ***I.Z. Indutnyy**, V.A. Dan'ko, I.Yu. Maidanchuk, V.I. Min'ko, P.E. Shepeliavyi*, V. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine

Nanocrystalline silicon (nc-Si) embedded in SiOx matrix recently have attracted much interest due to perspective of application in optoelectronics and photonics. One of the methods that allow forming nanocomposite Si-

SiOx films is vacuum deposition of amorphous SiOx with further anneal in vacuum or inert atmosphere. It leads to formation of nc-Si with diameter about 3-5 nm. Photoluminescence (PL) at room temperature is observed in such structures, position of PL band is in range of 700-950 nm. In recent papers we offered new method that allow to control nc-Si size and spectral range of PL by forming porous SiOx film using oblique deposition of silicon monoxide. Film obtained by oblique deposition has columnar structure (diameter of columns 10-50 nm). Annealing of such film leads to formation of nc-Si in volume limited by column size, that is nc-Si of smaller size are forming. Film obtained by oblique deposition is porous (porosity up to 57%). In this work we investigated the influence of chemical treatment in ammonia and acetone vapor on PL spectra of porous nc-Si-SiOx structures. Oblique deposited films were treated by saturated vapour of acetone or ammonia before anneal. This chemical treatment leads to the considerable changes in PL spectra effecting as on the band shape as on intensity. A new intensive PL band (with peak position near 590 nm) appears after annealing in samples treated in ammonia, and with peak near 600-610 nm in samples treated in acetone vapor. IR transmission spectra of treated and annealed films demonstrates appearance of silicon nitrides bands (for samples treated in ammonia) and bands connected with carbonization (for samples treated in acetone). It is assumed that the changes in PL spectra is caused by modification of nc-Si-SiOx interface with N or C atoms. Replacement of oxygen in Si-SiOx interface by N or C modifies electronic structure of excitons involved in light emitting process. Shortwave band (590-610 nm) that appears after chemical treatment is blueshifted for 0,6 eV in comparison with nontreated samples. The value of 0,6 eV is in good agreement with other works where oxide matrix with embedded nc-Si was replaced by nitride or carbon matrix. Thus chemical treatments in ammonia and acetone vapor are efficient methods that allow to increase PL intensity of the silicon nanocrystals embedded in the oxide matrix and vary PL peak position in wide range from 560 to 950 nm.

Surface Science

Room: 608 - Session SS1-TuM

Catalytic Chemistry of Hydrocarbons

Moderator: B.E. Koel, Lehigh University

8:00am **SS1-TuM1 Impact of Surface Analysis in Hydrocarbon Catalysis: Examples from Industry**, ***A.S.Y. Chan***, *S.R. Bare*, UOP - Honeywell

Isomerization of straight chain alkanes to their branched isomers is an important industrial process to upgrade the octane value of gasoline. A solid acid catalyst that is effective for the isomerization of light alkanes is sulfated zirconia. In 1990, Sun Refining and Marketing Co. patented a modified sulfated zirconia catalyst containing transition metals (e.g. Mn, Fe) as promoters. More recently, in 2003, UOP patented an improved catalyst that was promoted by at least one lanthanide. In this talk, we will focus on the surface characterization of model sulfated zirconia catalysts that are Mn-promoted and lanthanide-promoted. By using a combination of X-ray Photoelectron Spectroscopy (XPS) and Low Energy Ion Scattering (LEIS), the location of promoters and their subsequent effect on the structure of the zirconia support will be elucidated. In addition, the accessibility of active metal and acid sites on these two promoted catalysts will be discussed. Finally, we will generalize the combined XPS and LEIS studies to provide a more complete picture of other catalytic systems: examples will be drawn from novel zeolites used in alkylation reactions, and Pd-based selective hydrogenation catalysts.

8:20am **SS1-TuM2 The Influence of Steps on the Adsorption, Fragmentation, and Reactions of Ethylene and Ethanol on Rh Surfaces**, ***J.N. Andersen***, *E. Lundgren*, *A. Resta*, Lund University, Sweden

We have used high resolution core level photoemission to study how the adsorption, fragmentation, and reaction of ethylene and ethanol are influenced by low coordinated atoms found at the steps of vicinal Rh surfaces. The talk is naturally divided in two parts. In part 1, we describe how detailed analysis of the C1s spectra including the vibrational fine-structure of this level often facilitates determination of the adsorbed fragments of these molecules. In part 2, we use this method of identification to monitor the influence of steps. This was done by comparing results from Rh(111) and some of its vicinals. For ethanol adsorption, we find large differences in the fragmentation pattern at 300K between the Rh(111) and the Rh(553) surfaces, in particular, the steps on Rh(553) are found to be very effective in dehydrogenation reactions. We also find differences in the oxidation of ethanol, where Rh(553) is found to be more reactive. For ethylene adsorption we have studied the temperature induced ethylidyne formation and subsequent decomposition. Also in this case do we find that the steps increase the reactivity regarding fundamental reactions involved in both the formation and the decomposition pathways. In addition, comparison between Rh(553) and Rh(322) demonstrated a larger reactivity of (100)-type than of (111)-type micro-facets. Finally, we discuss the importance of the present results in the context of catalytic reactions on small metal particles.

8:40am **SS1-TuM3 Mechanistic Insights on Fischer-Tropsch Synthesis**, ***M. Mavrikakis***, University of Wisconsin - Madison **INVITED**

First-Principles methods can provide useful information regarding detailed reaction mechanisms. In this talk, we will present our recent work on the early steps of Fischer-Tropsch synthesis on iron and cobalt based catalysts. A number of elementary reaction steps leading to CO dissociation and hydrogenation of carbon-containing species have been analyzed both in terms of their thermochemistry and minimum energy paths. A comparison between our results and recent experimental results on realistic FTS catalysts leads to some interesting conclusions, including the role of hydrogen in CO dissociation on Fe and Co catalysts, and the possible role of identified surface reaction intermediates in the FTS polymerization reaction.

9:20am **SS1-TuM5 H Induced CO Dissociation on Nickel Surfaces**, *M.P. Anderson, F. Abild-Petersen, J. Engbaek, O. Lytken, S. Horch, J.H. Nielsen,* Technical University of Denmark, *J. Sehested, J.R. Rostrup-Nielsen,* Haldor Topsoe A/S, Denmark, *J.K. Norskov,* ***I. Chorkendorff***, Technical University of Denmark

The dissociation of CO is both a model test reaction on clean single crystals and a relevant reaction step for industrial methanation. Much attention has therefore been dedicated to understanding the details of the mechanism. First of all, there seems to be a lack of consensus on whether CO can dissociate on Nickel at low temperatures (400 K) in a UHV experiment. In this work we have used a Ni(14,13,13) crystal which is mis-cut in such a way that there is an atomic step for each 26 terrace atoms. We show that CO (which has carefully been cleaned from $Ni(CO)_4$) does not dissociate unless the temperature is larger than 400 K and there are atomic steps present on the surface. If the steps are blocked by sulfur no dissociation could be measured under UHV conditions. The activation energy for dissociation is found to be 1.6 eV, which is slightly larger than that for desorption. This observation is found to corroborate with DFT calculations indicating a barrier for dissociation of 1.7 eV. This is, however, in contrast with the activation energy of 1.07 eV and 1.01 eV observed for the methanation reaction on single crystals and real supported catalysts, respectively. Furthermore, surprisingly small prefactors for those reactions have been reported in both cases. By investigating the possible pathways using DFT, a much lower barrier for CO dissociation of 1.08 eV was identified when considering a COH intermediate. By incorporating this intermediate in the reaction pathway, the low activation energy and low prefactors can be explained in terms of a COH intermediate dissociating on step sites both in the single crystal experiments and on the nanoparticles constituting the real catalysts. In the latter case the conclusion is further confirmed by investigations of the relation between the particle size and the catalytic rate, where a strong deviation from a simple surface area effect is found.

9:40am **SS1-TuM6 Density Functional Theory Study of the Interconversion between HCO (formyl) and COH Surface Reaction Intermediate on Pt(111)**, ***L. Arnadottir***, *E.M. Stuve,* University of Washington, *H. Jónsson*, University of Iceland

Two forms of the reaction intermediate with H:C:O stoichiometry were studied on Pt(111) using density functional theory. Three cases were studied: the intermediate on a clean surface, the intermediate and one water molecule on the surface and the intermediate with a water bilayer. Both the H-C=O (formyl) and C-OH configurations were found to be stable on clean Pt(111) and when coadsorbed with a water molecule. Interconversion between the two configurations was studied using the nudged elastic band method. On the clean surface interconversion between the two forms goes through a CO_{ads} and H_{ads} intermediate, meaning that although both HCO and COH are stable on the clean surface they will not interconvert. In the presence of coadsorbed water molecule the activation barrier for the interconversion from HCO to COH was found to be 0.62 eV. While the HCO configuration is stable in the presence of a water bilayer, the COH configuration dissociates to CO_{ads} and H_{ads}. These results suggest that, in the presence of water, the HCO form will be the only stable form of the reaction intermediate of H:C:O stoichiometry.

10:40am **SS1-TuM9 Enantioselectivity and Structure of Naturally Chiral Metal Surfaces**, ***A.J. Gellman***, *Y. Huang*, *L. Baker*, Carnegie Mellon University

The high Miller index surfaces of single crystal metals have chiral structures and have been shown to interact enantiospecifically with chiral adsorbates. There are many demonstrations of this phenomenon originating from several laboratories around the world. One specific example is the adsorption of R-3-methylcyclohexanone on Cu(hkl)$^{R\&S}$ surfaces. Several years ago we demonstrated that the adsorption of R-3-methylcyclohexanone on the Cu(643)$^{R\&S}$ surfaces was enantiospecific. The desorption energies of R-3-methylcyclohexanone adsorbed at R and S kinks differed and the orientation of the molecule at the R and S kinks differed. Over the past two years we have completed a study of the adsorption of R-3-methylcyclohexanone on a set of 16 single crystal surfaces spanning the entire stereographic projection. In spite of the complex variety of surface structures, we find that the adsorption sites on all surfaces can be classified as terraces, step and kink type sites and have adsorption energies for R-3-methylcyclohexanone that are quite distinct from one another. One of the important observations is that some of the nominally straight step edges such as those found on the Cu(410) surface exhibit behavior similar to that of the kinks on the Cu(643) surface. This arises because these (410) step edges are in fact quite rough and are not formed by close packed rows of atoms. Recent work has focused on the structure of chiral Cu surfaces. Molecular simulation by various other groups has demonstrated that the kinked step edges of these surfaces are roughened by annealing to high temperatures and that such step edges expose a variety of different kinks sites that are not found on the ideally terminated high Miller index surfaces. Scanning tunneling micrographs of these surfaces that have been reported by other groups bear out this description of the structure of the high Miller index surfaces. Over the past year we have developed the use of Xe TPD and Xe UV photoemission as a means of obtaining spectroscopic characterization of the kink step and terrace site densities on these surfaces.

11:00am **SS1-TuM10 Tunneling Contributions in β-Hydride Elimination of Ethyl Groups on Cu(111) and Cu(100) surfaces**, ***Y. Huang***, *A.J. Gellman*, *D. Sholl*, Carnegie Mellon University

Ethyl groups decompose into ethylene through the β-hydride elimination on Cu(111) and Cu(100) single crystal surfaces. Density Functional Theory calculations for β-hydride elimination of ethyl groups on Cu(111) and Cu(100) have been conducted by Sholl et al. These calculations suggested that hydrogen tunneling influences the kinetics of β-hydride elimination of ethyl groups on Cu(111) but not on Cu(100). Based on the calculations the Deuterium isotope effect in β-hydride elimination of ethyl groups should be greater on Cu(111) than on Cu(100). To verify this temperature programmed desorption (TPD) spectra of ethyl iodide and ethyl-2,2,2-d$_3$ iodide on both Cu(111) and Cu(100) were obtained. The pre-exponential and activation barrier to β-hydride elimination reactions were determined and compared on both Cu(111) and Cu(100) surfaces.

11:20am **SS1-TuM11 CO Chemisorption on Cu(111) via Embedded Configuration Interaction Theory**, ***S. Sharifzadeh***, *P. Huang*, *E.A. Carter*, Princeton University

Although density functional theory (DFT) is often considered the electronic structure method of choice to study surfaces, situations exist where DFT fails, e.g. strongly correlated electrons and descriptions of unoccupied states. As an example, CO adsorption on Cu(111) is poorly described within DFT because the CO bond to Cu(111) involves Cu back-donation to the empty CO 2pi* orbitals, which are at too low an energy in DFT, leading to an overestimation of pi back-bonding. Measurements at low coverage are consistent with on-top site CO adsorption on Cu(111), whereas pseudopotential-based DFT methods predict hollow site adsorption, due to the overestimation of the importance of pi-back-bonding. In this work, we study CO/Cu(111) with a density-based embedding strategy, where a local region of interest, described by accurate ab initio quantum chemistry calculations, is embedded into a background described by DFT. The region of interest is represented by a cluster of atoms that includes CO and nearby metal atoms. A self-consistent, DFT-based embedding potential accounts for the effect of the background on this cluster. Since ab initio quantum chemistry methods, e.g. configuration interaction (CI), give a better description of the CO LUMO, we expect an improvement on the description of CO chemisorption. We will present site preferences and adsorption energies from embedded CI, as well as comparing to periodic DFT and finite cluster calculations.

11:40am **SS1-TuM12 Mechanistic Insights Into Methane Activation from State-Resolved Beam-Surface Scattering Measurements**, ***A.L. Utz***, *D.R. Killelea*, *V.L. Campbell*, *D.F. Del Sesto*, *N.S. Shuman*, Tufts University

State-resolved surface scattering experiments provide detailed insight into the mechanistic basis for methane activation. We use infrared laser excitation of molecules in a supersonic molecular beam to prepare reagents with a well-defined internal and translational energy. The state-resolved reaction probabilities that we measure reveal which molecular motions (methane stretching and bending, translation, and surface atom motion) best promote reaction. Earlier work in our lab has shown that on Ni(111), C-H stretching excitation is significantly more effective than translational energy or bending excitation in promoting methane dissociation. Recent measurements demonstrate our ability to exert bond-selective control over methane dissociation. We excite the C-H stretch in CHD$_3$ and detect exclusively reaction products from the C-H bond cleavage channel. In contrast, thermal excitation of CHD$_3$ vibrations leads to a preference for C-D bond cleavage. This observation contradicts statistical pictures of gas-surface activation and indicates that energy exchange during direct dissociation is not complete on the timescale of reaction. The presentation will highlight recent experimental results from our lab, discuss how these results teach us about the reaction coordinate for methane activation, and explore how limited energy flow during reaction impacts our understanding of the energetics of hydrocarbon activation.

12:00pm **SS1-TuM13 Preparation of Nickel Nanoparticles and their Catalytic Activity in the Cracking of Methane.**, ***J.C. De Jesus***, *I. Gonzalez*, PDVSA-Intevep, Venezuela, *M. Garcia*, *C. Urbina*, Universidad Central de Venezuela

In this study, a facile method for the preparation of nickel nanoparticles is employed to investigate the catalytic decomposition of methane into carbon nanotubes. Nickel acetate tetrahydrate decomposes readily below 350°C to form metallic nanoparticles (average size 10-80 nm), and weight changes measured inside a thermogravimetric analyzer (TGA) in methane streams can be related quantitatively to the production of carbon nanotubes by catalytic cracking. C to Ni atomic ratios (C/Ni) estimated directly from TGA data provided a systematic approach to study in-situ the catalytic activity of the nickel nanoparticles. Methane cracking starts at temperatures as low as 400°C and continues efficiently until approximately 600°C. Between 600°C and 660°C, methane decomposition momentarily breaks off, while presumably the catalytic system undergoes a self-reorganization. Cracking resumes at 660°C and continues slowly up to 950°C. The amount of carbon deposited in the 600-660°C interval shows a lineal dependence with methane concentrations, with C/Ni ratios ranging from 6 to 31. Transmission electron microscopy (TEM) images of the different C/Ni residues collected at 660°C showed that during cracking narrower carbon nanotubes are produced at elevated methane concentrations, suggesting dispersion of nickel nanoparticles.

Surface Science

Room: 611 - Session SS2-TuM

Surface Structure and Growth on Metals

Moderator: T. Risse, Fritz-Haber-Institut der MPG, Germany

8:00am **SS2-TuM1 Crystalline Structure of Sn/Cu(100) Across a Surface Phase Transition**, ***J. Martínez-Blanco***, *V. Joco*, Universidad Autónoma de Madrid, Spain, *C. Quirós*, Universidad de Oviedo, Spain, *P. Segovia*, *E.G. Michel*, Universidad Autónoma de Madrid, Spain

The crystalline structure of 0.5 monolayer of Sn atoms adsorbed on Cu{100} has been studied by surface X-ray diffraction (SXRD) measurements. This surface undergoes a temperature-induced phase transition at 360 K from a single domain $(\sqrt{2} \times \sqrt{2})R45°$ phase at high temperature to a two rotated domains $(3\sqrt{2} \times \sqrt{2})R45°$ phase at low temperature. In a previous work[1] this phase transition was identified as being due to the stabilization of a charge density wave (CDW), with gapping of nested regions of the high temperature Fermi surface in excellent agreement with the CDW periodicity. We performed temperature-dependent SXRD measurements in order to obtain information on the atomic displacements across the phase transition and to understand the nature of the two phases observed. A full data set including in-plane reflections, superstructure rods and crystal truncation rods was measured for each phase. The optimization method employed for fitting the experimental data for both the high and low temperature phases is a type of genetic algorithm called Differential Evolution,[2] used in this work for the first time to extract crystallographic information from SXRD data. For the low temperature phase, we compare the model obtained with a previous surface structure model.[3] Our results confirm the removing of every third row of copper in the alloyed top layer and a concomitant pairing of Sn atoms as the origin of the triple periodicity. However, we obtain slightly different values for the atomic displacements in deeper layers. For the high temperature phase, the overall dependence of the measured structure factors with the perpendicular momentum transfer is similar to the values extracted from the low temperature phase, suggesting a disordered nature for the high temperature phase. We propose a detailed model for this phase and for the nature of the thermal induced disorder. We discuss possible mechanisms to keep the local structure across the phase transition and the nature of the high temperature disordered phase.

[1] J. Martínez-Blanco et al., Physical Review B, 72 (2005), 041401(R)

[2] M. Wormington et al., Phil. Trans. Roy. Soc. London Sers A, 357 (1999), 2827-2848

[3] K. Pussi et al., Surface Science, 549 (2004), 24-30.

8:20am **SS2-TuM2 Self-assembled MnN Superstructure on Cu(001) Surface**, *X. Liu, B. Lu, T. Iimori, **K. Nakatsuji**, F. Komori*, University of Tokyo, Japan

Recently, self-assembled nanostructures have attracted tremendous interest. Among them, the ones with regular spatial array, uniform and well-defined geometric and structural characters, are especially desirable. However, it is still difficult to prepare such high-quality nanostructures. In the present paper, we describe the fabrication of self-assembled manganese nitride nano-islands on the Cu(001) surface and propose a new mechanism of the nano-self-assembling.[1] Each island shows a square shape and has a well-defined size of 3 nm x 3 nm. They are regularly arranged with a periodicity of (3.5 ± 0.1) nm and form a two-dimensional square superstructure. The depth of the trench between the islands is the same as the step height of the surface or the height of the island on the superstructure. The nano-islands adopt a NaCl-like structure which is oriented in the same way as the fcc Cu(001) substrate. They are reproducibly prepared in three steps in ultrahigh vacuum by mono-atomic layer of Mn deposition, atomic nitrogen exposure to the saturation and gradual annealing up to 630 K. The stoichiometry of the manganese nitride islands has been studied by in-situ X-ray photoelectron spectroscopy. It is determined that the formula of the manganese nitride is MnN. This stoichiometry is the same as that of the bulk MnN crystal, which has a face-centered tetragonal structure (distorted NaCl structure) with a lattice constant lager than that of Cu(001).[2] Thus, the nanostructure formation is attributed to strain-relief at the interface. However, different from the conventional stress-domain dominated self-assembly, the shape, size, and periodicity of the MnN islands do not change even when they coexist with the clean Cu(001) surface. This indicates that the self-assembling is driven not by the long-range strain relief, but by a short-range mechanism.

[1] X. Liu, B. Lu, T. Iimori, K. Nakatsuji and F. Komori, Phys. Rev. Lett. 98, 066103 (2007).

[2] K. Suzuki, T. Keneko, H. Yoshida, Y. Obi, H. Fujimori, and H. Morita, J. Alloys Comp. 306, 66 (2000).

8:40am **SS2-TuM3 Surface Morphology and Step Fluctuations on Ag Nanowires**, ***C.G. Tao****, *W.G. Cullen, E.D. Williams*, The University of Maryland, College Park, *S.E. Hunyadi, C.J. Murphy*, The University of South Carolina

Semiconducting and metallic nanowires have been the subject of intense research efforts for their potential applications in nanoscale electrical circuits and chemical sensors. For all the applications, and especially for sensors, the morphological and thermodynamic nature of the nanowire surfaces, including the presence of defects like steps and twin boundaries, play a crucial role in the functional response. Even though there have been many demonstrations of nanowire applications, extremely few studies directly address the issues of cleanliness and structural morphology of the surfaces of nanowires at the atomic scale. Here we will present the surface morphology and thermodynamic properties of Ag nanowires, characterized by scanning tunneling microscopy (STM) at room temperature. The Ag nanowires were prepared via a seedless, surfactantless wet chemical synthesis process and suspended in water. They then are redispersed into methanol by centrifugation, and are deposited onto atomically clean Ag thin films in ultra-high vacuum via a solution deposition method. By gently annealing the samples, methanol on the substrate and the surfaces of Ag nanowires is removed. The STM topography images reveal the facets of the penta-tetrahedrally twinned crystals which constitute the Ag nanowires, and sawtooth features of the boundaries of neighboring twinned crystals. On the facets, frizzy monatomic steps and rectangular shapes monolayer islands are clearly observed. Using a dynamic STM scan method, we obtain quantitative properties of step fluctuations, which are governed by periphery diffusion. Combing previous density functional theory (DFT) calculations and dynamics studies on low-index faces of Ag, we propose that the side facets are Ag(100) surfaces. Related studies about the time evolution of the twin boundaries and how the surface defects are associated with the electrical current flowing through the nanowires will also be discussed. --Supported by the NSF MRSEC (DMR 05) at the University of Maryland.

9:00am **SS2-TuM4 Capture-Zone Scaling and Universal Fluctuation Phenomena**, ***T.L. Einstein***, University of Maryland, *A. Pimpinelli*, Univ. of Maryland & U. Blaise Pascal--Clermont 2, France

As one approaches the nanoscale, fluctuations play an ever more important role in the physics of systems. Universal aspects of fluctuations are thus an especially timely topic. The Wigner distribution from random matrix theory has successfully described a vast array of physical phenomena, from energy spacings between nuclear levels to conductance fluctuations in wires, as well correlations of stock prices, spaces between parked cars, and times between successive unscheduled buses. It is easy to use, having the simple, one-parameter form a s^{β} exp $(-bs^2)$ [with a and b being constants assuring normalization and unit mean, and s the fluctuating variable divided by its mean]. Here we apply this approach to the long-standing problem of island-size distributions during growth. We consider the distribution of the areas of Voronoi polygons (proximity cells) around nucleation centers, i.e. the capture zones (CZ). Generalizations of the Wigner distribution (to allow more than the 3 values of β based on symmetry) account well for data generated in kinematic Monte Carlo studies by several groups, much as it did for terrace-width distributions (TWD) on vicinal surfaces. For CZ distributions we find $\beta = i + 1$, where i is the size of the critical nucleus. (In spatial dimension $d = 1$, $\beta = 2(i + 1)$.) We demonstrate excellent fits of numerical data for both $d = 1$ and $d = 2$. To clarify the underlying physics, we present a phenomenological derivation by constructing a Langevin equation similar to that used in accounting for the equilibration of TWDs; we discuss the competing forces that lead to the WD. Our expression also describes well experimental data for pentacene adsorption and for CZ distribution of growing quantum dots. We compare this analysis with others using less-well-motivated Gamma distributions or more complicated expressions.

Work at UMD supported by the MRSEC, NSF Grant DMR 05-20471. Visits to UMD by AP supported by a CNRS Travel Grant, and TLE partially supported by DOE CMSN grant DEFG0205ER46227.

9:20am **SS2-TuM5 Sulfur Adsorption on Ag(111): Self-Organization of Metal-Sulphur Complexes below 300K**, ***M. Shen***, Iowa State University, *D.-J. Liu, C.J. Jenks, J.W. Evans, P.A. Thiel*, Ames Laboratory - USDOE, Iowa State University

We have investigated the interaction of sulfur with Ag(111). Sulfur was deposited using an electrochemical evaporator, which generated gas-phase sulfur in the form of S_2. Sulfur coverage was measured with Auger electron spectroscopy.[1] Images from scanning tunneling microscopy (STM) showed different structures at temperatures between 135 and 300 K. Deposition at 135 K led to the formation of two-dimensional (2D) islands. After heating to 200 K, the surface exhibited a quasi-1D "dot-row" structure, in which each dot was about 0.7 nm in diameter. The dots were aligned in rows that were separated by distances ranging from about 1.6 to 5 nm. Cooling back to 135 K did not restore the initial 2D island structure, indicating that the 2D islands may consist of S_2 that dissociates irreversibly in the heating step. At 300 K, no ordered structures were visible, suggesting that the adsorbate becomes very mobile. The STM observations at 300 K and 200 K could be produced reversibly, pointing to a reversible phase transition below room temperature. Development of the dot-row structure at high S coverage was accompanied by pitting on the terraces, indicating participation of Ag. DFT calculations show that Ag_3S_3 is a candidate for the dots. This complex is analogous to a metal-sulfur complex that has been proposed to exist on Cu(111).[2]

[1] K. Schwaha, N.D. Spencer, R.M. Lambert, Surf. Sci., 81, 273 (1979).

[2] P.J. Feibelman, Phys. Rev. Lett., 85, 606 (2000).

9:40am **SS2-TuM6 Structure of the Al(100)-c(2x2)Ti Surface***, ***M. Kopczyk***, *W. Priyantha, H. Chen*, Montana State University, *D. Tonn*, Balwin-Wallace Collage, *R.J. Smith*, Montana State University, *D.S. Choi*, Kangwon National University, Korea, *G. Bozzolo*, Ohio Aerospace Institute

The atomic structure of sub-monolayer amounts of Ti deposited on the Al(100) surface at room temperature has been studied using low-energy electron diffraction (LEED) and low-energy ion-scattering spectroscopy (LEIS/ ISS). The Ti coverage was determined using Rutherford backscattering spectroscopy. From the symmetry of the observed c(2x2) LEED images we infer a structure which places the Ti atoms in every other Al unit cell. Analysis of the LEIS spectra, including both azimuth- and polar-angle scans, corroborates this hypothesis. This conclusion is relevant

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* Morton S. Traum Award Finalist

to recent studies of Ti as a catalyst in Na alinates presently being studied for their use in hydrogen storage applications important in fuel cell research.

*This work was supported by the National Science Foundation, NSF Grant DMR 0516603.

10:40am **SS2-TuM9 Hard Superconductivity in Soft Quantum Films,** ***H.H. Weitering***, University of Tennessee **INVITED**

Superconductivity is inevitably suppressed in reduced dimensionality. Questions of how thin superconducting wires or films can be before they lose their superconducting properties have important technological ramifications and go to the heart of understanding coherence and robustness of the superconducting state in quantum-confined geometries. In this talk, I will show how quantum confinement of itinerant electrons in a soft metal, Pb, can be exploited to stabilize superconductors with lateral dimensions of the order of a few millimeters and vertical dimensions of only a few atomic layers. These extremely thin superconductors show no indication of defect- or fluctuation-driven suppression of superconductivity and sustain enormous supercurrents of up to 10% of the theoretical depairing current density. Their magnetic hardness implies a superconducting critical state with strong vortex pinning that is attributed to quantum trapping of vortices. Our study paints a conceptually appealing, elegant picture of a model nanoscale superconductor with calculable critical state properties and surprisingly strong phase coherence. Finally, I will show how the quantum growth and superconductive properties of the films can be tailored by Fermi surface engineering, and I will discuss the possibility of multi-gap superconductivity in quantum-confined thin films. This work was done in collaboration with M.M. Ozer, J.R. Thompson, Yu Jia, and Z.Y. Zhang.

11:20am **SS2-TuM11 Initial Bilayer-by-Bilayer Growth of Ag Islands on NiAl(110): DFT Analysis of underlying Quantum Size Effects**, ***Y. Han***, *D.-J. Liu, B. Unal, F. Qin, C.J. Jenks, J.W. Evans, P.A. Thiel*, Iowa State University

Growth of Ag on NiAl(110) is distinguished by an almost perfect match of the lateral unit cell of the substrate to that of Ag(110). Thus, Ag/NiAl(110) provides an ideal system in which to study morphological evolution during heteroepitaxy in the absence of lateral mismatch strain. Our STM studies reveal the nucleation and growth of large rectangular Ag islands for deposition of submonolayer amounts of Ag between 130K and 300K. Subsequent deposition produces smooth growth with large rectangular islands forming on top of coalesced clusters of such lower layer islands. However, the step height for the first layer islands is ~0.33 nm, and only slightly lower at ~0.29 nm for the next two layers. These values far exceed the step height of ~0.15 nm for Ag islands on Ag(110). Thus, we propose that islands have a predominantly bilayer Ag(110) structure for the first three (bi-) layers. This claim is supported by DFT calculations which reveal step heights for this structure in close agreement with experiment, and also indicate that the driving force for this bilayer growth is the presence of a quantum size effect perpendicular to the surface plane for electrons confined in the Ag film. Specifically, there is a strong oscillation of period 2 monolayers (ML) in the surface energy, and also in the binding energy of single Ag atoms on top of flat Ag films, favoring film heights equal to an even number of monolayers. For thicker films, step heights decrease so film structure must deviate from the perfect Ag(110) bilayer structure (a feature also reflected in a weak height modulation across the tops of Ag islands).

11:40am **SS2-TuM12 Role of Surface Structure on Thin Film Nucleation on Quasicrystal Surfaces**, ***B. Unal****, Ames Lab., Iowa State Univ., *V. Fournee,* CNRS-UMR7584, France, *K.J. Schnitzenbaumer, C. Ghosh,* Iowa State Univ., *C.J. Jenks,* Ames Lab., Iowa State Univ., *A.R. Ross,* Iowa State Univ., *T.A. Lograsso,* Ames Lab., Iowa State Univ., *J.W. Evans,* Iowa State Univ., *P.A. Thiel*, Ames Lab., Iowa State Univ.

Quasicrystals are non-periodic but well-ordered solids. Their unusual atomic structures foster peculiar surface properties such as low friction and enhanced oxidation resistance. Using scanning tunneling microscope (STM) we have investigated clean surfaces of icosahedral (i) Al-Pd-Mn quasicrystals. By analyzing bulk structural models of i-Al-Pd-Mn quasicrystals, we suggest a relationship between the terminating layers and the clusters that form the basic building blocks of quasicrystals. Using STM, we have also investigated the nucleation and growth of Ag islands on the fivefold surface of an i-Al-Pd-Mn quasicrystal. The temperature dependence of island density suggests that trap sites control nucleation of Ag islands. We identify these trap sites as the cut clusters in the aforementioned structure analysis. Furthermore, we have developed a mean field rate equation model to explain this behavior. Our model suggests that the binding energy between Ag atoms at traps are significantly higher than that of Ag at regular terrace sites and the size of critical clusters is larger than one. This model will allow (qualitative) manipulation of experimental parameters to tailor island characteristic on quasicrystal surfaces.

12:00pm **SS2-TuM13 A Photoelectron Diffraction Study of $Cu_3Mn(100)$,** ***J. King-Lacroix,*** *N. Loh, D.-H. Yu, A.P.J. Stampfl,* Australian Nuclear Sci. and Tech. Org., *H. Ruppender, H. Over,* Justus-Liebig-Univ. Gießen, Germany, *E. Huwald, J.D. Riley,* La Trobe Univ., Australia, *A. Smith,* Monash Univ., Australia, *L.-J. Fan, Y.-W. Yang*, National Synchrotron Radiation Res. Ctr., Taiwan

In the Angstrom to nanoscale regime where electronic localisation blurs to itinerant behaviour, magnetic phenomena become highly dependent on dimensionality and local environment. Magnetic exchange between two different magnetic phases is one such phenomenon that is affected when dimensions are reduced to the nanoscale. We are specifically interested in studying the exchange properties at the interface of an antiferromagnetic or ferromagnetic material and a spin glass surface. Our first task however is to fully understand a spin-glass surface by mapping out the surface and bulk band structure as well as determine the surface crystalline structure. We have chosen the CuMn system because it represents a model spin-glass whose transition temperature is easily attainable. The bulk phase-diagram for the CuMn system displays a face-centered-cubic phase at room temperature for atomic percent concentrations of Mn from 0 to ~25% and the spin-glass transition temperature for CuMn in this percentage region increases linearly to ~110K at 25%at. Mn. We present here synchrotron-based azimuthal-scanned photoelectron diffraction measurements using the Cu and Mn 3p-orbitals from a $Cu_3Mn(100)$ surface and compare them to simulation and to corresponding data sets for Cu(100). The number of Mn-atoms in the upper-most layer is lower than expected from a truncated bulk surface suggesting surface segregation or oscillatory behaviour. Details of surface reconstruction and near-surface relaxation will be presented.

Thin Film

Room: 613/614 - Session TF-TuM

Two-Dimensional Carbon Nanostructures

Moderator: B.C. Holloway, Luna Innovations Incorporated

8:00am **TF-TuM1 Study of Growth Process and Structures of Carbon Nanowalls Synthesized Using Radical Injection Plasma Enhanced CVD**, ***S. Kondo,*** Nagoya University, Japan, *K. Yamakawa,* Katagiri Engineering Co., Ltd., Japan, *M. Hiramatsu,* Meijo University, Japan, *M. Hori*, Nagoya University, Japan

Carbon nanostructures, such as fullerene, carbon nanotubes and carbon nanowalls (CNWs) have received great attention for several applications, due to their outstanding physical, chemical and mechanical properties. Among a variety of nanocarbons, CNWs are considered as two-dimensional carbon nanostructures. CNWs are the graphite nanostructure with edges, which comprise the stacks of plane graphene sheets standing almost vertically on the substrate, forming a unique nanostructure similar to a maze with high aspect ratio. The large surface area and sharp edges of CNWs are useful as templates for the fabrication of other types of nanostructured materials, which have potential various applications such as in energy storage and electrodes for fuel cell as well as an electron field emitter. We have successfully synthesized CNWs using the radical injection plasma enhanced chemical vapor deposition (RI-PECVD) employing C_2F_6 and H_2 gases. The system consists of a parallel-plate capacitively coupled plasma (CCP) region and a surface wave microwave excited H_2 plasma (H_2-SWP) region over the CCP. Using this system, the heated substrate was showered with fluorocarbon radicals as well as plenty of H atoms in a controlled manner. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism and to control their structures and properties. Furthermore, it would be useful to investigate the etching characteristics of CNWs for the modification of CNWs structure or pattern transfer of CNWs to other materials. CNWs were evaluated by Raman spectroscopy, TEM, ellipsometry and XPS measurements. In the initial stage of CNWs growth on a Si substrate by RI-PECVD, we have confirmed that a thin layer of approximately 10 nm in thickness was deposited in the first 1 min, and subsequently CNWs grew in the vertical direction from a lot of nuclei on this thin film. This thin film was found to be amorphous carbon with a little amount of fluorine. The CNWs film with the bottom amorphous carbon layer was exfoliated from the Si substrate. Both sides of the detached CNWs film were etched by Ar/H_2 plasma. The etching rates of CNWs and amorphous carbon thin film were 140 and 15 nm/min, respectively. It is noted that after the removal of amorphous carbon thin film, the morphology of the CNWs was still maintained on the backside, resulting in the formation of free-standing CNWs filter or membrane.

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* Morton S. Traum Award Finalist

8:20am **TF-TuM2 Evaluation and Control of Electric Conduction of Carbon Nanowalls Fabricated by Plasma-Enhanced CVD**, ***W. Takeuchi**, M. Ura,* Nagoya University, Japan, *Y. Tokuda,* Aichi Institute of Technology, Japan, *M. Hiramatsu,* Meijo University, Japan, *H. Kano,* NU Eco-Engineering Co.,Ltd., Japan, *M. Hori*, Nagoya University, Japan

Carbon nanowalls (CNWs), two-dimensional (2-D) carbon nanostructure, consisting of graphite sheets standing vertically on the substrate, have attracted much attention for several applications, including field emitter arrays, gas storage, and membranes for electrochemical energy storage. Recently, it was reported that 2-D multilayer graphene sheet offers high mobility and huge sustainable currents. Therefore, CNW films potentially would possess high mobility and huge sustainable current density, since the CNWs are basically graphene sheet. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism and to control their structure and properties. In this study, we focused on the evaluation and control of electric properties of CNWs. CNWs were fabricated on the quartz substrate by the plasma enhanced CVD with H radical injection employing a mixture of C_2F_6/H_2. We investigated the influence of N_2 or O_2 addition to the process gas mixture on the morphology and electric properties of CNWs. Hall measurement and Raman spectroscopy were used to evaluate the electric properties and structure of CNWs. The Hall coefficient was positive for the CNW film grown without additives. When O_2 was added to the plasma, it was still positive. In the case of N_2 addition, it displayed negative value. The positive or negative value of the Hall coefficient implies p- or n-type, respectively. Therefore, it was found that the conduction type of CNW films was controllable by adding N_2 or O_2 to the C_2F_6/H_2 plasma. Morphology and crystallinity of CNWs were also changed by the addition of N_2 and O_2. In the Raman spectroscopy, all samples have a strong peak at 1590 cm^{-1} (G-band) indicating the formation of a graphitized structure, and another peak around at 1350 cm^{-1} corresponding to the disorder-induced phonon mode (D-band). The G-band width in the Raman spectrum increased when N_2 was added. In the case of O_2 addition, G-band width and peak intensity ratio of D band to G band of CNWs decreased. These results indicate that nitrogen would be included in CNWs and act as a donar, while accompanied by the slight degradation of graphite crystallinity. On the other hand, oxygen would play a role of etching of amorphous carbon content and contribute to the higher graphitization, while conduction type of CNW films would not change.

8:40am **TF-TuM3 Low Temperature Deposition of Carbon Nanosheets by C_2H_2/H_2 Plasma Enhanced Chemical Vapor Deposition**, ***M.Y. Zhu**, R.A. Outlaw, K. Hou, P. Miraldo, D. Manos*, College of William and Mary

Two-dimensional carbon nanosheets were previously deposited by radio frequency plasma enhanced chemical vapor deposition (PECVD) using CH_4/H_2 plasma on a variety of substrates. In this work, we report the deposition of the same nanostructure using C_2H_2/H_2 plasma at a substrate temperature more than 100 ºC lower than that for typical depositions using CH_4/H_2 plasma. The decrease of required substrate temperature is a great benefit to device fabrications. Carbon nanosheets were deposited on silicon substrates at temperatures ranging from 500 ºC to 600 ºC while other parameters were 100% C_2H_2 gas (5 sccm total gas flow rate), 35 mTorr gas pressure, 1000 W input RF power, and 10 minutes deposition duration. For substrate temperature from 550 ºC to 600 ºC, the carbon nanosheets deposited have sheet-like structures and flat surface morphologies, and are free-standing on substrate surfaces, as characterized by scanning electron microscope (SEM). High-resolution transmission electron microscopic (HR-TEM) results revealed that the edges of the nanosheets consist of about 3-8 atomic layers. Selected area electron diffraction pattern of carbon nanosheet samples matches that for polycrystalline graphitic structures. Raman spectra of carbon nanosheets have the characteristic D and G peaks for defective sp^2 graphitic structures. Detailed results showed faster growth rates and high Raman D/G peak ratios for samples deposited at higher substrate temperatures. Carbon nanosheets were also deposited using various (60-100%) C_2H_2 in H_2 concentrations while other parameters were fixed at 600 ºC substrate temperature, 5 sccm total gas flow rate, 1000 W input RF power, and 10 min deposition duration. With a decreasing C_2H_2 in H_2 concentration, both the nanosheet growth rate and the Raman D/G ratio were decreased, however, the basic nanosheet structures were maintained. Cross-sectional SEM images showed that carbon nanosheets deposited using C_2H_2/H_2 gas mixture have a straighter vertical orientation and a more uniform sheet height distribution than those deposited using CH_4/H_2 mixture, therefore are expected to have improved field emission properties. Field emission from C_2H_2/H_2 carbon nanosheets are measured under diode configuration and the results will also be presented.

9:00am **TF-TuM4 Field Emission Performance of Carbon Nanosheets**, ***K. Hou**, R.A. Outlaw,* College of William and Mary, *M.E. Kordesch,* Ohio University, *M.Y. Zhu, P. Miraldo,* College of William and Mary, *B.C. Holloway,* Luna Innovations Incorporated, *D. Manos*, The College of William and Mary

Carbon nanosheet, a novel two-dimensional carbon nanostructure consisting of vertically oriented ultra-thin graphitic sheets terminating with 1-3 graphene layers, are fabricated by inductively coupled radio frequency plasma enhanced chemical vapor deposition. Carbon nanosheet, with its atomic-scale edge structure, high purity, and uniform height distribution have been confirmed to be a promising candidate for the application as the cold cathode material in vacuum electronic devices. In this study, we present the latest field emission test results of carbon nanosheet thin film including total current, lifetime in a slow pulse mode, and lifetime in a dc mode. These tests were conducted using a diode configuration having an anode-cathode distance of 254 µm. Further, the emission uniformity of carbon nanosheet thin films was primarily studied by photoelectron emission microscopy. To date, we have routinely achieved total currents of more than 20 mA from ~30 mm^2 while maintaining a useful current density of ~0.1 A/cm^2. Among them, a maximum total current of 26 mA has been measured from a 32 mm^2 testing area at an applied electric field of 25.5 V/µm. The test result suggests that the field emission of nanosheet film is not saturated at this field level but is limited by the test apparatus. The lifetime in a slow pulse mode was conducted by applying a series of identical voltage ramps over a long time period with a duty factor of 21%. The maximum current on the order of 13 mA in each voltage ramp was recorded for 96 hours. The test result reveals that the standard deviation of the maximum is less than 2.1%. The lifetime in a dc mode was conducted by applying a constant negative bias to the sample. A stable ~1.5 mA emission current was obtained from the carbon nanosheet thin film for 200 hours. The standard deviation of the emission current is less than 3.6% during the test period. Photoelectron emission microscopy was used to investigate the field emission uniformity over the surface of carbon nanosheet thin films. In addition, field emission electron microscopy images, formed without photon illumination, were also captured. The analysis of these images show that a small number of nanosheet emission sites dominate the emission current.

9:20am **TF-TuM5 Enhanced Field Emission from Mo_2C Coated Carbon Nanosheets**, ***M. Bagge-Hansen**, P. Miraldo, R.A. Outlaw, M.Y. Zhu, M. Hou, D. Manos*, College of William and Mary

Carbon nanosheets, a new morphology of graphite, have shown remarkable promise as field emission cathodes for applications such as microwave tubes and flat panel displays. The sharp emission edges of the sheets are typically 1-3 graphite sheets thick (~1 nm) and thus provide a superior geometry for field emission enhancement. Fowler-Nordheim theory suggests further field emission enhancement is possible by lowering the work function. The effective work function of carbon nanosheets, previously undetermined, was calculated and found to be analogous to that of graphite, 4.8 eV. By applying a thin film coating of Mo_2C ($\Phi = 3.5$ eV), the field enhancement factor from the geometry, ß, was reduced by only a factor of two, yet field emission current substantially increased. A molybdenum coating was deposited on a carbon nanosheets sample by physical vapor deposition in very high vacuum (p ~1x10^{-8} Torr) and determined to be ~3 monolayers thick by Auger electron spectroscopy. The coated sample was radiatively heated to T~250°C to promote molybdenum reaction with adventitious carbon found in defects of the carbon nanosheets' emission edges and the underlying graphite structure. Auger electron spectroscopy and scanning electron microscopy were used to verify the composition and conformity of the coating, respectively. Field emission testing in an ultrahigh vacuum (p ~5x10^{-10} Torr) diode assembly with 250 µm spacing showed lowering of the effective work function after the coating procedure and consequently, increased emission current. At an applied field of 9 V/ µm, the emission current was found to be 100 µA compared ~0.1 µA for the carbon nanosheets. A comparison of linear ($R^2 = .999$) Fowler-Nordheim plots of coated and uncoated samples yielded values for the work function of uncoated CNS and the fractional emitting area of ~2% for carbon nanosheets. The experimental data of Mo_2C-coated CNS was significantly more repeatable and stable than the uncoated CNS.

9:40am **TF-TuM6 Production of Large Area Graphene Sheets by Si Desorption from SiC**, ***G.G. Jernigan**, J.C. Culbertson, B.L. VanMil, K.K. Lew, R.L. Myers-Ward, D.K. Gaskill, P.M. Campbell, E.S. Snow*, U.S. Naval Research Laboratory

With DeHeer's[1] initial report of graphene formation by the thermal desorption of Si from SiC, efforts have been underway to use this method to make large area sheets of graphene for device fabrication purposes. Mobility measurements of graphene on SiC, however, have not approached the values obtained with graphene exfoliated from graphite, indicating that material issues and other factors may be affecting the quality of graphene from SiC. We will report on our efforts to produce large area graphene sheets using 2- and 3-, Si-face, 4H and 6H SiC wafers. Using x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), atomic force microscopy (AFM), Raman spectroscopy, and electrical characterization, we have studied graphene sheets and graphite films formed on SiC by Si desorption in ultra-high vacuum (UHV). The wafers were initially subjected to hydrogen etches at 1400 °C and 1580 °C to remove polishing damage and to produce smooth surfaces prior to entrance into UHV. XPS measurements show the hydrogen-etched surfaces are initially covered by an oxide, which can be desorbed at 1000 °C in UHV resulting in a surface containing excess Si. At ~1300 °C, the surface becomes stoichiometric in Si and C and a √3 x √3 R30 LEED pattern is observed. At ~1350 °C, we observe a 6√3 x 6√3 R30 LEED pattern develop when graphene has formed, and a 1x1 LEED pattern for graphite films formed at temperatures greater than 1400 °C. AFM images show that the process of Si desorption from the surface results in the formation of hexagonal pits and that the liberation of carbon onto the surface produces the graphene layer. As more Si is desorbed from the surface, the carbon forms into 3-dimensional islands with a hexagonal shape. Interestingly, the sheet conductance remains constant while the islands coalesce into a thick graphite layer. Raman spectroscopy of the graphene sheets is complicated by strong transitions from the underlying SiC substrate. Nonetheless, D, G, and D' lines can be distinguished, and their intensities are observed to increase with increasing sheet thickness. The frequency of the D' line can also be used to distinguish the formation of graphene and graphitic material. We will discuss how process parameters affect the graphene quality as judged by the multiple techniques.

[1] J. Phys. Chem. B 108, 19912-19916 (2004).

10:40am **TF-TuM9 Epitaxial Graphene - A New Paradigm for Nanoelectronics*, W.A. de Heer***, Georgia Institute of Technology **INVITED**

Multilayer graphene grown on single-crystal silicon carbide by vacuum decomposition is a promising material for nanoelectronics. The material can be patterned using standard nanolithography methods. The transport properties, which are closely related to those of carbon nanotubes, are dominated by a single graphene layer at the silicon carbide interface. This epitaxial layer reveals the Dirac nature of the charge carriers. Unlike graphite, multilayer graphene is electronically related to single layer graphene with an anomalous Berry's phase as evidenced from transport measurements, from infrared absorption measurements and from Raman scattering measurements. Patterned structures show quantum confinement of electrons and phase coherence lengths beyond one micrometer at 4K, with mobilities exceeding 25000 cm2/Vs. These parameters suggest that all-graphene electronically coherent devices may be possible. Recent developments will be discussed including epitaxial graphene FETs.

11:20am **TF-TuM11 Rotational Stacking of Graphene Films Grown on 4H-SiC(000-1)*, J. Hass***, *J.E. Millán-Otoya, M. Sprinkle, X. Li,* The Georgia Institute of Technology, *F. Varchon, L. Magáud,* LEPES-CNRS, France, *P.N. First, E.H. Conrad*, The Georgia Institute of Technology

The presence of Dirac electrons and micron scale coherence lengths have been demonstrated in multi-layer graphene grown on SiC, suggesting that an all-carbon paradigm for electronic circuits may be possible.[1] It is now critical to understand the source of these unique transport properties and explain their dependence on: 1) graphene stacking order and 2) graphene/SiC substrate interactions. We will present surface X-ray reflectivity data that suggest a new structural model for multilayer graphene grown on the SiC (000-1) (C-terminated) face.[2] Reflectivity modeling indicates a high density of stacking faults with distinct rotational alignments. These complex rotational phases will be discussed in the context of recent ab initio calculations which show that this type of stacking effectively decouples adjacent graphene layers. This provides a potential explanation for transport being confined to a single graphene layer.

[1] C. Berger, et al., Science 312, 1191 (2006).

[2] J. Hass, et al., Phys. Rev. B, in press (2007).

11:40am **TF-TuM12 Probing the Interface between Graphene and SiC at the Atomic-scale*, *N.P. Guisinger,*** National Institute of Standards and Technology, *G.M. Rutter,* Georgia Institute of Technology, *J.N. Crain, E.A.A. Jarvis, M.D. Stiles,* National Institute of Standards and Technology, *P.N. First,* Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology

Graphene films on SiC exhibit coherent transport properties that suggest the potential for novel carbon-based nanoelectronics applications. Through controlled processing of SiC graphitization, large domains of single layer graphene can be realized opening the possibility for large area fabrication of carbon structures. Recent studies suggest that the role of the interface between single layer graphene and silicon-terminated SiC can strongly influence the electronic properties of the graphene overlayer. In the present study we have investigated this interface at the atomic scale, utilizing scanning tunneling microscopy and spectroscopic measurements at 4 K. These techniques allow us to probe both the graphene adlayer and the underlying electronic states associated with the SiC surface reconstruction. A novel imaging of the underlying interface is demonstrated by exploiting the energy dependence of the density of states of the SiC substrate versus the graphene overlayer. The first layer of graphene becomes semi-transparent at energies of 1 eV above or below the Fermi-energy, yielding images of the SiC interface. Our analysis of calculations based on density functional theory shows how this transparency arises from the electronic structure of a graphene layer on the SiC substrate. * This work was supported in part by the Office of Naval Research, by Intel Research, and by NSF grant ECS-0404084.

12:00pm **TF-TuM13 Quasiparticle Interference in Epitaxial Graphene*, *G.M. Rutter,*** Georgia Institute of Technology, *J.N. Crain, N.P. Guisinger,* National Institute of Standards and Technology, *P.N. First,* Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology

Understanding the role that defects play in the transport properties of graphene is essential for realizing potential carbon-based electronics. In this study, scanning tunneling spectroscopy was used to measure scattering from defects in epitaxial graphene grown on SiC(0001). Energy-resolved maps of the differential conductance reveal standing-wave modulations of the local density of states on two different length scales, corresponding to two classes of allowed scattering vectors. While backscattering is normally suppressed due to the chiral symmetry of Dirac quasiparticles in graphene, the presence of atomic defects is shown to mix quasiparticle wavefunctions of different symmetries. From Fourier transforms of the spectroscopic conductance maps we determine the energy-momentum dispersion relation for both occupied and unoccupied states near the Fermi level of single-layer and bilayer epitaxial graphene. * This work was supported in part by the Office of Naval Research, by Intel Research, and by NSF grant ECS-0404084.

Tuesday Morning, October 16, 2007

Exhibitor Workshops

Room: Exhibit Hall - Session EW-TuB

Exhibitor Workshops

Moderator: R. Childs, Consultant

10:00am **EW-TuB1 New AFM Imaging Technique-Dual AC^{TM} Mode**, *R. Proksch, D. Bocek, C. Callahan, J. Cleveland, T. Day, **J. Li**, A. Moshar*, Asylum Research

In a new AFM imaging technique, Dual AC Mode, the cantilever is driven at or near two of its resonant vibrational modes. For commercially-available cantilevers, these resonant modes are not harmonic. The amplitude and phase signals measured at the different frequencies show very different contrast on a variety of samples.[1] The workshop will discuss how Dual AC mode works and show application examples of Dual AC on magnetic samples, material and bio samples. In addition to images of a variety of samples, we will also discuss amplitude and phase vs. the tip sample distance curves which further elucidates the physics of the contrast formation.

[1] R. Proksch. Multifrequency, repulsive-mode amplitude-modulated atomic force microscopy. Applied Physics Letters 89, p. 113121, (2006).

10:20am **EW-TuB2 What a Certified Rebuilt Pump Really Is - And Why It's Important**, ***G. Govola***, FMG Enterprises

What is FMG Certified Program? For those who want their remanufactured pumps to work right the first time, and keep their line technicians focused on maximum tool productivity, FMG Certified Program^{TM} is a validation process of the technical competencies and expertise needed to plan, deploy, support, and service FMG's Pumps. The FMG Certified Program^{TM} is a structured certification with emphasis on precision, reliability, durability and performance. Each Rebuild Pump that leaves FMG has been thoroughly inspected by our factory certified technicians and backed by our Certification process. FMG has geared up to be equal if not better than the factory specifications for high quality Rebuild Vacuum Pumps. FMG Certified^{TM} assures that you will get products as good or better than new because FMG goes the "extra mile" at every step. Procedure of Rebuild: FMG has developed our own internal disassembly, cleaning, reliability, testing, detailing and shipping; Technicians: All of FMG's technician's are factory trained and Certified on each pump type; Documentation: Disassembly, evaluation, build sheet, data sheet, final assembly sheet. Test and Quality Assurance sheet, Paint QA and shipping documentation are recorded; Pump Tracking: Internal database monitors incoming rebuilds in every stage of the rebuild process. Features: Electrical 100 point inspection, Electrical/Module/Software, Mechanical parameters, Perform vacuum integrity leak check beyond OEM specifications, 36 performance burn-in reliability checks, Final Quality Assurance Inspection check, Check and record pump parameters including fluid levels, temperatures, pump flows, Perform visual and vacuum integrity leak check, and Check any facility issues directly associated with the pump; system leak check. Advantages: Foresee potential problem areas before any occurrences may arise-through extensive evaluations; Extends pump life, positively affects bottom line with reduced numbers of pump rebuilds or purchases; Maximize overall equipment uptime for production; Cost Savings; and Statement of work performed.

Exhibitor Workshops

Room: Exhibit Hall - Session EW-TuL

Exhibitor Workshops

Moderator: R. Childs, Consultant

12:20pm **EW-TuL1 Thermo Scientific Surface Analysis*, R.G. White***, Thermo Fisher Scientific, UK

There is a wide range of requirements within the surface analysis community, including the need for multi-technique and preparation options. High quality data and reliability are common requirements for both academic and industrial users. ESCALAB 250 is principally a high-sensitivity, high energy resolution imaging XPS instrument. The flexible configuration of this system allows additional analytical options, chamber configurations and sample preparation facilities. Analytical options include additional X-ray anodes, UV lamp and a 95nm electron source. Theta Probe is an integrated XPS system designed with the unique ability to collect small and large area angle resolved XPS without the need to tilt the sample. This, in combination with the suite of accompanying software, makes this instrument a very powerful tool in the analysis of nano-scale layers. This method of rapid data collection allows the analyst to combine mapping with ARXPS to provide uniformity, thickness and composition maps of ultra-thin films. The latest offering from Thermo is K-Alpha. This is designed to provide XPS analysis with the highest possible throughput. It achieves this by combining high-sensitivity, monochromated XPS with a degree of automation that removes the need for the analyst to be involved with routine repetitive tasks. This is the ideal instrument for a multi-user environment. Each of the above instruments is controlled by the market leading data system, Avantage. This is a comprehensive, integrated data system based on Windows XP. In addition to instrument control and data processing, it provides the capability of remote control via a network and a simple interface to Office applications for automatic reporting.

12:40pm **EW-TuL2 New Developments in Surface Analysis Instrumentation from Physical Electronics*, S. Bryan***, Physical Electronics

This presentation will provide an update on the latest product developments from Physical Electronics. At the AVS National Symposium in 2006 PHI introduced two new products to the market, the PHI 5000 VersaProbe and the PHI TRIFT V nanoTOF. Over the past year, additional options have been added to these two new products. In addition, the top-of-the-line Quantera XPS Microprobe and the 700 Scanning Auger Nanoprobe will be discussed.

1:00pm **EW-TuL3 Commercially Available High-Throughput Dip Pen Nanolithography®*, T. Levesque***, NanoInk, Inc.

Dip Pen Nanolithography® (DPN®) is an inherently additive SPM-based technique which operates under ambient conditions, making it suitable to deposit wide range of biological, organic, and inorganic materials. Further, massively parallel two-dimensional nanopatterning with DPN is now commercially available via NanoInk's 2D nano PrintArray^{TM}, making DPN a high-throughput, flexible and versatile method for precision nanoscale pattern formation. By fabricating 55,000 cantilevers (each with its own nanoscale tip) across a 1 cm^2 chip, we leverage the inherent versatility of DPN and demonstrate large area surface coverage, routinely achieving throughputs of $3x10^7$ µm^2 per hour.

1:20pm **EW-TuL4 Modern Aluminum Vacuum Chambers***, J. Bothell*, ***K. Coates***, *E. Jones*, Atlas Technologies

Modern Aluminum Vacuum Chambers: Low cost and superior vacuum performance to stainless steel. Historical evolution of aluminum: With the invention of the ConFlat knife-edge sealing system by Varian stainless steel became the recommended material to achieve high and ultra high vacuum. Aluminum was dismissed because of a lack of a robust sealing system, a misunderstanding of oxide surfaces and a lack of understanding of welding techniques. This paper will present: 1. Aluminum surface preparation methods techniques and instruction on cleaning and detailing materials. 2. Welding methods and techniques, materials, equipment and processes to weld aluminum surfaces 3. Aluminum sealing techniques such as the Atlas Flange. 4. Why aluminum vacuum chambers are lower cost than stainless steel. Finally the paper will present data as to the vacuum properties of aluminum vacuum chambers.

1:40pm **EW-TuL5 Pfeiffer Vacuum Introduces Complete Vacuum System for Mobile Analytical Equipment*, J. Keller***, Pfeiffer Vacuum, Germany

Pfeiffer Vacuum, one of the world's leading producers of vacuum products and services, introduces a durable, reliable and compact vacuum system for mobile mass spectrometry. Able to run at lower power levels, Pfeiffer Vacuumsâ?T compact vacuum system integrates a turbopump and a specially designed dry diaphragm pump that allows analytical equipment to provide real time analysis in the field. This mobile vacuum systems runs on 24 volts with a power save mode when idling. The vacuum system is available with TMH 071 or TPD 011 l/s turbopumps and the MVP 006, a new diaphragm backing pump. This system can be configured to fit analytical OEM requirements. Pfeiffer Vacuumsâ?T TMH 071 turbopump is a 70 l/s, hybrid magnetic design with excellent specifications and highest reliability for mass spectrometry. This pump is currently integrated into dozens of mass spectrometers with thousands sold each year. The TPD 011 turbopump is designed with a unique dual end supported bearing making it the most rugged and smallest commercially available turbopump in the world. The TPD 011 makes possible the design of several portable mass spectrometers that could not have been built with any other pump. The MVP 006 dry diaphragm backing pump is ideal for small mass spectrometry systems because smart electronics communicate with the turbo directly automatically speeding the pump up and down based on demand. This feature optimizes power consumption, vibration, and diaphragm life. In addition, only one power supply is needed for both pumps, and the 24 VDC input simplifies electronic requirements.

Applied Surface Science

Room: 610 - Session AS-TuA

3-Dimensional Characterization

Moderator: S.J. Pachuta, 3M Company

1:40pm **AS-TuA1 XPS, TEM, and SIMS Analysis of FIB Bombarded Surfaces Over the Range 500 eV to 30 keV**, ***J.E. Fulghum***, *K. Artyushkova,* University of New Mexico, *L.A. Giannuzzi, B. Van Leer, J. Ringnalda,* FEI Company, *F.A. Stevie, D.P. Griffis*, North Carolina State University

Focused Ion Beam (FIB) instruments are known for the ability to provide material removal with a lateral resolution less than 10nm using a Ga+ beam. FIB capabilities continue to improve with low energy performance that allows routine use of glancing angle 2kV Ga+ beams for final polishing of TEM specimens. The lower energy reduces the penetration of gallium into the material under study and minimizes sample damage.[1] It is now routinely possible to reduce the energy of the Ga+ beam to 500eV. Previous work has shown that low energy Ga+ impinging at normal incidence results in Ga deposition.[2] There is also TEM evidence indicating that the use of Ga+ for glancing incidence polishing at energies below 2 keV does not further reduce surface damage in Si, but rather creates a Ga rich region since the sputter yield at these energies drops to a value less than 1.[3] An FIB was used to sputter craters into (100) Si using normal incidence Ga energies from 500eV to 30keV. XPS and SIMS analyses were performed on these craters to determine the Ga surface concentrations and depth distributions at these energies. From 30keV down to 2keV, a decreasing Ga penetration was noted. For the SIMS analyses below 2keV, a surface effect was observed in the SIMS depth profiles which may be the result of an enhancement of silicon secondary ion yield. It my be that glancing incidence polishing at Ga+ energies below 2keV will not result in additional reduction of surface damage. However, the low energy FIB capabilities can provide a means for site specific deposition of Ga when the low energy Ga impinges at normal incidence.

[1] L. Giannuzzi, R. Geurts, J, Ringnalda, Microscopy and Microanalysis Proceedings 11 (Suppl 2) 2005, p.828

[2] D.H. Narum and R.F.W. Pease, J. Vac. Sci. Technol. B6(6) (1988) p. 2115

[3] L. A. Giannuzzi, B. Van Leer, J. Ringnalda, Microscopy and Microanalysis Proceedings (2007).

2:00pm **AS-TuA2 3-D XPS Characterization of Organics Surfaces**, ***J.S. Hammond***, *S. Raman, J. Moulder,* Physical Electronics, *N. Sanada, R. Inoue, M. Suzuki*, ULVAC-PHI

For many industrial products, non-uniform surface segregation and contamination of organic constituents on micro-areas of polymeric materials is of great concern. Over the past three years, C60 ion beams have been shown to be very effective for the sputter removal of a surface layer of many organic materials, leaving the remaining surface with minimal chemical damage. By combining a C60 ion gun system with a scanning x-ray microprobe XPS specifically designed for optimum performance for micro-area spectroscopy, chemical state mapping and depth profiling, it is now possible to obtain a three dimensional characterization of organic surfaces. To illustrate this new analytical technique, surface area mapping and micro-area depth profiling of a coated human hair and a micro-area contamination analysis on a thick polymer will be discussed. By using high energy resolution core level spectroscopy as well as valence band chemical state mapping, information on the coating thickness and the spatial dimensions of contamination areas can be obtained. Finally, a comparison between the chemical state damage induced by the C60 ion beam versus the x-ray beam damage during a depth profile will be discussed. Initial experiments indicate that for some polymers, the x-ray beam damage is of greater significance than the chemical changes observed after C60 sputtering. The use of a scanning x-ray beam may facilitate chemical state depth profiling with minimal data artifacts.

2:20pm **AS-TuA3 C60 Molecular Depth Profiling: A Fundamental Study using a 3D Organic System**, ***A.G. Shard***, *I.S. Gilmore*, National Physical Laboratory, UK

C_{60} sputtering of organic materials enables the possibility of producing 3 dimensional reconstructions of the distribution of organic compounds. We demonstrate that many organic materials have identical yield volumes (volume sputtered per incident ion) and that, in general, sputtering yield is a well behaved function of ion dose. Irganox layers were created by vacuum evaporation to create well-defined stacks of organic materials with controllable layer thicknesses. These layered materials were employed to determine the energy dependence of sputtering yield, depth resolution and damage accumulation during C_{60} depth profiling. We show that sputtering yield increases with C_{60} ion energy and that depth resolution concomitantly becomes poorer. The multilayers are also used to demonstrate how the depth resolution degrades with depth and a comparison with AFM data shows that the resolution is mainly limited by topography. Examples are also shown of the lateral and depth distribution of mixed organic systems.

2:40pm **AS-TuA4 Prospects for Electron Tomography with Atomic Resolution**, ***C.F. Kisielowski,*** Lawrence Berkeley National Laboratory, *F.R. Chen*, National Tsing Hua University, Taiwan **INVITED**

Since several decades Transmission Electron Microscopy (TEM) is a primary tool for characterizing the inner structure of materials including interfaces and surfaces. A most limiting factor of the transmission-imaging mode comes with the projection of the probed crystal volume into one image plane, which causes loss of information about the materials structure along the electron beam direction. In recent years electron tomography was developed and successfully applied to soft and hard materials yielding the three dimensional materials structure with a resolution that can approach 1-2 nm.[1,2] However, it is still impossible to achieve truly atomic resolution because radiation damage can limit the electron dose and because quantitative procedures need yet to be established that would allow recovering the materials structure at atomic resolution reliably from the recorded images. In order to achieve this goal it is essential to solve the phase problem and to remove effects that relate to the dynamic scattering of electrons in a solid. In this talk we describe current efforts that aim at reaching this goal. Our investigations build on recent hardware and software developments that relate to the DoE's TEAM Project,[3] which will provide a next generation of electron microscopes operating between 80 and 300 kV and providing deep sub Ångstrom resolution. We show that the phase problem is reliably solved and that dynamic scattering can be indeed inverted. As a result a full quantification of the samples mean inner potentials becomes possible, which can be used to determine the number of atoms in each imaged atom column together with its chemical composition. If such experiments are executed along a few zone axes it is possible to reconstruct the atomic structure of materials with atomic resolution.[4] Experimental validations of the developed concept include gold surfaces and bi-crystals of Al:Cu.

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[2] Q. Yang, J. Mardinly, C. Kübel, C. Nelson, C. Kisielowski, International Journal of Materials Research 97, (2006) 880-4

[3] http://www.lbl.gov/LBL-Programs/TEAM/index.html

[4] J.R. Jinschek, H.A. Calderon, K.J. Batenburg, V. Radmilovic, C. Kisielowski, Mat. Res. Soc. Symp. Proc. 839 (2005) 4.5.1 - 4.5.6.

4:00pm **AS-TuA8 Retrospective and Multivariate Statistical Analysis of Three-Spatial-Dimension ToF-SIMS Data Sets**, ***V.S. Smentkowski***, *S.G. Ostrowski,* General Electric Global Research, *M.R. Keenan, J.A. Ohlhausen, P.G. Kotula*, Sandia National Laboratories

3 spatial dimension (3D) Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis can be performed if an X-Y image is saved at each depth of a depth profile. We will show how images reconstructed from specified depths, depth profiles generated from specific X-Y coordinates, as well as 3 spatial dimensional rendering provides for a better understanding of the sample than traditional depth profiling where only a single spectrum is collected at each depth. We will also demonstrate that multivariate statistical analysis (MVSA) tools can be used to perform a rapid, unbiased, analysis of the entire 3D data set. Color overlays of the MVSA components and animated movies showing the visualization (in 3D) from various angles will be provided. The MVSA results will also be represented as depth profile traces. 3D ToF-SIMS analysis is performed using only 1 primary ion shot/pixel. Under these conditions, detector dead time effects can introduce non-linearities into the data sets; examples of non-linear data sets will be shown. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:20pm **AS-TuA9 3D Molecular Characterization of a Drug Delivery System**, ***G.L. Fisher***, Physical Electronics, *A. Belu,* Medtronic Inc.*, K. Wormuth*, SurModics Inc.

Coronary implants that incorporate a drug delivery system are being developed at an increasing rate. It is important for a variety of reasons to characterize such in vivo drug delivery devices and to relate the chemical and physical properties to how the system will function. This study focuses on the characterization of a drug eluting stent coating that consists of rapamycin in a poly(lactic-co-glycolic acid) (PLGA) matrix. The goal is to understand the lateral and depth distribution of the drug in the polymer matrix. Additionally, the drug distribution is studied as a function of elution time. Information regarding the lateral and depth distribution of rapamycin in PLGA, and the distribution as a function of elution time, was determined by TOF-SIMS depth profiling with a C$_{60}$ cluster ion source. Where appropriate, the TOF-SIMS results will be compared to the results obtained by XPS and confocal Raman. The experimentally-determined 3D chemical structure as a function of elution time, in conjunction with the elution profiles, may be used to enhance the design of future in vivo drug delivery systems.

4:40pm **AS-TuA10 3D Image Acquiring and Spectrum Extraction from 2D Elemental Mapping in Auger Electron Spectroscopy**, ***N. Urushihara***, *S. Iida, N. Sanada,* ULVAC-PHI, Inc., Japan, *D.F. Paul, S. Bryan,* Physical Electronics, *M. Suzuki,* ULVAC-PHI, Inc., Japan, *Y. Nakajima, T. Hanajiri*, Toyo University, Japan

Auger electron spectroscopy (AES) is widely used for observation of two-dimensional map (surface elemental distribution) with a high spatial resolution as well as in-depth elemental distribution. An elemental map is generally obtained at an as-received surface or a sputtered surface. Though it is easy to visually recognize elemental distribution in a plane surface, it is difficult to display it three-dimensionally. On the other hand, an energy dispersal spectrum is not stored at each pixel of an elemental map in AES, and it leads a difficulty to investigate spectral shapes at specified points in an elemental map. In order to solve the former issue we have tried to acquire a three-dimensional elemental map and for the latter issue we have studied to extract an energy dispersal spectrum from successive two-dimensional images at fixed kinetic energies. Specimens used were two kinds of SOI (Silicon on insulator) in the study of 3D image acquiring and a part of sputtered crater at the interface region of a silicon dioxide layer on silicon substrate in the study of spectrum extraction from 2D elemental maps. The interface regions were ion-sputtered at the interval of 0.5nm and intensity distributions of Si LVV and O KLL were mapped at a respective depth with 256 x 256 pixels. One can easily recognize three-dimensional features at the interface regions, seeing successive display of 2D maps. It is clearly seen that silicon oxide is formed island structure for the interface in one of the specimens. For the second issue, two-dimensional signal intensities were stored at the region located adjacent to the interface of SiO$_2$ and Si on a graded sputtered surface. Maps consisted of 64 x 64 pixels and imaged signal intensities were defined as raw intensities including background components. The maps were obtained in the energy ranges of 77 eV to 100 eV for Si LVV with an energy step of 3 eV. At every pixel point energy dispersal spectra were extracted from the 9 maps obtained at the fixed energy. It is obviously distinguished for extracted Si LVV spectra for silicon elemental component and oxide component. All of extracted spectra were processed with linear least square (LLS) method, resulting in separation of elemental and oxide components. In the presentation, results from other material systems for both issues will be demonstrated.

5:00pm **AS-TuA11 Nanospectroscopy of Single Silicon Nanowire Surface using Energy Filtered X-ray PhotoElectron Emission Microscopy (XPEEM)**, ***O. Renault***, *A. Bailly,* CEA-LETI Minatec, France, *N. Barrett, L.-F. Zagonel,* DSM/DRECAM/SPCSI, France, *N. Pauc, P. Gentile,* CEA DRFMC, SiNAPS, France, *T. Baron*, CNRS-LTM, France

Interest in silicon nanowires (Si NWs) continues to grow, fuelled by novel applications in nanotechnology. This requires precise wire engineering in order to tailor specific surface properties of Si NWs like electron emission properties and surface chemistry, which can be altered by the growth process.[1] Within this perspective, the implementation of novel, non destructive experimental techniques offering both spectroscopic and microscopic capabilities is needed. In this contribution, we present recent results of a surface study using synchrotron radiation induced X-ray PhotoElectron Emission Microscopy (XPEEM) of 250 nm-diameter single NWs dispersed on gold after growth by the Vapour-Liquid-Solid process from gold-silicon catalysts. Here, XPEEM is implemented with the first commercially available NanoESCA spectromicroscope featuring a fully electrostatic PEEM column together with an aberration-corrected energy filter (double hemispherical energy analyser) allowing both a high lateral and energy resolutions.[2-4] The instrument allows laboratory XPEEM experiments with a bright AlKα source, and can also be periodically moved to the European Synchrotron Radiation Facility (ESRF) to benefit from the high brightness and energy tunability of ID08, a soft X-ray beamline.[4] We focus on results related to the energy-filtered, secondary electron images at the photoemission threshold that reveal differences in the local work function and enable investigation, along the nanowire, of the sidewall wetting by the catalyst and the catalyst properties. The double-photoemission threshold shape of the generated nanospectra along the NW surface is a superposition of that characteristic of the Si NW surface and of the gold substrate indicating that gold diffusion and dewetting along the NW sidewall occurs, giving rise to the formation of a non-continuous gold layer. This is confirmed by the Au4f core-level images and SEM observations on the same nanowire. This experiment demonstrates the powerful capabilities of XPEEM nanospectroscopy with the NanoESCA for the surface chemical characterization of single nanostructures.

[1] J.B. Hannon et al., Nature 440 (2006) 69.

[2] M. Escher et al., J. Phys.: Condens. Matter 17 (2005) S1329.

[3] O. Renault et al., Surf. Interface Anal. 2006 ; 38 : 375-377.

[4] O. Renault et al., Surf. Sci. 2007 (in press).

Biomaterial Interfaces

Room: 609 - Session BI-TuA

Engineered Cellular Interfaces

Moderator: H.E. Canavan, University of New Mexico

1:40pm **BI-TuA1 Simultaneous Deposition of Endothelial Cells and Biomaterials for Human Microvasculature Fabrication**, *X. Cui, P.V. Kreuk,* ***T. Boland***, Clemson University

The current tissue engineering paradigm is that successfully engineered thick tissues must include vasculature. As biological approaches alone such as VGEF have fallen short of their promises, one may look for an engineering approach to build microvasculature. Layer-by-layer approach for customized fabrication of cell/scaffold constructs have shown some potential in building complex 3D structures. With the advent of cell printing, one may be able to build precise human microvasculature with suitable bioink. Human Microvascular Endothelial Cells (HMEC) and fibrin were studied as bioink for microvasculature construction. Endothelial cells are the only cells to compose the human capillaries and also the major cells of blood vessel intima layer. Fibrin has been already widely recognized as tissue engineering scaffold for vasculature and other cells, including skeleton/smooth muscle cells and chondrocytes. In our study, we precisely fabricated micron-sized fibrin channels using a drop-on-demand polymerization. This printing technique uses aqueous processes that have been shown to induce little, if any, damage to cells. When printing HMEC cells in conjunction with the fibrin, we found the cells aligned themselves inside the channels and proliferated to form confluent linings. Current studies to characterize the biology and functionality of these engineered microvascular structures will be presented. The preliminary data suggests that a combined simultaneous cell and scaffold printing can promote HMEC proliferation and microvasculature formation.

2:00pm **BI-TuA2 Cells, Surfaces, Spaces and Forces: What makes a tissue?**, ***K.D. Hauch***, *D.J. Mortisen, M.A. Laflamme, C.E. Murry, B.D. Ratner*, University of Washington **INVITED**

Tissue engineering strives to combine parenchymal and other cells with porous biomaterial scaffolds; to grow tissue like constructs that can be used to repair diseased or damaged tissues and organs. The natural course of development, as well as some (but not all) processes of wound repair and regeneration, depend upon complex parameters including: the changing composition and capabilities of the cells that populate the tissue; molecular cues from the interface between cell and its environs; the structural space wherein the cells reside; and mechanical forces. All these and more act to guide the processes that results in a hierarchical living tissue with appropriate structure and function. Here we explore these issues in the context of cardiac tissue engineering. Adult cardiomyocytes demonstrate little if any proliferative potential. However, using an appropriate schema of soluble cues, large quantities of proliferating cardiomyocytes as well endothelial cells can be derived from cultures of human embryonic stem cells, to be used for tissue engineering. Postulating the importance of scaffold geometry, novel scaffolds were constructed with appropriately sized spaces and shapes, providing an engineered support structure that mimics aspects of native muscle architecture. Molecular cues are provided by immobilizing adhesion proteins on the scaffold and delivering other soluble factors to stimulate cell survival, proliferation, and ultimately vascularization. huESC-derived cardiomyocytes populate these scaffolds and survive at high cell densities in culture. Finally, the application of cyclical mechanical stress during in vitro culture is seen to enhance cardiomyocyte size, survival and functional organization. The analysis of these engineered tissues depends on both standard immunohistochemical observations, as well as newer visualization tools, including Digital Volumetric Imaging, a microscopic 3D serial sectioning and reconstruction technique. Together, the appropriate application of proliferative cardiomyocytes to carefully engineered scaffolds featuring spaces of appropriate size and shape, in conjunction with soluble and mechanical cues can lead to the development of a robust functional unit of cardiac muscle.

2:40pm **BI-TuA4 Expanding Human Embryonic Stem Cells without Feeder Cells on Chitosan-Alginate 3D Porous Scaffolds**, ***M.C. Leung***, *L. Zhensheng, M. Zhang*, University of Washington

The tremendous interest in human embryonic stem (hES) cells is motivated by a wide range of potential therapeutic, diagnostic, and fundamental research applications. To preserve their undifferentiated state, two-dimensional co-culture with feeder cells is standard practice.[1,2,3] In order to develop therapeutic applications, a system for the undifferentiated expansion of hES cells in pure culture must be developed to prevent xenogenic contamination.[4,5,6] With BG01V cells as a model, porous chitosan-alginate (CA) scaffolds were studied as a three dimensional (3D) substrate for undifferentiated hES cell proliferation. It was observed that hES cells attached, proliferated, expressed relevant transcription factors, translated appropriate markers, and retained pluripotency after 21 days of cultivation. Furthermore, the 3D CA culture system replicates the structure of natural extra cellular matrix, creating additional opportunities for regenerative medicine. This method realizes the goal of expanding pure hES cell populations in vitro while preserving undifferentiated state, and represents a significant advancement in hES cultivation technique.

[1] Choo, A., Padmanabhan, J., Chin, A., Fong, W. J. & Oh, S. K. Immortalized feeders for the scale-up of human embryonic stem cells in feeder and feeder-free conditions. J Biotechnol 122, 130-41 (2006).

[2] Oh, S. K. et al. High density cultures of embryonic stem cells. Biotechnol Bioeng 91, 523-33 (2005).

[3] Richards, M., Fong, C. Y., Tan, S., Chan, W. K. & Bongso, A. An efficient and safe xeno-free cryopreservation method for the storage of human embryonic stem cells. Stem Cells 22, 779-89 (2004).

[4] Stacey, G. N. et al. The development of 'feeder' cells for the preparation of clinical grade hES cell lines: challenges and solutions. J Biotechnol 125, 583-8 (2006).

[5] Amit, M. & al., E. Feeder Layer- and Serum-Free Culture of Human Embryonic Stem Cells. Biol Reprod 70, 837-845 (2004).

[6] Hoffman, L. M. & Carpenter, M. K. Characterization and culture of human embryonic stem cells. Nat Biotechnol 23, 699-708 (2005). .

3:00pm **BI-TuA5 Stem Cell Adhesion and Proliferation Correlated with Surface Properties of Copolymer Libraries Synthesised as Micro Arrays**, *A.J. Urquhart, M. Taylor,* University of Nottingham, UK, *D.G. Anderson, R. Langer,* Massachusetts Institute of Technology, *M.R. Alexander,* ***M.C. Davies***, University of Nottingham, UK

In the field of tissue engineering, the search is on for the optimum polymer scaffold material to support the adhesion and proliferation of stem cells for organ regeneration. To accelerate this process, Anderson et al., developed a high throughput screening methodology for the assessment of stem cell interactions with a large combinatorial library of over 500 copolymers1. Initial cellular behaviour with these materials will be driven by surface-cell interactions but until very recently, there was no rapid method of measuring the surface chemistry of such spatially patterned arrays. We report on the first high-throughput screening of the surface chemistry (ToF-SIMS and XPS) and wettability (contact angle, surface energetics) of large copolymer library array spatially patterned as 300 micron islands and polymerized in-situ on a single poly(HEMA) slides. The copolymer library is designed to exhibit a range of surface phenomena and their ability to support the growth of cells (eg, endothelial stem cells, bacteria) was assessed. Statistical analysis of the large surface and biological data sets reveals important relationships linking surface properties and cell interactions that point to the key surface phenomenon that could lead to the development of optimised copolymer surfaces for the development of polymeric scaffolds.

4:00pm **BI-TuA8 Hierarchical Control of Form and Function in the Heart**, ***K.K. Parker***, Harvard University **INVITED**

Expression of sarcomeric proteins is necessary, but not sufficient, for contraction of cardiac myocytes. Posttranslational processes contribute to regulation of muscle growth during cardiac development, normal function, and disease. However, little is known about the mechanisms and signals that potentiate directional muscle growth and the self-assembly and organization of sarcomeres, myofibrils, cells, and tissues. These structures appear to be optimized for their contractile function. In order to elucidate the structure-function relationships that govern contractility, we have developed computational and experimental models of self-assembly and organization in cardiac myocytes in vitro. By controlling only 2D boundary conditions imposed on the myocyte, we are able to engineer predictable myofibrillar patterns and contractility of individual myocytes. These experiments have revealed how the extracellular matrix provides an important set of instructions for self-assembly of the myocyte cytoskeleton architecture which serves as a template for myofibrillar patterning. Our results suggest the post-translational mechanisms that regulate cardiac organo- and pathogenesis.

4:40pm **BI-TuA10 BioArtificial Matrices to Control Blood Vessel Network Formation**, ***E.A. Phelps***, *A.J. García*, Georgia Institute of Technology

Vascularization of engineered regenerative constructs is a major obstacle in the development of clinically significant regenerative medicine. The ability of regenerative constructs to recapitulate normal blood vessel wiring is central to their successful integration with host tissue, proper physiological function, and long term survival. The natural formation of new blood vessel networks is driven by spatially and temporally controlled presentation of positive and negative cues that direct cell behavior to initiate vessel sprouting, migration, and stabilization.[1] We have developed a strategy for engineering regenerative constructs with spatially patterned biomolecules to direct the formation of orderly networks of blood vessels in artificial biomaterials. Our approach employs a photopatterning technique to convalently link bioactive peptides to poly(ethylene glycol) (PEG) hydrogels to modulate and direct cell function. In this system, peptides are attached to the surface of PEG hydrogel through the use of a photoactive crosslinking agent. Peptides are patterned on the hydrodel by exposing the peptide and crosslinker solution on the surface to UV light through a Mylar photomask. We achieved sharply defined patterns of fluorescently labeled peptide with 10 µm features. We anticipate that the system can easily produce higher resolution patterns. We employed the photopatterning technique to create various patterns of the adhesive ligand RGDS on a nonadhesive PEG background. We have shown that we can constrain the adhesion and morphology of NIH fibroblast cells to the patterned RGDS with this system. We have also used RGDS functionalized PEG hydrogels to induce tubule formation of human aortic endothelial cells, and we have successfully created patterns of labeled RGDS resembling branching microvasculature. We plan to use these patterns to direct the growth of vascular sprouts from explanted sections of mouse aorta into a vascular network. Ultimately we will employ a system to pattern ligands in 3D to direct vascularization of an implanted hydrogel in vivo. The central hypothesis of this work is that spatiotemporal presentation of bioactive cues will result in directed vascularization of engineered hydrogels from the host tissue and that increased vascularization will result in improved healing, integration, and function of regenerative constructs.

[1] M. P. Lutolf and J. A. Hubbell, Nature biotechnology 23 (1), 47 (2005).

5:00pm **BI-TuA11 Cytoskeleton Structure and Focal Contact Points on a Micro 3D Patterned Film**, ***H. Sunami***, *E. Ito,* Hokkaido University, Japan, *M. Tanaka,* Tohoku University, Japan, *S. Yamamoto,* Hokkaido University, Japan, *M. Simomura*, Tohoku University, Japan

Micro fabrication of cell culture substrates is one of the most significant subjects in the field of biomaterial research. Recently we found that endothelial cells can proliferate rapidly on a micro 3D patterned film (honeycomb film). The cell shape and cytoskeleton structure on the honeycomb films were clearly different from those on a flat film. In order to elucidate the effect of honeycomb films as a 3D scaffold for cell culture, it is needed that the 3D observation of cell behaviors such as the morphological change, expression of cytoskeleton, expression of contact points on extracellular adhesion molecules, and migration on the honeycomb films during cell culture. In this research, effects of 3D honeycomb pattern on above cell behaviors were observed.

Electronic Materials and Processing

Room: 612 - Session EM+NS-TuA

Semiconductor Nanostructures for Electronics and Optoelectronics II

Moderator: S.E. Mohney, The Pennsylvania State University

1:40pm **EM+NS-TuA1 Epitaxial NiFe Contacts on GaAs via Electrodeposition**, *Z.L. Bao,* ***K.L. Kavanagh***, *A.S. Arrott,* Simon Fraser University, Canada, *A.A. Talin*, Sandia National Laboratories

We report the electrodeposition of epitaxial FexNi(1-x) films on n-GaAs (001) substrates from aqueous metal ammonium sulphate solutions. Structural measurements using x ray diffraction show that the films have single crystalline BCC or FCC structure at Fe and Ni-rich compositions, respectively. The ratio of Fe concentration in the FCC films to that in the electrolyte is surprisingly close to unity (1.1). BCC FexNi(1-x)/GaAs diodes have constant Schottky barrier heights independent of Fe composition consistent with a constant interfacial composition while the

FCC Ni-rich alloys barriers increase with increasing Ni composition consistent with room temperature reactions.

2:00pm **EM+NS-TuA2 Medard W. Welch Award Lecture - Growth of Semiconductor Nanostructures: Simple Models for Complex Behavior**, ***J. Tersoff****, IBM T.J. Watson Center **INVITED**

Epitaxial islands and wires can "self assemble" during growth, producing quantum dots and nanowires with sub-lithographic dimensions. Such growth exhibits many remarkable and puzzling features, which must be understood in order to grow well controlled nanostructures. I will describe simple models that can explain many of the phenomena observed during growth of quantum dots in strained-layer heteroepitaxy, and also some recently discovered phenomena in growth of nanowires via the vapor-liquid-solid mechanism.

2:40pm **EM+NS-TuA4 Fast Synthesis Method for Binary and Ternary alloy Quantum Dots**, ***N. Shukla***, *M.M. Nigra*, *A.J. Gellman*, Carnegie Mellon University

We have developed a one step synthesis process for binary and ternary alloy quantum dots with photoluminescence ranging from the red through to the violet region of the solar spectrum. This synthesis method allows us to control particle size and composition of quantum dots. We have also studied the effect of solvent boiling point and the addition of various chemical precursors on the synthesis and the photoluminescence properties of quantum dots. The photoluminescence peak in this synthesis method can be controlled by using different reaction time to produce quantum dots of different sizes. Photoluminescence peaks can also be controlled through varying composition of the chemical precursors. In addition, we have also studied the effect of solvent boiling point and the type of solvent on the physical and photoluminescence properties of these quantum dots. The type of solvent plays an important role in the photoluminescence properties of quantum dots. High boiling point non-polar solvents shift the photoluminescence peak to higher wavelength and low boiling point polar solvents shift the photoluminescence peak to lower wavelength.

3:00pm **EM+NS-TuA5 Zinc Oxide Nanowalls and its Optical and Field Emission Properties**, *D. Pradhan*, ***K.T. Leung***, University of Waterloo, Canada

Vertically grown ZnO nanowalls, with typical dimensions of 40-80 nm thick and several micrometers wide, were electrodeposited on an ITO-glass substrate at 70 °C. XRD study shows that these nanowalls have the wurtzite structure and are highly crystalline. The corresponding Raman and photoluminescence spectra further indicate the presence of oxygen deficiency. These ZnO nanowalls exhibit excellent field emission performance, with not only a considerably lower turn-on field of 3.6 V/µm (at 0.1 $\mu A/cm^2$) but also a higher current density of 0.34 mA/cm^2 at 6.6 V/µm than most of ZnO nanowires and other one-dimensional nanostructures reported to date. We will also discuss a plausible growth mechanism for these nanowalls, and our recent work on the growth of these and other novel ZnO two-dimensional nanostructures on ITO-plastics.

4:00pm **EM+NS-TuA8 Bright and Color-Saturated Light Emitting Devices Based on Colloidal Nanocrystal Quantum Dots**, ***J. Xu***, Pennsylvania State University, *Q. Sun*, University of Dayton, *T. Zhu*, Pennsylvania State University, *A. Wang*, Ocean NanoTech LLC., *Y. Li*, Chinese Academy of Science, China **INVITED**

Recently, the development of low cost, solution-based synthesis of monodisperse, well characterized colloidal quantum dots (QDs) has generated a new class of material for the next generation-light emitting devices. Electroluminescent (EL) devices have been fabricated from thin films of colloidal QDs and exhibit saturated colors and broad wavelength coverage. Emission of EL devices can be easily tuned by varying the size and/or the material composition of nanoparticles during the synthesis process, while their chemical properties remain largely the same. Therefore, one device fabricating procedure can be adopted for different nanocrystals to produce emissions over a broad wavelength, covering the visible (0.4µm – 0.8µm) and NIR (0.8µm - 2.5µm) regions of the spectrum.In addition to the broad wavelength tunability, high fluorescence quantum yield and photochemical stability can be achieved by careful modification of the nanocrystal surface, and this may favor the efficiency of the EL device. All these unique properties have made semiconductor NQDs promising candidates for a broad range of applications, including flat panel display (FPD), light illumination, lightwave communication, and bio/chemical sensing. In this talk we present our work on the design and optimization of colloidal quantum dot (QD)-based light emitting diodes (LEDs) by tailoring the structure and layer thickness of the emissive QDs in the LED active region, the device configuration, as well as the electrode composition. The maximum brightness of red (?peak=619nm), orange (?peak=595nm), yellow (?peak=575nm), and green (?peak=526nm) QD-LEDs were measured to be 9064 cd/m2, 3200 cd/m2, 4470 cd/m2, and 3700 cd/m2, respectively, representing the highest brightness reported for QD-based EL devices. These devices were characterized with low turn-on voltages (3-4 V), high efficiency (1.1-2.7 Cd/A), and longer operation time at high brightness (t50%=300hrs at 1100 cd/m2) , indicative of the superior radiative properties and adequately-tailored carrier-injection and transport functions of the QD-active region in the LEDs.

4:40pm **EM+NS-TuA10 Ligand Quenching of CdSe Quantum Dot Photoluminescence Investigated by Single Molecule Spectroscopy**, ***A.M. Munro***, *I. Jen-La Plante*, *D.S. Ginger*, University of Washington

Colloidal quantum dots are a unique class of solution processable chromophores with high photoluminescence quantum yields, good photostability, and narrow, size-tunable emission spectra that make them potentially useful for many optoelectronic and photonic applications. Surface chemistry strongly affects the optical and electrical properties, as well as the solubility and stability of the quantum dots. However, many properties of ligand-quantum dot interactions remain unresolved. For instance, it is not known exactly how different ligands alter quantum dot photoluminescence and a better understanding of ligand effects is necessary in order to tailor quantum dot surface chemistry for specific applications. We investigate changes in the photoluminescence of colloidal CdSe quantum dots as we bind different ligands to quantum dot surfaces using both single-molecule and ensemble averaged spectroscopy. Using single-molecule spectroscopy, we monitor the photoluminescence of single CdSe quantum dots over time in the presence of varying concentrations of octadecanethiol and determine the average quantum dot intensity, the average number of emissive quantum dots, and the blinking statistics of the quantum dots. This allows us to determine that the binding of a single thiol molecule to the surface of a CdSe quantum dot creates a trap state that decreases the photoluminescence intensity of the individual quantum dot by a significant amount, but that there is no change in the quantum dot blinking rate. We use this single-molecule data to refine our previously reported Langmuir isotherm quenching fits to ensemble solution photoluminescence spectra. By modeling the effects of octadecanethiol on CdSe quantum dots, we develop a better general understanding of ligand exchange and ligand binding to quantum dots.

5:00pm **EM+NS-TuA11 Controlling the Electronic Structure of Graphene Layers**, ***T. Ohta***, LBNL; Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *A. Bostwick*, LBNL, *J.L. McChesney*, LBNL; Montana State University, *T. Seyller*, Univ. Erlangen-Nürnberg, Germany, *K. Horn*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *E. Rotenberg*, LBNL

Much recent attention has been given to the electronic structure of graphene, the honeycomb carbon sheet which is the building block of graphite, carbon nanotubes, C_{60}, and other mesoscopic forms of carbon. Following recent developments in synthesizing or isolating graphene films, experiments have revealed many interesting and physical properties, including an anomalous quantum Hall effect, ballistic electron transport at room temperature, and micron-scale coherence lengths. These unconventional properties are the direct consequence of graphene's peculiar and structure, with massless "Dirac Fermions" as charge carriers at the Fermi level. We have determined the layer-dependent electronic properties of graphene sheets prepared on silicon carbide, using angle-resolved photoemission spectroscopy. We examine this unique two-dimensional system in its development from single layers to multilayers in the π band, the highest occupied state, and the dispersion relation in the out-of-plane electron wave vector in particular.[1] By exploiting the sensitivity of graphene's electronic states to the charge carrier concentration, changes in the on-site Coulomb potential leading to a change of π and π^* bands can be examined. We demonstrate that, in a graphene bilayer, the gap between π and π^* bands can be controlled by selectively adjusting relative carrier concentrations, suggesting a potential application in switching functions in electronic devices.[2]

[1] T. Ohta, A. Bostwick, J. L. McChesney, T. Seyller, K. Horn, E. Rotenberg, Phys. Rev. Lett., 2007, in press.

[2] T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, Science 313, 951, 2006.

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* Medard W. Welch Award Winner

Exhibitor Workshops

Room: Exhibit Hall - Session EW-TuA

Exhibitor Workshops

Moderator: R. Childs, Consultant

3:20pm **EW-TuA6 High Speed, High Resolution XPS Imaging*, C. Blomfield, S. Page, S. Hutton, D. Surman*,** Kratos Analytical

XPS imaging is an established method for determining the qualitative lateral distribution of chemical species across a sample surface. Early methodologies for this technique involved XPS maps where a virtual or X-ray probe was scanned a cross a sample surface and an image built up pixel by pixel as the analysis point was moved across the sample. Other methods involved the parallel detection of a predefined field of view over one specific binding energy range. Improvements in detector technology and instrument design have lead to the development of truly quantitative pulse counting methods which give high lateral resolution XPS images with quantitative intensities over short time intervals. This presentation describes the technology required to achieve this level of performance and illustrates some applications which benefit from a quantitative chemical state imaging technique.

3:40pm **EW-TuA7 Chemical Sample Characterisation on the Nanoscale: Imaging XPS with Ultimate Spatial Resolution*, M. Green*,** *M. Maier*, Omicron NanoTechnology, Germany

In this contribution we briefly summarize the current status of novel instrument design in imaging XPS (iXPS) achieving ultimate resolution beyond today's traditional limits. In iXPS a great obstacle for higher resolution is the limited X-ray brilliance in the analysis area in combination with the small electron acceptance angle of current spectrometers. Today commercial laboratory instruments are limited to approx. 3 µm resolution. Acquisition times as well as time for experiment set up increase unacceptably when the attempt is made to utilize this kind of resolution routinely. In particular with those instruments acquiring each image pixel sequentially by either scanning the X-ray beam or the analysis spot. We present first results acquired with a NanoESCA instrument installed at LETI. A new lens concept provides a huge progress for the acceptance angle of photoelectrons. This is combined with a patented aberration compensated analyzer allowing the acquisition of typically 640x512 image pixels in a single shot. This offers the unique possibility to achieve sub micron image resolution routinely as well as small spot spectra from well-defined areas below 1µm diameter, within reasonable acquisition times.

The Industrial Physics Forum 2007: The Energy Challenge

Room: 602/603 - Session IPF-TuA

Frontiers in Physics

Moderator: J. Hobbs, American Institute of Physics

2:00pm **IPF-TuA2 Probing the Intrinsic Magnetism of the Electron (and Measuring the Fine Structure Constant)*, G. Gabrielse*,** Harvard University **INVITED**

A single electron is suspended by itself for months at a time. The electron and apparatus together form an artificial, home-made atom whose energy levels we probe using quantum jump spectroscopy. Much as measurements of the magnetism of the earth reveal something about the inner structure of the earth, measurements of the electron's intrinsic magnetism tells about the inner structure of the simplest of elementary particles. For the first time since 1987 the electron's magnetic moment is measured with a higher accuracy. The new measurement, together with quantum electrodynamics theory, determines the important fine structure constant about ten times more precisely than does any rival method. Many interesting techniques are employed, including the inhibition of spontaneous emission and the a single-particle self-excited oscillator, some of which are now applicable in MRI imaging and for ICR analysis of pharmaceuticals.

2:40pm **IPF-TuA4 Nanopores & Systems Biology*, J.J. Kasianowicz,*** *J.W.F. Robertson,* National Institute of Standards and Technology*, O.V. Krasilnikov,* UFPE, Recife, Brazil*, V.M. Stanford*, National Institute of Standards and Technology **INVITED**

Proteins that form nanometer-scale pores in cell membranes are the basis of many biological processes including nerve activity and cell-cell communication. Research over the past two decades demonstrated that they could also be used for the selective detection and characterization of molecules (e.g., proteins, anthrax toxins, and DNA). More recently, a single nanopore was used as the transducer for a novel aqueous-based mass spectrometry technique. The ability to detect and discriminate between molecules with nanopores should provide useful analytical systems for health care applications.

4:00pm **IPF-TuA8 Circuits with Light at the Nanoscale*, N. Engheta*,** University of Pennsylvania **INVITED**

For many years, the familiar notion of lumped circuit elements has been extensively and successfully used in microelectronics. This concept has allowed "modularization" of various functions at the circuit level, and thus has been proven to be a powerful tool in design, innovation, and discovery of new functionalities in the radio frequencies (RF) and microwaves. Can the concept of lumped circuit elements, and the mathematical machinery of circuit theory, be extended into the nanometer scale and into the optical domain? In other words, can we envision nanostructures that may act as a "module" representing a lumped circuit element, such as a nanoinductor, a nanocapacitor, a nanoresistor, and a nanodiode, etc. that will work with light, instead of electricity? Utilizing the notion of metamaterials and plasmonic materials with unusual values for material parameters such as negative or near-zero parameters, we have developed the concept of lumped circuit elements at the higher frequency regimes, such as terahertz (THz), infrared (IR), and optical domains. With this approach, nanoelements such as nanoinductors, nanocapacitors, nanoresistors, and nanodiodes can indeed be envisioned at optical frequencies by properly arranging plasmonic and nonplasmonic nanostructures as a tapestry of nanoparticles. This new circuit paradigm, which we coin "meta-nanocircuits" inspired by metaplasmonics, provides us with the possibility of tailoring and manipulating optical electric fields with desired patterns in sub-wavelength regions, and thus allows the mathematical tools of circuit theory to be used in the THz, IR and optical frequencies. This will open doors to many innovations in future optical nanoelectronics and nanosystems, and may likely lead to a new paradigm for information processing, detection, and storage, in the nanometer scales. In our theoretical and computational works, we have shown how more general circuits with various transfer functions can be considered by using blocks of nanostructures, providing new ways of designing nano-scale optical lumped components and devices such as filters, switches, etc. at optical wavelengths. Such meta-nanocircuits may one day be also interfaced with biological circuits, leading to the possibility of hybrid nano-bio circuits. In this talk, I will present an overview of some of our theoretical results and computational simulations on this concept of metactronics - metamaterial electronics.

4:40pm **IPF-TuA10 Understanding the Near Earth Object Population,** ***W.F. Bottke***, Southwest Research Institute **INVITED**

Near Earth Objects (NEOs) are asteroids and comets on orbits that allow them to approach and, in some cases, strike the Earth. This population is comprised of bodies ranging in size from dust-sized fragments to objects tens of km in diameter. It is now recognized that the impact of diameter D > 0.1 km NEOs represent a small but non-negligible hazard to human life and infrastructure. Interestingly, however, the potential threat represented by these bodies may also be one of easier ones to mitigate against, provided adequate resources are allocated to identify all of the NEOs of relevant size. Using our knowledge of the collisional and dynamical mechanisms that transport asteroids and comets from their source regions all the way to NEO space, we now have a working model of the steady-state orbital, size, and albedo distributions of the NEO population. This model does an excellent job of reproducing observations from various NEO surveys (e.g., LINEAR). We predict the existence of approximately 1000 NEOs that are roughly 1 km in size. The mean impact interval for these objects with the Earth is 0.5 My, with most impactors being asteroids rather than comets. We also find that the Earth should undergo a 1000 megaton (MT) collision every 64,000 years. Only a tiny fraction of the 300 m diameter bodies capable of producing these kinds of blasts have been discovered to date. These predicted impact rates are in good agreement with the terrestrial and lunar crater record and have been confirmed by recent work. Our NEO model has recently been used to predict the future rate of NEO discoveries using current and next-generation survey technology. We find that 90% of the potentially hazardous (diameter D > 140 m) NEOs could be found within 20 years or so using new ground- or space-based surveys. The cost of these systems vary, but much can be accomplished for a budgetary equivalent to a NASA Discovery-class mission ($200-$400 million). Our understanding of the processes that produce NEOs has also led to new insights into how the terrestrial impact flux has changed over time. We can now show that large breakup events in the inner portion of the main asteroid belt may trigger so-called asteroid showers, events that can dramatically increase the impact flux on Earth for prolonged periods (e.g., in some cases for as long as 100 My). In fact, one particular breakup event occurring within the last 200 My may have had important implications for our understanding of mass extinction events and life on Earth.

Nanomanufacturing Topical Conference

Room: 615 - Session NM+TF-TuA

Nanomanufacturing of Materials

Moderator: M. Tuominen, University of Massachusetts, Amherst

1:40pm **NM+TF-TuA1 Nanoscale Patterning with S-layer Proteins and Area Selective Atomic Layer Deposition**, ***J.R. Liu***, *C.M. Tanner, E. Lan, B.S. Dunn, J.P. Chang*, University of California at Los Angeles

Nano-sized crystalline bacterial cell surface layer (S-layer) proteins have the intrinsic property to reassemble into two-dimensional arrays with ordered pores of identical size onto solid supports,[1] ideal as a template for nanoscale patterning. In this work, we demonstrated that, when combined with area selective atomic layer deposition (ALD), the reassembled S-layer proteins can be effective nanotemplates to pattern nano-sized dielectrics. S-layer proteins were reassembled on Si wafer from the solution containing protein units and $CaCl_2$. Atomic force microscopy (AFM) and transition electron microscopy (TEM) images showed that the protein unit size and the pore diameter are about 10 nm and 5 nm, respectively. Octadecyltricholorosilane (ODTS) was used to modify the more hydrophilic protein surface since ODTS has been demonstrated to be an effective monolayer resist on a hydrophilic SiO_2 surface toward ALD of HfO_2.[2] High-k oxides were only deposited in the pores built by the protein units by an area selective ALD after the S-layer nano-template was modified by ODTS. Attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR), contact angle measurement, and x-ray photoelectron spectroscopy (XPS) were employed to analyze the reassembling, modification, and removing process of S-layer proteins. FTIR analysis of the reassembled S-layer proteins before and after ODTS treatment revealed NH (3297 cm^{-1}), CH_3 (2968 and 2866 cm^{-1}), CH_2 (2922 cm^{-1}), CO (1645 cm^{-1}), and CN (1525 cm^{-1}) from S-layer proteins, while the intensity of CH_2 increased after modified by ODTS, due to the 17 CH_2 groups in ODTS. The ODTS treated S-layer proteins surface became more hydrophobic, evident by a contact angle change from 59° to 84° for 2h and 101° for 40h. After cleaning, the peaks of NH (3297 cm^{-1}), CH_3 (2968 and 2866 cm^{-1}), CH_2 (2922 cm^{-1}), CO (1645 cm^{-1}), and CN (1525 cm^{-1}) from S-layer proteins disappeared, confirming that S-layer proteins have been removed completely. The current-voltage (I-V) of oxide nanopatterns is characterized by a conductive AFM.

[1] U. B. Sleytr, P. Messner, D. Pum, and M. Sara, Angew. Chem. Int. Ed., 1034-1054, 38, 1999.

[2] R. Chen, H. Kim, P. C. McIntyre, and S. F. Bent, Appl. Phys. Lett., 4017-4019, 84, 2004.

2:00pm **NM+TF-TuA2 Plasmonic Nanoparticle Complexes for Diagnostics and Therapeutics**, ***N.J. Halas***, Rice University **INVITED**

The combination of metallic nanostructures and molecular adsorbates provides a broadly adaptable route to the development of optically addressible, functional nanocomplexes. In particular, nanostructures based on this approach can be designed to sample, and, via Raman scattered light, report on specific aspects of their chemical environment. Combining this sensing functionality with photothermal heating of the local environment of the nanocomplex provides an important strategy for functional therapeutics for cancer and beyond.

2:40pm **NM+TF-TuA4 Conduction Nature of Nanochannels of Track Etched Polymeric Membranes**, ***K. Awasthi***, University of Rajasthan, India

The nanopores are developed by using one side etching of swift heavy ion irradiated polymeric membrane. In an electrolytic cell, the chemical solution serves as well as etchant and as an electrolyte. In the moment breakthrough of a track the beginning and increasing electrical current supplies information of the birth and growing of the track. The membranes used can be seen as model systems acting as interconnects between two separate liquids. There is a significant difference in the electrical conduction behavior of the electrolytes having common anion. It is clear from the voltage current characteristics that electrical conduction through the etched membrane of polycarbonate is dependent on size of cation.

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3:00pm **NM+TF-TuA5 Laser Sintering of Nano-Silver coated Polyetheretherketone Powder**, ***D. Pohle***, *C. Damm,* University Erlangen-Nuremberg, Germany, *T. Rechtenwald,* BLZ, Bavarian Laser Center gGmbH, Germany, *A. Rösch, H. Münstedt*, University Erlangen-Nuremberg, Germany

The effectiveness of silver as oligodynamic bactericide is proven and well investigated. The silver ions inhibit vital activities of the bacteria, such as breathing and metabolism. Elemental silver particles provide a large reservoir of antimicrobial silver ions, as in contact with water and dissolved oxygen they release small amounts of silver ions, only. The oxidation occurs on the surface of the particles. Accordingly the ion concentration and the rate of silver ion release are dependent on the surface to volume ratio of the elemental silver particles. The polymer matrix used in this investigation is polyetheretherketone. PEEK is a high performance thermoplastic with melting temperature of 345°C, very good mechanical properties and outstanding stability against chemicals and radiation. Its water uptake is below 0.5%. Because of this an antimicrobial equipment of the bulk material by use of silver is difficult. Silver nanoparticles were generated. Polyvinyl alcohol was dissolved in distilled water and silver nitrate was added. Sodium borohydride was used as reduction agent. Formation of elemental silver nanoparticles occurred, which were stabilized by the PVA. PEEK powder (PEEK 150 PF, Victrex, UK) was coated with silver nanoparticles by giving the polymer powder into the silver dispersion for 24h. The coated PEEK powder was used in a laser sintering (LS) process to generate antimicrobially equipped polymer specimens. LS of PEEK is a challenge because of its very high melting temperature and the irregular shape of the polymer particles. A modified laser sintering machine (EOSINT P 380, EOS, Germany) was used to obtain powder bed temperatures up to 350°C. After a pre-treatment of the polymer powder, including sieving and adding a small amount of carbon black to increase the flow ability, it was possible to manufacture discs with a diameter of 10mm and a height of 3mm. By use of LS specimens with open porosity are generated, so water can easily infiltrate the polymer parts. Stripping voltammetry showed that the sintered specimens released much more silver ions than hot pressed dense PEEK specimens. The silver release as function of time plot indicates that the release is governed by diffusion. To investigate the antimicrobial efficacy of the polymer specimens Escherichia coli was used. The antimicrobial tests were made by use of a solid agar plate method. As expected by the silver ion release test the specimens are active against E. coli.

4:00pm **NM+TF-TuA8 TEM-Based Metrology and Structural Characterization of HfO_2 ALD Films Formed in Anodic Aluminum Oxide Templates**, ***I. Perez***, *E. Robertson, L. Henn-Lecordier, P. Banerjee, S.J. Son, S.B. Lee, G.W. Rubloff*, University of Maryland, College Park

A broad variety of nanotechnology applications are poised to exploit the self-assembly that occurs in forming anodic aluminum oxide (AAO) films, which can be structured to comprise cylindrical nanopores with uniform dimensions (15-300nm diameters) spaced closely and regularly in AAO films microns in thickness. Such AAO films comprise templates for manufacturing of energy devices (capacitors, batteries, solar cells), electrochromic displays, or – if released by AAO dissolution - nanoparticle systems for targeted, imageable drug delivery, in which ultrathin highly conformal layers are formed in the nanopores by atomic layer deposition (ALD) or electrochemical deposition (ECD). Nanomanufacturing of such structures relies on the availability of fairly rapid metrologies and material characterization techniques which are precise at the nanoscale. We have achieved this goal based on transmission electron microscopy (TEM) methods, demonstrated here for ALD HfO_2 nanotubes formed in AAO templates. The HfO_2 nanotubes are first released by dissolution of the surrounding AAO template, then captured on standard TEM grids for observation in the TEM, whose high spatial resolution readily allows determination of nanotube diameters and wall thicknesses as a function of distance along the nanotube. We have developed image analysis codes to extract this metrology information in semi-automated fashion, so that ALD deposition profiles can be readily compared with ALD and AAO process parameters to optimize nanostructure manufacturing and to validate further models for process conformality. Furthermore, we have used HRTEM to identify HfO_2 crystal phases at different locations along the nanotubes upon annealing, carried out on nanotubes either while embedded in the AAO template or after release. For annealing at 650°C for 30 minutes, we find the expected monoclinic phase of HfO_2 is formed. These results demonstrate that the ability to release nanotubes from the AAO template, coupled with rapid HRTEM characterization and metrology, comprises an effective means to support AAO-based nanodevice manufacturing.

4:20pm **NM+TF-TuA9 Nano-Manufacturing of Materials at Oak Ridge National Laboratory's NanoApplications Center*, S.M. Robinson***, Oak Ridge National Laboratory

The NanoApplications Center (http://nanotech.ornl.gov/) at Oak Ridge National Laboratory (ORNL) employs state-of-the-art facilities and multidisciplinary R&D capabilities to transition the discoveries of nanoscience to innovative technologies for energy environment, and economic competitiveness. It fosters innovation of new energy-related nanotechnologies and helps transform industry by enabling the responsible development of processes for mass production and application of nano-scale materials, structures, devices, and systems that provide unprecedented energy, cost, and productivity benefits. Capabilities within the NanoApplications Center include 1) materials processing and fabrication, 2) characterization, and 3) responsible nanomanufacturing, and 4) rapid prototyping for development and deployment. This paper describes example nano-manufacturing projects for materials processing and real-time measurements for process control. These include investigation of infrared-based processing for high temperature processing of metals to enhance metallurgical and mechanical properties by controlling grain size and development of coating processes that infuse alloys several hundred nanometers deep into the surface of a metal to create enhanced durability. To better enable nanomanufacturing, researchers at ORNL have developed and applied novel real-time characterization techniques to process monitoring and control. A commercial differential mobility analyzer is being used to sample and characterize nanoparticles in real time.

4:40pm **NM+TF-TuA10 Nanometrology: A Key Element for Successful Nanomanufacturing*, M.T. Postek***, National Institute of Standards and Technology **INVITED**

Nanomanufacturing is the essential bridge between the discoveries of nanoscience and real world nanotech products - it is the vehicle by which this Nation will realize the promise of major technological innovation across a spectrum of products that will affect virtually every industrial sector. For nanotech products to achieve the broad impacts envisioned, they must be manufactured in market-appropriate quantities using reliable, repeatable, and commercially viable manufacturing processes. In addition, they must be manufactured so that environmental and human health concerns are met, worker safety issues are appropriately assessed and handled, and liability issues are addressed. Critical to this realization of robust nanomanufacturing is the development of the necessary instrumentation, metrology, and standards. This will allow the physical dimensions, properties, functionality, and purity of the materials, processes, tools, systems, products, and emissions that will constitute nanomanufacturing to be measured and characterized. This will in turn enable production to be scaleable, controllable, predictable, and repeatable to meet market needs. If a product cannot be measured it cannot be manufactured. This presentation will discuss some of the challenges confronting the effective development of the nanometrology needed for the success of nanomanufacturing.

Nanometer-scale Science and Technology

Room: 616 - Session NS+MS-TuA

Characterization of Nanostructures

Moderator: R.F. Klie, University of Illinois - Chicago

1:40pm **NS+MS-TuA1 Atomic-scale Deformation in N-doped Carbon Nanotubes**, ***C.-L. Sun***, Academia Sinica, Taiwan, *H.-W. Wang, M. Hayashi, L.-C. Chen,* National Taiwan University, *K.-H. Chen*, Academia Sinica, Taiwan

We present the N-doping induced atomic-scale structural deformation in N-doped carbon nanotubes (CNTs) by using energy-filtered transmission electron microscopy (EFTEM) and density functional theory calculations. EFTEM N mapping image shows that N is indeed incorporated in the bamboo-like CNTs with non-uniform distribution. The interlinked parts in CNTs are brighter than the sidewall, indicating that they contain higher N concentration. We then construct the finite cluster models for CNTs with pure and two doping types in order to study the detailed structural changes in atomic scale. For substitutional-N-doped nanotube clusters, the N dopant with an excess electron lone pair exhibits the high negative charge and the homogeneously-distributed dopants enlarge the tube diameter in both zigzag and armchair cases. On the other hand, in pyridine-like-N-doped ones, the concentrated N atoms result in positively curved graphene layer and thus can be responsible for tube wall roughness and the formation of interlinked structures. Several examples for its relevant applications in energy conversion and storage will be briefly introduced in the end.

2:00pm **NS+MS-TuA2 Four-Tip Scanning Tunneling Microscope for Measuring Transport in Nanostructures*, S. Hasegawa***, University of Tokyo, Japan **INVITED**

Since the establishment of techniques for surface conductivity measurement by microscopic four-point probes (M4PP).[1-5] with four-tip scanning tunneling microscope (4T-STM) and monolithic four-point probes, electronic transport through single-atomic layers on semiconductor crystals has attracted considerable interests. The electrical conduction through atomic chains and nanowires can also be measured by the methods. Interesting transport properties of such atomic-scale structures have been revealed; the instability and atomic-scale defects intrinsic to such nano-scale structures play decisive roles in transport. I will introduce and summarize the following several topics in the talk. Recent advancements with metal-coated carbon nanotube tips in 4T-STM are also introduced.[11]) (1) A metal-insulator transition and strong anisotropy in conductivity of Indium atomic wire arrays.[1,6] (2) Resistance caused by monatomic steps on surface .[12] (3) Non-metallic conduction of metallic Au wires and monolayers[7,10] (4) Conductance of individual silicide nano-wires and carbon nanotubes.[8,9,13]

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[2] T. Tanikawa, et al., e-J. Surf. Sci. Nanotech. 1, 50 (2003)[http://dx.doi.org/10.1380/ejssnt.2003.50]

[3] S. Hasegawa, et al., J. Phys.: Condens. Matter 14, 8379 (2002).

[4] S. Hasegawa, et al., Surf. Rev. Lett. 10, 963 (2002).

[5] R. Hobara, et al., Rev. Sci. Inst. 78, 053705 (2007).

[6] T. Tanikawa, et al., Phys. Rev. Lett. 93, 016801 (2004).

[7] H. Okino, et al., Phys. Rev. B 70, 113404 (2004).

[8] H. Okino, et al., Appl. Phys. Lett., submitted.

[9] R. Hobara, et al., Jpn. J. Appl. Phys. 43, L1081 (2004).

[10] S. Yamazaki, et al., submitted to Phys. Rev. Lett.

[11] Y. Murata, et al., Jpn. J. Appl. Phys. 44, 5336 (2005); S. Yosimodo, et al., ibid. 44, L1563 (2005).

[12] I. Matsuda, et al., Phys. Rev. Lett. 93, 236801 (2004).

[13] S. Yoshimoto, et al., Nano Letters 7, 956 (2007).

2:40pm **NS+MS-TuA4 A Novel Approach for Electronic Nanotechnology of Carbon Nanotubes*, K.E. Hurst,*** National Institute of Standards and Technology, *R.K. Ahrenkiel,* National Renewable Energy Laboratory, *T. Campbell,* ADA Technologies, *J.H. Lehman*, National Institute of Standards and Technology

We present a new measurement technique for measuring the recombination lifetimes of carbon nanotubes called the resonant-coupled photoconductive decay (RCPCD) method.[1] The carrier recombination lifetime is a fundamental property of carbon nanotubes which is typically determined by contact-based techniques or spectroscopic methods which do not readily allow characterization of bulk material properties. The measurement is based on a pump-probe technique in which an optical pump and a low frequency microwave probe are employed. RCPCD offers the first rapid, non-contact technique for routine nanometrology of carbon nanotube electronic properties. We demonstrate measurements of carrier lifetimes for multi-walled carbon nanotube and single-walled carbon nanotube thin films, where the ~30 μm thick films are deposited on a glass slide by an air-brush technique. We also consider the influence of material purity on the measurement of lifetimes in these nano-scale systems. Raman spectroscopy and UV-VIS absorption measurements provide further identification and characterization of nanotube samples to enable correlation of nanotube properties with the efficiency of charge transport in these samples. RCPCD is shown to be a fast and effective method for measuring the lifetimes of bulk carbon nanotubes, thereby overcoming present issues of routine carbon nanotube electronic nanometrology.

[1] R.K. Ahrenkiel, S.W. Johnston Mater. Sci. Eng. B 102 (2003) 161

3:00pm **NS+MS-TuA5 Properties of the Surface and Core Region of Single CdS Nanowires*, S.F. Alvarado***, IBM Research, Zurich Research Laboratory, Switzerland, *O. Hayden*, Siemens AG, Germany

The properties of the surface and core region of single CdS nanowires are characterized by STM-based cathodoluminescence under ultrahigh-vacuum conditions at room temperature. The CdS nanowires were fabricated using pulsed laser deposition via metal-cluster-catalyzed growth. A diluted nanowire suspension was used to flow-align the nanowires on a p-type Si substrate using microfluidic channels. Cathodoluminescence is excited by using the tip of an STM as a source of low-energy electrons ($100 < E_{kin} < 1000$ eV) at currents in the pico- to microampere range. The penetration depth of the incident electrons is approx. 1 nm at 100 eV and increases with kinetic energy up to a few nanometers at 1 keV. Therefore this technique allows one to probe the surface region of single nanostructures. A typical spectrum collected on a single nanowire exhibits a relatively sharp emission line centered at approx. 510 nm, with a full width at half maximum of 20 nm, and a much broader band centered at 750 nm. The intensity ratio of the 510 nm to the 750 nm line increases with increasing electron energy, indicating that the 750-nm emission arises from the surface regions of the nanowires, whereas the 510 nm line originates mainly from their core regions. In addition, cathodoluminescence images of single CdS nanowires, collected at different wavelengths, exhibit regions of enhanced emission as well as local variations of the ratio of surface and core contributions. A comparison of cathodoluminescence spectra collected on nanowires, on a CdS nanosheet, and on other structures, suggests a relationship between the ratio of surface-to-core emission and the quality of the nanowires.

4:00pm **NS+MS-TuA8 Helium-ion Microscopy for Nanostructure Characterization**, ***N.P. Economou***, *B. Ward, J. Notte, R. Hill, L.A. Stern*, Carl Zeiss SMT **INVITED**

We have developed the first practical He ion microscope, based on a unique gas field ion source. The source has highly desirable performance characteristics for building scanning ion microscopes with sub-nanometer probe sizes. A unique construction allows the source to provide stable output over useful lifetimes of several hundred hours, thus enabling the development of practical systems for microscopy and nanostructure characterization. An important aspect of the He ion microscope is the interaction of He ions with the sample being observed. As compared with electrons interacting with the same sample, He ions penetrate less deeply, scatter less and produce higher yields of secondary electrons; back-scattered ions are also present. Images produced with a He ion beam exhibit greater material contrast, higher resolution due to reduced interaction volume, and better signal-to-noise ratio. These factors combine to produce He ion images that often contain more and better information than electron images. Because of these inherent advantages, we believe the He ion microscope will become an important tool for the study of nanostructures. We will discuss the unique characteristics of the source, and present images produced from the microscope that demonstrate its advantages over currently available instruments.

4:40pm **NS+MS-TuA10 Study of Characteristic Fragmentation of Nano Carbon by the Scanning Atom Probe**, ***O. Nishikawa***, *M. Taniguchi*, Kanazawa Institute of Technology, Japan, *Y. Saito*, Nagoya University, Japan, *M. Ushirozawa*, Japan Broadcasting Corporation

Since the characteristic fragmentation of a material is closely related with the binding state between the atoms forming the material, multiwall carbon nanotubes (MWCNT), graphite nanofibers (GNF) and ultrapure graphite are studied by field evaporating these specimens and by mass analyzing the fragmented cluster ions with the scanning atom probe. Two kinds of MWCNT were analyzed: commercially available and laboratory fabricated MWCNTs. GNF is grown on a 304 stainless steel tip by thermal CVD. Purity of the analyzed graphite is 99.9999%. The mass spectra of both MWCNTs are quite similar, particularly mass to charge ratio M/n from 0 to 100. However, the commercial MWCNT exhibits many unidentifiable small mass peaks throughout the mass range up to a few thousands. The most significant feature is the large mass peak at M/n = 340 which could be $C_{28}H_4$. The proposed structure of this cluster is a squarely arranged 8 hexagonal rings. This structure is suitable to form a tube. The mass spectrum of GNF is quite different from that of MWCNT and shows the highest mass peak at M/n = 278, $C_{23}H_2$. The proposed structure of this cluster is the triangularly arranged six hexagonal cells. Two corner carbon atoms of the triangle are hydrogen-terminated and third corner carbon atom is bound with an extra carbon atom. Two dimensional extension of the fragments shows a hexagonal ring formed by 6 hydrogen atoms terminating the carbon bonds and 6 extra carbon atoms forming a hexagon. The hydrogen hexagonal ring is quite similar to that of a kekulene molecule. The graphite exhibits two completely different mass spectra. One is quite similar to that of MWCNT showing the characteristic large mass peaks. The other closely resembles those of silicon and diamond. The number of detected ions decreases with mass. Thus, the largest mass peak is C^{2+} and then C^+. The clusters formed by the odd number of carbon atoms are more abundant than those of even number. Most clusters are doubly charged. This implies that the binding between carbon atoms in this analyzed section is strong and uniform and that the graphite has two phases: diamond and graphite. Although only few H^+ ions are detected from MWCNTs and GNF, most fragments contain more than 1 hydrogen atom. On the other hand few ions detected from the diamond-like graphite are bound with hydrogen.

5:00pm **NS+MS-TuA11 Nano-scale Surface Effects of Field Electron Emission from Zirconium and Hafnium Carbide**, ***W.A. Mackie***, *G.M. Magera, K.J. Kagarice*, Applied Physics Technologies

An electron source for a high resolution SEM/TEM application should produce a high brightness, have a minimal energy distribution, and should be highly stable. In an application in which the resolution is limited by chromatic aberrations, one can improve the performance over a commonly used thermal field emission source, such as a ZrOW Schottky emitter, by using a cold field emission source (CFE). In CFE, the emitting area of the usable beam is small and understanding surface chemistry and effects are crucial to controlling emission stability. Single crystalline transition metal carbides have electron emission properties making them attractive candidates for CFE applications. We are reporting on field emission from (310) oriented single crystal ZrC and HfC. ZrC(310) has a relatively low work function axial emitting surface (3.4 eV) that has a low evaporation rate, is resistant to ion bombardment and sputtering, has a high melting point (~3800 K), and a very low surface mobility. The robustness of this material allows for repeated cleaning via high temperature flashing without changing the geometry of the emitting end form. These crystals are electrochemically etched and mounted in a mini Vogel mount to enable flash cleaning. Experimental I(V) data were taken from which angular intensity and reduced brightness were calculated. Experimental I(t) data were then taken and analyzed for current stability in both long term drift and short term noise. Results are highlighted from a 160 nm ZrC (310) operating at 0.02 mA/sr. Noise spectra were analyzed by FFT and found to be consistent with step and spike like noise associated with foreign atom migration and ion bombardment. Emission from small areas comprising <100 atom sites are dominated by the mobility of foreign atoms from ion back streaming and surface diffusion both arising from the high electric field. Using an annular area surrounding the beam emission area as a current monitor we were able to control fluctuations in the beam. This control ability results from the overlapping currents from both areas. Data are presented which demonstrate improved stability over a variety of vacuum conditions.

Understanding Biointerphases and Magnetism with Neutrons Topical Conference

Room: 618 - Session NT-TuA

Magnetism

Moderator: M. Grunze, University of Heidelberg, Germany

2:00pm **NT-TuA2 Introduction to Magnetic Neutron Scattering**, ***S.E. Nagler***, Oak Ridge National Laboratory **INVITED**

Neutron scattering is arguably the most powerful experimental technique available for characterizing magnetic structures and excitations. This talk will provide a brief introduction to neutron scattering, with emphasis on its application to problems in magnetism. The talk is intended for scientifically literate non-specialists.

2:40pm **NT-TuA4 Polarized Neutron Reflectometry and Diffraction on Magnetic Thin Film Structures**, ***F.R. Klose***, Oak Ridge National Laboratory **INVITED**

In this presentation, I will review applications of polarized neutron reflectivity and diffraction in regard to magnetic thin film research. Polarized reflectivity is an ideal tool for investigating vector magnetization profiles in thin film systems with a vertical depth-resolution of a few monolayers. The method has been used for many years, for example, to demonstrate oscillatory exchange coupling in magnetic multilayers, the effect which is causing giant magneto-resistance. Recently developed polarized "off-specular / diffuse" scattering methods also allow investigations of lateral (in-plane) magnetic correlations on length-scales between 1 nm and 100 µm. High-angle magnetic neutron diffraction is an extremely powerful technique for investigating atomic-scale antiferromagnetism in thin films. The latter is very important in regard to the exchange bias effect which is used in magnetic storage technology. Recent research results on Fe-Pt based films for magnetic recording applications will be presented.

4:00pm **NT-TuA8 Opportunities for Neutron Scattering in Thin Magnetic Films for Sensor Technology.**, ***M.L. Plumer***, Memorial University of Newfoundland, Canada **INVITED**

With the continued demand for ever smaller and faster magnetic sensors based on thin-film technology the requirements for deeper understanding of the relevant processes involved continue to grow. Simple modeling methods based on Maxwell's equations, and simple experimental techniques that measure only bulk magnetic properties, served the industry well for the latter part of the twentieth century but are no longer adequate research tools for the engineering of the nanometer magnetic devices of today and tomorrow. This talk will review some of the detailed knowledge of both static and time-dependent behavior of interacting magnetic grains within films and multilayers that can be gained through micromagnetic simulations based on the Landau-Lifshitz-Gilbert (LLG) equations. Opportunities for the use of a variety neutron scattering techniques to measure such detailed equilibrium and dynamic properties will be discussed.

4:40pm **NT-TuA10 Nanostructures and Ordering Phenomena in Magnetic Colloids Probed by Small Angle Neutron Scattering**, ***A. Wiedenmann***, Hahn-Meitner-Institut Berlin, Germany **INVITED**

Small Angle Neutron Scattering (SANS) allows fluctuations of density, composition and magnetization to be analysed simultaneously on a nanometers length scale. This non-destructive technique was used to characterise magnetic colloids which are of growing interest for advanced medical applications. Such "Ferrofluids" consist of nanosized magnetic particles coated by nonmagnetic organic surfactants and dispersed in carrier liquids. Isotope contrast variation combined with the newly developed technique of polarised neutrons ("SANSPOL") allowed size distributions, compositions and magnetic moments of magnetic core-shell particles and magnetic aggregates to be evaluated precisely beside non-magnetic micelles of similar sizes.[1] In concentrated Ferrofluids an unconventional pseudo-crystalline ordering has been monitored by SANS resulting from strong field-induced inter-particle correlations.[2-3] New stroboscopic techniques have been developed which allowed the dynamics of ordering and realxation to be studied in a time range similar to that of X-ray photon-correlation spectroscopy.[4]

[1] Wiedenmann, A., Kammel, M., Heinemann, A., Keiderling, U. J. Phys. : Condensed Matter: 18 (2006) S2713-2736

[2] Wiedenmann, A., Hoell, A., Kammel, M. , Boesecke, P. Phys Rev. E 68 (2003) 031203

[3] Klokkenburg, M., Erné, B. H., Meeldijk, J.D., Wiedenmann, A., Pethukov, A.V., Philipse, A.P, Physical Revue Letters 97, 185702 (2006)

[4] Wiedenmann, A., Keiderling, U., Habicht, K., Russina, M., Gähler, R., Physical Review Letters 97, 057202 (2006)

Plasma Science and Technology

Room: 606 - Session PS1-TuA

Plasma Etching for Advanced Interconnects II

Moderator: D.J. Economou, University of Houston

1:40pm **PS1-TuA1 Process Performance of CO_2 In Situ Photoresist Ashing Processes and Their Influence on ULK Materials Modifications**, ***M.S. Kuo***, *G.S. Oehrlein*, University of Maryland at College Park, *S. Sirard, E.A. Hudson*, Lam Research Corp.

An in situ ashing process for removing photoresist (PR) layers is desired by industry as an alternative to remote plasma ashing processes since it could be more easily integrated with plasma etching processes. In this work, we examined the feasibility of CO_2 as source gas for in situ PR ashing processes compatible with ULK materials, and performed characterization of 193 nm PR ashing along with ULK (JSR LKD 5109, and several other candidate materials) damage evaluation. Reducing CO_2 pressure from 100 to 10 mTorr increased the ion density and led to a higher PR ashing rate (substrate at 10 °C, line of sight interaction), while suppressing ULK damage (non-line-of-sight interaction). Low pressure operation using CO_2 enabled a high ashing efficiency (AE) which is defined as the amount of PR removed over the amount of ULK material damaged (for a given time). The CO_2 AE at 10 mTorr is ~5 times improved relative to O_2 and comparable to the best values we have measured for typical H_2 based remote plasma ashing processes. For the CO_2 in situ ashing processes, we examined sidewall damage introduced in ULK trench structures employing scanning electron microscopy (SEM). We also used a gap structure to simulate exposure of ULK materials in actual trench sidewalls. This allowed characterization of ULK surface modifications induced by the indirect plasma exposure using ellipsometry, X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). These results will be presented, along with a discussion of issues derived from real pattern transfer processes such as etching/ashing interaction and the influence of slight ion bombardment to ULK sidewall during in situ ashing.

2:00pm **PS1-TuA2 SiOCH Damage in N_2/H_2 Plasma**, ***M. Fukasawa***, *T. Tatsumi, K. Nagahata*, Sony Corporation, Japan, *S. Uchida, S. Takashima, M. Hori*, Nagoya University, Japan, *Y. Kamide*, Sony Corporation, Japan

Reducing the damage to low-k dielectrics caused by plasma is one of the key issues for achieving high-performance devices. We report the root cause of the dielectric constant increase (Δk) of SiOCH that occurs after N_2/H_2 plasma exposure. The plasma damage of SiOCH (k=2.65) was investigated in a dual-frequency (60/2 MHz) capacitively coupled plasma reactor equipped with a surface wave probe, quadruple mass spectrometer, high-voltage probe and optical emission spectroscope. Measurements were performed as a function of an N_2/H_2 flow rate ratio, while maintaining total ion and neutral fluxes, and ion energies. The amount of moisture uptake during air exposure, Δk, water contact angle, and chemical bonding were analyzed. The behavior of Δk strongly depends on the N_2/H_2 flow rate ratio. Thermal disorption spectroscopy revealed that the Δk is almost proportional to the amount of moisture uptake.[1] The amount of Si-CH_3 bond in the bulk SiOCH measured by FT-IR decreased monotonically with an increasing H_2 flow rate ratio. These results suggest that the Si-CH_3 bonds were broken by H, and the dangling bond (or one weakly terminated by H) was generated during plasma exposure. During air exposure, the Si-H bonds are replaced with Si-OH bonds, which then adsorb moisture. However, in the case of H-rich plasma, the Δk decreased, while the total number of adsorption sites increased. We analyzed the depth profile of incident ions since the SiOCH damage gradually varies from the surface depending on the depth distribution of ion, light, and radical diffusion from the surface. In relatively H-rich plasma, the small mass number of dominant ion species (H_3^+) results in the deeper damage caused by the longer projected range (10 nm). Thus, more Si-CH_3 bonds remained on the surface and generated more hydrophobic surface, compared with that generated by relatively N-rich plasma. The hydrophobic surface was found to suppress the moisture permeability and lead to the Δk reduction. To suppress Δk, it is important to precisely control the incident radical/ion flux ratios and ion energies thus reducing the adsorption sites in the bulk and keeping the hydrophobic surface that suppresses the water permeation during air exposure.

[1] M. Fukasawa et al., in Proceedings of International Conference on Dry Process, Nagoya, Japan (2006) p.5.

2:20pm **PS1-TuA3 Study of Downstream O_2 Plasma Damage to Blanket and Patterned CDO Low k Films**, ***J. Bao***, *H. Shi, H. Huang, J. Liu, P.S. Ho, E. Paek, G.S. Hwang*, The University of Texas at Austin

Carbon Doped Oxide (CDO) low k films were treated by downstream O_2 plasma. The effects of O_2 plasma on blanket and patterned low k dielectric surfaces were studied by in-situ angle resolved X-ray photoelectron spectroscopy (ARXPS) and Fourier transform infrared spectroscopy (FTIR). The reaction byproducts were analyzed by residual gas analyzer. Roles of ions and radicals in the plasma to cause carbon depletion were investigated using a plasma source that was capable of separating ions from plasma beam. Energetic ions in oxygen plasma contributed much to the loss of film hydrophobicity and dielectric constant through the formation of C=O and Si-OH. Coupled with RGA analysis, three possible reaction paths leading to carbon depletion were proposed. Effects of ions and radicals on blanket low k films at different tilt angles (0^0 to 90^0) were analyzed. Finally, O_2 plasma damage to patterned CDO film was studied by XPS and SEM. And the damage behavior was simulated with Monte Carlo method. It was found that the charging potential distribution induced by plasma was important in determining low k film carbon loss. The charging potential distribution was mainly related to the geometry of low k trench structures.

2:40pm **PS1-TuA4 Ion- and Radical-Induced Ultra Low-k Damage Mechanisms**, ***M.A. Goldman***, *S.H. Kim, D.B. Graves*, University of California, Berkeley

It is widely understood that photoresist strip following dielectric etch often damages ultra low-k films. We measured the effects of molecular beams of ions and radicals impacting porous, ultra low-k dielectric films in a vacuum beam chamber to simulate damage induced by photoresist stripping under controlled conditions. Damage was characterized by ex-situ FTIR, contact angle measurements, SEM coupled with damaged layer etching, and AFM. We find that rare gas ions (Ar^+ and Xe^+) alone appear to damage only the near-surface region of the film. In addition, we report results on the mechanism of damage due to radical beams, including O, N, NH_x, NO, and H. For oxygen radical damage on porous ultra low-k films, carbon abstraction and subsequent moisture uptake is shown to be a diffusion-limited process that occurs as a front of carbon depletion that penetrates through the film. Rare gas ion bombardment at normal incidence is shown to significantly reduce the damaging effects of O atoms, apparently by closing pores at the surface of the film.

3:00pm **PS1-TuA5 Evaluation of Plasma Damages due to VUV Light, UV Light, Radicals, Ions and Interaction of Light and Radicals on Low-k Films**, ***S. Uchida***, *S. Takashima, M. Hori*, Nagoya University, Japan, *M. Fukasawa, K. Oshima, K. Nagahata, T. Tatsumi*, Sony Corporation, Japan

The low-k films are wildy used as the insulating materials of ULSIs in order to reduce the RC delay. The low-k films receive the damages from the plasmas in the etching and ashing processes. The plasma damages induce the increase of the dielectric constant of the films. In order to realize the damage free plasma processes, it is necessary to clarify the influences of the light, the radicals, and the ions from the plasmas on the low-k films. In our previous study, in order to separate the effects of the light, the radicals, and the ions in the process plasmas, we have developed a new technique, where the four kinds of etching samples were prepared. We call the technique a pallet for plasma evaluation (Pape). These samples were as follows. The MgF_2 and the quartz windows were put directly on the film, respectively, to clarify the influence of the vacuum ultraviolet (VUV) light and the ultraviolet (UV) light from the plasmas. The MgF_2 and the quartz windows transmit the light of wavelength 115nm or more and 170nm or more, respectively. Si plate was put 0.7 mm above the film surface to investigate the influence of radicals. In order to clarify all the influences of the light, the radicals, and the ions, nothing was put on the film. In this study, we have improved the Pape in order to evaluate the effect of the interaction of the light and the radicals. The advanced Pape is the methods of putting the MgF_2 and the quartz windows 0.7 mm above the film surface. The low-k film used in this study was the porous SiOCH film. The dual frequency capacitively coupled plasma employing H_2 and N_2 gases was used in this study. The refractive index and the film thickness were measured by an ellipsometer. At a VHF power of 500W, a bias power of 500W, a gas flow rate ratio of 50%, and a pressure of 5.3 Pa, the ions induced the largest damage on the films. Moreover, the damage due to the interaction of the lights and radicals was larger than that due to the individual lights and radicals.

4:00pm **PS1-TuA8 Low-Damage Low-k Etching by CF_3I Plasma with Low Global Warming Potential**, ***E. Soda***, *S. Kondo*, Selete, Japan, *Y. Ichihashi*, *A. Sato*, *H. Ohtake*, *S. Samukawa*, Tohoku University, Japan, *S. Saito*, Selete, Japan

The CF_3I gas has been developed to reduce the recent global warming[1] because it has a low global warming potential (GWP) of 1.0 while most of conventional etching gases have considerably higher potentials of more than 1000 (CF_4: 6500, C_4F_8: 8700). The feasibility of CF_3I plasma etching and its damage to the porous low-k film (SiOC, k=2.6) were studied in this work. When an SiOC film was exposed to the CF_3I plasma, increase in the k-value and decrease in CH_3 group of the film (FTIR) were found to be suppressed compared with those caused by conventional CF_4 plasma because intensity of the ultra violet (UV) light in CF_3I plasma was lower than that of CF_4 plasma. To investigate etching property of CF_3I gas, we used a photolithography patterned wafer with the resist mask of 200-nm pitch size. As a result, the etching profile of CF_3I plasma was comparable with that of CF_4 plasma. Since the etching selectivity (SiOC/ArF) of CF_3I plasma was higher than that of CF_4 plasma, the remaining resist thickness after etching increased, thereby line edge roughness (LER) was suppressed. Moreover, the pulse operation in CF_3I plasma drastically increased etching rate and minimized UV damage to the low-k film because injection of negative ions in pulsed plasma enhanced the low-k film etching. Accordingly, we found that CF_3I plasma is one of the promising candidates for low-damage and highly selective low-k etching. This work is supported by the New Energy and Industrial Technology Development Organization (NEDO).

[1] N. Nagasaki et al., "The Development of a Novel Catalytic Technology for CF_3I Manufacture", Halon Options Technical Working Conference, May 2000.

4:20pm **PS1-TuA9 Ash Plasma Exposure of Hybrid Material (SiOCH and Porogen): Comparison with Porous SiOCH**, ***M. Darnon***, CNRS, France, *T. Chevolleau*, LTM-CNRS, France, *T. David*, CEA-LETI-MINATEC, France, *L. Vallier*, LTM-CNRS, France, *J. Torres*, STM, France, *O. Joubert*, LTM-CNRS, France

In CMOS technology, the dominant strategy to achieve future generation of ultra low-k interlayer dielectric materials with a dielectric constant close to 2.2 is to introduce porosity into a SiOCH matrix. However, porous materials are very sensitive to etch and ash plasma exposure and one of the major integration challenges is to reduce the impact of plasma processes on the ultra low-k degradation. To solve this issue, one of the emerging solutions is the late porogen removal process. In this approach, the porosity is generated by a sacrificial carbon based porogen which is desorbed after patterning or copper filling. Such hybrid materials (SiOCH matrix and porogen) are expected to behave like dense materials and therefore to be less sensitive to plasma processes (etching and ashing). In this work, the hybrid material and the porous material are compared in terms of sensitivity to ash plasmas. The ash plasmas are performed in an industrial MERIE (Magnetically Enhanced Reactive Ion Etcher) and in an ICP (Inductively Coupled Plasma) reactor using oxygen-, ammoniac- or methane-based plasmas. X-ray photoelectron spectroscopy studies shows that the surface composition of the porous SiOCH is modified after the ash plasma treatments (SiO, SiON, and SiOC after O_2, NH_3 and CH_4 treatments, respectively) and X-ray reflectometry measurements indicate an increase of the surface density. Hybrid materials and porous SiOCH after ash plasma treatments present similar surface composition but no surface densification is evidenced. After the pore release process of the treated hybrid material, the surface composition remains close to the treated porous SiOCH and the top surface is denser than as deposited porous SiOCH. Infrared spectroscopy (FTIR) shows an important bulk modification of the porous SiOCH after ash plasma exposure (carbon depletion and new absorption bonds depending on ashing plasmas), whereas the hybrid material volume is hardly modified. After the pore release process of the treated hybrid materials, FTIR spectra are identical to an untreated porous SiOCH indicating an almost unmodified porous SiOCH. The porogen of the hybrid material prevents the bulk modification potentially induced by the different ash plasmas. Consequently, after the pore release process the material is similar to an unmodified porous SiOCH with only a slight modification of the top surface.

4:40pm **PS1-TuA10 Effects of Combining H Radical Treatment and Low-k Restoration for Extreme Ultra Low-k**, ***L.H. Chen***, *S. Tahara*, Tokyo Electron AT LTD, Japan, *R. Asako*, Tokyo Electron LTD, Japan, *K. Yamazaki*, Tokyo Electron AT LTD, Japan, *Y. Ohsawa*, Tokyo Electron LTD, Japan, *Y. Chiba*, Tokyo Electron AT LTD, Japan, *H. Nagai*, Tokyo Electron LTD, Japan, *K. Kubota*, Tokyo Electron AT LTD, Japan, *K. Maekawa*, Tokyo Electron LTD, Japan

Extreme Ultra low-k (eULK) dielectrics with k-value of below 2.2 have been extensively evaluated for 32 nm technology and beyond. The eULK dielectrics exert new challenges in etch/ash plasma process and post treatment process. In photo resist stripping, hydrogen radical is known as a reactant to minimize low-k damage compared to oxygen. Hydrogen radical, however, does not restore etch-induced low-k damage. Thus, a low-k restoration following to hydrogen radical stripping should be processed subsequently. At this point, we picked up the silylation process with vaporized silazanes as a low-k restoration technique so that all processed from etch to low-k restoration could be integrated in a dry system for high restoration effectiveness and productivity. In this study, we investigated the effects of combining H radical treatment and low-k restoration by using spin on dielectric blanket film (k=2.2). It was confirmed that a hydrogen process/treatment did not only minimize low-k damage in photo resist stripping but also reduce oxygen in copper, and decrease fluorine in low-k film by Thermal Desorption Spectroscopy (TDS) analysis. Moreover, the combination of a hydrogen treatment and low-k restoration in a dry system without air exposure showed that k value, leakage current, H2O degas amount by TDS, and carbon profile by Secondary Ion Mass Spectroscopy (SIMS) were improved and recovered to near pristine low-k material.

5:00pm **PS1-TuA11 Process Induced Damages and Their Recovery for Highly-Porous Self-Assembled Porous Silica Low-k Film**, ***K. Kinoshita***, *S. Chikaki*, *M. Nihei*, Selete Inc., Japan, *H. Tanaka*, *K. Kohmura*, Mitsui Chemicals, Inc., Japan, *T. Nakayama*, ULVAC, Inc., Japan, *T. Kikkawa*, ASRC, AIST, Japan

To realize the low-k film of k<2.1 with silica material, it is necessary to achieve the porosity higher than 50%. We have been developing porous silica materials. The characteristics of the porous silica is; (a) scalability of the k-value by controlling pore structure with self-assembled process, and (b) post reinforcing and hydrophobizing treatment.[1] The new process technologies to apply such highly porous low-k films to the interconnect module process have been developed, simultaneously. Especially, introduction of the damage recovery process is inevitable.[2] This paper describes about damage recovery process for the porous silica materials. The porous silica blanket films with k~2.07 and E~6.5 GPa were formed on 300 mm wafers. They were half-etched by fluorocarbon plasma, and were exposed to high-temperature He/H_2 down flow ashing plasma. Then, wet clean by two different types of chemical were examined, followed by the damage recovery process by TMCTS vapor annealing. The samples were evaluated by k-value measurement, FT-IR, and TDS after each step. The porous silica films after the etching and the ashing were first treated by the organic acid type wet chemical solution. The k-value of the films increased from 2.07 (pristine) to 2.66 (etching), 2.67 (ashing), and 2.96 (wet clean). The TDS spectrum showed the desorption of the species originated in the wet chemical solution. In contrast to that, the k-value increased to 2.78 after the treatment by the dilute aqueous solution type chemical. The FT-IR and TDS spectra showed almost no change compared with those after the ashing. The recovery process at the pressure of 4 kPa or 30 kPa were evaluated. The recovery of the k-value was remarkable under the high pressure 30 kPa conditions (k=2.17). The collision probability enhancement between silanol groups on the pore surface and TMCTS molecules diffusing into the pore is important to improve recovery effect. When the incident ion-energy during etching was reduced to change the initial damage level with keeping final film thickness, the k-value recovered clearly at the lower ion-energy condition. The recovery effects by the other molecules, and electrical properties of Cu interconnect structure will be presented. Part of this work was assisted by NEDO.

[1] K. Kohmura, et al., Thin Solid Films, 515, 5019 (2007)

[2] T. Ono, et al., Jpn. J. Appl. Phys., 45, 6231 (2006).

Plasma Science and Technology

Room: 607 - Session PS2-TuA

Plasma Sources

Moderator: D.L. Keil, Lam Research Corporation

1:40pm **PS2-TuA1 Influence of Gas Heating on Microplasma I-V Characteristics**, ***S.G. Belostotskiy***, *V.M. Donnelly, D.J. Economou*, University of Houston

Experimental I-V characteristics of DC microdischarges in helium were obtained at different operating pressures (P = 300 - 800 Torr). Since the interelectrode gap was relatively small (L = 300 μm), the voltage drop across the discharge was approximately equal to that across the cathode sheath. It was found that the scaling laws obtained by the classical theory of the cathode layer developed by von Engel and Steenbeck (i.e., the cathode voltage is a function of current density divided by the square of the pressure - $V_c = f(j/p^2)$) are not applicable to microdisharges due to the influence of gas heating. For example, the voltage drop at p = 700 Torr was 40 Volts higher than that at p = 300 Torr for the same reduced current density J = 3 $\mu A/(cm^2*Torr^2)$. A new semi-analytical model of the cathode layer that accounts for neutral gas heating was developed. Model predictions were in agreement with the experimental I-V characteristics. The model can be used to quantify the influence of neutral gas heating on microdischarge performance.

2:00pm **PS2-TuA2 RF Discharge under the Influence of a Magnetic Field**, ***E.V. Barnat***, *P.A. Miller*, Sandia National Laboratories, *A.M. Paterson*, Applied Materials

We examined the effects of an externally applied magnetic field (0 to 150 Gauss) on a capacitive 13.56 MHz argon discharge in a Gaseous Electronics Conference (GEC) reference cell. The electrical characteristics of the discharge were measured as functions of applied magnetic field and rf power. At fixed power the rf voltage decreased with increasing magnetic field. The discharge impedance was predominantly capacitive and became more resistive as the electron mobility decreased with increasing magnetic field. We also measured the effect that the magnetic field had on the spatial distribution of the plasma in vertical planes parallel and perpendicular to the direction of the magnetic field using Langmuir probes, optical emission, and laser induced fluorescence. Due to ExB forces, the distribution of excited states in the plasma remained radially symmetric in the plane parallel to the magnetic field and became skewed in the plane perpendicular to the magnetic field. The degree of skew depended on the state probed. Finally, we examined the temporal evolution of the electric fields in the plasma. In the presence of magnetic field, the sheath thickness decreased and most of the voltage drop was contained within the sheath. Consistent with dc voltage trends, there was no significant sheath reversal observed at higher magnetic fields. Comparisons of the results presented here are made to trends predicted by models and simulations found in the literature.

2:20pm **PS2-TuA3 Characterization of a High Power Surface Wave O_2/N_2 Plasma Jet for Removing Photoresist from Semiconductor Wafers**, ***M. Bhargava***, *B. Craver, H. Guo,* University of Houston, *A.K. Srivastava,* Axcelis Technologies, *J.C. Wolfe*, University of Houston

We describe a plasma system for removing photoresist from silicon wafers where reactant gas flowing in a quartz tube is activated by a high power, 2.45 GHz surface wave discharge at pressures near 80 Torr.The plasma applicator is based on Moisan's 'surfaguide' design[1] where the discharge tube passes through a thin-walled coupling aperture in a reduced-height wave-guide section. Microwave electric fields loop out of the aperture and launch surface waves in both directions along the interface between the discharge tube and the plasma. The directional flow (3slm) of process gas in the tube (6 mm inside diameter) effectively suppresses the discharge on the upstream side of the waveguide. This same flow, in conjunction with the downstream surface wave, produces a plasma jet that emerges from the end of the discharge tube and carries hot, activated gases to a scanning wafer below.The discharge tube is cooled by a counter-flow of clean, dry air confined in a coaxial outer tube; this enables extended operation at 2.5 kW for O_2/N_2 discharges. The wafer is clamped to a heated, 200 mm chuck with a backside pressure of about 35 Torr. An x-y stage, actuated by in-vacuum linear motors, translates the wafer with speed and acceleration up to 1.1 m/s and 2 g, respectively. The efficiency of converting microwave power to thermal jet power is 21% and 19% for respective substrate-to-source distances of 0.9 cm and 2.9 cm, independent of oxygen concentration. For an O_2:N_2= 9:1 plasma jet operating at 2.5 kW, 80 Torr pressure, and a flow of 3slm, the etched track profile is Gaussian in shape with a full-width-at-half-maximum of 1.5 cm. A serpentine raster pattern with 7 mm pitch is used to cover an entire 200 mm wafer. The time to clear 1.2 μm thick, unimplanted photoresist is about 10 seconds for a 70 cm/s scan speed and 200 °C chuck temperature. This corresponds to an instantaneous etch rate of about 4000 μm/min. A detailed analysis of the transient heating process will be presented at the conference. Acknowledgements: Partially supported by the Texas Center for Superconductivity at the University of Houston. The authors are grateful to Ivan Berry for insightful discussions. The opinions expressed are solely the responsibility of the authors.

[1] M. Moisan et al., IEEE Trans. Plasma Sci. PS-12, 203-214 (1984).

2:40pm **PS2-TuA4 Effect of DC Superposition on the Selective Etching of SiO_2 over Si_3N_4 in Dual Frequency Capacitively Coupled Plasma**, ***S.-O. Lee***, *M.-S. Lee, S.-H. Cho, Y.-S. Cho, S.-C. Moon, J.-W. Kim*, HYNIX Semiconductor Inc., Republic of Korea

The characteristics of negative external DC superposition with the top electrode in dual frequency $C_4F_6/O_2/Ar$ gas capacitively coupled plasma (CCP) on the selective etching of SiO_2 over Si_3N_4 have been studied as a function of supplying DC voltage, ranging from 0V to -1500V. It is reported that the accelerated 2nd electron which is generated near top electrode sheath by using DC superposition irradiates the wafer, and polymer molecular structure such as C/F ratio and C-C bond structure etc. is reformed. To analyze the effect of DC superposition in dual frequency CCP source, we investigated the chemical species such as CF_2 radicals and other radicals that have influence on polymerization, in the gas phase with optical emission spectroscopy (OES). The thickness and components of fluorocarbon polymer on etched surface were investigated with high resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS).

3:00pm **PS2-TuA5 Frequency and Pressure Effects in Plasma Etching of High Aspect Ratio Features in Dielectric Films**, ***E.A. Hudson***, *C. Hayden, D.L. Keil, S. Engelmann, C. Rusu, L. Romm, M. Srinivasan*, Lam Research Corp.

Microelectronics processing requires etching of many different dielectric films and structures. Among these applications, some of the most challenging are the etching of high aspect ratio contacts and memory cells. Dual-frequency capacitively-coupled discharges at high power are widely used for these applications. Typically a lower excitation frequency provides the capability for high energy ion bombardment while a higher frequency allows decoupled control of plasma density. This paper examines the effect of applying three different excitation frequencies at the wafer electrode to access this process regime, using a mechanically confined plasma in a narrow-gap etch reactor. The effects of process pressure and 27MHz vs 60MHz, in combination with 2MHz, were characterized by plasma diagnostic measurements of ion flux and radical densities. Dense arrays of high aspect ratio holes were etched to measure the feature-level influence of these process control parameters. Results indicate that the combination of 60MHz and lower pressure allows operation at higher ion:radical flux ratios, which may help to prevent early etch stop. Additionally the radical chemistry is controlled by the ratio of 27MHz to 60MHZ power. Therefore the combined use of three frequencies improves the tuning of feature profiles and the control of striations.

4:00pm **PS2-TuA8 Numerical Investigation of Wave Effects in High-Frequency Capacitively Coupled Plasmas***, ***Y. Yang***, *M.J. Kushner*, Iowa State University

The trend in dielectric etching using capacitively coupled plasmas is use of multiple frequencies where a high frequency (tens to hundreds of MHz) dominates ionization and a low frequency (a few to 10s MHz) is used to control ion energy distributions. As the effective wavelength in the plasma waveguide represented by the reactor decreases with increasing frequency, electromagnetic wave propagation effects become a concern and may give rise to limitations on processing uniformity. These effects have been investigated experimentally but are difficult to address computationally in arbitrary geometries due to the coupling between the electromagnetic and the electrostatic fields, the latter of which is responsible for the formation of the sheath. In this talk, we discuss results from a computational investigation of high frequency effects in capacitively coupled plasmas. A full Maxwell solver based on the concept of vector and scalar potentials, and capable of resolving wave effects in a self-consistent manner in arbitrary geometries, was developed and incorporated into the Hybrid Plasma Equipment Model, a two-dimensional hybrid simulation. In particular, the capability to address multiple frequencies in the time domain are included. To properly capture high frequency heating, excitation rates are provided by spatially dependent electron energy distributions generated by a Monte Carlo simulation. The method of solution will be discussed and comparisons made to using a conventional electrostatic method for electric fields. Results from investigations of dual frequency CCPs (low frequency < 10 MHz, high frequency > 50 MHz) in 10s of mTorr polymerizing and non-polymerizing gas mixtures will be discussed. Assessments of the change in power deposition profile as a function of frequency will be made.

*Work supported by the Semiconductor Research Corp. and the National Science Foundation.

4:20pm **PS2-TuA9 Physics of Very High Frequency (VHF) Capacitively Coupled Plasma Discharges**, ***S. Rauf***, *K. Bera*, *K. Collins*, Applied Materials, Inc.

Capacitively coupled plasma (CCP) discharges are widely used for dielectric etching in the semiconductor industry. Operating frequencies, especially the source frequency in multi-frequency CCP systems, have generally increased in recent years to be able to generate high electron-density discharges with moderate ion energy. Concomitantly, economic considerations are driving towards radially larger plasma discharges. The combination of higher driving frequencies and larger plasma size means that electromagnetic effects start to play a more important role in determining plasma behavior. Understanding the physics of VHF plasmas is therefore critical for assessing the scalability of CCPs to future generations of dielectric etching technologies. This paper uses a computational model to elucidate the physics of VHF CCP discharges. The 2-dimensional model includes the full set of Maxwell equations in their potential formulation. The equations governing the vector potential, A, are solved in the frequency domain after every cycle for multiple harmonics of the driving frequency. Current sources for the vector potential equations are computed using the plasma characteristics from the previous cycle. The coupled set of equations governing the scalar potential, φ, and drift-diffusion equations for all charged species are solved implicitly in time. The model also includes the electron temperature equation, Kirchhoff equations for the external circuit, and continuity equations for neutral species. Our simulations focus on a 180 MHz CCP discharge, and examine the effect of inter-electrode spacing, driven electrode diameter, grounded electrode size and magnetic field on the plasma characteristics. It is found that the electrostatic component of the electric field peaks in the sheath region, where there is an imbalance between positive ion and electron concentrations. Electromagnetic fields are generated by current flowing through the discharge. The electromagnetic component of the electric field peaks in the center of the chamber due to the standing wave effect. The electromagnetic fields have a strong influence on charged species location and concentration at 180 MHz. However, besides the operating frequency, the plasma reactor design (inter-electrode spacing and electrode sizes) also determines the relative importance of the electromagnetic fields in plasma dynamics.

4:40pm **PS2-TuA10 Electron Heating Mechanisms, Mode Transitions, and Non-Uniformities in Dual Frequency Capacitive Discharges**, ***P. Chabert***, École Polytechnique, France **INVITED**

The physics of capacitive discharges has recently been reinvigorated with the rise of interest in multiple-frequency excitation and the related need to widen the range of frequencies that are used. A major attraction of dual-frequency excitation is that it promises independent control of the ion flux and the ion energy. In some circumstances, a third frequency is added to further control the etching processes by modifying the ion energy distribution function at the substrate. In this paper, we focus on the consequences of multiple-frequency excitation on the electron heating mechanisms, and in turns on the plasma uniformity. We will discuss the collisionless and collisional electron heating mechanisms within rf sheaths, when they are driven by two frequencies. For typical discharge parameters, we find the result that the collisionless heating produced by the combination of two frequencies can be much larger than that of either acting alone. We will also address the issue of electromagnetic effects arising when the wavelength associated with the highest frequency becomes comparable to (or shorter than) the electrode size. In this situation, the electric field has two components, (i) the usual capacitive field perpendicular to the electrodes, (ii) and the inductive field, parallel to the electrode. The power deposited by the inductive field may be greater than the capacitive power. As in classical inductive discharges, the high frequency capacitive discharge experiences capacitive-to-inductive (E to H) transitions when the injected power, i.e. the voltage between the electrodes, is increased. Finally, both the capacitive and inductive powers are radially non-uniform, which can lead to severe problems of process uniformity.

Advanced Surface Engineering

Room: 617 - Session SE-TuA

Naturally and Artificially Nanolaminated Coatings

Moderator: D. Gall, Rensselaer Polytechnic Institute

1:40pm **SE-TuA1 Optical Characterization of ZnO/Ag/ZnO Multilayer Films with Ag Layer Deposited by High Power Pulsed Magnetron Sputtering**, ***J. Li***, *S.R. Kirkpatrick*, *S.L. Rohde*, University of Nebraska-Lincoln

ZnO/Ag/ZnO multilayer films can be used in Low-E glass, solar cells and flat panel displays. Thin silver layers sandwiched between layers ZnO have been deposited by High Power Pulsed Magnetron Sputtering (HPPMS). By varying the deposition conditions during HPPMS, a thin, dense and uniform silver layer with low resistivity, high transmittance in visible light range have been obtained. The optical properties of ZnO/Ag/ZnO multilayer films with silver layer deposited by HPPMS have been studied using spectroscopic ellipsometry and infrared spectroscopic ellipsometry. The results have also been compared with multilayer films with silver layers deposited by conventional DC magnetron sputtering. For ZnO/Ag/ZnO multilayer films, the Ag-HPPMS multilayer films showed lower resistivity, lower IR transmittance than DC magnetron sputtered films. The optical properties of ZnO/Ag/ZnO multilayer films with different silver layer thickness deposited by HPPMS have also been investigated, with respect to their potential in an array of optical applications.

2:00pm **SE-TuA2 Synthesis and Elastic Properties of MAX Phases**, ***J.M. Schneider***, *D. Music*, RWTH Aachen University, Germany **INVITED**

$M_{n+1}AX_n$ phases (space group $P6_3/mmc$), where M is a transition metal, A is mostly IIIA or IVA group element, X is either C or N and n = 1–3, can be referred to as nanolaminates, where MX layers are interleaved with A layers. We have investigated the valence electron concentration induced changes in the elastic properties of M_2AlC phases (M = Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) using ab initio calculations.[1,2] In terms of bulk moduli [1], we have suggested that M_2AlC phases can be classified into two groups based on the coupling between MC and Al layers: M_2AlC phases with M = VB and VIB are strongly coupled, while M_2AlC with M = IVB are weakly coupled. In terms of shearing,[2] we have proposed that these phases can also be classified into two groups: one group comprises M = VB and VIB, where the C_{44} values are independent of the corresponding MC. The other group includes M = IIIB and IVB, where the C_{44} shows a linear dependency with the corresponding MC. This may be understood based on the electronic structure: shear resistant bands are filled in M_2AlC phases with M = VB and VIB, while they are not completely filled when M = IIIB and IVB. These classification proposals exhibit identical critical valence electron concentration values for the group boundary. Experimental efforts have been dedicated towards exploring the correlation between the valence electron concentration, constitution, and the elastic properties of M_2AlC phases (M = Ti, V, Cr). Ti_2AlC can be deposited onto sapphire substrates at a growth temperature of 800 °C using a compound target and an additional source of Ti.[3] V_2AlC was grown at a substrate temperature of 850 °C. We report that 450 °C is sufficient to grow crystalline Cr_2AlC thin films. This is the lowest deposition temperature ever reported for a MAX phase and is significantly lower than the crystallization temperature of an amorphous Cr_2AlC thin film based on our differential scanning calorimetry data.[4]

[1] D. Music, Z. Sun, R. Ahuja, J.M. Schneider, Phys. Rev. B 73 (2006) 134117.

[2] D. Music, Z. Sun, A.A. Voevodin, J.M. Schneider, Solid State Commun. 139 (2006) 139.

[3] C. Walter, C. Martinez, T. El-Raghy, J.M. Schneider, Steel Research Int. 76 (2005) 225.

[4] C. Walter, D.P. Sigumonrong, T. El-Raghy, J.M. Schneider, Thin Solid Films 515 (2006) 389.

2:40pm **SE-TuA4 Deposition of $M_{n+1}AX_n$(n=1-3)Phase Coatings by Magnetron Sputtering from Compound Targets and High Velocity Oxy-Fuel Spraying**, ***H. Högberg***, Linköping University, Sweden**INVITED**

Magnetron sputtering has proven to be a favorable route for synthesis of films of the ternary carbides or nitrides referred to as the $M_{n+1}AX_n$(n=1-3) phases. Sputtering from elemental targets has enabled the growth of several materials systems; predominately carbidic phases with Ti as the carbide-forming transition metal (M) and with either Al, Si, Ge or Sn as the A-element, but with extensions to other metals as in the V-Ge-C system or to nitride based systems as in the Ti-Al-N system. The majority of the films have been deposited on Al_2O_3(0001) substrates to promote epitaxial growth at temperatures typically above 700 °C, but for V_2GeC as low as 450 °C. In addition to deposition of the known phases in each of the studied systems this type of process also enables the growth of new phases such as Ti_3SnC_2 and so-called intergrown structures in the Ti-Si-C and Ti-Ge-C systems. Using sputtering from compound targets of Ti_3SiC_2 and Ti_2AlC in either Ar or Ar/N_2 plasmas we are currently investigating the growth conditions for the respective phases as well as potentially quaternary Ti-Si-CN and Ti-Al-CN phases. The studies show that sputtering of the compound targets in pure Ar plasmas favors epitaxial growth conditions for Ti_3SiC_2 and Ti_2AlC when the sources are co-sputtered with Ti. The as-deposited coatings consist predominately of MAX phase, but with intergrown layers of TiC. This behavior is attributed to higher carbon content in the deposited films compared to the target composition. Addition of N_2 during growth of both systems results in films of lower crystalline quality, and with preferential nucleation of TiC or TiCN for higher N_2 flows. XPS shows that up to 30 at. % N_2 is incorporated in the Ti-Al-CN films, and that the content of nitrogen in the deposited films scales with the amount of nitrogen available in the plasma. For deposition of thick (appr. 200 µm) Ti_2AlC coatings, we have applied high velocity oxy-fuel (HVOF) spraying. Characterization shows that dense and well-adherent coatings can be deposited on steel. Structural analysis shows that the HVOF coatings consist of Ti_2AlC (the powder phase) together with Ti-Al melting phases and residual TiC and Ti_3AlC_2. Vickers indentation experiments and scanning electron microscopy imaging of the indented area showed a hardness of appr. 6 GPa, with concentric cracks at the indent.

4:00pm **SE-TuA8 Effect of Swift Heavy Ion Irradiation on the Hardness of Chromium Nanorods**, ***R. Nagar***, Indian Institute of Technology Delhi, India, *K. Sai, D. Gall*, Rensselaer Polytechnic Institute, *D. Jain*, UGC-DAE, CSR, India, *B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi, India

This presentation discusses the use of ion irradiation to controllably tailor the hardness of Cr columnar thin films. Regular arrays of slanted Cr rods, 2 µm long and 250 nm wide, were grown by glancing angle dc magnetron sputter deposition on patterned Si(100) substrates. The patterns consist of 500-nm-diameter polystyrene spheres that self-assemble to form hexagonal close-packed monolayers. The Cr rod arrays were irradiated with 100 MeV Ag^{+8} ions at three different fluences of 10^{13}, $5x10^{13}$ and 10^{14} ions/cm^2, while maintaining the sample at a constant temperature of 80K. The ion-irradiation induced defect formation is dominated by electronic energy losses, with a very small contribution (approximately 0.5%) from the nuclear energy losses and negligible Ag-implantation. The average nanohardness of pristine Cr rods, as determined using a Berkovich diamond tip attached to an atomic force microscope, was found to be 0.6 GPa. Irradiation of the rods with 10^{13} ions/cm^2 does not lead to a measurable change in the hardness. However, for the fluence of 10^{14} ions/cm^2, the hardness increases to about 4 GPa, leading to an about eight-fold increase. The fluence-dependent hardness in these Cr rods is attributed to the ion-irradiation induced defect formation that may lead to dislocation pinning which is particularly effective due to the nanoscale dimensions of the Cr rods. These results are very promising as they demonstrate the use of swift heavy ion irradiation to tune the hardness of nanorod coatings.

4:20pm **SE-TuA9 Formation of Surface Relief of As2S3 Films using Glancing Deposition**, ***M.V. Sopinskyy***, V. Lashkaryov Institute of Semiconductor Physics, Ukraine, *V.I. Min'ko*, V. Lashkaryov Institute of Semiconductor Physics NAS, Ukraine, *I.Z. Indutnyy, O.S. Lytvyn, P.E. Shepeliavyi*, V. Lashkaryov Institute of Semiconductor Physics, Ukraine

In this report we present the first results on the surface morphology and optical properties of 1-3 mkm thick As2S3 films that were thermally evaporated on the glass and silicon substrates within 70-80° range of the vapor incidence angles. The AFM has revealed the details of the surface relief of glancing-deposited films showing quasi-regular grating-like structure, with the spatial frequency of quasi-gratings being in the 3000-6000 mm^{-1} range, and relief depth of 10-60 nm range. Ordering degree also depends on the substrate. The preliminary deposition of thin Cr film on the glass substrate results in more pronounced surface self-ordering of glancing-deposited As2S3 films. Multiangle ellipsometric measurements have been performed to determine the refractive index, and check the anisotropy of the films. It has been found that the refractive index values in these films are lower compared to the values for the films with the normal (perpendicular) deposition. In addition, there is anisotropy of refractive index in the plane of the film. This indicates that the structure of the films is columnar, with the columns tilted relative to the substrate normal. The most probable explanation for the observed effect is the surface stress that plays significant role in the self-organized ordering of nanostructures at the mesoscopic length scales (several nm - hundreds of nm). It is the known fact that the thermally deposited As2S3 films are mechanically stressed, especially in the near-surface area. Thus, due to the structural anisotropy of the obliquely deposited As2S3 films, the stress forces are also anisotropic. The more pronounced columnar structure of these samples provides a lot of free space where the bond breaking and atomic movements are facilitated. Both of these factors result in anisotropic plastic shears in the film' near-surface region. The effect is a cheap and easy way to create quasi-gratings on the surface of amorphous chalcogenide films and could be used for fabrication of nano- and microdevices.

Surface Science

Room: 608 - Session SS1-TuA

Bimetallics and Alloys

Moderator: I. Chorkendorff, Technical University of Denmark

1:40pm **SS1-TuA1 Atomic-Scale Assembly of a Heterogeneous Catalytic Site**, *P. Han*, Texas A&M University, *I. Lyubinetsky*, Pacific Northwest National Laboratory, ***D.W. Goodman***, Texas A&M University

The distance between surface Pd atoms is known to control the catalytic formation of vinyl acetate from ethylene and acetic acid by AuPd catalysts. In this study, we use the thermodynamic properties and the surface lattice spacing of a AuPd(100) alloy single crystal model catalyst to control and optimize the number of Pd monomer-pair sites with a specific Pd-Pd distance. Scanning tunneling microscopy reveals that sample annealing has a direct effect on the surface Pd arrangements: short-range order preferentially forms Pd-pairs located at local c(2 x 2) sites, sites known to be active for vinyl acetate synthesis. This methodology should be useful in the optimization of bimetallic industrial catalysts.

2:00pm **SS1-TuA2 Mechanistic Studies of the Steam Reforming of Methanol on PdZn Alloy Catalysts**, *E. Jeroro*, ***J.M. Vohs***, University of Pennsylvania

Methanol and other alcohols are potential bio-renewable sources of hydrogen. The use of alcohols, however, as a H2 source or storage medium requires stable reforming catalysts that have high activity and selectivity at low temperatures. One such catalyst that has received much attention for steam reforming of CH_3OH (SRM) [$CH_3OH + H_2O$? $CO_2 + 3H_2$] is Pd supported on ZnO. Pd/ZnO catalysts have unusually high selectivity (>95%) for the production of CO_2 and H_2 from methanol, in spite of the fact that bulk Pd exhibits nearly 100 % selectivity for the dehydrogenation of CH_3OH to CO and H_2 under typical SRM conditions. While it has been demonstrated that formation of a PdZn allow is required to obtain high selectivity, the mechanism by which Zn alters the reactivity of the Pd is not understood. In this talk we will present results of a study of model PdZn catalysts consisting of submonolayer amounts of Zn supported on Pd(111) that provide insight into the synergistic interactions between Zn and Pd and how they alter the reactivity of the Pd surface. Temperature programmed desorption (TPD) data for the reaction of methanol, formaldehyde and carbon monoxide on Pd(111) as a function of Zn coverage as well as results of a high resolution electron energy loss spectroscopy (HREELS) study of the bonding configurations of these molecules on Zn/Pd(111) surfaces will be presented. The TPD data show that the formation of the PdZn alloy significantly decreases the activity of the Pd surface for the dehydrogenation of CH_3OH and CH_2O. This change in reactivity is found to be due in part to a change in the bonding configuration of adsorbed formaldehyde intermediates. The experimental results also provide evidence for a strong electronic interaction between the Pd and Zn which affects the adsorption energies of CO and methanol.

2:20pm **SS1-TuA3 Revisiting the CO oxidation on a Au/Ni(111) Surface Alloy**, ***J. Knudsen***, *L.R. Merte, R.T. Vang*, University of Aarhus, Denmark, *A. Resta, J. Schnadt, J.N. Andersen*, Lund University, Sweden, *F. Besenbacher*, University of Aarhus, Denmark

In the early 1990s our group showed that deposition of gold onto nickel single-crystal surfaces results in the formation of a stable alloy in the crystal's topmost layer, a surprising discovery considering that the two metals are immiscible in the bulk. This surface alloy was later shown to display interesting catalytic properties; for example, the presence of small amounts of gold in nickel catalysts hinders graphite formation during steam reforming of hydrocarbons.[1] Other studies explored the use of gold to inhibit CO dissociation on Ni(111) and the stability of the surface alloy under high-pressure conditions.[2] Most recently, Lahr and Ceyer reported that the Au/Ni(111) surface alloy catalyzes oxidation of CO to CO_2 at temperatures as low as 70K.[3] They conclude that gold atoms substituted into the top layer of the Ni(111) surface stabilize chemisorption of a reactive, non-dissociated O_2 species in a similar manner as has been reported for gold nanoclusters. We have used scanning tunnelling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) to study the adsorption, coadsorption and reaction of CO and O_2 on the Au/Ni(111) surface alloy and the clean Ni(111) surface with the goal of clarifying the mechanism or mechanisms behind this interesting phenomenon. In agreement with the work of Lahr and Ceyer we find that molecular oxygen is required to produce CO$_2$ on the surface but our results seem to indicate a different reaction mechanism than the one proposed in their article.

[1] Besenbacher, F.; Chorkendorff, I.; Clausen, B. S.; Hammer, B.; Molenbroek, A. M.; Norskov, J. K.; Stensgaard, I., Design of a surface alloy catalyst for steam reforming. Science 1998, 279, (5358), 1913-1915.

[2] Vestergaard, E. K.; Vang, R. T.; Knudsen, J.; Pedersen, T. M.; An, T.; Laegsgaard, E.; Stensgaard, I.; Hammer, B.; Besenbacher, F., Adsorbate-induced alloy phase separation: A direct view by high-pressure scanning tunneling microscopy. Physical Review Letters 2005, 95, (12), 126101.

[3] Lahr, D. L.; Ceyer, S. T., Catalyzed CO oxidation at 70 K on an extended Au/Ni surface alloy. Journal Of The American Chemical Society 2006, 128, (6), 1800-1801.

2:40pm **SS1-TuA4 General Trends in the Electronic and Chemical Properties of Monolayer Bimetallic Surfaces**, ***J.G. Chen***, University of Delaware **INVITED**

It is well known that bimetallic surfaces often show novel properties that are not present on either of the parent metal surfaces. The modification effect is especially important at the admetal coverages in the submonolayer and monolayer regime. However, it is difficult to know a priori how the chemical properties of a particular bimetallic surface will be modified relative to the parent metals. We have investigated the electronic and chemical properties of model bimetallic surface structures, in particular subsurface and surface monolayers, using a combination of experimental and theoretical modeling to gain further insights into these factors. In the current presentation we will first utilize the adsorption and desorption of hydrogen to demonstrate the correlation between the hydrogen binding energy and the center of the surface d-band in various bimetallic surfaces. We will also provide a general equation that allows one to predict how the electronic properties, especially the d-band center, will be affected in bimetallic systems. We will then use several probe reactions, including hydrogenation of alkenes and reforming of oxygenates, to show the correlation between the chemical activities and the surface d-band center of bimetallic surfaces. Finally, we will discuss the relative stability of surface and subsurface bimetallic structures in vacuum, and in the presence of adsorbed hydrogen and oxygen.

4:00pm **SS1-TuA8 Real-time STM Observations of the Oxidation of a Ti/Pt(111)-(2x2) Surface Alloy using O$_2$ and NO$_2$**, *S. Hsieh*, National Sun Yat-Sen University, Taiwan, *G. Liu*, ***B.E. Koel***, Lehigh University

We have used scanning tunneling microscopy (STM), low energy diffraction (LEED), and Auger electron spectroscopy (AES) to study the nascent oxidation of an ordered Ti/Pt(111)-(2x2) surface alloy exposed to oxygen (O$_2$) or nitrogen dioxide (NO$_2$) under ultrahigh vacuum conditions. The Ti/Pt(111)-(2x2) surface alloy was formed by depositing an ultrathin Ti film on Pt(111) and annealing to 1050 K. This produces an alloy film in which the surface layer is pure Pt and the second layer contains Ti atoms in a (2x2) structure that causes the pattern observed by STM and LEED. Real-time imaging of the surface at 300 K was carried out by continuously scanning with the STM while either O$_2$ or NO$_2$ was introduced into the chamber. O$_2$ exposures did not cause any gross structural changes, however oxygen was detected on the surface afterwards using AES. Annealing this surface to 950 K resulted in the formation of an ordered TiO$_x$ overlayer as characterized by both LEED and STM. In contrast, NO$_2$ exposures caused definite changes in the surface morphology at 300 K, and the RMS roughness increased from 3.5 to 7.1 Å after a 93-L NO$_2$ exposure. No ordered structures were produced by this exposure, but annealing the surface to 950 K formed an ordered pattern in LEED and corresponding clear, well-resolved structures in STM images. Disruption or reconstruction of the Ti/Pt(111)-(2x2) surface alloy because of Ti oxidation is an activated process. The energetic barrier to TiO$_x$ formation can not be surmounted at room temperature at low oxygen coverages and annealing the surface was necessary to initiate this reaction. However, the higher oxygen coverages obtained using the more reactive oxidant NO$_2$ lowered the chemical potential in the system sufficiently to overcome the activation barrier to extract Ti from the alloy and form a disordered TiO$_x$ film at room temperature. These results illustrate the importance of the surface oxygen coverage in nucleating the room temperature oxidation of the Ti/Pt(111)-(2x2) surface alloy.

4:20pm **SS1-TuA9 CO Tolerance of Pt Islets on Ru(1000) and their Implications for PtRu Nanocatalysts: Insights from First Principles Calculations**, ***T. Rahman***, *S. Stolbov*, *M. Alcantara-Ortigoza*, University of Central Florida

Proton exchange fuel cells are promising tools for hydrogen economy. However, CO traces which are inevitably present, block active sites of the Pt anode and hence poison its reactivity. Recently, Ru nanoparticles with submonolayer Pt coverage are found[1] to be much more tolerant to CO than commercial catalysts. To understand the rationale for this tolerance, we have performed density functional theory based calculations of the energetics of adsorption and diffusion of CO on Pt islets on Ru(0001). We find that the total energy of the system gradually decreases as the CO molecule moves from the center of the islets to its edge and further onto substrate. Diffusion barriers for CO are found to be low: 0.06 eV to move from the center of the island to its edge, 0.27 eV to "jump" from the Pt island edge to a neighboring substrate site, and 0.3 eV to move further along the Ru surface. Assuming the pre-factor of CO diffusion to be 1012 sec-1, the diffusion rate at the operating temperature 350K is estimated to be around 107 sec-1. These results suggest that this catalyst is CO tolerant because of the propensity of CO to move from active Pt island site to the Ru substrate. We trace this effect to the features of the local densities of electronic states around the Fermi-level.

[1] S. R. Brankovic, J. X. Wang, and R. R. Adžic, Electrochem. Solid State Lett.4, A217 (2001).

[2] Work supported in part by DOE-BES under grant DE-FG02-07ER15842.

4:40pm **SS1-TuA10 Effect of Quantum Well States on Adsorption of CO Molecules**, ***W. Kim***, *S. Han*, *D. Lee*, *C. Hwang*, Korea Research Institute of Standards and Science, *C. Min*, Seoul National University, Republic of Korea, *H. Lee*, *H. Kim*, Pohang Accelarator Laboratory, Republic of Korea

Formation of quantum well states in the metallic thin film systems satisfying specific boundary conditions leads to the oscillation of the electron density of states at Fermi level as the thickness of the film increases.[1] We investigated the effect of the oscillation on adsorption of CO molecules in case of the Cu/Co/Cu(100) system. The quantum well states and resulting oscillation of density of states at Fermi level in wedge-shaped Cu/Co/Cu(100) system were confirmed by angle-resolved photoemission spectroscopy. After adsorption of CO molecules at the substrate temperature of 100 K, we observed the shift of binding energies of quantum well states, which could be understood in the scheme of phase accumulation model. C 1s core level photoemission spectra of the adsorbed molecules were measured as a function of temperature for each Cu thickness. The initial feature of the C 1s spectra show well-known three peak structure similar to that of CO molecules adsorbed on Cu(100). From the temperature dependence of the intensity of measured C 1s core level spectra, we could determine the desorption temperature of CO molecules for each Cu thickness, which showed clear dependence on the density of states of Fermi level with oscillating variation of 15 K. We also evaluated the relative ratio of the first satellite peak to main peak in C 1s core level spectra and found out that the ratio showed oscillatory behavior and strong correlation with the density of states at Fermi level. Our observations confirm the old theoretical explanation on the origin of three peak structure of C 1s core level spectra of CO molecules adsorbed on the Cu(100) surface.[2]

[1] Z. Q. Qiu and N. V. Smith, J. Phys.: Condens. Matter vol.14, R169.

[2] O. Gunnarsson, and K. Schöhammer, Phys. Rev. Lett. vol 41, 1608.

5:00pm **SS1-TuA11 Modifying the Adsorption of Molecules at Metal Surfaces by Quantum Confinement of Electrons**, ***L. Tskipuri***, *R.A. Bartynski*, Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. Quantum confinement of electrons forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. In previous studies we found that MQW states modify the strength of CO bonding to Cu MQW overlayers on the pseudomorphic fcc-Co/Cu(100) and fcc-Fe/Cu(100) systems.[1] In these systems, the CO-metal bond strength oscillates, in correlation with MQW states, as a function of Cu overlayer thickness. Here we extend these studies with IR studies of CO adsorbed on Cu MQWs and report on the adsorption properties of the pseudomorphic transition metal layers themselves. These systems have partially filled d-bands may be grown in a metastable structure. We have examined the unoccupied electronic structure and CO bonding strength on the n-ML fccNi/Cu(100) and n-ML fccCo/Cu(100) systems using inverse photoemission (IPE), reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). In the case of Co, the as-grown films exhibit well-defined unoccupied MQW states, but they do not cross the Fermi level. This allows us to investigate adsorbate-MQW interactions that involve MQW states away from the Fermi level. Upon CO adsorption a well-defined structure centered about 3.8 eV above the Fermi level appears and is assigned to the unoccupied CO 2π orbital. CO adsorbs molecularly at room temperature and in TPD measurements we find a desorption temperature of approximately 375 K, which is about 30 K lower than what is observed for CO adsorbed on the hcp Co surfaces. When Co films are dosed at low temperatures (~ 100K), we find a second CO desorption peak around 230 K, once again similar to what is seen for hcp Co, but as a markedly lower temperature. These peak desorption temperatures change as a function of film thickness and are correlated with two different C-O stretch vibrational frequencies observed in the IR spectra. We have observed similar desorption peak temperature shifts when CO desorption from the Ni/Cu(100) system as a function of thickness and as compared to single crystal Ni(100). The role of quantum confinement and surface strain in producing the observed effects will be discussed.

[1] A. G. Danese, F. G. Curti, and R. A. Bartynski, Phys. Rev. B 70, 165420 (2004).

Surface Science

Room: 611 - Session SS2-TuA

Excitations at Surfaces

Moderator: G.A. Kimmel, Pacific Northwest National Laboratory

2:00pm **SS2-TuA2 Electronic Excitation and Bond Dissociation via Transient Anion Formation at the Surfaces of Molecular and Biomolecular Solids**, ***L. Sanche***, University of Sherbrooke, Canada **INVITED**

Electrons with energies in the range 0-30 eV can induce at interfaces and surfaces specific reactions which are relevant to applied fields such as nanolithography, dielectric aging, radiation waste management, radiation processing, astrobiology, planetary and atmospheric chemistry, surface photochemistry, radiobiology, radiotherapy and ballistic electronics. The action of low energy electrons (LEE) at the surface of molecular and biomolecular solids has been investigated with model systems consisting of pure or doped thin molecular films. Some of the results will be presented at the conference. In these experiments a target film is deposited on a metal or semi-conductor substrate and bombarded by a LEE beam under ultra high vacuum (UHV) conditions. Backscattered electrons are energy analysed to determine the energy and characteristics of electronic excited states at the surface of the molecular solid. Bond dissociation is analysed by mass spectrometry (MS); i.e., we determine the energy, mass and intensity of the neutral fragments and ions emanating from the films vs electron energy. The products remaining in the films are analyzed in situ by X-ray photoelectron and electron energy loss spectroscopies; they can also be removed from the UHV system and analyzed by HPLC and LC/MS. By comparing the results of the theory and different experiments, it is possible to determine fundamental mechanisms that are involved in the processes induced by LEE. Such mechanisms involve the formation of transient anions which play a dominant role in the fragmentation of all molecules investigated and dipolar dissociation which produces an anion and a cation. The transient anions fragment the parent molecules by decaying into dissociative electronically excited states or by dissociating into a stable anion and a neutral radical. These fragments usually initiate other reactions with nearby molecules, causing further chemical damage. The damage caused by transient anions is dependent on the molecular environment. This research is financed by the CIHR.

2:40pm **SS2-TuA4 An Atomic Seesaw Switch by Tunneling Carrier Injection on Ge (001)**, ***K. Tomatsu***, *K. Nakatsuji, T. Iimori*, University of Tokyo, Japan, *Y. Takagi*, Riken Harima, Japan, *H. Kusuhara, A. Ishii*, Tottori University, Japan, *F. Komori*, University of Tokyo, Japan

Reversible switching of electronic conduction through atom manipulation is one of the main subjects of nanoscience. However, different conducting pathways have not been clearly observed with atomic resolution. Here, we demonstrate the correlation between the change of surface atomic position by tunneling carrier injection and that of the reflection of one-dimensional (1D) surface-state electrons on the Ge (001) surface with a low density of heterogeneous Sn-Ge dimers.[1] On the clean Ge(001) surface, two atoms form a buckled dimer, and bonding π- and antibonding π^*-states localize on upper and lower atoms of the dimer. The Ge dimers align in the [110] direction and form a dimer row. The π^*-electron behaves like a 1D free electron along the dimer row. It has been shown that the buckling orientation of the Ge dimer can be reversibly controlled by surface bias voltage of STM.[2] This conformation change is induced by inelastic scattering of injected carriers from the STM tip to the surface under the electric field due to the bias voltage. When Sn atoms are deposited on the clean Ge(001) surface at room temperature, buckled dimers originating from the Sn atoms are formed at the Ge dimer position in the surface.[3] We identify the dimer as a heterogeneous Sn-Ge dimer by reversing its buckling orientation with STM and observing the change of the STM images at 80 K. An atomic seesaw switch is realized for the 1D π^* electrons in the Ge dimer-row direction by using the STM to reversibly flip the buckling orientation of a single Sn-Ge dimer in the dimer row. When the Sn atom of the heterogeneous dimer is at the lower position, the 1D electrons are reflected and a standing wave of this state is observed in the dI/dV image. Whereas, when it is at the upper position, the 1D electrons pass through the heterogeneous dimer, and no standing wave is observed. In this state, the lower atom of the dimer is Ge, and the π^* state of the dimer is little different from that of the Ge-Ge dimers. These are confirmed using first-principles calculations.

[1] K. Tomatsu, K. Nakatsuji, T. Iimori, Y. Takagi, H. Kusuhara, A. Ishii, F. Komori; Science 315, 1696, 2007.

[2] Y. Takagi, Y. Yoshimoto, K. Nakatsuji, F. Komori; Phys. Rev. B75, 115304, 2007.

[3] K. Tomatsu, K. Nakatsuji, T. Iimori, F. Komori; Surf. Sci. 601, 1736, 2007.

3:00pm **SS2-TuA5 Detection of Hydrogen During Low-Energy (5-50 eV) Electron Bombardment of Acetylene Adsorbed on Si(111) Surfaces**, ***K.R. Shepperd***, *T. Li, P.N. First, T.M. Orlando*, Georgia Institute of Technology

The interaction of hydrocarbons with Si surfaces is a topic of wide interest. This is generally related to the technological importance of SiC and the growing interest in graphene. In an effort to grow SiC interfaces and graphene overlayers, we have investigated the interaction of C_2H_2 (C_2D_2) with Si(111) surfaces and the low-energy electron-beam induced chemistry of this adsorbate-substrate system. We monitor the production and release of hydrogen using sensitive and selective resonance enhanced multiphoton ionization laser detection schemes. We have measured the threshold energy and the yield vs. incident electron energy. We discuss the structure in the yields vs. energy in terms of direct dissociative excitations and dissociative electron attachment. We also have investigated the remaining carbon deposit using Auger electron spectroscopy, scanning electron and scanning tunneling microscopy. Initial results indicate facile formation of SiC at low coverage but no clear signature of graphene.

4:00pm **SS2-TuA8 Mechanism of Negative Ion Formation during the Laser Ablation of Alkali Halides[1]**, ***J.T. Dickinson***, *K. Kimura, S.C. Langford*, Washington State University

Pulsed excimer laser radiation produces a variety of surface and near surface defects in the alkali halides that contribute to particle emission. Quadrupole mass spectrometry during pulsed 248-nm laser irradiation of cleaved LiF, NaCl, KCl, and KBr shows intense emissions of positive alkali ions at fluences well below the threshold for visible plume formation. We argue that these ions are emitted directly from surface defect sites when nearby electron traps are photoionized. In this work, we describe somewhat weaker emissions of negative alkali ions with kinetic energies similar to that of the positive ions. Measurements of induced charge on a metal sheet mounted behind a thin sample show that the surface develops a positive charge during the laser pulse. Thus the direct emission of negative ions at these low fluences is not expected. In previous work, we have shown that the cloud of positive alkali ions is accompanied by enough electrons to compensate much of the positive charge. These electrons are electrostatically confined to the ion distribution to produce a mixed charge cloud. Although these electrons are available for electron attachment processes, detailed measurements on KCl show no Cl^- at our level of sensitivity, despite the presence of the neutral Cl, with its high electron affinity. We attribute the lack of Cl^- to the absence of spatial overlap between neutral Cl and the charge cloud. Since the detected neutral K and Cl have similar velocity distributions, negative ion formation by electron attachment to neutral K desorbed directly from the surface is similarly difficult. These considerations suggest that K^- is formed by double electron attachment to K^+. Measurements of the total ion and electron emissions imply that the electron and ion densities immediately after the laser pulse are sufficient to account for the production of the observed negative alkali ions by collisional electron-ion and electron-neutral recombination. Although electron attachment is frequently observed among the products of ablation at high fluences, it is remarkable that the conditions required for double electron attachment are attained at the low fluences probed in this work. Further study of the behavior of charged emissions in this well-studied system is required to clarify how these conditions develop.

[1] This work was supported by the US Department of Energy under Grant DE-FG02-04ER-15618.

4:20pm **SS2-TuA9 Dissociative Attachment of Adsorbed Methyl Halides by Dielectric Layer Image State Electrons**, ***E.T. Jensen***, University of Northern British Columbia, Canada

We have studied the transfer of low-energy electrons through thin films of n-hexane (C_6H_{12}) on a Cu(110) substrate. The band structure of the thin n-hexane layers allows relatively long-lived image states to be formed at the hexane-vacuum interface.[1,2] In our experiments, these image states are occupied by sub-vacuum level photoelectrons from the Cu(110) substrate that are generated by a near-UV laser, and tunnel through the n-hexane film into the image states. These image state electrons can couple to the unoccupied electron affinity levels of coadsorbed CH_3X (X=Br, I). Dissociative electron attachment (DEA) of the CH_3X is detected by the fission of the C-X bond, with the CH_3 fragment escaping into the vacuum and subsequently detected by a quadrupole mass spectrometer. The intermediary role of the image states in this DEA process is determined from the coverage dependencies of the CH_3 fragment yields and the distinctive translational energy distribution of the CH_3- the image state electrons constitute a nearly monochromatic electron source for DEA of the CH_3X.

[1] M.W. Cole, Phys. Rev. B 3 (1971) 4418.

[2] K. Nagesha and L. Sanche, Phys. Rev. Lett. 81 (1998) 5892.

4:40pm **SS2-TuA10 Photo-induced Surface Functionalization of Carbon Surfaces: The Role of Photoelectron Ejection**, ***P.E. Colavita**, B. Sun, K.-Y. Tse, R.J. Hamers*, University of Wisconsin-Madison

Carbon based materials are attractive for a wide range of applications, from biomaterials to fuel cells; however their effective use often requires controlling the surface chemistry to incorporate recognition moieties or reactive centers. The high stability of carbon also makes it a challenging material to functionalize; recently, the use of ultraviolet light (254 nm) to initiate functionalization of carbon surfaces has emerged as a way to obtain carbon/organic interfaces with tailored properties. We have investigated the mechanism of covalent grafting of amorphous carbon surfaces with functional organic molecules using the photochemical reaction of terminal alkenes. Measurements comparing the reactivity of different n-alkenes bearing different terminal groups at the terminus opposite the olefin showed pronounced differences in reactivity. We characterized the rate and final coverage of the resulting organic layers using X-ray Photoelectron Spectroscopy (XPS) and Infrared Reflection Absorption Spectroscopy (IRRAS). Ultraviolet Photoelectron Spectroscopy (UPS) and photocurrent measurements suggested that the reaction involves photoelectron emission from the carbon surface into the liquid phase. Density functional calculations show a strong correlation between the electron affinity of the alkenes and the observed reactivity. The specific terminal group opposite to the olefin was found to play an important role in the stabilization of excess negative charges on the molecule, thus explaining the strong dependence of reactivity on the particular terminal group. These findings suggest that the reaction involves injection of photoelectrons into the alkene acceptor levels, leading to the formation of radical anions in the liquid phase. Finally, we demonstrate that the grafting of marginally reactive alkenes can be enhanced by seeding the surface with a small amount of good electron accepting groups. These results provide fundamental new insights into the role of electronic excitations in controlling rates and mechanisms of olefin reactions at surfaces. While demonstrated here for amorphous carbon, these results may also be significant for the UV initiated grafting of olefins on other semiconductors.

5:00pm **SS2-TuA11 Electron Stimulated Reactions in Thin Water Films Adsorbed on TiO_2(110)**, ***N.G. Petrik***, Pacific Northwest National Laboratory, *C.D. Lane, T.M. Orlando*, Georgia Institute of Technology, *G.A. Kimmel*, Pacific Northwest National Laboratory

The electron-stimulated desorption of molecular water from TiO_2 (110) surface was investigated as function of coverage (0-5 ML), incident electron energy (5-100 eV), and other parameters. The two main water adsorption sites - 5-fold coordinated Ti^{4+} ions and bridge-bonded oxygens (BBO)- have significantly different cross-sections for electron-stimulated desorption, but similar cross-sections for electron-stimulated dissociation. Isotopic layering experiments show that both desorption and dissociation of water adsorbed on the Ti^{4+} sites is suppressed by deposition of water molecules on the BBO sites. The results suggest that electronic excitations in water molecules adsorbed on the Ti^{4+} sites can produce reactions (desorption or dissociation) in water molecules on the BBO sites. The experimental observations are discussed in terms of specific structural characteristics of thin water films on TiO_2 (110).

Thin Film

Room: 613/614 - Session TF-TuA

Surface Chemistry for Atomic Layer Deposition

Moderator: S. Rossnagel, IBM

1:40pm **TF-TuA1 Infrared Characterization of Atomic Layer Deposition and Post Annealing of Lanthanum Oxide Films**, ***J. Kwon**, M. Dai*, Rutgers University, *E. Langereis*, Eindhoven University of Technology, The Netherlands, *Y.J. Chabal*, Rutgers University, *K. Kim, R. Gordon*, Harvard University

La_2O_3 is a potential material for high-k gate dielectrics in microelectronics due to its relatively large permittivity, thermal stability in contact with Si, suitable band gap and conduction band offset. Uniform and conformal thin layers of metal oxides can be realized by a self-limiting atomic layer deposition (ALD) process. Surface nucleation and overall interface formation mechanisms are unfortunately not well understood since most of film characterization has been performed with ex-situ measurements. We report on in-situ Fourier transmission infrared (FTIR) studies of ALD growth and post-deposition annealing of La-oxide thin films on Si substrates using a metal-amidinate precursor[1] and D_2O. Film growth rates were determined from ex-situ RBS measurements. Atomically flat hydrogen-terminated Si(111) surfaces were used as substrates for La-oxide film growth. IR spectra were obtained at every half-cycle of the initial stages and post-deposition annealing was studied up to 800°C by performing IR measurements after 20 cycles of ALD process at 100°C increments. Between 200 and 300°C substrate temperatures, the first La-precursor exposure consumes approximately 30% of surface hydrogen, as measured by the intensity loss of the monohydride Si-H stretching mode (2083 cm^{-1}). A D_2O exposure is used each time to complete the cycle. More than 90 % hydrogen is consumed after the third metal-precursor dosing (2.5 cycle) at 300°C deposition temperature. La_2O_3 grown at 200°C shows higher concentration of carbonate species (modes in the 1390 ~ 1470 cm^{-1} region) incorporated into the film compared to 300°C grown films, probably due to incomplete elimination of the metal precursor by D_2O. The intensity of these modes decreases with increasing annealing temperature and almost completely disappears at 400 ~ 500°C annealing. Carbonate groups in the films grown at 300°C are lower, but profound ligand decomposition is observed around 2000 cm^{-1}. Si-O-Si modes (900 ~ 1200 cm^{-1}) are observed to increase from the very initial ALD cycle, consistent with interfacial SiO_x formation at 300°C. Films grown at 200°C show much slower interface oxide formation, but even a mild (400°C) post-deposition anneal triggers substantial interfacial SiO_x formation.

[1] B. S. Lim et al., Appl. Phys. Lett. 84, 3957 (2004).

2:00pm **TF-TuA2 Understanding the Long Nucleation Period for Pd ALD on Alumina Substrates**, ***D.N. Goldstein**, S.M. George*, University of Colorado

Palladium (Pd) atomic layer deposition (ALD) can be performed on alumina substrates using $Pd(hfac)_2$ (hfac= hexafluoroacetylacetone) and formalin. However, this system requires a nucleation period of 50-100 cycles before Pd grows steadily at 0.2 Å/cycle. To understand the long nucleation period, this study explored the details of the surface reactions occurring during Pd ALD nucleation. This research utilizes in situ Fourier Transform Infrared (FTIR) spectroscopy on nanopowder substrates to observe the surface species. $Pd(hfac)_2$ dissociatively adsorbs on the Al_2O_3 substrate to yield surface Pd(hfac) and Al(hfac) during the initial $Pd(hfac)_2$ exposure. During the first formalin exposure, only the hfac ligands attached to Pd are removed and the Al(hfac) species remain on the substrate. In addition, the formalin exposure adds formate species to the available Lewis acid sites on Al_2O_3. After the first cycle, no more surface Pd(hfac) is observed and formalin exposures remove some of the Al(hfac) species. These Al(hfac) species are believed to be the cause for the long nucleation period. Surface Al(hfac) is continually produced from $Pd(hfac)_2$ exposures and competes with Pd metal for the same surface sites. The fate of Al(hfac) is either thermal decomposition to trifluoroacetate groups or removal from the surface as a volatile enol isomer. Formalin provides hydrogen to release the enol of hfac but cannot remove the trifluoroacetate groups. Trifluoroacetate groups may be a source of fluorine contamination in the films. The nucleation period ends when the volatile hfac products desorb and Pd can cover the original Al_2O_3 surface. At this point, only Pd(hfac) species are observed in the FTIR spectra. Transmission electron microscopy studies reveal Pd nanocrystallites that increase in number with increasing number of ALD cycles. These crystallites eventually coalesce to a conformal Pd film.

2:40pm **TF-TuA4 Simulations of the Surface Chemistry of HfO2 Atomic Layer Deposition*, C.B. Musgrave*, *A. Mukhopadhyay*, Stanford University, *J.F. Sanz*, Universidad de Sevilla, Spain **INVITED**

We have used a combination of theoretical techniques to explore the surface chemistry of atomic layer deposition of metal oxides and nitrides, including HfO2, HfN, HfOxNy and WN. Our main focus has been on the chemical mechanisms involved in the ALD of HfO2. Density functional theory has been employed using both the cluster and periodic supercell models of the reacting surface to determine detailed mechanisms of the surface chemistry of ALD. In addition to locating transition states and applying transition state theory to predict reaction rates, we also simulate ALD surface reactions using Born-Oppenheimer quantum molecular dynamics. These simulations provide a rich and complex picture of the atomistic detail of the ALD process which shows that the chemistry of ALD is much more complicated than initial descriptions suggested. In addition to finding various reaction pathways and predicting their relative rates, we also investigate processes such as dissociation of adsorbed precursors via microsolvation and the effect of surface hydration on the ALD mechanism.

4:00pm **TF-TuA8 Passivation and Atomic Layer Deposition on Halide-Terminated Ge Surfaces*, P. Ardalan*, *C.B. Musgrave, S.F. Bent*, Stanford University

Because of the poor oxide of germanium, alternative passivation methods are required for practical use of Ge in devices. We have studied the passivation of germanium surfaces by alkanethiolate self-assembled monolayers (SAMs) and by ALD-deposited titanium dioxide (TiO_2). We have also investigated the ability of the SAMs to block TiO_2 deposition for application to area selective ALD. Our studies started with halide-terminated (Cl- or Br-) Ge(100) and (111) surfaces, which have been shown to exhibit good stability and resistance to oxidation. The initial functionalization of Ge surfaces by HCl and HBr was investigated by various experimental and theoretical methods, including x-ray photoelectron spectroscopy and density functional theory. Next, these surfaces were exposed to 1-alkanethiols to form alkanethiolate self-assembled monolayers (SAMs), where the formation and bonding of such SAMs were studied by the same methods. We also investigated the ALD of TiO_2 on halide-terminated Ge surfaces, with the results showing a strong temperature dependence of the growth process. Finally, we have explored the area selective ALD of TiO_2 at the Ge surfaces. We observe that the 1-alkanethiolate SAMs protect the Ge surfaces from ALD, leaving TiO_2 to deposit only at regions of the Ge surfaces which are functionalized by halides but not protected by the SAMs. The results demonstrate a new route to Ge surface functionalization and passivation.

4:20pm **TF-TuA9 Step by step in-situ X-ray Photoelectron Spectroscopy Investigation on ALD Al_2O_3 Films using TMA and Water*, K.J. Choi*,** University of Texas at Dallas, *S.J. McDonnell*, Dublin City University, Ireland, *R.M. Wallace, J. Kim*, University of Texas at Dallas

In atomic layer deposition (ALD) of Al_2O_3 on H-terminated silicon substrates, it is often observed that the initial growth rate of Al_2O_3 films is much slower than that in the steady-state condition after several cycles. This phenomenon is frequently called an incubation period, which has been extensively investigated by using various in-situ surface characterization methods, such as quartz crystal microbalance, quadrupole mass spectroscopy, FT-IR etc. Although X-ray photoelectron spectroscopy (XPS) provides useful chemical binding information at the surface, a relatively few papers have been published regarding in-situ XPS investigations possibly due to a ultra-high vacuum (UHV) requirement which is not easily compatible to ALD system. In this study, in-situ XPS is used to investigate on chemical binding status during formation of Al_2O_3 thin films on an HF-last Si wafer. All experiments were carried out in an UHV system consisting of various deposition tools, including atomic layer deposition, sputter deposition, molecular beam epitaxy/deposition, and e-beam evaporation, as well as surface characterization methods including XPS, UPS, STM and AFM. The Al_2O_3 film was grown at 300^{o}C on HF-last Si substrate using trimethylalumium [$Al(CH_3)_3$, TMA] as the aluminum precursor and H_2O as the oxidizing agent. A cycle of the deposition process consisted of 0.1 s of TMA pulse, 10 s of N_2 purge, 0.1 s of H_2O pulse and 10 s of N_2 purge. The growth rate is about 0.11nm/cycle. XPS analysis was conducted on Al_2O_3 thin films resulting from a 3-cycle deposition. The Al_2O_3 thin films were grown in half cycle steps (TMA pulse+N2 purge or H_2O pulse + N_2 purge) and analyzed in-situ so that the initial growth of Al_2O_3 could be observed. The Al2$_{P3/2}$ photoelectron emission peak appears after the 1 cycle + TMA pulse + N_2 purge. As the number of cycles is increased, the peak intensity of Al2$_{P3/2}$ increases in TMA pulse + N_2 purge step, and does not increase in H_2O pulse + N_2 purge step. In addition, we will also present in-situ vs. ex-situ XPS analysis of ALD Al_2O_3 in this presentation.

4:40pm **TF-TuA10 Multi-Scale Simulation of High-κ Gate Dielectrics Deposited by Atomic Layer Deposition*, Z. Hu*,** *C.H. Turner*, The University of Alabama

Two of the most critical issues currently facing the semiconductor industry are the discovery of high-κ gate dielectric replacement materials for SiO_2 and the development of deposition processes that will afford high surface uniformity and controlled growth at the atomic scale. Atomic layer deposition (ALD) is an ideal candidate for meeting these challenges, enabling the deposition of a material through highly uniform and conformal growth, with thickness control at the atomic layer level. Our current work involves the use of a multi-scale modeling strategy to gain theoretical insights into the structure, properties and deposition process of high-κ dielectrics materials, which can provide a better understanding of experimental results and accurate predictions of specific properties of the thin films deposited by atomic layer deposition (ALD). In this work, we present results obtained from ab-initio quantum mechanical cluster calculations and periodic density functional theory (DFT) calculations based on tight-binding techniques. A series of calculations were carried out to study the initial ALD surface reactions. We present detailed chemical mechanisms and kinetic data at typical ALD temperatures range from 150°C to 450°C. This information can be used to understand experimental results and optimize operating conditions. The effects of surface functionalities and precursors on the thin film deposition process are discussed. Our DFT calculations show the complexity of the growth mechanisms during ALD processing. In addition, we predicted a new oxygen incorporation mechanism, which is relevant to the formation of the SiO_2 interfacial oxide layer during the ALD of Al_2O_3. As a replacement material for SiO_2, the potential high-κ oxide should form a high-quality interface with Si. We used molecular dynamics (MD) simulation to study the TiO_2/Si interface. A variable-charge inter-atomic potential was developed to describe the TiO_2/Si interface where the coordination environment may change. The TiO_2/Si interface structure was investigated by using MD with simulated annealing technique. The post-annealing oxidization process of the Si substrate was simulated by introducing external O atoms into the system to create concentration gradient. The atomic-scale mechanisms that govern the oxidation process can provide fundamental insight into the formation of the SiO_2 interfacial oxide and a better understanding of the TiO_2/Si interface structure.

5:00pm **TF-TuA11 Branched Interfacial Organic Layers: Controlling Nucleation and Growth of Thin Films*, M. Sharma*,** *A. Dube, K.J. Hughes, J.R. Engstrom*, Cornell University

Organic layers hold great potential for use in modern electronic and optoelectronic devices, owing to both their unique material properties, and their processing properties, such as their tendency towards self-assembly. In the work we describe here we have investigated the use of self-assembled monolayers (SAMs), or more accurately interfacial organic layers (IOLs), that possess a branched backbone for use as nucleation site multipliers and amplifiers. Here we describe the synthesis and characterization of two branched IOLs, their reactivity with precursors for atomic layer deposition (ALD), and the subsequent nucleation and growth of ALD thin films of TiN on these layers. The first IOL we consider is a layer that possesses a regular branched backbone with terminal $-NH_2$ groups, based on a sequential chemical reactions and application of polyamidoamine (dendrimer) chemistry. Here, an appropriately chosen $-NH_2$ terminated SAM serves as the anchor, from which additional growth is seeded, forming an IOL with a "Y" backbone and $-NH_2$ termination. A second IOL we consider is a randomly branched organic film, possessing -OH groups both at terminal points and along the backbone, which have been grown using anionic ring-opening polymerization of glycidol. In both cases the IOLs themselves have been characterized using X-ray photoelectron spectroscopy (XPS), ellipsometry and contact angle measurements. Furthermore, the layers have been characterized concerning their reactivity with two precursors for ALD, $Ti[N(CH_3)_2]_4$ and $Ta[N(CH_3)_2]_5$, using XPS. For the dendrimer we find that the adsorptive capacity of the surface scales with the generation of the dendrimer, i.e., the branching step effectively doubles the reactivity of the surface. For the poly-G layer, however, we find that sufficiently thick layers can virtually strip the Ta complex of all of its ligands, forming a TaO_x core. These observations are borne out in the subsequent growth of ALD thin films of TiN on these layers. Nucleation on the dense $-NH_2$ terminated dendrimer is relatively facile, and STEM shows a highly conformal layer. Growth on poly-G depends sensitively on its thickness-thin layers behave in a manner similar to the dendrimer IOL, whereas thicker poly-G layers behave more akin to unreactive long-chain $-CH_3$ layers. We will conclude with a discussion of our results on porous low-κ materials.

Applied Surface Science

Room: 4C - Session AS-TuP

Aspects of Applied Surface Science Poster Session

AS-TuP1 Exploring the Complementary Nature of ToF-SIMS and ESCA Depth Profiling, ***K.G. Lloyd***, *L. Zhang, J.R. Marsh, M.A. Plummer*, The DuPont Company

Depth profiling -- the removal of material with nanometer depth resolution while analyzing with surface-specific techniques that probe only the newly-revealed surfaces – is an important characterization component of the electronics industry. Secondary Ion Mass Spectrometry (SIMS) and X-ray Photoelectron Spectroscopy (XPS, a.k.a. ESCA) depth profiling are currently offered by the DuPont CCAS (Corporate Center for Analytical Sciences) organization and DuPont Analytical Solutions. Characteristics of the technique and the sample to be studied often determine which technique is more appropriate. These include detection limits, lateral resolution, thickness regime, and the type of chemical information required (elemental vs. functional group/oxidation vs. molecularly-specific). More recently, SIMS depth profiling with a Time-of-Flight (ToF) analyzer offers high mass resolution, spatially-resolved chemical information, and the collection of the entire mass spectrum at each depth interval. In addition, the combination of ToF-SIMS depth profiling and chemometric/multivariate methods of data analysis allows better definition and characterization of interfacial regions between layers, as well as buried defects. This has called for a reassessment of how and when the two depth-profiling techniques (ESCA and ToF-SIMS) can provide complementary information. Topics including oxidation state, organic information, and influence of different sputter sources will be discussed with examples.

AS-TuP2 Ultra-thin Titanium Films as Deuterium Storage Material; Thermal Desorption Kinetics Studies Combined with Microstructure Analysis, ***E.G. Keim***, University of Twente. MESA+ Institute, The Netherlands, *W. Lisowski*, Polish Academy of Sciences, Poland, *M.A. Smithers*, University of Twente, MESA+ Institute, The Netherlands, *Z. Kaszkur*, Polish Academy of Sciences, Poland

Thin titanium films can be applied as hydrogen storage material due to titanium hydride (deuteride) formation. However, the morphology of the Ti films, which depends strongly on the Ti film thickness, affects both the deuterium sorption and titanium deuteride decomposition properties.[1] Here we present the results of TDMS, XRD, SEM and TEM, showing adsorption-desorption properties of ultra-thin Ti films as well as surface and bulk film morphology changes due to titanium deuteride (TiDy) formation. Ti films, 10-20 nm thick, were prepared in a UHV glass system[2] at 300 K. Both volumetrically controlled deuterium adsorption and TDMS[3] monitored deuterium evolution was carried out in situ, all other analyses ex situ. It was found that ultra-thin Ti films of fine grained bulk morphology (average grain size about 10 nm) form a TiDy phase with low deuterium content ($y \leq 1.2$) after deuterium treatment at 1 Pa pressure. SEM and TEM/XRD analyses reveal a very fine grained (smaller than 8 nm) surface and bulk film morphology. TDMS heating induced decomposition of ultra-thin TiDy films proceeds at low temperature (maximum peak temperature T_m about 500 K) and its kinetics is dominated by a low energy desorption ($E_D = 0.61$ eV) of deuterium from surface and subsurface areas of the Ti film.

[1] W. Lisowski, E.G. Keim, Z. Kaszkur, M.A. Smithers, Langmuir, 2007, submitted.

[2] W. Lisowski, Vacuum, 54, 13 (1999).

[3] W. Lisowski, E.G. Keim and M.A. Smithers, J. Vac. Sci. Technol. A21, 545 (2003).

AS-TuP3 Scanning Auger Microanalysis of M316LN Alloy Used as a Superconducting Magnet Conduit Material, *H.M. Meyer III, R.M. Trejo*, Oak Ridge National Laboratory, ***S.T. Downey II***, *P.N. Kalu, K. Han*, FAMU-FSU College of Engineering

This poster presents the characterization of chemically modified 316LN used as a conduit alloy in Superconducting Outsert of the 45T Hybrid Magnet System housed at the NHMFL. The conduit material acts as a protective jacket and carrier of the Nb_3Sn superconductors formed within the magnet coil. This alloy was developed to withstand the deteriorative effects of the Nb_3Sn reaction heat treatment while maintaining high strength, toughness and ductility at liquid helium temperatures. This heat treatment, necessary for forming the Nb_3Sn superconductors within the magnet coil, is known to cause sensitization in most unmodified austenitic steel grades. Sensitization is the formation of brittle, chromium rich phases which degrade the mechanical behavior of this structural material. Cryogenic mechanical testing of M316LN upon exposure to the high temperature, long duration heat treatment (700C for 100 hours) was used to validate its current use. Mechanical tests show a significant loss in fracture toughness (~45%), although little microstructural characterization has been performed to support these findings. This poster describes our effort to provide microstructural and chemical characterization of the M316LN alloy exposed to the prescribed environments. In particular, we present scanning Auger microanalysis of the changes in chemical composition at the grain boundaries of M316LN caused by the heat treatment and resultant precipitate formation. Correlation of the Auger results with nanohardness tests at the grain boundaries will be presented. Research sponsored in part by the NSF through the Partnership for Research and Education in Materials Science under Grant No. DMR-0351770 and in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

AS-TuP4 Chemical Reaction of Alkali Metal with 1,3-butadiene on Si(100)2x1 Surface, ***H.Y. Park***, Korea Research Institute of Chemical Technology, *S.H. Kim, J.R. Ahn*, Sungkyunkwan University, Korea, *K.-S. An*, Korea Research Institute of Chemical Technology

The chemical adsorption of Na with 1,3-butadiene (BD)overlayer on Si(100)2x1 surface have been studied using X-ray photoelectron spectroscopy and synchrotron radiation photoemission spectroscopy in order to investigate the possibility of organic molecule-metal multilayered structure on semiconductor surface using unsaturated functional group of molecule on the top layer. As well known, the ethylene-like overlayer was induced by BD adsorption on Si(100)2x1 surface with [4+2] cycloaddition reaction (Diels-Alder reaction) at RT without breaking Si dimer. At low coverage of Na adsorption on the BD overlayer, large binding energy shift of C 1s core level spectrum was induced, which may be explained by Fermi level shift due to charge transfer from adsorbed Na to anti-π bonding state of C=C. Interestingly, the BD overlayer induces metallic Na layer beyond the RT saturation at higher coverage although Na adsorption on clean Si(100)2x1 surface has a saturation coverage (1 monolayer by double layer model) at RT. In this study, from work function changes, core level shifts, and valence band spectra, the chemical reaction of Na with ethylene-like BD overlayer on Si(100)2x1 surface are discussed.

AS-TuP5 Coding and Functionalization of Nanoparticles for Forming Photonic Bandgap Structures, *Y.-T. Kao, H.-T. Su*, ***C.-C. Chang***, National Taiwan University

Developing chemical strategies for synthesizing and characterizing functionalized nanoparticles and microspheres on which atomic aggregates of unique properties are coded for forming a lattice of repeating patterns as the photonic crystal are of great challenge for elevating photonic crystal research towards practical photonic device fabrication. When used in the photonic circuitry system, the crystal containing property-enhancing, functionalized microspheres must possess, among others, high degrees of optical clarity. This mandates high quality dispersions of the functionalized nanomaterials within the host matrix. Nanoparticles and microspheres of different chemical compositions and refractive indexes have been synthesized using a variety of chemical synthetic approaches. They were then coated with metal nanoparticles or functionalized with inorganic linkers, which were well dispersed on the surface of unit spheres. Photonic crystals were produced by self-assembly of these unit spheres through gravity or pressure. A variety of analytical methods were employed to reveal the chemical process involved in the synthesis, coding and functionalization of the unit spheres. Selective binding of species with unique functions to the surface of the unit materials was achieved by pretreating the materials surface, designing precursor molecules, and controlling the reactions involved in coding and functionalization. The bonding, reaction chemistry as well as the chemical identification of the species that were coded on the model unit materials surface will be discussed.

AS-TuP6 Addition of Surface-Modified Silsesquioxane Nanofillers for Thermal Stabilization of Polymer Thin Films, ***N. Hosaka***, *K. Miyamoto, H. Otsuka*, Kyushu University, Japan, *N. Yamada, N. Torikai*, KENS, Japan, *A. Takahara*, Kyushu University, Japan

Polymer thin films have numerous technological applications which require the homogeneous film. However, producing stable films is problematic since the polymer thin films tend to dewet from the substrates. Various approaches have been adopted to stabilize these films against dewetting, and recently, much interest has focused on the use of additives to improve the thin film stability. In this paper, polyhedral oligomeric silsesquioxanes

(POSS) were used as a nanofiller. POSS have gained considerable attention due to their organic-inorganic hybrid structure which consists of a silica cage with organic groups. The salient feature of this nanosized material is the ability to functionalize the silicon corners with a variety of organic substituents. Our previous study showed that the blending of cyclopenty substituted-POSS (CpPOSS) with the polystyrene (PS) thin films led to an inhibition of dewetting in the films.[1] Structural analyses of the films revealed that CpPOSS segregated to the film surface and film-substrate interface, and the inhibition of dewetting can be attributed to the segregation of CpPOSS, accompanying modification of the energetics and morphologies of the interfaces. However, the film with CpPOSS had a problem that its surface was roughened by the aggregation of CpPOSS. Present work is focused on the surface modification of POSS with several organic groups and PS chains to improve the dispersibility of POSS in PS films. Furthermore, the dispersion state of the surface-modified POSS in the film, especially at the surface and interface of the films, was investigated, and the relationship between dewetting inhibition and structure of the film was discussed. The dispersibility of POSS in PS films depended on the surface composition, and POSS with PS chains dispersed well in the films and also stabilized the film against dewetting.[2] Smooth surface morphology of the PS film with POSS modified by PS chains was observed by atomic force microscopy. Neutron reflectivity measurements revealed that the POSS still had the tendency to segregate to the film surface and interface even after the introduction of a PS chain on its surface, and this structure seems to be preferable for the inhibition of dewetting of the films.

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AS-TuP7 2 Dimensional Map of Field Emission Properties of CNT Emitters Fabricated by a Screen Printing Process, ***W.H. Han***, *T.Y. Park, C.J. Kang, Y.S. Kim, J.W. Kim, Y.J. Choi*, Myongji University, Korea

The spatial uniformity and durability of field emission is one of the main issues in the carbon nanotube (CNT) field emission devices fabricated by a screen printing process. In this paper, we propose novel method to visualize field emission sites of CNT films two-dimensionally by adopting scanning probe microscopy technique and verify the conditions where the field emission of CNT emitters is spatially uniform and durable. While the anode probe with a small tip diameter of <100nm was scanned over CNT emitter surface whose dimension is 200um*200um, the field emission current was recorded through Keithley 6517A, converted into 256 grayscale level and displayed on monitor through LabView program. The anode probe was made by electro-chemically etching tungsten wire and the CNT emitter sample was fabricated by screen printing multiwall CNT whose diameter is 4-6nm and length is 1-2um on the indium-tin-oxide (ITO) glass. During scanning, the gap between W anode and ITO glass surface was maintained to be few tens of um. For the large scale imaging, we used the inertial nano positioner whose model number is ANPxyz100 made by Attocube Systems as a long range scanner. With this system, we could not only measure the emission turn-on field at fixed locations but also obtain the electron emission current map over large surface areas under constant anode voltage. We will discuss the relation between the local geometry and field emission properties of CNT emitter, and the fabrication condition of CNT emitters where the field emission is uniform and stable.

AS-TuP8 Characterization of Vertical Arrays of ZnO Nanorod by AFM, ***Y. Hou***, *A. Andreev, C. Teichert*, University of Leoben, Austria, *G. Brauer*, Forschungszentrum Dresden-Rossendorf, Germany, *A. Djurisic*, University of Hong Kong, P.R. China

Solar cells made from an array of high-quality vertical ZnO nanorods filled with a light-absorbing, hole conducting polymer are promising devices for efficient low-cost solar energy conversion.[1] However, achieving full control over the growth of such nanostructures leading to proper dimensional confinement (like nanorod diameter, length, density and orientation) is still a challenging task. On the other hand, Atomic Force Microscopy (AFM) is well known as a valuable tool for nanometer scale characterization of different types of nanostructures.[2] The capabilities of AFM technique are demonstrated for the characterization of vertical arrays of various ZnO nanorods.[3] In detail, the topography of the ZnO nanorods grown on Si and ITO substrates was examined. It was found that tapping mode AFM is an appropriate tool to reveal the morphological features of vertical ZnO nanorods on the nanoscale, i.e. 3D rod shape, lateral size, average height and rod height uniformity. The results are compared with those obtained by Scanning Electron Microscopy. Moreover, by cross-sectional AFM measurements it was also established that intermediate facets appear between the top (0001) and side facets. Further, polymer coated ZnO nanorods have been investigated by AFM.

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AS-TuP9 Characterization of Ceramic Materials using Electron, Ion, X-ray, and Optical Techniques, ***B.W. Schmidt***, *B.R. Rogers, J.M. Burst, R.D. Geil, M.R. George, N.D. Vora*, Vanderbilt University

Ceramic materials are widely used because of their hardness, thermal stability, and electrical properties. However, these characteristics also present issues when it comes to processing. Powder pressing is commonly used, but due to the variability in powder sizes and structures, reproducibility is difficult. Therefore, fundamental understanding of interfaces and surfaces is critical to modeling efforts. Our group uses thin film experiments to gain insight into basic mechanisms, which can then be applied to more complicated systems. We are focusing on aluminum and hafnium-based materials. Al_2O_3 is used extensively today because of its low cost and excellent protective properties. Chemical vapor deposition of Al_2O_3 typically includes trimethylaluminum (TMA), a dangerous pyrophoric compound. Dimethylaluminum isopropoxide (DMAI) is an alternative precursor that displays the same high vapor pressure that makes TMA desirable, but also shows stability as a liquid in ambient conditions. Hafnium oxide materials have received recent emphasis as high-κ replacements of silicon dioxide in CMOS devices. In addition, the borides and carbides of hafnium also can be used in high temperature applications such as hypersonic flight and atmospheric re-entry. In this work, we provide examples of how Auger electron spectroscopy, Rutherford backscattering spectrometry, time-of-flight medium energy backscattering spectrometry, X-ray photoelectron spectroscopy, and spectroscopic ellipsometry have been used to characterize these ceramics.

AS-TuP10 Room Temperature Nanoimprinting of Crystalline Poly(fluoroalkyl acrylate) Thin Films, ***K. Honda***, Kyushu University, Japan, *M. Morita*, Daikin Industries, Japan, *A. Takahara*, Kyushu University, Japan

Various studies have been done on the nanofabrication of polymeric materials. However, most of the studies utilize conventional polymers and little attempt has been done for the design of polymeric materials for nanofabrication. In this study, room temperature nanoimprinting of polymer thin films will be presented. Nanoimprinting technology using compression molding of thermoplastic polymers is a low cost mass manufacturing technology and has been around for several decades.[1] The polymer used for nanoimprint experiment is Poly(2-(perfluoroocthyl ethyl) acrylate) with long fluoroalkyl group (PFA-C_8). In previous report, the authors studied wetting properties and surface molecular aggregation of PFA-C_8 thin films and clarified that PFA-C_8 showed the high water repellency because of crystaliization of long fluoroalkyl group.[2,3] PFA-C_8 was spin-coated on the Si-wafer. The film thickness was estimated as approximately 500 nm by atomic force microscopy (AFM). The mold patterned with lines (L/S of 500 nm) was imprinted onto a spin-coated PFA-C_8 thin film under various imprinting conditions and nanoimprinting characteristics of PFA-C_8 was investigated on the basis of scanning elerctron microscopy (SEM), AFM and contact angle measurement. The line patterns were observed on PFA-C_8 film surface by AFM and SEM. In addition, PFA-C_8 film was sucessfully nanoimprinted at room temperature because of the weak interaction among rigid fluoroalkyl groups in crysatallite. The nano-textured PFA-C_8 exhibited super hydrophobicity as well as high oleophobicity. Also, line imprinted surface showed anisotropic wetting behavior. The super hydrophobicity was explained by the notion of heterogeneous wetting proposed by Cassie. In this case, the space between the solid surface and probe liquid was occupied by air and consequently the contact angle was increased.

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AS-TuP11 Short and Long-term Sputter Rate Constancy Measurements, ***A.S. Lea***, *M.H. Engelhard, D.R. Baer, P. Nachimuthu*, Pacific Northwest National Laboratory

The use of ion sputtering to obtain relative and absolute depth information about surface layers and films is a common application of Auger and photoelectron spectroscopy. Accurate information about sputter rates for different materials and reproducible information for similar systems requires that the conditions of operation of an ion gun be fairly well characterized and the parameters needed to obtain reproducible sputter conditions be understood. Unfortunately, most of us do not have a good sense of how stable and reproducible our actual sputter rates are. We have undertaken a study to determine the constancy of sputtering over short and long periods of times as these determine how long of a warm-up time is necessary prior to conducting sputter rate profiles, how much variability occurs during the course of an experiment, and how often one must perform sputter rate calibrations. We have three surface analysis systems, either manually or digitally controlled, in which we are conducting these constancy measurements. We have found that for one digitally controlled system, sputter rate are fairly constant over a period of a year. In the short term, sputter rates are constant following a short warm-up time. For a manually controlled system, the sputter rate is constant over a period of days provided the settings do not change over that period of time. Determination of the long-term variability of a manually controlled system for argon ion sputtering at fixed energies is part of an on-going effort. These sputter rate constancy measurements are being conducted in a Phi Quantum 2000 XPS system, a Phi 680 Auger Nanoprobe system, and a Kratos Axis 165 multitechnique system. We will provide comparisons of sputter rate constancy for these systems over the short and long-term.

AS-TuP12 Interaction of Cobalt with Weathered Steel Surfaces Studied by XPS*, D.L. Blanchard Jr.*, *I.E. Burgeson, G.J. Lumetta, J.R. DesChane,* Pacific Northwest National Laboratory*, G.W. Wagner*, Edgewood Chemical Biological Center

Researchers at the U.S. Army Edgewood Chemical Biological Center have developed and tested a solution for decontaminating surfaces from biological and chemical warfare agents: DECON GREEN^{TM}. Prior tests conducted at the Pacific Northwest National Laboratory (PNNL) to examine the efficacy for removal of radionuclides showed that the effectiveness of DECON GREEN^{TM} in removing Co from aged steel, though better than water, was considerably lower than that observed for other surfaces. Only about 50% of the Co could be removed from the steel surface using DECON GREEN^{TM}. In the current work, the mechanism of the Co adhesion to the steel was investigated using X-ray Photoelectron Spectroscopy (XPS). Cobalt(II) chloride ($CoCl_2$) aqueous solution was pipetted onto a weathered steel coupon and allowed to air-dry. The coupon was examined by XPS to determine the chemical state of the resulting cobalt deposit. An untreated, weathered steel coupon was examined as a control, and samples of cobalt metal foil and $CoCl_2$ powder were examined as reference compounds. The steel coupon treated with the $CoCl_2$ was rinsed with water after the initial XPS analysis, then re-examined to identify any changes in the cobalt chemical state. The coupon was then treated with DECON GREEN^{TM} and rinsed with water, and re-examined. The key observations are: 1) The cobalt on the weathered steel coupon was mainly metallic, based on the shape and position of the Co $2p_{3/2}$ XPS peak, indicating that cobalt(II) in the applied solution was reduced to metal at the surface. The appearance of shoulders on the high binding energy side of the main peak suggested the presence of a small amount of oxidized cobalt. The iron in the weathered steel coupon was somewhat oxidized before the cobalt deposition; the deposition further oxidized the iron. 2) Rinsing with water did not significantly change the shape of the Co $2p_{3/2}$ XPS peak; the shape and position still indicate mainly Co metal with some oxidized cobalt, probably a cobalt hydroxide or oxide. Rinsing oxidized all the iron metal at the surface, and greatly increased the fraction of oxygen on the surface. 3) Treating with DECON GREEN^{TM} increases the fraction of oxidized cobalt at the surface, but the majority is still metallic. The iron may undergo some additional oxidation. The DECON GREEN^{TM} treatment left carbon at the surface, probably from organic constituents.

AS-TuP13 Plasma Enhanced Chemical Vapor Deposition of Trimethylsilane on Ion Vapor and Physical Vapor Deposited Aluminum*, P.R. Scott*, *D.M. Wieliczka*, University of Missouri - Kansas City

X-ray photoelectron spectra were obtained after each stage of a plasma deposition process with depth profiles to the aluminum layer. Spectra were obtained from Silicon wafers prior to processing; and after Argon ion plasma etching, vapor deposition of Aluminum, and DC plasma deposition of trimethylsilane. The samples were transferred under vacuum from the plasma chamber to a Kratos AXIS HS x-ray photoelectron spectrometer. Spectra were taken with magnesium K-alpha x-rays at a base pressure of 10^-9 Torr. Argon plasma etching removed carbon contamination, but left a residual oxide on the surface. Aluminum ion vapor deposition films were created at 100mTorr of Argon while physical vapor deposition films were created at a pressure of 10^-7 Torr. Results of a comparison between the ion vapor deposition and physical vapor deposition films will be presented. Various plasma deposition parameters were used to produce the trimethylsilane thin films.

AS-TuP14 Sputter Rate Determinations for Different Forms of ZnO, TiO2, and Al2O3*, M.H. Engelhard*, *T.C. Droubay, L.V. Saraf, P. Nachimuthu, A.S. Lea,* Pacific Northwest National Laboratory*, W. Stickle,* Hewlett Packard*, C. Mathews, B. Lee, J. Kim, R.M. Wallace,* University of Texas at Dallas*, D.R. Baer*, Pacific Northwest National Laboratory

Oxide films play increasingly important roles in several modern technologies, including integrated circuits, fuel cells, and sensors. Important to the use of surface analysis techniques to characterize a variety of these materials systems is the knowledge of the sputter rates for different oxides. Since research in our laboratories and for users of the US Department of Energy's Environmental Molecular Sciences Laboratory (EMSL) user facility involves the use of oxide films and particles, we have been building an oxide sputter rate database by examining thin films grown by oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). These studies demonstrate that we can usually obtain sputter rate reproducibility of better than 5% for similar oxide films grown by OPA-MBE. However, it is well known that there are many sputtering artifacts that can occur including those due to crystal orientation, structure, or the presence of impurities. In order to examine the general applicability of the information from the epitaxial film "standards" to other materials, we are measuring the sputter rates for oxide films for a different crystal structures and/or deposition techniques. Here, we report measurements of sputter rates for ZnO, TiO2 , and Al2O3 films prepared by pulsed laser deposition, chemical vapor deposition, or atomic layer deposition. We are currently examining the dependency of density as well as crystal structure on sputter rates. X-ray reflectivity (XRR) has been used to measure the thickness and density of these films and sputter rates are measured using a PHI Quantum 2000 Scanning ESCA Microprobe. The measured sputter rates are compared to rates for known thicknesses of SiO2/Si. Work at PNNL is supported by the Department of Energy and work at UT-Dallas is supported in part by the Semiconductor Research Corporation.

AS-TuP15 Ion Beam Tuning and Optimization of Nova Ion Gun in Kratos Axis Ultra DLD Spectrometer*, H. Piao*, *J. Chera, V. Robinson*, General Electric Co.

The first part of this study focuses on the Nova ion gun beam tuning and the resulting XPS depth profiling measurements based on a standard SiO2/Si sample under different measuring conditions (ion beam energies from 0.5-4 keV). The quantitative evaluation of depth profiles in terms of sputter rate and depth resolution is discussed in more details. Changes of topography resulting from sputtering (roughness increases with sputtering time and depth) are also given a full attention. Then we report the advantages of the "float" mode with the production of relatively high current, low energy ion beams for enhanced depth resolution. Practical application of its depth profiling at interfaces is further elucidated by a typical example: SiOxNy(40nm)/SiOxCy(300nm)/SiOxNy(40nm) thin film. Finally, the improvement of the depth resolution by rotating the sample azimuthally is demonstrated.

Biomaterial Interfaces

Room: 4C - Session BI-TuP

Biomaterials Interfaces Poster Session

BI-TuP1 Investigating the Adhesion of Biomolecules on Plasma Polymerized Thin Films*, R. Foerch*, *S. Brueninghoff, E.-K. Sinner, W. Knoll, R. Berger*, Max-Planck-Institut for Polymer Research, Germany

The controlled adhesion of biomolecules on surfaces has become a major topic of interest in biomaterial surface design. The interest in this has been triggered by a broad range of biomaterial applications. For example, those that rely on proteins and cells immobilized on solid surfaces for the development of new implant materials and tissue regeneration. It is generally accepted that both the surface morphology and the surface chemistry need to be in concert to ensure optimum conditions for biomaterial adhesion. However, the surface interactions are very complex and are not completely understood. Further, there are only very few analytical tools available that deliver reliable, real time insights into the biomaterial/ surface interactions. We present recent results in which plasma polymerization techniques have been used to prepare "model" surfaces that can be conditioned towards the adhesion of a particular mammalian cell line (P19 progenitor cells). Techniques such as Surface Plasmon Resonance (SPR), Micro-Cantilever Sensor technology (MCS) and standard optical microscopy have been used to study in real time the adsorption of proteins and P19 cells on such surfaces. Correlations to the chemical environment at the interface are made.

BI-TuP2 Tailoring Surface Properties of Spider Silk Protein Films for Biomaterial Applications*, P.A. Johnson*, *H. Zhang, C. Skinner, T.G. Martinez-Servantez*, University of Wyoming

Spider silk is well known for its unique, outstanding material properties. Dragline spider silk in particular is one of the strongest natural materials with a high degree of elasticity. These properties, together with its inherent biodegradability and biocompatibility, make it a promising biomaterial for tissue engineering applications. Though the best material properties are derived from native dragline spider silk, producing spider silk naturally is not practical to generate sufficient quantities for biomedical applications. Recombinant spider silk proteins have been successfully produced in bacterial expression systems as well as in goat's milk. In our studies we compared the surface properties and biological responses of native major ampullate silk from N. clavipes, the major ampullate proteins produced in E. coli, and the major ampullate proteins produced in goats' milk. Thin films were cast from hexafluoroisopropanol and then treated with 90% methanol. The films with and without methanol treatment were characterized by AFM, SEM and contact angle analysis. The untreated films initially had very different surface properties, but after methanol treatment the contact angles and surface roughness converged to similar values. Once processes for generating consistent films were established, the biological response of the films was determined. Protein adsorption studies were conducted via mass sensitive techniques (QCM-D). Cellular responses were established to determine cell adhesion, cell morphology and cell proliferation. The films were protein resistant and inhibited cell adhesion. Therefore, to promote cell attachment and growth the spider silk films were modified with cell binding peptides.

BI-TuP3 Self-Assembly of Biomolecules at Surfaces, Characterized by NEXAFS*, **X. Liu**, F. Zheng,* University of Wisconsin-Madison*, A. Jürgensen,* Canadian Synchrotron Radiation Facility, Synchrotron Radiation Center*, V. Perez-Dieste,* Universitat Autònoma de Barcelona, Spain*, D.Y. Petrovykh,* University of Maryland and Naval Research Laboratory*, N.L. Abbott, F.J. Himpsel*, University of Wisconsin-Madison

Surface science has made great strides towards tailoring surface properties via self-assembly organic molecules. It is now possible to functionalize surfaces with complex biomolecules, such as DNA and proteins. However, probes of the chemical orbitals involved in this process have remained scarce. Here we show how NEXAFS (Near Edge X-ray Absorption Fine Structure spectroscopy) can be used to characterize the assembly of biological molecules at surfaces in atom- and orbital-specific fashion. The technique is illustrated by self-assembled monolayers with customized terminal groups. Applications are demonstrated by DNA oligonucleotides and Ribonuclease A[1], a small protein containing 124 amino acids. The N 1s absorption edge is particularly useful for characterizing DNA and proteins, because it selectively interrogates the π^* orbitals in nucleobases and the peptide bonds in proteins. Information about the orientation of molecular orbitals is obtained from the polarization dependence. Quantitative NEXAFS models are developed to explain the polarization dependence in terms of molecular orientation and structure.

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BI-TuP4 Adsorption of an S-layer Bacterial Protein by Total Internal Reflection UV Absorption Spectroscopy, ***M.A. Bratescu***, Nagoya University, Japan*, D.B. Allred,* Nagoya University, Japan, and University of Washington*, N. Saito,* Nagoya University, Japan*, M. Sarikaya,* University of Washington*, O. Takai*, Nagoya University, Japan

Surface-layer (S-layer) proteins from many species of bacteria and archaea self-assemble into two-dimensional supramolecular arrays and form specific space groups. Although S-layer proteins are now used as molecular and nanoscale templates for nano- and bio-nanotechnology, the fundamental bases of assembly and ordered organization are still under study. The purpose of our research is to characterize adsorption specificity, surface interactions, and assembly of S-layer proteins on solid surfaces. We use absorption of UV evanescent light produced by multiple total internal reflections in a quartz IRE sensor which is sensitive to a depth of a few tens of nanometers. The S-layer proteins were prepared as described in Ref. [1], starting from a cell culture of Deinococcus radiodurans. A final concentration of protein in sodium dodecyl sulfate was estimated to be 0.5 mg mL $^{-1}$. For experiments, the protein solution was diluted in deionized water to a concentration of 0.2 mg mL $^{-1}$. A comparative analysis of the S-layer protein adsorption was performed on different functionalized surfaces (amino- and hydroxyl- terminated) or surfaces deposited with noble metals (platinum and gold). The amino-terminated monolayer was obtained by dipping freshly cleaned quartz into a 1 wt % solution of (3-aminopropyl) trimethoxysilane in toluene for 3 hours at 60 ° C. The hydroxyl-terminated surface was obtained by photochemical exposure of quartz to VUV radiation at 172 nm. The noble metals were deposited by magnetron sputtering. S-layer protein absorption bands were found at 274 nm and 307 nm, characteristic of tryptophan and tyrosine residues, which have UV absorption bands in the spectral region 270 - 350 nm. The strongest absorption was obtained when S-layer proteins were adsorbed on an amino-terminated surface. Time dependence of protein adsorption will be correlated with data obtained by atomic force microscopy analysis of S-layer proteins on different solid surfaces to derive a better understanding of the adsorption process.

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BI-TuP5 Adsorption Kinetics and Dynamics of Fibrinogen with Surface Interactions, ***N. Saito**, Y. Sato, O. Takai*, Nagoya University, Japan

The control of blood coagulation on biomaterial surfaces is an urgent issue in the medical field. The main process occurring in blood coagulation is the polymerization of fibrinogen into erythrocyte-trapping fibrin. Other plasma proteins are also involved in initiating this process. The multi-interactions among proteins and material surface govern the process. The molecular structure of fibrinogen as a free molecule has been investigated in detail. However, its adsorption state on a biomaterial surface has yet to be elucidated. Recently, the adsorption state of fibrinogen on various substrates has been the subject of intensive investigation employing atomic force microscopy (AFM). Such use of AFM has been crucial in the study of molecular biology on surfaces. In this study, the adsorption kinetics and dynamics of fibrinogen with the interaction of heparin onto hydrophobic and hydrophilic surfaces is investigated with AFM analysis and QCM (quartz crystal microbalance). CH3-terminated self-assembled monolayer (SAM) and SiOH-terminated substrates were utilized as the hydrophobic and hydrophilic surfaces. Fibrinogen adsorption proceeded following Langmuir type. On the process, the orientation of fibrinogen on the sample surface was changed. Heparin did not promote desorption of fibrinogen but the adsorption on the hydrophilic surface though it is well known as an anti-coagulation factor. On the other hands, heparin promoted the adsorption on the hydrophobic surface. The differences were discussed based on 3-body interactions analysis.

BI-TuP6 In situ Analysis of Fibrinogen on Self-Assembled Monolayers by Evanescent Optical Spectroscopy, ***M. Matsuno**, T. Ishizaki, O. Takai, N. Saito*, Nagoya University, Japan

Fibrinogen is one of proteins in blood plasma and plays a great important role on blood coagulation. Many researchers have investigated the adsorption of fibrinogen on various substrates in order to develop inactive biomaterials for fibrinogen. However, the coagulation mechanism has not been understood yet, since it is due to interactions among many factors, ex. other proteins and ions. The research on fibrinogen adsorption from molecular viewpoints has been required. In this study, we aimed to understand fibrinogen adsorption on OH-terminated, CH_3-terminated, NH_2-terminated and poly(ethylene glycol) (PEG) surfaces using an evanescent optical spectroscopy, an atomic force microscopy (AFM) and a zeta potentiometry. The evanescent optical spectroscopy allows us to detect few fibrinogens on surfaces with high-sensitivity. A quartz glass was used as a substrate, which worked as an optical waveguide. A vacuum ultraviolet (VUV) lamp with a wavelength of 172 nm irradiated the quartz substrates. The surface changed to OH-terminated surface. CH_3-terminated surface was prepared from n-octadecyltrichlorosilane (OTS) dissolved in toluene through liquid phase method. NH_2-terminated and PEG surfaces were prepared from n-(6-aminohexyl)aminopropyltrimethoxysilane (AHAPS) and 2-methoxy[polyethyleneoxy]propyltrimethoxysilane (MPEOPS) through a vapor phase method. Dried fibrinogen was dissolved in phosphate buffered saline (PBS). The concentrations of fibrinogen were adjusted to 0.1, 1 and 10μM. Fibrinogen adsorption process was monitored by the evanescent optical spectroscopy. An absorption peak was observed at wavelength of ca. 280nm, which is attributed to tyrosine and tryptophan in fibrinogen. The change of the intensity against time was determined by types of surfaces. In order to reveal the difference, the fibrinogens on the surfaces were observed by AFM. In addition, zeta potentials of the fibrinogen and the sample surfaces were obtained in order to elucidate the effect of electrostatic interaction among them on adsorption. Finally, we propose a kinetic model of the adsorption.

BI-TuP7 Determining the Surface Release Kinetics of KGF Protein from a Biodegradable Polymer Film, ***S.A. Burns**, J.A. Gardella Jr.*, SUNY Buffalo

Biodegradable polymers are of interest in developing strategies to control protein drug delivery. The protein that was used in this study is Keratinocyte Growth Factor (KGF) which is a protein involved in the re-epithelialization process. The protein is stabilized in the biodegradable polymer matrix during formulation and over the course of polymer degradation with the use of an ionic surfactant Aerosol-OT (AOT) which will encapsulate the protein in an aqueous environment. The release kinetics of the protein from the surface of the polymer matrix requires precise timing which is a crucial factor in the efficacy of this drug delivery system. Determining the release kinetics was accomplished by a two fold method. The first step was to measure the accumulation of the surfactant and protein at the surface of the polymer film. X-ray Photoelectron Spectroscopy (XPS) was used to measure the surface concentration of the surfactant and polymer using the unique elemental composition of these compounds. The surfactant has been identified from the polymer matrix using the sulfur region while protein identification utilizes the nitrogen signal. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used in the same capacity to identify the molecular ion peak of the surfactant and polymer and use this to determine surface concentration. The surfactant molecular ion peak was observed in the positive and negative mode at m/z 467 and 422, respectively. These peaks were determined to be [AOT + Na+]+ and [AOT-Na+]-. These methods are used to identify the surfactant and protein from the polymer matrix and are used to measure the rate of surface accumulation. The second step was to compare this accumulation rate with the release rate of the protein into an aqueous solution during the degradation of the biodegradable film. This rate is compared to fluorescence spectroscopy measurements that were done using the autofluorescence of the protein that has been released into an aqueous solution. This study was done to determine the release kinetics of an unmodified biodegradable system containing only a polymer, surfactant, and protein. One method that is currently being used to tune the release rate of the polymer is micro-patterning. The pattern will determine the rate at which the polymer degrades and the rate at which protein is released.

BI-TuP8 Protein Encapsulation in Organo-Functionalized Mesostructured Silica and Titania, *C.T. Burns, S.Y. Choi, **M.A. Firestone***, Argonne National Laboratory

Interfacing biomolecules to inorganic frameworks is essential for fabricating robust, functionally integrated biocomposites that may prove useful in a wide range of technologies including biocatalysis, biosensors or protein-based devices. Our work is directed at developing means to integrate biomolecules (e.g., proteins) into 'active' mesostructured inorganics. These active frameworks serve to both improve the mechanical stability (robustness) of the proteins and to facilitate communication with the encapsulated guests. Toward that end, we have synthesized and characterized a variety of photoactive mesoporous silicas and have examined the encapsulation of soluble proteins within them. Specifically, we have both carried out post-synthesis modification of the silica pore surface and prepared organosilicas in which spiropyran groups are homogeneously incorporated throughout the walls of the mesoporous silicas as a means to introduce photo- and redox active moieties within the frameworks. Protein incorporation within mesostructured titania thin films has also been achieved. The synthetic strategies used to prepare these materials, and details of the characterization of the frameworks and the biocomposites will be presented.

BI-TuP9 Dynamic Visible Spectroscopic Ellipsometry Studies of Protein Adsorption and Conformational Change, ***S. Sarkar**, L. Castro, D.W. Thompson, A. Subramanian, J.A. Woollam*, University of Nebraska, Lincoln

Protein adsorption onto surfaces continues to be widely researched, as it is an everyday occurrence either improving or impeding the quality of life. Often investigated are kinetics of adsorption. In the present work we monitored protein adsorption to surfaces with different chemistries. Modified chitosan surfaces and silicon wafers were used. Spin-cast Chitosan was cross-linked and activated with diepoxides and selected chemical ligands (n-butyl amine, t-butyl amine, n-octyl amine, 2,4,6 Tris and 2-t-Ethyl(butyl amine)) and anti-human albumin molecule. These surfaces were created to preferentially adhere to human serum albumin (HSA). Protein solutions consisting of HSA, immunoglobulin and fibrinogen dissolved in phosphate buffered saline were used to study adsorption processes. Solutions were introduced onto modified chitosan using a fluid cell, and dynamic data optically modeled to obtain protein adsorption profiles. Chitosan is a well known hydro-gel, and spun cast chitosan is anisotropic. Our EMA-based optical model accounts for this anisotropy. A thermodynamic adsorption model was formulated which accounts for changes in protein surface binding capacity during dynamic conformational changes. The model assumes irreversible binding of proteins and a process that is not diffusion limited. The adsorption profiles were then modeled and the parameters compared. Our studies indicate typical protein adsorption processes differ from a simplistic Langmuir model. It also describes changes in protein binding rates during a given adsorption cycle. We propose these regions of data result from surface bound protein conformation changes.

BI-TuP10 Performance and Properties of Poly(N-isopropylacrylamide) Based Switchable Coatings, ***M.A. Cole***, University of South Australia, *H. Thissen*, CSIRO Molecular and Health Technologies, Australia, *N.H. Voelcker*, Flinders University, Australia, *H.J. Griesser*, University of South Australia

Surface modification of biomedical and biotechnological devices using thin polymeric coatings is a popular method employed to alter the interactions of synthetic materials with biomolecules and cells from surrounding biological media and environments. Advancements in this field have been made largely from an interdisciplinary approach combining surface modification and polymer science with biomaterials science and biological studies. Recent research into stimuli-responsive or switchable materials has focused on means to control protein-material and cell-material interactions with respect to directing the spatial location, temporal location and biological function of biomolecules. Controlling the interfacial interactions of biological components is of interest for a wide range of biomedical/biotechnological applications including microarrays, biosensors, drug delivery, cell sheet engineering and 'lab on a chip' devices. As part of ongoing research we report our findings on the grafting and properties of stimuli-responsive coatings incorporating poly(N-isopropylacrylamide) (pNIPAM). Thin films of pNIPAM were prepared via 'grafting to' and 'grafting from' techniques and investigated at temperatures above and below the lower critical solution temperature (LCST) of approximately 32 °C. Switching of coatings between hydrated and collapsed states below and above the LCST was investigated with respect to the degree of change in phase transition and the ability to induce protein adsorption. Surface analysis was carried out using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and time of flight secondary ion mass spectrometry (ToF SIMS). Adsorption of model proteins, lysozyme and bovine serum albumin were investigated using a quartz crystal microbalance (QCM), optical waveguide lightmode spectroscopy (OWLS), TOF SIMS, and AFM. Results from switching and protein adsorption experiments show the transformation of pNIPAM coatings between low fouling (protein resistant) and fouling (protein adsorbent) states. Colloid probe force analysis of pNIPAM coatings reveal considerable changes in protein-pNIPAM interactions at different temperatures. The present study is expected to assist the development of switchable coatings for biomedical and biotechnological applications.

BI-TuP11 Molecular Dynamics Parameterization for Electrostatic Interactions between Proteins and Biomaterial Surfaces, ***G. Collier***, Clemson University, *B.R. Brooks*, National Institutes of Health, *S.J. Stuart, R.A. Latour*, Clemson University

Since protein-biomaterial interactions govern the biocompatibility of implanted materials, controlling biocompatibility through material design must begin with the study of protein-biomaterial interactions at the atomic level. All-atom molecular dynamics simulation provides an excellent approach to investigate this type of problem. However, current molecular dynamics simulation methods and parameters are generally not designed to accommodate the unique types of atomic interactions that exist for the case of a protein interacting with a functionalized surface. To address this problem, we have begun adapting the molecular modeling community's range of tools to develop a set that is specifically designed for the simulation of the adsorption behavior of proteins to functionalized surfaces. Protein adsorption behavior is predominantly governed by nonbonded interactions, with electrostatic effects representing the strongest type of these interactions and the type that is most difficult to accurately represent. In an effort to establish the most appropriate method of treating electrostatic interactions for the simulation of adsorption processes, we are evaluating the calculated differences in ion distribution over a charged surface using a variety of nonbonded interaction techniques. Our 4.5 x 4.3 x 10.0 nm^3 model system is comprised of a 150 mM NaCl aqueous solution with TIP3P water over a 50% deprotonated COOH-SAM surface ($pK_a = 7.4$) with Na^+ counterions. Nanosecond-scale molecular dynamics simulations are then conducted to model the structure of the electric double layer over the surface using a series of different methods to represent the electrostatic interactions of the system, including particle-mesh Ewald, radial cutoffs, isotropic periodic sum, and anisotropic periodic sum methods. The results of these simulations are then compared to the analytical solution of the ion distribution based on the Poisson-Boltzmann equation to gauge the accuracy of each of the different simulation methods. Within each different method, the parameters defining the limits of atomic interactions, such as interaction cutoff distances in the case of radial cutoffs, have been varied to establish a balance between computational cost and simulation accuracy. The results of this study will establish the most efficient and accurate method for the representation of nonbonded electrostatic interactions for the simulation of protein-surface interactions.

BI-TuP12 Photogenerated Surfaces for Carbohydrate-Protein Interactions, ***O. Ramstrom***, Royal Institute of Technology, Sweden, *M. Yan*, Portland State University

Photogenerated bioactive surfaces have been developed following a perfluorophenylazide-based, double ligation strategy. Gold-plated quartz crystal microbalance crystals were initially coated with different polymers, either covalently or non-covalently, and the resulting surfaces were subsequently used as substrates for photoinsertion of active photoprobes. A range of different polymers were evaluated, where high biocompatibility and durability could be shown. The photoprobe insertion yielded a range of different carbohydrate-based recognition motifs presented at the surfaces, which were subsequently used as sensor recognition elements in a flow-through quartz crystal microbalance instrumentation. A series of different carbohydrate-binding proteins (lectins) were analyzed, and selectivity and affinity of protein binding could be efficiently monitored. The results clearly show the predicted protein selectivities, demonstrating the applicability of the approach.

BI-TuP13 Microlens Array Patterning of Glass and Silicon for Protein Bioarray Formation, *M.R. Linford, M.C. Asplund, R. Gates, F. Zhang,* ***G. Saini***, Brigham Young University

Microlens arrays (MLAs) are powerful tools for surface modification. These commercially available optics offer a wide range of shapes and packings for their microlenses. Here we describe the use of MLAs for patterning monolayer-coated glass and silicon substrates. In this process, a nanosecond pulse of laser light is directed through a MLA. In the region where the microlenses focus the light onto the surface the protective monolayer is removed leaving a pattern of spots. A wide variety of proteins, including ferritin and ferritin analogs, adsorb directly onto these spots. A reactive polymer will also adsorb to these spots and undergo subsequent reactions that are typical of bioconjugate chemistry. This process is further demonstrated with 266 nm light on glass, where glass is the substrate material of choice for bioarrays.

BI-TuP14 Protein Adsorption Correlated with Surface Properties of Copolymer Libraries Synthesised as Microarrays, ***M. Taylor***, *A.J. Urquhart,* University of Nottingham, UK, *D.G. Anderson, R. Langer,* Massachusetts Institute of Technology, *M.R. Alexander, M.C. Davies*, University of Nottingham, UK

Combinatorial methods have become increasingly popular as a means of material development, allowing rapid discovery and optimisation of new materials. Micro patterned combinatorial material libraries have been shown to be a useful method of screening materials for a number of biological applications. Protein adsorption to surfaces underpins biological response and is therefore of great importance in both implantation and tissue culture situations. Adsorbed proteins effectively translate the structure of a surface into a biological language that ultimately influences the way cells adhere and function. Hence, understanding why and how different proteins adsorb to different surfaces and the effect this has on cell adhesion and growth is of major importance. In this abstract, we report on the adsorption of fluorescently labelled fibronectin to a spatially patterned micro-arrayed library of 480 novel copolymers designed to illicit a range of surface phenomena. Using partial least squares models, protein adsorption has been related to the data generated from the high-throughput surface analysis of the array, including surface chemistry (ToF-SIMS and XPS) and wettability (contact angle, surface energetics), as well as the data derived from the screening of the adhesion and proliferation of the chicken embryonic stem cells to the copolymer library. Interesting correlations between surface phenomena and biological response have been derived from the large data sets, information that will provide important pointers for controlling cellular interactions with such polymeric surfaces.

BI-TuP15 On the Thermodynamics of Protein Adsorption Processes, ***J.C. Hower***, *Y. He, S. Jiang*, University of Washington

While significant advances in biocompatible and environmentally benign materials have been made, one of the remaining challenges is to understand surface resistance to protein adsorption. Significant experimental efforts have produced only a small number of nonfouling materials and coatings. Moreover the mechanisms of protein resistance are poorly understood and a majority of new material breakthroughs are made fortuitously. Molecular simulations can aide in material development. By simulating in-silico, one can perform costly experimentation after candidates are selected by initial screening. Molecular simulations also provide access to interactions at the protein-surface-solution interface. We have performed extensive work quantifying the repulsive forces that nonfouling surfaces generate on proteins and analyzing the cause of these forces. Yet, the thermodynamic criterion of adsorption or resistance is the change in free energy as a protein approaches a surface. In this work, molecular simulations were used to calculate the free energy change as model peptides in solution approach surfaces of varying nonfouling ability and to develop simulation-based evaluation criteria. The simulations were supported by protein adsorption experiments. By combining simulations and experiments we verified our simulations and evaluated the relative influence of the surface and hydrating water on the process. This combined approach provides feedback on our simulation parameters and a deeper understanding of the mechanisms of protein resistance and adsorption. Our research has demonstrated a strong link between surface hydration and non-fouling ability. Thus simulations and experiments were conducted to evaluate the hydration of functional moieties representing a wide range of nonfouling abilities. The extent of hydration of biologically relevant functional groups, like oligo-ethylene glycol and sugar alcohols, was evaluated by calculating the partial molar volume change due to hydration. This data was then compared to protein adsorption to self-assembled monolayer surfaces presenting the same functional groups. By using a simple measurement of hydration, it is possible to rapidly screen candidate non-fouling moieties. By combining molecular simulations and experimental techniques, we are able to develop a fundamental description of the interactions present at the molecular and macro scale. This in turn supports rational material design based on desired molecular function.

BI-TuP16 Correlation of Changes in Protein Bioactivity Post-Adsorption to Adsorbed Orientation and Conformation, ***K.P. Fears***, *R.A. Latour*, Clemson University

It has long been known that proteins rapidly and irreversibly adsorb onto biomaterial surfaces upon contact with bodily fluids. The structure and bioactivity of the adsorbed protein layer are recognized to be critical factors that influence subsequent cellular responses; however, the molecular mechanisms involved are mostly unknown. The bioactivity of an adsorbed protein could be inhibited due to adsorption-induced conformational changes, orientation effects causing the active site to be sterically blocked, or a combination of both. We have developed experimental methods to measure the bioactivity of an adsorbed protein layer and probe protein orientation and/or adsorption-induced conformational changes. Alkanethiol self-assembled monolayers (SAMs), with different surface chemistries, were used as model surfaces and standard spectrophotometric bioactivity assays were used to measure the percent of protein bioactivity retained post-adsorption. The secondary structure of the adsorbed protein layers was determined using circular dichroism (CD) and compared to the native structure of the proteins. Solvent accessible tryptophan residues were successfully modified using 2-hydroxy-5-nitrobenzyl bromide (Koshland's Reagent) and quantified via spectrophotoscopy. The specific locations of the modified residues are being determined by mass spectrometry to further assess the adsorbed orientation and tertiary structure of the proteins for correlation with changes in their bioactivity.

BI-TuP17 Screening Protein-Surface Interactions with Surface Gradients and TIRF, ***Y.-X. Ding***, *B. Wright, V. Hlady*, University of Utah

Macroscopic surface gradients with negative to neutral surface charges were created by reacting 3-mercaptopropyltrimethoxysilane (MTS) with fused silica and selectively oxidizing surface-bound MTS by controlled UV exposure. XPS analysis and contact angle titrations of the MTS gradients showed that UV oxidation of the MTS sulfhydryl group converts it into a charged sulfonate-like moiety. The MTS gradients were also characterized by AFM in topography, adhesion, and friction modes. The reactivity of unoxidized sulfhydryl groups in the gradient region was assessed by quantitative fluorescence microscopy. The MTS gradients were then used to screen protein interactions with model surfaces. Adsorption kinetics of three human blood proteins, albumin, IgG and fibrinogen, were measured at 1% of their plasma concentrations using a dual channel total internal reflection fluorescence (TIRF) technique. For each protein, two binding experiments were carried out using the same surface gradient sample. In one TIRF channel the solitary binding of one of the fluorescently labeled plasma proteins was observed, and in the other the adsorption of the same was observed from a mixture with the other two unlabeled proteins. The TIRF experiments were later quantified using autoradiography. The adsorption behavior of the three proteins along the sulfhydryl-sulfonate surface gradient was analyzed by taking into account the convective/diffusive transport processes. The on- and off-binding rate constants were obtained as a function of the gradient position by fitting the experimental data to a simple model. Because the unoxidized MTS sulfhydryl can be further derivatized, these techniques have potential to be used as screening tools to study protein-surface interactions on a wide variety of gradient surface chemistries.

BI-TuP18 Detection of Lp-PLA2 as a Biomarker for Atherosclerosis Using Superquenching, ***S. Chemburu***, *Y. Wu,* University of New Mexico, *K. Ogawa, K. Schanze,* University of Florida, *D. Whitten, G.P. Lopez*, University of New Mexico

Lipoprotein associated phospholipase A2 (Lp-PLA2) is being recognized as a new biomarker for the prognosis and diagnosis of atherosclerotic patients. Lp-PLA2 cleaves the sn-2 acyl bond of glycerol-phospholipids yielding a fatty acid and a lysophospholipid as byproducts, which play an important role in the generation of pro-inflammatory moieties. The assays that have been developed for quantifying its catalytic activity or its concentration are time consuming and involve tedious experimental procedures. We have developed a simple bead based fluorescent assay for the quantification of the catalytic activity of Lp-PLA2. Using the layer-by-layer coating of surfaces approach, borosilicate glass beads (5uM dia) were coated with a cationic fluorescent conjugated polyelectrolyte poly(phenylene ethynylene) (PPE). The polymer-coated beads were then covered by a layer of an anionic lipid bilayer that is a natural substrate for PLA2. The lipid bilayer acted as a barrier protecting the fluorescence of PPE from being quenched by anthraquinone disulfonate (AQS). Upon the addition of PLA2, the hydrolysis of the lipid bilayer is catalyzed exposing the PPE to AQS and hence the fluorescence of PPE is turned off. The decrease in fluorescence quenching of the PPE in the presence of the lipid bilayer by AQS has been termed as frustrated superquenching and the authors have used this to develop a simple assay for the quantification of Lp-PLA2 activity.

BI-TuP19 Nanoscale Patterning of Photosynthetic Light Harvesting Proteins*, **N. Reynolds**, S. Janusz, J. Olsen, C.N. Hunter, G.J. Leggett*, The Univ. Of Sheffield, UK

Here we present the patterning of light harvesting 2 (LH2) complexes from the photosynthetic bacterium Rhodobacter sphaeroides. LH2 complexes consist of circular arrays of bacteriochlorophyll and carotenoid molecules, held together by a cylindrical assembly of polypeptides. As many as 100 LH2 complexes are organised in the membrane to form an interconnected energy transfer networks comprising thousands of bacteriochlorophyll molecules that absorb photons, channelling the excitation energy down an energy gradient towards the reaction centre (RC), leading to a charge separation that drives subsequent biosynthetic reactions in the cell. When removed from the photosynthetic membrane, LH2 complexes retain the ability to absorb light, and they emit the energy as fluorescence. This property has been utilised in order to gain insight into the biological functionality of the LH2 after immobilization. Alkanethiol SAMs on gold surfaces have been used in conjunction with photolithographic techniques to produce patterned assemblies of LH2. Selective exposure of alkanethiols to UV light (wavelength 244 nm) leads to their photo-oxidation to alkylsulfonates, which may be displaced by a second thiol in a solution-phase process. The adsorption of LH2 onto SAMs with a variety of functional groups has been measured in order to determine which surfaces resist non-specific adsorption. In contrast to plasma proteins, which adsorb strongly to most surfaces, simple patterns consisting of hydrophilic and hydrophobic regions may be used effectively to pattern LH2. Covalent attachment to carboxylic acid groups using carbodiimide activation methods is an effective means of immobilising LH2 at the surface. Fluorescence spectroscopy measurements of proteins immobilized by attachment to patterned SAMs have confirmed that biological function is retained, leading to the observation of absorption spectra qualitatively identical to those of complexes in solution. Nanoscale chemical patterns have been fabricated using scanning near-field photolithography (SNP), in which a scanning near-field optical microscope coupled to a UV laser is used to selectively expose regions of a SAM. Using SNP, lines of carboxylic acid functionalised thiols as small as 70 nm have been fabricated in monolayers of perfluorinated thiols, and used to form LH2 structures with a width of less than 100 nm.

BI-TuP20 Molecular Simulation Studies of Protein Interactions with Phosphorylcholine Self-Assembled Monolayers*, **Y. He**, J.C. Hower, S. Chen, M.T. Bernards, S. Jiang*, University of Washington

We performed molecular simulations to study the interactions between a protein (lysozyme) and phosphorylcholine(PC) self-assembled monolayers (SAMs) in the presence of explicit water molecules and ions. The all-atom simulations were performed to calculate the force generated on the protein as a function of its distance above the SAM surfaces. The structural and dynamic properties of water around PC-SAM surfaces were analyzed. These properties were also compared with those for the oligo(ethylene glycol) (OEG) SAM systems. Results show that the water molecules above the PC-SAM surfaces create a strong repulsive force on the protein as it approaches the surfaces. Further studies show that the dynamics of the water molecules are significantly slowed around both the PC-SAM and OEG-SAM surfaces as compared with that of bulk water, suggesting that the PC-SAM surface generates a tightly bound, structured water layer around their head groups, similar to the OEG-SAM surface. Our results also show that the PC-SAM surface is holding water more strongly than the OEG-SAM surface. The water molecules in the hydration layer of the PC-SAM surface stay longer and reorients slower than those in the hydration layer of the OEG-SAM surface. The most significant difference observed between these two surfaces is that the dipole of non-hydrogen bonded interfacial water molecules reorients much slower on PC-SAM than on OEG-SAM, which can be due to the zwitterionic nature of PC head groups. The application of PC-SAM in bio-lubrication studies will also be discussed.

BI-TuP21 First Direct Observation of Membrane Lipid Asymmetry Induced by Polypeptide Association*, **N. Biswas**, J.C. Conboy*, University of Utah

Cellular membranes of eukaryotic cells are characterized by a heterogeneous distribution of phospholipids, which is key to many physiological functions. While some membranes (such as the endoplasmic reticulum) are symmetric, others (as the plasma membrane) are asymmetric with phosphatidylethanolamine and phosphatidylserines being primarily localized in the inner leaflet. The loss of asymmetry in plasma membranes has been thought to have direct relevance to numerous physiological and pathological events, such as phagocytosis and cell apoptosis. Although much is know about the biosynthesis of phospholipids, little is known about their mechanism of translocation and even less is known about the mechanism which produces or maintains lipid asymmetry in membranes. The present study shows for the first time, spontaneous development of asymmetry in a DSPC-d$_{70}$/DSPS (1,2-distearoyl-sn-glycero-3-phosphocholine /1,2-distearoyl-sn-glycero-3-[phospho-L-serine] planar supported lipid bilayer, in the presence of a positively charged polypeptide (polylsyine). The negatively charged DSPS molecules selectively localize in the top leaflet of the bilayer due to the electrostatic association with the polypeptide. The highly surface specific, second order nonlinear spectroscopy, sum frequency vibrational spectroscopy (SFVS), has been used since it offered the opportunity to study the kinetics of unlabeled lipids that were not modified by a fluorescent or spin-probe.

BI-TuP22 Smart Polymers and Cancer Cell Culture: Investigating The Effects of Film Deposition and Cell Culture Parameters on Cellular Behavior*, **J.A. Reed**, E. Romero, A. Wandinger-Ness, H.E. Canavan*, University of New Mexico

Cell/surface interactions are mediated via the extracellular matrix (ECM). Many important proteins extend into the ECM, such as epidermal growth factor receptor (EGFR). EGFR is often up-regulated in cancer cells, resulting in uncontrollable cell growth and metastasis, which makes them key candidates for in vitro cancer therapeutic models. However, the methods traditionally used to detach cells from surfaces destroy the integrity of proteins in the ECM, resulting in damaged protein and receptors, making them incompatible with the solution-based analysis. In this work, we describe the use of a thermo-responsive polymer, poly(N-isopropyl acrylamide) or pNIPAM, for non-destructive release of cells into suspension. Many cell types, ranging from fibroblasts to epithelial cells, have demonstrated cell sheet detachment on pNIPAM surfaces. However, there is presently very little data on primary cells, cell culture parameters, or the method of film fabrication. To optimize the pNIPAM substrates, pNIPAM films were prepared using different methods (e.g., dissolution in silica vs. plasma deposited films) and compositions (10-40 wt% pNIPAM). The surface chemistry of the resulting films was characterized using X-ray photoelectron spectroscopy (XPS), film thickness was ascertained via interferometry and XPS, and the thermo-responsivity was determined by contact angle analysis. The cell releasing properties of the films was characterized by incubating baby hamster kidney (BHK) cells to confluency, introducing a variety of solvents (e.g., PBS vs. serum free media) below the LCST, and observing the rate of detachment via microscopy. We find that plasma deposited films exhibited the best detachment behavior when rinsed with PBS and allowed to detach in 4C serum free media.

BI-TuP23 Development of Antimicrobial Materials Based on Surface-Active Biocides in a Resin Matrix*, **R.A. Brizzolara**,* NSWC, Carderock Division, *J.H. Wynne,* Naval Research Laboratory, *J. Jones-Meehan*, Department of Homeland Security

The goal of this work is to develop a surface that demonstrates biocidal activity with less than 0.5% biocide concentration in the bulk material. The incorporation of an amphiphilic biocide as a surface-active component in a resin matrix is being investigated as a means of achieving a higher biocide concentration at the surface (and therefore better biocidal efficacy), while maintaining low bulk biocide concentrations. The amphiphilic quaternary ammonium compounds containing both aliphatic and oxyethylene moieties afforded greatest biocidal activity. These molecules were synthesized via simple condensation of a tertiary dimethyl-N-alkylamine with the corresponding halo-oxyethylene. Purity was confirmed using 1H- and 13C-NMR. The biocide-containing urethane coating was dried on glass slides for microbiological analysis and on gold surfaces for x-ray photoelectron spectroscopy (XPS) analysis. Microbiological analysis was performed to determine biocidal efficacy of coating formulations against S. aureus (Gram-positive bacterium). 10 µL of bacterial culture was placed on the surface of the slide. After 2 hours, the slide surface was swabbed. Swab contents were resuspended in appropriate neutralization media, serial dilution was performed with plating on LB agar plates. XPS was used to determine the quantity of biocide at the coating surface compared to the bulk to determine the segregation of biocide to surface, and to correlate surface concentration of biocide to the coating's biocidal efficacy. The N1s binding energy shift between nitrogen in quaternary ammonium and nitrogen in polyurethane was used to differentiate biocide from polyurethane. The XPS analysis demonstrated surface enrichment of two quaternary ammonium-based biocides in a polyurethane coating by approximately a factor of 10 compared to the bulk. The quaternary ammonium-containing materials exhibited increased killing of - S. aureus cells compared to the control (polyurethane containing no biocide). These results indicate that the use of surface-active biocides can result in significant biocidal efficacy with small bulk biocide concentrations. This work was sponsored by the DARPA Defense Sciences Office.

BI-TuP24 Immobilization of Live Salmonella on Abiotic Surfaces for AFM Investigation, ***Z.Y. Suo***, *R. Avci, L. Kellerman, X.H. Yang, D.W. Pascual*, Montana State University

High-resolution AFM images of gram-negative pathogenic Salmonella typhimurium reveal the morphological features of bacterial cells, including CFA/I fimbriae with a diameter of ~3 nm, flagella with a diameter of ~11 nm, and the extracellular polymeric substance surrounding the bacteria. The fine details of the CFA/I fimbriae and the lipopolysaccharides decorating them are clearly resolved when imaged with ultrasharp tips in tapping mode. For studies in liquid, however, it is necessary to immobilize bacterial cells through some sort of "leash," or cross-linker. Live S. typhimurium and their adhesins were successfully immobilized through interactions between bacterial surface antigens and their corresponding antibodies covalently linked to a substrate. Cells immobilized in this way remain viable for hours in PBS buffer and are capable of regenerating if incubated in a growth medium. Immobilized live S. typhimurium cells were imaged in PBS buffer in contact mode and force-volume mode. This approach opens up new fields of investigation, such as quantification of adhesin-receptor interactions, affinity mapping and patterning of bacterial cells on surfaces, which will be discussed in our presentation.

BI-TuP25 Development of Multi-Phasic Scaffolds for Ligament Tissue Engineering via Melt Electrospun Polyurethanes: Cytotoxicity of Melt Electrospun Aliphatic Polyurethane Fibers, ***A. Karchin***, *J.E. Sanders*, University of Washington

Towards the goal of developing electrospun polyurethane (PU) scaffolds for tissue engineering applications, the cytotoxicity of basic aliphatic PUs based on (CH2)4-content diisocyanates, polycaprolactone and 1,4-butane diamine or 1,4-butanediol were tested. These biodegradable polymers were chosen due to their general biocompatibility, excellent mechanical properties, and designed so that in vivo degradation products can be cleared through normal metabolic pathway. Electrospinning from melt, compared to from solution, is an attractive manufacturing process as it allows for the formation of small diameter fibers while eliminating the use of solvents which can be cytotoxic. A two-tiered experimental design was employed to determine the suitability of the specific PUs for use as tissue engineering scaffolds from a biocompatibility perspective. First, the effect of atmosphere, temperature and time at elevated temperature on the polymer cytotoxicity was assessed. Second, an investigation into the relationship between melt electrospinning and cytotoxicity was explored by performing cytotoxicity tests on electrospun meshes. These experiments are useful as a guide for subsequent development of the novel electrospun biohybrid enzymatically biodegradable PUs into a tissue engineering scaffolds.

BI-TuP26 "Smart" Biopolymer for Reversible Stimuli-Responsive Platform of Cell-Based Biochips, ***K. Na***, *O. Kim, J. Jung, J. Lee*, Seoul National University, Korea, *J.W. Park, T.G. Lee*, Korea Research Institute of Standards and Science, *J. Hyun*, Seoul National University, Korea

In the presentation, we describe the genetical synthesis of lysine tagged ELP (ELP-K) with inverse phase transition temperature (Tt) of 30? for fabricating a thermo-responsive culture surface. For the micropatterning of ELP-K a removable polymer template was microcontact-printed on the glass surface derivatized with epoxide. After conjugating ELP-K onto the glass surface followed by dissolving a polymer template, highly resolved ELP-K micropatterns were efficiently created on the surface. The successful micropatterning of the polypeptide was confirmed using ELP-K conjugated with fluorescence dye by confocal microscopy as well as atomic force microscopic images. TOF-SIMS images of ELP-K micropatterns verified the highly resolved ELP microstructure on the surface.

BI-TuP27 Growth Behavior of Fibroblast Cell in Culture Medium Containing Nanoparticles, ***S. Fujita***, *T. Ishizaki, N. Saito, O. Takai*, Nagoya University, Japan

1. Introduction Nanoparticles of metal alloy, metallic oxides, semiconductors and ceramics have unique properties compared with bulk materials since they have high reactivity and catalysis by the large specific surface area. Thus, nanoparticles have been paid attention in the various fields and utilized as electric devices, biomedical materials and cosmetics. On the other hand, it has been reported that nanoparticles could have a harmful effect on human body. For example, nanoparticles such as soot in exhaust fumes are inhaled into lung and cause pulmonary and cardiac diseases. In some recent researches, it is reported that nanoparticles could activate an adverse reaction in the body because they pass through cell walls and move through the blood or lymph vessel. However, nobody knows their interactions with the body in detail. In this study, we aimed to investigate the influence of the nanoparticles on the cell growth and assess the risk of nanoparticles. 2. Experimental procedure Au, Pt, and Ag nanoparticles were synthesized by a wet reduction process. Citric acid was used as a reducing agent. Mouse fibroblast cells (NIH-3T3) were cultured in medium (DMEM, pH: 7) containing the nanoparticles in humidified atmosphere containing 5.0% CO_2 at 37°C for 3 days. The cultured cells were counted using blood cell counting chamber and observed with phase-contrast microscope and transmission electron microscope (TEM). 3. Result Only Ag nanoparticles prevented the cells from growing onto the culture dish. Number of cells after the culture for 72 hours decreased with the increase of concentration of Ag nanoparticles. TEM images showed that the Ag nanoparticles were engulfed into a cell tissue. In addition, the ingested Ag nanoparticles were aggregated around the nuclear. However, such aggregation is not the reason that the cell cannot be cultured in the medium containing Ag nanoparticles, because Au and Pt nanoparticles were also aggregated around the nuclear. At least, Ag nanoparticles are toxic to cells. We believe that nanoparticles may provide us many types of risk; damage of DNA, disappear of proteins and so on. We must investigate the mid- and long-term influence of the nanoparticles on human being.

Marine Biofouling Topical Conference

Room: 4C - Session MB+BI-TuP

Marine Biofouling Poster Session

MB+BI-TuP1 Contact Angle Analysis for Barnacle Adhesives, ***E.R. Holm***, *R.A. Brizzolara*, Naval Surface Warfare Center, Carderock Division

The key step in the accumulation of biofouling on immersed surfaces is the permanent attachment of fouling organisms. Patterns of attachment and adhesion of biofouling, in response to surface properties, vary both among and within species. This variation may be mediated by interactions between surfaces and biological adhesives. We have been studying this interaction for the barnacle, Balanus amphitrite. Our initial approach addresses the propensity of barnacle adhesive to wet modified glass surfaces and commercially-available and experimental silicone fouling-release coatings. Glass surfaces were modified with various organosilane coatings to produce a range of water wettabilities. We verified attachment of organosilane to glass with XPS. We have been quantifying wetting by barnacle adhesive as contact angle. Preliminary results, for modified glass surfaces, indicated that for hydrophilic surfaces, contact angles for adhesive were equivalent to that for water. As surfaces became more hydrophobic, however, contact angles for barnacle adhesive became more variable than those for water. Individual measurements were occasionally substantially lower than typical water contact angles. Differences in contact angle among adhesive samples may be related to the protein content of the adhesive, which varies strongly among individual barnacles. Results will be related to attachment of larval barnacles and adhesion of adult barnacles. Funded by the NSWC Carderock Division In-House Laboratory Independent Research Program.

MB+BI-TuP2 Poly(ethylene glycol)-based Anti-biofouling Surfaces, ***T. Ekblad***, *G. Bergström, C.-X. Du, T. Ederth, B. Liedberg*, Linköping University, Sweden

This work describes the fabrication, characterization and biological evaluation of homogeneous and patterned hydrogel films, used as model coatings in anti-fouling experiments. The work is a part of an EC-initiative on Advanced Nanostructured Surfaces for the Control of Biofouling, AMBIO. The hydrogels consist of poly(ethylene glycol)-containing methacrylate monomers that are UV-grafted onto solid supports, e.g. silanized glass. The physical and chemical properties of these films have been studied using ellipsometry, FT-IR, AFM and a range of other surface characterization techniques. A key property of the hydrogels is that they appear to be resistant to protein adsorption from complex biofluids, including plasma and serum.[1] These observations encouraged us to test the hydrogels as anti-fouling surfaces. Hydrogels, ca. 30 nm thick, were prepared and evaluated in settlement and removal assays using a range of organisms, including barnacle cyprids of the species Balanus amphitrite, Ulva linza zoospores, Navicula diatoms and the three bacteria species Cobetia marina, Marinobacter hydrocarbonoclasticus and Pseudomonas fluorescens. It is clear from the results that the hydrogel surfaces display excellent antifouling properties. All tested organisms displayed significantly reduced settlement compared to reference coatings. The removal of settled organisms generally appeared to be less affected by the surface coating. Though the relationship is not yet confirmed, this study demonstrates that a surface with low protein adsorption also can have advantageous anti-biofouling properties. The broad-spectrum effect of the hydrogel coating does undoubtedly imply that the selected poly(ethylene glycol) chemistry acts on a fundamental stage in the settlement process of biologically diverse organisms. This stage may be the adsorption of biomolecules from glues released by the settling organisms.

[1] A. Larsson, T. Ekblad, O. Andersson, B. Liedberg, Biomacromolecules 2007, 8, 287-295.

MB+BI-TuP3 The Dynamics of Two Species of Megabalanus (Crustacea: Cirripedia: Balanidae) by a Cellular Automata Model*,* *M. Apolinário,* PETROBRAS, Brazil*, A. Racco*, LNCC, Brazil

The Cellular Automata (CA) model was used in a computational simulation between an introduced species in Brazilian, Rio de Janeiro State's waters Megabalanus coccopoma and a cryptogenic species Megabalanus tintinnabulum (Crustacea: Cirripedia: Balanidae), obtaining a time series where M. tintinnabulum firstly occurs alone and then it interacts with the entrance of M. coccopoma in the system. The simulation also gets data about spatial distribution of both species and column formation, representing the specimens' assessment one above the other, as it occurs at the natural environment. The results show that total recruitment of each species within the maximum height of the columns is important for the predominance of the introduced species in comparison with the cryptogenic one. The comparison between CA model and natural distribution of both species shows that CA represents significantly the interaction between both species of barnacles in the studied area.

MEMS and NEMS

Room: 4C - Session MN-TuP

MEMS and NEMS Poster Session

MN-TuP1 Surface Potential and Resistance Measurements for Detecting Wear of Chemically-Bonded and Unbonded Molecularly-Thick Perfluoropolyether Lubricant Films Using Atomic Force Microscopy*,* *M. Palacio,* *B. Bhushan*, The Ohio State University

The wear of perfluoropolyether (PFPE) lubricants applied on Si (100) and a Au film on Si (100) substrate at ultralow loads was investigated by using atomic force microscopy (AFM)-based surface potential and resistance measurements. Surface potential data is used in detecting lubricant removal and the initiation of wear on the silicon substrate. The surface potential change is attributed to the change in the work function of the silicon after wear, and electrostatic charge build-up of debris in the lubricant. It was found that coatings that are partially bonded, i.e., containing a mobile lubricant fraction were better able to protect the silicon substrate from wear compared to the fully bonded coating. This enhanced protection is attributed to a lubricant replenishment mechanism. However, an untreated lubricant coating exhibited considerable wear as it contains a smaller amount of lubricant bonded to the substrate relative to the partially bonded and fully bonded coatings. A sample subjected to shear is shown to have improved wear resistance, and this enhancement is attributed to chain reorientation and alignment of the lubricant molecules. The detection of wear of PFPE lubricants on Au by an AFM-based resistance measurement method is demonstrated for the first time. This technique provides complementary information to surface potential data and is a promising method for studying the wear of conducting films.

MN-TuP2 Wetting Behavior During Evaporation and Condensation of Water Microdroplets on Superhydrophbic Patterned Surfaces*,* *Y.C. Jung*, *B. Bhushan*, The Ohio State University

Superhydrophobic surfaces have considerable technological potential for various applications due to their extreme water repellent properties. The superhydrophobic surfaces may be generated by the use of hydrophobic coating, roughness and air pockets between solid and liquid. The geometric effects and dynamic effects, such as surface waves can destroy the composite solid-air-liquid interface. The relationship between the water droplet size and geometric parameters governs the creation of composite interface and affects transition from solid-liquid interface to composite interface. Therefore, it is necessary to study the effect of droplets of various sizes. We have studied the effect of droplet size on contact angle by using evaporation studies with droplet radii ranging from about 700 to 300 µm. Experimental and theoretical studies of wetting properties of silicon surfaces patterned with pillars of two different diameters and heights with varying pitch values are presented. We propose a criterion where transition from Cassie and Baxter regime to Wenzel regime occurs when the droop of the droplet sinking between two asperities is greater than depth of the cavity. Based on the experimental data and the proposed transition criteria, the trends are explained. For the first time, environmental scanning electron microscopy (ESEM) is used to form smaller droplets of about 20 µm radius and measure the contact angle on the patterned surfaces. The investigation has shown that ESEM provides a new approach to wetting studies on the microscale.

MN-TuP3 The Effect of Sliding and Peeling Motion on Gecko Adhesion*, T.W. Kim, **B. Bhushan***, The Ohio State University

The attachment pads of geckos exhibit the most versatile and effective adhesive known in nature. Their fibrillar structure is the primary source of high adhesion and their hierarchical structure produces the adhesion enhancement by giving the gecko the adaptability to create a large real area of contact with surfaces. Although geckos are capable of producing large adhesive forces, they retain the ability to remove their feet from an attachment surface at will. Detachment is achieved by a peeling motion of the geckoâ?Ts feet from a surface. Recent investigations have shown that a load applied normal to the surface was insufficient for an effective attachment of seta. The maximum adhesion force was observed by sliding the seta laterally along the surface under a preload. Therefore, in this study, for the three-level hierarchical model recently developed by the authors, the sliding motion of a gecko seta is considered to understand how the sliding contributes the adhesion and friction forces. In addition, the peeling motion of a gecko seta has also modeled. The peeling force is obtained as a function of peeling angle for the gecko setae contacting with the different random rough surface. This works are useful for understanding biological systems and for guiding of fabrication of the biomimetic attachment system.

MN-TuP4 Nanotribological Studies of Platinum Coated Probes Sliding against Coated Silicon Wafers For Probe-based Recording Technology*,* *K.J. Kwak*, *B. Bhushan*, The Ohio State University

Some of the new alternative information storage technologies being researched are probe-based recording techniques. In one of techniques, a phase-change medium is used and phase change is accomplished by applying either high or low magnitude of current which heats the interface at different temperatures. Tip wear at high temperature is a serious concern. For wear protection of the phase-change chalcogenide media, diamondlike carbon (DLC) film and various lubricant overcoats were deposited on the recording layer/silicon substrate. Nanotribological properties of platinum (Pt) coated probes with high electrical conductivity have been investigated in sliding against the coated media using an atomic force microscope (AFM). A silicon grating sample and SPIP software of Image Metrology were used to characterize the change in the tip shape and evaluate the tip radius. The wear tests were performed at the sliding velocity ranging from 100 µm/s to 100 mm/s. Pt-tips on the lubricant coated DLC film surfaces showed less sensitivity to the velocity and the load as compared to the unlubricated DLC film surfaces. The lubricant coatings could be used to reduce Pt-tip wear and friction between Pt-tip and DLC film surfaces. The results suggest that wear mechanism at low speed appears to be adhesive. At high speeds, the wear primarily depends on surface chemistry of the coated layers such as tribochemical oxidation.

MN-TuP5 A Microfluidic Device for the Spring Constant Calibration of Micro-Cantilevers and for Measuring Fluid Flow Velocities*,* *G.V. Lubarsky*, *G. Haehner*, University of St. Andrews, UK

We present a new microfluidic device and method based on cantilever sensing technology. Utilizing an artificially created force gradient the method can be applied for the non-destructive calibration of the normal spring constant of micro-cantilevers. In contrast to the most recent efforts to advance cantilever calibration, our method can be performed in situ, is easy to use, reliable, accurate, and non-destructive, i.e., does not involve any contact between the cantilever and another surface. The method has great potential for the calibration of modified probes, bio-sensor cantilevers etc. In addition, provided the dynamic properties of the cantilever sensor are designed and clearly defined, the device can be easily incorporated in microfluidic systems to measure the velocity of fluid flows.

MN-TuP6 Improvement of Surface Roughness of Cerium Oxide Thin Film by Chemical Mechanical Polishing for Oxygen Gas Sensor*, P.-J. Ko, Y.-K. Jun, P.-G. Jung,* Chosun University, Korea*, **N.-H. Kim***, Sungkyunkwan University, Korea, *W.-S. Lee*, Chosun University, Korea

Cerium oxide (CeO2) is one of the most widely used materials for the oxygen gas sensors. Surface roughness of CeO2 thin films must be improved because the electrical and sensing properties of CeO2 thin films are determined by these characteristics. Chemical mechanical polishing (CMP) processing was selected for improving the surface roughness of CeO2 thin films. Surface roughness and within-wafer non-uniformity (WIWNU%) of spin coated CeO2 thin films were examined with a change of CMP process parameters. The optimized process condition, reflected by both the surface roughness and the hillock-free surface with the good uniformity, was obtained. The effects of the improved surface roughness on the sensing property of CeO2 thin films were also confirmed. The improved sensing property of CeO2 thin films for oxygen sensors were obtained after

CMP process by the improved surface morphology. Therefore, we conclude that sensing property of CeO2 thin film is strongly dependent on the surface roughness of CeO2 thin films. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2006-005-J00902).

MN-TuP7 Fabrication of Body Insulated Conductive Cantilever with Metalic Nano Tip, ***S.H. Park,*** Myongji University, Korea, *S.H. Kim,* Korea Electronics Technology Institute, *C.J. Kang, Y.J. Choi, J.W. Kim, Y.S. Kim*, Myongji University, Korea

Scanning Probe Microscopy (SPM) can be used to analyze specimens at sub-micrometer scale either by profiling their surface morphology or by measuring their electrical property. SPM has become one of the essential research tools in the field of biology because of its lateral resolution superior to optical microscopy. For the application to biological samples, the SPM probe should be occasionally immersed into an aqueous environment in the form of buffer solution. If we want to get electrical information of the sample in the aqueous environment with commercially available surface conductive cantilevers, electrical leakage from the cantilever body to the solution takes place, which results in poor image resolution. In this study, we fabricated body insulated conductive cantilever in order to avoid leakage current through cantilever surface. Electron Beam Induced Deposition (EBID) technique was used to fabricate well localized conductive nano probe. By optimizing the EBID tip growth condition, we could acquire probe whose base diameter and effective length are below 300nm and a few µm. Tungsten hexacarbonyl [W(CO)6] is a popular precursor material used in placing conductive deposits with the EBID method. We analyzed the constituents of fabricated nano probe by Energy Dispersive X-ray Spectroscopy (EDXS) and microscopic Fourier Transform Infrared spectroscopy (µ-FTIR) which detects element species and chemical bond. We also examined resolution of the fabricated nano probe compared with the conventional metal probe by recording topographic images and electrostatic force images (EFM) of gold electrodes simultaneously. When measuring an electric signal in buffer solution, we could reduce a leakage electric current. This result suggests the possibility of direct fabrication of high aspect ratio and conducting nano SPM probe on the body insulated conductive cantilever.

MN-TuP8 A Robust Parametrically Excited MEMGyroscope, ***L.A. Oropeza-Ramos,*** *C.B. Burgner, C. Olroyd, K.L. Turner*, University of California, Santa Barbara

We present a novel scheme for a robust micro gyroscope which is actuated parametrically and is less sensitive to parameter variations. We experimentally demonstrate that using a parametric resonance based actuator, the drive mode signal has rich dynamic behavior with a large response in a large bandwidth. In this way the system is able to induce oscillations in the sense mode due to Coriolis force, despite that there is a clear disparity on the drive and sense natural frequencies. Thus we propose a scheme that reduces the sensitivity loss due to mismatching in the drive and the sense natural frequencies, which is a common problem in micro gyroscopes based on harmonic oscillators, and also increases significantly the range of frequencies where the gyroscope can operate due to its inherent dynamical properties. Rate table characterization is given. Extensive effort has been applied to gyroscopic structures based on two or more degree of freedom (DOF) harmonic oscillator.[1] For the 2 DOF type, the drive and the sense resonant modes are tuned to be equal (or nearly equal) in most cases, in such a way that the output is amplified by the quality factor Q, resulting in high sensitivities. Due to the current fabrication processes, structural asymmetries are inevitably present; therefore matching of frequencies commonly requires external trimming or implementation of control schemes. In this paper we present the realization of a novel Micro Electro Mechanical Gyroscope actuated by a set of noninterdigitated comb fingers which generate a force with time and displacement dependent stiffness coefficients. Thus, parametric resonance excitation amplifies the drive mode response over a wide set of frequencies. In this way, differences in drive and sense natural frequencies do not compromise the sensitivity in 1kHz range. The 2 DOF micro gyroscope is fabricated using the standard SOI process flow and rate table characterization is presented under 50 mTorr pressure. The sensor response is detected with a capacitive readout hybrid wire bonded to the gyroscope on a chip. Our device has demonstrated a scale factor nonlinearity of 0.8% within ±150 °/sec. Thus, in this demonstration the micro gyroscope is robust to parameter variations.

[1] Yazdi, N., et.al., IEEE Proceedings, Vol.86, No.8, 1998.

MN-TuP9 Modeling of Asymmetric Microelectrode Array and Capillary Forces for Fluidic Self Assembly in MEMS, ***A. Dang,*** Netaji Subhas Institute of Technology, India, *M. Dhayal*, National Physics Laboratory, India

Modeling and quantitative design play a key role in MEMS to explore the difference parameter space that can influence the performance of micro fluidic devices. In this study the effects of actuation profile incorporated with geometrical dimensions has been investigated on self-assembly of different types of fluids in micro fluidic devices. Different types of asymmetric electrode array were designed and associated electric field profile had been modeled. The optimization of operating conditions of asymmetric field profile with controlled geometrical dimensions on self-assembly of different type of polar solutions has been investigated for different biological applications.

MN-TuP10 Effect of Au Promoter Layers on NOx Sensitivity of Indium Oxide Solid State Sensor, ***S. Kannan,*** *M. Sorenson, L.W. Rieth, F. Solzbacher*, University of Utah

Stricter global emission regulations have generated an immediate need to develop high temperature compatible (>500°C) gas sensors for monitoring exhaust. Indium Oxide (In_2O_3) thin films with Au promoter layers have exhibited excellent sensitivity (S ~ 20) for detection of NO_x at temperatures greater than 500°C. Gas sensitivity results will be interpreted as a function of In_2O_3 film structure and morphology. Thin film In_2O_3 layers (~150 nm) were RF sputter deposited in an ambient of pure argon (10 mtorr, 600 W, 2.4 nm/min) on Pt inter-digitated electrodes (IDE). Au promoter layers (~3nm) were deposited on top of the In_2O_3 film in a separate sputtering system. The thin films were annealed in nitrogen, oxygen, forming gas (2% H_2 in Ar) or mixtures of nitrogen and oxygen up to 15 hours at temperatures from 700°C to 1000°C. X-ray diffraction (XRD) results reveal as-deposited and films annealed in oxygen have cubic crystallite structure with several reflections present. In_2O_3 films annealed in nitrogen show the presence of (321) (411) grains in addition to the as-deposited peaks. Atomic force microscopy (AFM) reveals as-deposited films having an average particle size of 25 nm (RMS = 1.5 nm) which increase to a particle size of up to 65 nm with annealing (RMS = 2.6 nm). These images also suggest all annealed samples with Au promoter change in morphology and increase roughness to 6.5 nm. X-ray photoelectron spectroscopy (XPS) revealed the annealed films to be In rich (45% In, 55% O). Films annealed in forming gas islanded exposing Si XPS peaks from the substrate.Four point probe measurements show the resistivity increase from as-deposited values of 0.0045 Ω-cm to larger than probe can measure(~ 7 Ω-cm) for forming gas annealed films and the results suggest the annealing ambient is important. In_2O_3 films were tested for gas sensitivity (S) towards NO_x (0-25ppm), NH_3 (25 ppm), CO_2 (1000 ppm), H_2 (5000 ppm) in synthetic air (80% N_2, 20% O_2) and nitrogen as carrier gas. In_2O_3 films with Au as a promoter annealed in N_2 at 900°C for 5 hours exhibited excellent sensitivity (S~5) operating at 500°C and S~1 at operating temperature 650°C for detection of NO_x. Sensitivity to NH_3 as well as CO_2 was low relative to NO_x at 500°C and 650°C (S~0.1).

MN-TuP11 XeF_2 Etching of Metallic Films, ***O. Celik,*** *N. Shankar, A.V. Ermakov, L. Goncharova, Q. Jiang, L. Wielunski, E. Garfunkel,* Rutgers University, *X.M. Yan, A.L. Londergan, E. Gousev*, Qualcomm MEMS Technologies

The controlled etching of micro/nano structures is very important for a variety of technological applications, including MEMS fabrication. XeF_2 is an isotropic and selective vapor phase etchant used to etch Si and metals in MEMS and other devices. For better process control and device functioning, it is important to understand the etching mechanism at the molecular level. In this study we have explored the surface and gas phase chemistry of XeF_2 etching of metallic films. Down stream mass spectrometry is used to identify the gas phase by-products in the etching process. RBS and MEIS are used to measure the thickness of the films and the depth profile of near-surface species after etching. The etch rate is calculated from film thickness changes. The etched surface composition and chemical state are further investigated by XPS. Based upon the gas phase by-products during etching, surface species and their depth profiles, and the etching rate, a reaction mechanism of XeF_2 etching is proposed.

MN-TuP12 Parametric Amplification in Electromagnetically Actuated Resonant Chemical Sensors, ***K. Lukes,*** *K.L. Turner,* University of California, Santa Barbara, *J. Rhoads, S. Shaw*, Michigan State University

This work presents a novel implementation of mechanical domain, parametric amplification in electromagnetic microcantilevers. Parametric amplification is the amplification of a signal due to pumping energy into the system parametrically. This class of resonators shows great potential for implementation as chemical sensors, since they exploit the induced electromotive force (emf) for sensing[1] giving potential for complete onchip integration. It is difficult to recover the sense signal because it is several orders of magnitude smaller than the drive signal. Parametric amplification offers low noise gain for signal recovery. We describe the model and experimental validation of parametric amplification. A measure of merit for the amplifier is its gain. Gain is defined as the ratio of sensor's amplified to harmonic response. Analysis of the gain function shows the response is amplified asymptotically as the pump approaches the limiting magnitude defined by the onset of parametric resonance, and depends on the square root of sin(2φ), where φ is the phase shift between the input signals. Parametric amplification is achieved by the microcantilevers. Each cantilever has metal wires deposited on the surface, making it a closed current loop. The device sits on an angled permanent magnet. An AC current, consisting of the sum of the harmonic and parametric signals, passes through the device producing the Lorentz force. The force can be broken into a normal component, the harmonic forcing, and axial component, the parametric pump. The dynamics of the resonators are measured using a single point laser vibrometer in vacuum.[2] These devices have shown the capability for emf sensing;[1] vibrometry is used for proof of concept. Experimental data confirms the expected relationship of gain to φ and pump magnitude. We have successfully shown parametric amplification in electromagnetically actuated microcantilevers. Theoretical results anticipate large gains and experimental data confirms that these gains are feasible. The ability to mechanically amplify the signal of the transducer shows potential for a complete on-chip chemical sensor.

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MN-TuP13 Capacitive Displacement Sensing for Comb Drive Actuators Operating in Aqueous Media*, P. Ponce*, *V. Mukundan, B. Murmann, B.L. Pruitt*, Stanford University

We present a system that is capable of measuring displacements in a comb drive actuator operating in aqueous electrolytes. Underwater electrostatic actuators are promising tools for manipulation of biological samples in media.[1,2] Optical techniques have been reported for measurement of these actuator displacements.[3] Apart from accuracy and portability, electrical measurements are beneficial in setting up feedback systems for controlled actuation. Relative changes between the capacitances of the comb drive are measured by connecting them to parallel oscillator circuits. The operational frequencies of each oscillator depend directly on its corresponding capacitance value. In order to avoid electrolysis and electrostatic shielding effects in ionic media, the oscillators resonate at high frequencies (around 2-10 MHz) and the voltages across the comb drive electrodes are limited to approximately 100 mV, peak-to-peak. A major advantage of the described system is its ability to operate in ionic media without common adverse effects, such as electrolytic breakdown and electrode corrosion. The resultant oscillating signals are multiplied with each other and filtered to obtain a sinusoidal signal whose frequency is determined by the capacitance offset between the parallel oscillators. The sine wave is then applied to a frequency-to-voltage converter that yields a DC voltage signal. The system exhibits a change of approximately 16 kHz for each pF offset in capacitance. Based on the performance of the circuitry used, these results translate into a capacitive offset measurement accuracy on the order of 10 fF. The signal that contains information of the measured comb drive displacement is a DC voltage. This purely electrical signal allows the current device to be considered as an abstract "black box" for the purposes of creating a controllable feedback system. One plausible use for this system topology is the development of a method for applying specific forces onto cells adhered to the comb drive actuator.

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MN-TuP14 Assembly and Testing of Metal-based Microchannel Heat Exchange Devices*, F.H. Mei*, *J. Jiang, W.J. Meng, P.R. Parida, S.V. Ekkad*, Louisiana State University

Since Tuckerman and Pease suggested the use of microfluidic devices for high heat flux removal in 1981, intense studies of heat transfer within microchannel devices at the mm to µm length scales have been carried out over the last two decades.[1,2] A majority of studies on microscale fluid flow and heat transfer have been conducted in Si-based microchannels because of the prevalence of Si microfabrication technology[3] and the lack of suitable microfabrication techniques for metal-based microchannel devices. Metal-based microchannel heat exchangers (MHEs) have important potential advantages over Si-based devices due to their higher thermal conductivities and better mechanical characteristics. Realization of metal-based microdevices requires the fabrication of metallic high-aspect-ratio microscale structures (HARMS). We have demonstrated successful HARMS replication in Pb,[4] Zn,[5] Al,[6] and Cu[7] from HARMS mold inserts by compression molding. To form any functional metal-based microdevice from such replicated metallic HARMS, proper assembly and packaging are required. Recently, we have successfully bonded Al-based and Cu-based HARMS by using eutectic bonding with Al-Ge composite thin films as intermediate layers, utilizing the Al-Ge eutectic with an eutectic temperature of 424°C.[8] We also evaluated the bond quality through measurements of the tensile bond strength in Al-based specimens.[9] In this paper, we report successful assembly of Cu-based microchannel devices and investigation of their heat transfer characteristics. Further studies on the bond quality of Cu-based specimens will be carried out, and results of assembly of metal-based MHE prototypes and testing of their overall heat transfer performance will be reported.

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Nanometer-scale Science and Technology

Room: 4C - Session NS-TuP

Nanometer-scale Science and Technology Poster Session I

NS-TuP1 Orderly Fabrication of Nanometer-Scaled Triangular Structure using Bridge Phenomenon of Polystyrene Beads*, B.K. Lee*, *K.S. Kim, J.H. Lee, N.H. Kim, Y.H. Roh*, Sungkyunkwan University, Republic of Korea

Recently, nanometer-scaled materials have used for fabrication of nanostructure. Polystyrene bead (PSb) has many advantages for fabrication of nanostructure. For example, the PSb could fabricate the particular pattern array structures using for its self-assembled monolayer property. The PSb could be integrated with the established semiconductor process technologies because the PSb has excellent compatibility with silicon substrate. In this experiment, a spin coating was used for well-ordered array of the PSb. The PSb could be reduced its size using an oxygen plasma ashing process. During the plasma ashing process, the bridge phenomenon was occurred between the adjacent PSbs according to the plasma ashing conditions. The main reason for the occurrence of PSb bridges during the plasma ashing process is estimated that the PSb on the silicon surface was not sufficiently ashed by plasma. The ashed PSbs showed the triangular structures and the adjacent bridge distance was under 35 nm. The metal thin film was deposited on the bridges of the PSbs and then the PSbs as a deposition mask were removed by ultra sonication process. After the metal deposition on the ashed PSbs mask, we could obtain the nanometer-scaled triangular island less than 30 nm with the well-ordered array. Consequently, the triangular island would be applied to the nanometer-scaled devices such as single-electron transistor and biosensors.

NS-TuP2 Deposition of Gold Nanoparticles on HOPG using Atmospheric Plasma*, F. Demoisson*, Universite Libre de Bruxelles, Belgium, *M. Raes, J. Vereecken,* Vrije Universiteit Brussel, Belgium, *F. Reniers*, Universite Libre de Bruxelles, Belgium

The interest for gold nanoparticles in the field of nanocatalysis and of nanosensors is growing. Nanotubes covered with gold nanoclusters could present interesting properties in these fields. However, due to the weak carbon-gold bond, the adhesion of this metal to carbon is not trivial. It is generally accepted that the carbon surface must be activated, either by the creation of surface defects and/or by the adsorption of reactive species, such as oxygen containing groups. Most of the time, activation is done using wet chemistry techniques, such as hot nitric acid solutions. Some studies present activation and deposition experiments realized using vacuum techniques, with ion guns, low pressure plasmas, and/or thermal evaporators. In this preliminary study, we used highly oriented pyrolitic graphite (HOPG) as a model surface that could present the same chemical properties as the one of carbon nanotubes. An atmospheric plasma torch was used to activate the HOPG surface and to realize the gold deposition. The atmospheric plasma torch runs in the RF mode (13,56 MHz), using argon as the main gas. Oxygen was added as secondary gas, in order to provide the active species able to activate the surface. The plasma post discharge was spatially characterized by optical emission spectrometry. Immediately after activation, metal particles were injected into the plasma post-discharge. The surface Au/C elemental composition was analysed using XPS and shows the presence of gold, whereas field emission gun scanning electron microscopy allowed to study the size distribution of the gold particles on the surface as a function of the plasma parameters. This work is financially supported by the Nano2Hybrids (EC-STREP-033311) and PAI 7/3 (Plasma surface interactions - Belgian federal government) projects.

NS-TuP3 Laser Transfer of Organic Molecules through a Liquid Layer, *Y. Pihosh, M. Goto, A. Kasahara, M. Tosa*, National Instituteof Materials Science (NIMS), Japan

Previous results of implantation of Coumarin 6 (C6) molecules on a target polymer surface by laser molecular implantation technique showed that the achieved minimum size of dots could be 3 µm in diameter. However, the implantation of organic molecules into conductive organic or inorganic materials on the nanometer scale is one of the challenging problems in materials research that has to be solved. Here, we report the process of laser molecular implantation of pyrene acid and pyrene sublimed molecules onto different materials by generating a laser-induced water channeled jet through a liquid-filled space-gap between the source film and target materials. This process leads to significant reduction in the size of implanted organic molecular dots to a sub-micrometer region on the surface of solid materials such as glass and copper. The pyrene source films were prepared by means of thermal evaporation onto a cover glass with the thickness of about 600 nm. The source film and the target were brought into contact, and the distance between them was filled with liquid. A four nanosecond pulse laser beam was focused on the surface of the source film by special array of lenses, and those photo-excited organic molecules. As a result, the molecules could be ejected from the source film in a form of a plume through a strait path, which was created by laser induced plasma. Later the molecules were implanted onto or into the target materials in the form of dots or rings depending on laser fluence. Those experiments focused on the implantation process of pyrene organic molecules in the submicron region on glass and copper substrates through polar and non-polar liquids. The size of the smallest implanted pyrene acid dots implanted through water and diidomethane layer was estimated to be about 0.4 µm and 0.3 µm at laser fluences of 235 Jcm^{-2} and 326 Jcm^{-2} , respectively. From fluorescence spectra it was noticed that the implanted molecules did not decompose during the implantation process no matter which liquid filled the gap. In the case of pyrene sublimed molecules it was found that implantation occurs only through a water layer, and, also, that the implanted dots have a very short life time.

NS-TuP4 Effect of Surface Potential on Formation of DNA-Templated Gold Nanowires by pH Change of Gold Nanoparticles, *S.W. Cha, J.-S. Kim, H.J. Kim, N.H. Kim, Y.H. Roh*, Sungkyunkwan University, Republic of Korea

Biological molecules such as DNA are especially useful as the material for the nanoscale electronic construction because their strand is possible to regulate and their width has nanometer-size diameter of about 2 nm. And also, the negatively charged phosphate group in DNA is possible to bind the surface-functionalized gold nanoparticle (AuNP). However, the location of AuNP with the uniform interval along DNA molecules as template is generally considered to be difficult because precise control of the electrostatic force for conjugation between negatively charged DNA molecules and positively charged AuNPs is hard. In this study, we developed a new method to control the interval between AuNPs on stretched DNA molecules by changing pH of oxidized aniline-capped AuNPs (AN-AuNPs). DNA molecules were stretched and fixed on 3-aminopropyltriethoxysilane (APS) coated Si wafer by the tilting method. Then, pH of AN-AuNPs solution was changed by adding NaOH solution, and DNA molecules were treated with AN-AuNPs solution for the certain time. As NaOH solution was added in AN-AuNPs solution, the surface electric charge of AN-AuNPs was decreased. Atomic force microscopy (AFM) was used to analyze the intervals of AN-AuNPs attached on DNA molecules. The surface electric charge of AN-AuNPs was measured with the change of pH by the Zeta-potential measurement to confirm the interval of AuNPs when the surface electric charge of AN-AuNPs was changed. The effect of AN-AuNPs size on the intervals of AN-AuNPs was also investigated because the AuNPs would be aggregated with the change of pH of AN-AuNPs.

NS-TuP5 Nanostructured Growth of Cobalt on Cu(775): An STM and Photoemission Study, *M. Yilmaz, N. Zaki, S. Wang, K. Knox, D.V. Potapenko, J. Dadap, R.M. Osgood,* Columbia University, *T. Valla, P. Johnson*, Brookhaven National Laboratory

Vicinal metal surfaces have attracted much attention in recent years as templates for self assembled nanostructures. We will present an STM and photoemission study of Co/Cu(775). Using STM, we observed that the substrate acts as a template for the growth of Co. Cobalt grows in the form of anisotropic islands, the structure of which changes with coverage. The effect of these nanostructures on the surface electronic structure is investigated by means of high resolution angle resolved photoemission spectroscopy (ARPES). At very low coverages, cobalt alters the modulation plane of the Cu surface state from surface modulation to terrace modulation. As the coverage increased an additional Cu derived surface state at a higher binding energy appears. Both states are supressed as more cobalt is deposited on the surface. Cobalt d-band features are relatively flat and consistent with experiments performed on other Co/Cu systems.

NS-TuP6 Influence of Preparation Condition on Electrical Properties of Cobalt(Co2+)-Metallic-DNA Molecules, *S.D. Cheon, N.H. Kim, Y.H. Roh*, Sungkyunkwan University, Korea

Recent works have showed many attractive interests in the formation of nanowires to make nano-device using the deoxyribonucleic acid (DNA) molecules. Because of DNA molecule has narrow width (2nm) and the length of DNA easy to control. Metallic DNA (M-DNA) is a modified DNA by incorporating divalent metallic ions (i.e., Zn^{2+}, Co^{2+}, Ni^{2+}, etc.) to the each base pair of B-DNA. It is one of the methods to form the metallic nanowires with metallic electrical conductivity by contrast with B-DNA of semiconductor like electrical properties. M-DNA has the higher and the more stable current-voltage (I-V) characteristic than B-DNA. Most experiments of electrical properties of M-DNA were made up by Zn-M-DNA. Cobalt and nickel divalent ions are generally known to be also possible to make M-DNA. Particularly, cobalt (Co^{2+}) is comparatively easy to make M-DNA because of its good synthesis rate and fast incorporating speed. In this work, Co-M-DNA could be made using poly(dG)-poly(dC), poly(dA)-poly(dT) or lambda DNA. The Co-M-DNA was prepared with the various conditions such as concentration of divalent metallic ions, preparation pH and temperature. The Co-M-DNA was prepared with heating processes, which contributed to decrease of incorporating time. The prepared Co-M-DNA molecules were attached on Au electrodes with the nanometer size gap. The current through Co-M-DNA measured on vacuum (10^{-2}torr) to minimize humidity effects by HP4145 semiconductor parameter analyzer. The current through Co-M-DNA showed the metallic electrical properties and larger conductivity than B-DNA. The conductivity of Co-M-DNA became larger by preparation over pH 8. Furthermore, the conductivity of M-DNA was affected by Co^{2+} concentration.

NS-TuP7 A Study on the Patterned Molecular Wires Based on Cartenoids by Electrostatic Force Microscopy and I-V Measurement, *J.W. Yoo, J.W. Kim, Y.J. Choi, Y.S. Kim, S.H. Koo, C.J. Kang*, Myongji University, Korea

Electrical properties of single carotenedithiol molecules lithographed on Au by micro channel have been investigated by electrostatic force microscopy (EFM) and current versus voltage (I-V) measurement. The Carotenedithiol molecules have three different species of end-groups substitutive. To make a wire pattern, polydimethylsiloxane (PDMS) micro channel carrying carotendithiol molecules are used and the molecules are inserted into an octadecane monolayer that is previously patterned on Au substrate. After removing the PDMS channel, EFM and I-V measurement was performed on the remained wire pattern. For the efficient microscopy, we adopted cantilever oscillation method using Lorentz force. The results show that the organic molecules of cartenoid based patterned nano wires can be a candidate of the element for nano devices.

NS-TuP8 Real-time Single-molecule Detection on Random Arrays for Biosensing Applications using Total Internal Reflection Fluorescence, *A. Gunnarsson, P. Jönsson, R. Marie, J. Tegenfeldt, F. Höök*, Lund University, Sweden

Development of ultrasensitive biological sensors has attracted significant scientific interest due to its many possible application areas such as biomedical diagnostics, proteomics and forensic analysis. DNA sensing using nanoscale devices based on electrical[1,2] or optical[3,4] detection has shown great promise for achieving high sensitivity and specificity. We report of a novel biosensor assay capable of detecting non-labeled low-abundant DNA targets based on surface adsorption of lipid vesicles through DNA hybridization. Using total internal reflection fluorescence (TIRF) microscopy, single DNA molecule detection at 10 fM concentrations is achieved. Various biomolecules besides DNA can be probed with the assay, including soluble and membrane proteins utilizing the lipid bilayer of the vesicles. Not only achieving ultra-sensitive detection, the novel approach also offers great potential for studies of biomolecular interactions on a single molecule level in real time.

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NS-TuP9 Siloxane, including Amine Terminal, Coated Stable Silicon Nanoparticles for Interaction with Negative Charged Materials, ***B.-Y. Jeong***, SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Republic of Korea, *J.-W. Park,* Sungkyunkwan University, Republic of Korea, *J.-S. Kim,* SAINT, Sungkyunkwan University, Republic of Korea, *N.H. Kim, Y.H. Roh*, Sungkyunkwan University, Republic of Korea

Silicon nanoparticles (Si NPs) have many interesting electronic properties such as controllable electron mobility and energy band-gap through doping impurities despite their nanometer-scaled size. They are widely used in LED, photo-luminescent label, sensor, etc. Si NPs could be also applied to nano-size semiconductor. However, pure Si in nature makes natural oxide-layer. Moreover, Si NPs which were not functionalized lost their characteristics of nanoparticles for aggregating each other because the pure Si has unsatisfactory stability. Therefore, the surface of Si NPs should be modified in order to disperse and stabilize Si NPs. In this study, Si NPs were coated by siloxane that has amine terminal to stabilize and modify the surface of Si NPs to the positively charged surface coincidently. It led to prevent an aggregation and chemical reactions of surface. After treatment, Si NPs were dispersed in solution and had positively charged surface. The raw Si NPs were treated with piranha etch to remove the oxide layer and make a hydroxyl surface. In order to induce hydrosilylation, we added 3-aminopropyltriethoxysilane with gentle stirring. TEM was carried out to check the rate of dispersion. EDX and FTIR analyses were performed to confirm the hydrosilylation reaction. Zeta-potential was measured in order to estimate the charge of particle surface. Consequently, we expected that the stable siloxane-coated Si NPs with positively charged surface have possible applications to conjugate with phosphate of DNA or other polymer with negative charge.

NS-TuP10 Fabrication of Well-defined Microdomains Composed of Aldehyde- and Carboxy-terminated Self-assembled Monolayers, ***A. Hozumi,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan, *H. Taoda, T. Saito*, AIST, Japan

Organosilane self-assembled monolayers (SAMs) have been widely applied to the artificial control of surface chemical functionalities. Among the various types of SAMs, both aldehyde (CHO)- and carboxy (COOH)-terminated SAMs are of particular interest owing to their chemical reactivities to biomolecules. Here, we report on the fabrication of microdomains composed of CHO- and COOH-terminated SAMs on a Si substrate covered with native oxide. The cleaned substrate was first exposed to a vapor of 12.5 vol % solution of triethoxysilylundecanal (TESUD) diluted with absolute toluene for 3 h at 403 K. This vapor phase treatment produced the CHO-terminated SAM on the native oxide/Si surface. The thickness of this SAM was estimated by ellipsometry to be about 1.2 nm. Next, some of the samples were irradiated for 1~60 min with 172 nm vacuum UV light in air. Due to this treatment, the hydrophobic surface became hydrophilic gradually with irradiation time. Although film thickness remained almost unchanged even after irradiation for 25 min, water-contct angle decreased from 86 degree to about 25 degree. Both contact angle and film thickness decreased markedly after aound 25 min and reached their minimum of 5 degree or less and 0.3 nm, respectively, at the irradiation time of 60 min. We further confirmed by X-ray photoelectron spectroscopy and attenuated total reflection spectroscopy, the irradiation time of 25 min was determined the optimum time to yield reproducible COOH-terminated SAM. Finally, the CHO-SAM was irradiated site-selectively through a photomask. As confirmed by lateral force microscopy, the microstructures composed of 5 micron x 5 micron square features photoprinted on the CHO-terminated SAM surface were clearly imaged through the friction force contrast between the photoirradiated and masked regions. The former regions were expected to have been converted to COOH-terminated SAM.

NS-TuP11 Conducting Polymer Nanofilm Growth on a Nanoscale Linked-Crater Pattern Fabricated on an Al Surface, *H. Kato,* ***S. Takemura****, A. Ishii, Y. Takarai, Y. Watanabe, T. Sugiyama, T. Hiramatsu, N. Nanba,* Kanto Gakuin University, Japan, *O. Nishikawa, M. Taniguchi*, Kanazawa Institute of Technology, Japan

A nanoscale linked crater structure was fabricated on an Al surface by wet chemical and electrochemical processes. The surface of an Al plate was treated with Semi Clean and Semico Clean in order to create crater-shaped erosion on the surface. The successive electrochemical anodization in H2SO4 solution created a nanoscale finer linked-crater structure on the surface. The authors conducted the nanofilm growth of conducting polymer polythiophene on the nanoscale structured Al surface by the electrochemical polymerization method. The electrochemical polymerization was performed in acetonitrile containing thiophene monomer and (Et)4NBF4 as a supporting electrolyte and the polymerization on the linked-crater surface was conducted by applying positive voltage to the Al plate. The dynamic force microscopy (DFM) image of the Al surface after the polymerization process suggested that the polymer was grown on the nanoscale linked-crater structure. In the DFM measurements, the dimmer contour image of each crater was still recognized even after the polymerization process was fulfilled suggesting that the polymer film was grown on the Al surface. The cross section analysis of the DFM measurement demonstrated that the nanofilm was grown on the linked crater because the crater depth became shallow. X-ray photoemission spectroscopy (XPS) measurement also supported the polymer growth because C 1s and F 1s due to the polymer origin were detected. Furthermore, the authors tried to inject copper phthalocyanine (CuPc) molecules into the polythiophene nanofilm on the nanoscale structured Al in order to functionalize the nanoscale hybrid materials. The XPS measurement detected C 1s, N 1s and Cu 2p lines due to the injected CuPc molecules. This work was supported by High-Tech Research Center Project aided by MEXT.

NS-TuP12 Fabrication of Nanoscale Organic Patterns on a Highly-Oriented Grooved Structure Created on an Electrochemically Treated Aluminum Surface, *H. Kato,* ***Y. Watanabe****, S. Takemura, S. Kimura, D. Okumura, R. Nakano, T. Sugiyama, T. Hiramatsu, N. Nanba*, Kanto Gakuin University, Japan

The surface of an aluminum plate was treated with a combination of chemical and electrochemical processes. A chemical treatment with acetone and a successive electrochemical process created a nanoscale highly-oriented grooved structure on an aluminum surface. The distance between the oriented lines was estimated as 30-40 nm by dynamic force microscopy (DFM) measurements. The present work intended to make an organic-inorganic nanoscale pattern using this nanoscale structure. Copper phthalocyanine (CuPc) and fullerene C60, which were highly-functional molecules, were selected in fabrication of nanoscale patterning. CuPc and C60 molecules were deposited on the highly-oriented line-structure on Al. A toluene droplet containing CuPc molecules was cast on the Al plate and extended on the surface. CuPc deposition on the Al surface was made by evaporation of toluene. Cross section analysis of the DFM measurements clarified that each aligned groove was filled with CuPc molecules because the depth of the channel became shallow and in some area the row width became narrower after the CuPc deposition. X-ray photoemission spectroscopy (XPS) measurements clarified that N 1s and Cu 2p lines appeared, which also supported the CuPc deposition on the nanoscale structure creating a nanoscale organic line-pattern. The spectral profile difference of Al 2p pre- and after deposition of CuPc suggested the molecular-surface interaction. Furthermore, the authors tried to make a polyaniline nanowire along the row channel fabricated on an Al surface. A droplet of HCl solution containing aniline molecules was cast and extended on the nanoscale-structured Al plate. Successively, a droplet containing APS was put and extended on the surface in order to trigger the polymerization in the nanoscale area. The DFM and XPS measurements clarified that aniline molecules were polymerized in the channel. This work was supported by High-Tech Research Center Project aided by MEXT.

NS-TuP13 Quenching of Photoluminescence in Silicon Oxide Layers with Silicon Nanocrystals under Ion-Beam Irradiation: Analysis of Experimental Data, ***V.A. Stuchinsky****, S.G. Cherkova, G.A. Kachurin, D.V. Marin*, Russian Academy of Sciences

A quantitative analysis of experimental data on photoluminescence (PL) quenching in silicon oxide layers with embedded Si nanocrystals (nc's) under ion-beam irradiation is presented. The analysis was performed using the data of[1], obtained for an nc-system with mean nc size R=2.9 nm irradiated with 2 MeV He, Ge, and Au ions, and our data obtained for an nc-system with R=3.8 nm, irradiated with 130-200 keV He, F, and P ions. A method to allow for the PL lifetime degradation is proposed, which can be applied if the available dataset for a particular nc-system contains data obtained using irradiation of this system with light ions. A simple model is considered to predict the number N_{lum} of luminescing nc's versus the fraction η of atoms displaced in the system at low irradiation doses with allowance for the density of collision cascades and the size distribution of nc's. In this model, the well-known expression for N_{lum} vs η in the case of random rare displacements is used (see, e.g.,[1]), with the density of atomic displacements corrected for the damage factor of individual nc's. The experimental PL quenching curves were used to determine the average number of stable nonradiative centers introduced into one nc (N_{exp}). The quantity N_{exp} was then compared with the mean number N of displacements per nc obtained in a computer analysis of TRIM simulation data on 3D coordinates of displacements. The yields N_{exp}/N of stable nonradiative centers with respect to primary displacements in the nc-systems irradiated with the various ions were determined. The obtained values suggest that in dense collision cascades close vacancies choose to combine in divacancies, whereas in rare cascades they prefer to form nonradiative centers individually, possible coming to the nc/matrix interface with the formation of dangling bonds there. A physical interpretation is given to the curves of PL lifetime versus the damaged fraction of nc's. The exciton tunneling times between adjacent nc grains in the nc-systems under consideration were evaluated (120 and 15 µs for the systems with R=2.9 and 3.8 nm). Based on these values, estimates of the decay length of the excitonic wavefunction into the dielectric matrix, and the excitonic recombination cross section at deep traps introduced by ion-beam irradiation in the host dielectric, were obtained.

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NS-TuP14 Segmented Nanowire Fabrication Through Templated Electrodeposition

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Metal oxide nanowires have recently attracted considerable attention in electrochemical sensing. Templated electrodeposition of metals within porous aluminum oxide (PAO) membranes has proven to be a simple and reliable method of nanowire synthesis.[1] The PAO self ordered pore array consists of honeycomb packed hexagonal cells with central cylindrical pores. Pore diameters exhibit high uniformity across the membrane can be easily tailored from 4 to 400 nm, while a pore depth of several hundred nanometers has been achieved. Electrodeopsition of WO$_3$ has been explored for its electrochromic effects. Application of WO$_3$ to gas sensing was first explored by Reyes et al.[2] We here report on the development of WO$_3$ segmented nanowires for chemical sensing. The basic layout of these sensing structures consists of a short metal oxide segment intercalated between gold electrical contacts. During the initial step, a 500 nm silver layer is sputtered onto the back of Whatman Anodisc 25 PAO filters. The resistive nature of aluminum oxide forces wire growth to initiate at the seeding layer, the deepest point within each pore, and continue towards the surface of the membrane. Silver (Technic Inc. Cy-less Silver RTU Plating solution) is backfilled into the pores and acts as a sacrificial contact, restricting gold and metal oxide growth to a uniform portion of the membrane. 3 µm of gold is subsequently deposited from Techni-Gold 25 E (Technic Inc.) at a current density of 250 µm/cm^2. A 0.1 molar aqueous sodium tungstate (Na$_2$WO$_3$) solution is then prepared and subsequently deposited at 0.5 mA/cm^2. Plating is completed with a final 3 µm Au deposition. The resulting wires are then released by selective etching of the silver seeding layer and the porous alumina template. Extensive structural characterization of these nanowires using XPS, SEM and Auger will be presented. We plan to present both morphological material analysis as well as preliminary electrical response and chemical sensing results.

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NS-TuP15 Local Gating Behaviors in Nanowire Heterojunction Transistors

***J.-H. Lim**, H.J. Ji, G.E. Jeong, G.T. Kim, J.S. Ha, S.-J. Kahng*, Korea University

Electronic transport properties of ZnO nanowire transistors were studied with atomic force microscope (AFM). The nanowire transistors were fabricated with ebeam lithography and characterized in a probing system embedded in the AFM. Clear gate dependence was observed in the source-drain current by using the non-local back-gate in the transistor. When Ti-Pt-coated AFM tip was used as a local and mobile gate, it was observed that the gating behavior is strongly dependent on the position of the local gate. The transistor could be made on and off repeatedly with the AFM tip locating above the nanowire heterojunction, implying that the active region in the transistor behavior is mostly confined to the small junction area.

NS-TuP16 Nanoindentation Rate Depend Mechanical Properties of Nickel and Titanium

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Rate dependent nano-indentation experiments have been performed on pure polycrystalline nickel and titanium and also on anodized titanium samples. During indentation, the load is linearly increased, then held constant for various intervals of time then reduced linearly to zero. The extent of "creep", sample displacement at constant load, varies with the loading rate. Finite element calculations have been performed to model these experiments. Using time independent material properties, the slope of the loading curve is significantly underestimated. When rate-dependent material properties are used in the model calculations accurate load slopes and creep behavior are obtained. Additional experiments have been carried out to analyse the effect of sample roughness and indentation depth. Implications for determination of material properties trough nano-indentation will be discussed.

NS-TuP17 Flipping of Atomic Image Contrast of Graphite

***J. Choi**, G.S. Khara*, Wayne State University

Flipping of atomic image contrast of graphite is studied by using scanning tunneling microscopy (STM) and spectroscopy (STS). Tunneling gap-distance, gap-voltage and bias polarity play an important role in the flipping of atomic image contrast. The study revealed that the flipping of atomic image contrast is natural because of the electronically active and mechanically soft beta-carbon atoms of graphite. The brightest contrast in the scanning tunneling microscopic images does not always represent a specific site of graphite such as beta-site. The flipping mechanism of atomic image contrast will be discussed.

NS-TuP18 Construction of a Ultra Low Temperature Scanning Tunneling Microscope System[1]

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We describe the design and construction of an ultra-low-temperature (20 mK), high magnetic field (15 T) scanning tunneling microscope (ULT STM) system. This ULT STM consists of an ultra-high-vacuum-compatible dilution refrigerator (DR) and associated UHV systems. The DR was designed and constructed to allow two independent modes of ^{3}He condensation: a traditional 1K pot condenser, or a Joule-Thomson condenser for possible lower noise operation. The system includes extensive vibration isolations and RF shielding. We describe the cooling power characteristics and temperature measurement system of this versatile DR, which reaches a base temperature of 10 mK without STM running. For STM/STS measurements a custom-designed STM module suitable for operation at mK temperatures is described. The STM body is made from coin silver which is rigid and thermally conductive in the mK regime. The whole STM module can be transferred from the upper, room-temperature chamber where the sample and tip can be easily exchanged. The sample holder has five isolated electrical contacts which are also used for kinematic mounting of the sample. This allows 4-probe electrical measurements to be performed simultaneously with STM measurements for microscopic transport studies. This STM module has ± 2 mm of x and y travel and in-situ deposition capabilities on the STM sample mount. Current progress and research plans will be discussed.

[1] This work is supported in part by the Office of Naval Research and Korea Research Foundation.

NS-TuP19 High Selectivity Detection of Trace Explosives using Piezoresistive Microcantilevers

***A.R. Krause**,* University of Tennessee, Oak Ridge National Laboratory, *D. Yi, T.G. Thundat*, Oak Ridge National Laboratory

Microcantilever arrays offer a miniature, cost effective, and real-time sensor platform for trace explosive detection for combating the terrorist threat. Selectivity in detection in microcantilever arrays is achieved by using receptor layers immobilized on the cantilever surfaces. Despite their high sensitivity and the ability for array-based detection of multiple analytes in real-time, cantilever-based sensor platforms exhibit poor selectivity due to the lack of highly selective receptor layers. Selectivity based on array-based detection and pattern recognition often fails due to the lack of orthogonality in sensor array responses due to the limited number of interactions forming a basis for receptor-analyte interactions. We have developed a receptor-free detection method that can provide high selectivity in explosive vapor detection. In this method adsorbed explosives molecules are allowed to undergo chemical reactions with locally generated ozone to provide an analyte specific cantilever response. The explosive molecules from a vapor generator calibrated with GC-mass spectrometer were first allowed to condense on the cantilever surface. The adsorbed molecules were then exposed to ozone created by a miniature UV lamp for a short period of time and the cantilever responses were recorded as a function of exposure time. We have used a piezoresistive cantilever array in common mode rejection to achieve high selectivity and sensitivity. Recent results for selective and sensitive detection of TNT, RDX, and PETN using this method will be presented.

NS-TuP20 Reactions of Atomic Oxygen on Nanoporous Gold Sponges

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In recent years there has been a rising interest in nanoporous gold sponges due to their promising features in low temperature heterogeneous catalysis. Preparation by selectively leaching silver from a gold-silver alloy with acid or a combination of applied voltage and acid leads to a sponge-like morphology with structures in the range of only a few nanometers. Model studies on Au(111) single crystals show a strong interaction of atomic oxygen with the gold surface.[1] The chemisorbed oxygen extracts Au atoms from the surface leading to gold-oxygen complexes on top of it . Inspired by this work we treat nanoporous gold-sponges with atomic oxygen under an ozone-containing ambient atmosphere. We show that in contrast to molecular oxygen the atomic oxygen reacts strongly with the surface leading to a macroscopically detectable shrinking. Measurement of shrinking depending on the concentration of ozone is carried out with a dilatometer. We detect a change of length of nearly 0.5 % of the edge size.

The process was accompanied by a black staining which affirms that the oxygen reacts with gold and leads to the formation of gold oxide clusters in the range of a few nanometers on top of the surface. Staining and shrinking can be changed reversibly by reduction with carbon monoxide. In catalytic measurements it is shown that the surface oxygen produced by ozone reacts immediately with carbon monoxide leading to the product of oxidation, the carbon dioxide. These results provide fundamental insight into the allocation of reactive oxygen on catalytically active gold surfaces, the key step of the oxidation reaction on gold catalysts. Furthermore, ozone detection is of great interest in the context of environmental monitoring. Our experiments show that application of gold sponges as chemical gas sensors for determination of ozone is an interesting and promising possibility.

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Plasmonics Topical Conference

Room: 4C - Session PL-TuP

Plasmonics Poster Session

PL-TuP1 A Hydrogel Chip for Biosensing Studied by Imaging Surface Plasmon Resonance, ***O. Andersson***, *A. Larsson, B. Liedberg*, Linköping University, Sweden

In protein microarray biosensors the use of surface enhancing matrices, or hydrogels, is of great interest. Properly constructed biosensor hydrogels exhibit low non-specific binding while allowing for covalent immobilization of ligands with maintained bio-functionality. In earlier work we have developed such a matrix, based on graft copolymerization of poly(ethylene glycol) and 2-hydroxyethyl methacrylate monomers.[1] The matrix was graft polymerized using UV light and was subsequently modified by chemical introduction of carboxyl groups. In this contribution, we demonstrate the construction of a microarray consisting of proteins covalently immobilized to well defined spots of different thicknesses of our PEG-matrix. By using a photo mask and a movable shutter we are able to vary the UV light exposure time of different spots on our surface. This enables construction of surfaces consisting of arrays of spots with physical thicknesses ranging from a few to tens of nanometers. These surfaces were pre-activated with EDC/NHS and proteins were delivered through piezo-dispensation. Biomolecular interactions involving the immobilized proteins were monitored using imaging surface plasmon resonance (iSPR). More specifically, the proteins Human Serum Albumin and Fibrinogen were piezo-dispensed and the response upon flow delivery of their respective antibodies was monitored with iSPR. The dynamic range of iSPR in the Kretschmann configuration is typically limited by the width of the resonance dip. In this work, however, we have employed iSPR at multiple wavelengths to extend the dynamic range and enable measurements in surface spots of different thicknesses.[2] Our results indicate that our sensor surfaces exhibit excellent properties for use as a template in protein micro-array fabrication. This type of thickness gradient surfaces are also useful when optimizing the properties of the hydrogel, for instance with respect to ligand binding, activity and non-specific binding.[3] In addition, the hydrogel thickness gradient array is interesting as a scaffold in the immobilization of nano-particles and as a platform for the construction of more complex heterogeneously composed biosensor matrices.

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[3] Larsson A, Liedberg B. To appear in Langmuir.

PL-TuP2 Enhanced Optical Response in CdSe Semiconductor via Surface Plasmon Excitation in Gold Nanoparticles, ***R.B. Konda***, *A.K. Pradhan*, Norfolk State University

Recently, surface plasmon resonance in metallic nanoparticles are being explored for a variety of applications including powerful and evolving toolkit for biological detection and molecular sensing, focusing of light, subwavelength photonics, and near-field optical microscopy. Here we show the enhancement of Raman intensity, photoluminescence and absorption in CdSe semiconductor via excitation of surface plasmon resonances in Au nanoparticles insitu pulsed-laser deposited on CdSe semiconductor film surface. CdSe was selected as a model material to illustrate our fabrication method and to demonstrate the physical concept of the enhanced optical properties, such as improving the functionality or performance of photodetectors and related optoelectronic devices, due to plasmon resonance in proximate noble metal nanoparticles. We have also demonstrated enhancement of photocurrent response in p-Si/n-CdSe junction diodes that correspond closely to the nanoparticle plasmon resonance wavelengths via the excitation of surface plasmon resonances in spherical Au nanoparticles deposited on the semiconductor surface. Our results suggest a variety of approaches for improving the performance of devices such as related to enhanced photodetection.

PL-TuP3 Thermoplasmonic Processes in Continuous and Nanostructured Metallic Thin Films, ***A. Passian***, Oak Ridge National Laboratory, *A. Lereu*, ICFO-The Institute of Photonic Sciences, Spain, *R.H. Farahi*, Oak Ridge National Laboratory, *N.F. van Hulst*, ICFO-The Institute of Photonic Sciences, Spain, *T.G. Thundat*, Oak Ridge National Laboratory

Thermoplasmonic processes in continuous and nanostructured metallic thin films The development of optical integrated components such as modulators, filters or switches, has been of continuing interest during recent decades, also in conjunction with developing a new generation of opto-electronic components. In this context, the capability of modulation of light by light naturally appears as a basic goal to achieve toward the emergence of such components. In parallel tremendous progresses have been made in nanofabrication such that nanostructured thin films and surface features may be accomplished with nanometric control. We introduce the concept of surface plasmon (SP) mediated thermo-optical processes to achieve optical modulation. In the first part, SP excitation, supported in thin gold films in the Kretschmann configuration, is demonstrated to lead to a new form of low-frequency modulation of light by light. Thermo-optical processes are shown to be the origin of such a modulation. We report experimental results of the surface response regarding a coupling between several spectrally different Gaussian beams, where a modulated infrared beam is taken as the pump beam and multiple visible continuous beams represent the probes. In the second part, to achieve higher modulation frequency rate, we study nanostructured thin films and nanoparticles where it is expected to see higher dissipation of thermal effects and bring the optical aspect to light. In order to get first some insights, we investigate using spectroscopy and near field scanning optical microscopy (NSOM) the optical response of gold nanostructures placed on a transparent substrate by electron beam lithography. In a second step, a modulated pump beam will be applied to the nanostructured film/nanoparticles and the local illumination from the NSOM tip will be used as a probe signal. We are aiming to achieve higher modulation frequency as well as to utilize lower excitation power. Moreover, the limitation of the excitation power corresponds well with the damage threshold of the nanostructures, a parameter to be taken into account.

PL-TuP4 Gold Nanocrescents with Highly Tunable Infrared Plasmonic Properties for Surface-Enhanced Infrared Absorption Spectroscopy, ***R. Bukasov***, *J.S. Shumaker-Parry*, University of Utah

Gold crescent-shaped nanostructures with uniform size and orientation were fabricated using nanosphere template lithography. The nanocrescents have broadly tunable (900-3600 nm) and strong plasmon resonances (effective cross sections up to 30). The plasmons resonances in the crescents have been shown to be sensitive to the dielectric environment with shifts of the plasmon resonance peak position of up to 880nm/RIU. We will present a new approach to investigate the tunability of nanocrescent plasmons in the infrared (IR) spectral region based on controlling the distance between the tips of the open crescent structures. The tip-to-tip distances in the nanocrescents were varied until a continous ring formed. The crescents were fabricated by controlling the angle of deposition and the angle of rotation between subsequent metal depositions. The number of plasmon resonance peaks in the IR increases from two for completely open crescents to four peaks for closed, continuous crescents. The magnitude of those resonances is dependent upon the orientation of the nanocrescents with respect to the polarization of the incident light. The application of the crescents as a tunable substrates for surface-enhanced infrared absorption (SEIRA) spectroscopy is being investigated. The ability to tune the crescent plasmon resonances farther into the IR by using substrates with higher refractive indices (e.g., from a refractive index of ~ 1.5 for glass to ~3.4 for silicon) is being explored.

PL-TuP5 Single-Nanoparticle Light-Scattering Spectra of Flat Gold Nanoparticles (FGNPs): A Study of the Effect of Nanoparticle Treatment, ***W.D. Tennyson***, *C.E. Allen, D.S. Hartnett, M.D. McCutchen, D.H. Dahanayaka, L.A. Bumm*, The University of Oklahoma

We have investigated the effects of a range of treatments on the surface plasmon modes of individual FGNPs using single-nanoparticle far-field light-scattering spectroscopy. We have explored thermal annealing, surface cleaning, and nanomechanical manipulation of the FGNPs. We can directly measure the effect of the treatments to an individual nanoparticle by correlating the before-and-after spectra with before-and-after microscopy (AFM and SEM). Finding the same nanoparticle again and again can be a significant barrier in correlation, however we have developed a photolithograpically- prepared addressed-grid system to assist finding the particles in multiple measurement platforms. This method also allows facile correlation of the light-scattering spectra to size, shape, thickness, and local environment.

PL-TuP6 Sol-gel Encapsulated Gold-Silica Nanoshells for SERS Based Sensors, *S. Bishnoi*, ***Y.-J. Lin***, Illinois Institute of Technology

Gold-silica nanoshells are important materials for surface enhanced Raman scattering (SERS) based sensors. The individual particles have been found to have enhancements on the order of 10^{10} over normal Raman,[1] preventing the need for the pre-aggregation of particles. The resulting sensors are significantly more reproducible than SERS sensors based on aggregated gold colloids. One challenge in the use of such particles for the creation of in-line Raman sensors lies in the immobilization of such particles to prevent long-term aggregation and other storage issues. To this end, we have used sol-gel methods to immobilize gold-silica nanoshells to create robust SERS based sensors. Using a protocol commonly used to immobilize proteins,[2] we have created biologically friendly SERS sensors for the study of gold binding peptides and proteins. Specifically, by combining tetraethyl orthosilicate (TEOS), methyltrimethoxysilicate (MTMS), phosphate buffer, and gold nanoparticles we have created sol-gels with reduced fluorescence and Raman backgrounds. Since organic solvents have been eliminated in the synthesis, these porous materials are ideal for studying the attachment of biological molecules to gold nanoparticles.

[1] Jackson, J. B.; Halas, N. J. Proc. Natl. Acad. Sci. U.S.A. 2004, 101, 17930-17935.

[2] Soyoun Kim, Youngdeuk Kim, Philseok Kim, Jeongmin Ha, Kyunyoung Kim, Mijin Sohn, Jin-San Yoo, Jungeun Lee, Jung-ah Kwon, and Kap No Lee. Anal. Chem. 2006, 78(21), 7392 -7396.

PL-TuP7 Plasmonic Detection of a Model Analyte in Serum by a Gold Nanorod Sensor, ***S.M. Marinakos***, *S. Chen, A. Chilkoti*, Duke University

We describe the fabrication of a label-free, chip-based biosensor based on the localized surface plasmon resonance (LSPR) of gold nanorods. Gold nanorods were chemisorbed onto a mercaptosilane-modified glass substrate, followed by conjugation of biotin to the nanorods. Streptavidin-binding to biotin was monitored by the wavelength shift of the LSPR peak in the UV-visible extinction spectrum of the immobilized gold nanorods due to the change in local refractive index at the gold nanorod surface induced by streptavidin binding. The limit of detection of the sensor is 94 pM in PBS and 19 nM in serum, and the dynamic range spans 94 pM to 0.19 µM. The advantages of the nanorod-based sensor over a LSPR sensor that we had previously fabricated from gold nanospheres are the significantly lower detection limit and the internal self-reference that the signal of the nanorod sensor provides based on the measurement of peak wavelength shift.

PL-TuP8 Controlled Assembly of Asymmetrically Functionalized Gold Nanoparticles, ***R. Sardar***, *T.B. Heap, J.S. Shumaker-Parry*, University of Utah

Metal nanoparticles have received great attention due to their unique optical properties and wide range of applicability. In this context, programmable assembly of nanoparticles to control particle-particle interactions is a major challenge for the application of nanoparticles in device fabrication and detection systems. Different methods have been developed to achieve asymmetrically functionalized gold nanoparticles including the use of organic bridged ligands, oligonucleotides, and solid phase approaches to form gold nanoparticle dimer, trimer and tetramer assemblies. Of these architectures, dimers are of special interest because of their application as substrates in surface-enhanced Raman spectroscopy (SERS). In addition, one-dimensional nanoparticle chains show potential usefulness in fabrication of optoelectronic devices. We have developed a versatile solid phase synthesis of gold nanoparticle dimers using commercially available organic reagents through an asymmetric functionalization pathway. The method may be used to synthesize dimers for a wide size range of gold nanoparticles. In addition, we demonstrate the synthesis of dimers consisting of two particles with different sizes. The dimer yield varies from ~30% to ~65% depending on the nanoparticles' size. The dimers demonstrate remarkable stability in ethanol without further processing. We have also developed a simple synthetic route to prepare one-dimensional gold nanoparticle chains using asymmetrically functionalized gold nanoparticles and poly(acrylic acid) via a simple amide couple reaction. The length of the synthesized nanoparticle chains varies from 256-400 nm with regular interparticle spacing (~2.7 nm). The synthesized chains display distinct optical properties compared to individual nanoparticles. This methodology also is applicable for gold nanoparticle with different sizes.

PL-TuP9 Optical, Magnetic and Magneto-Optical Properties of Noble-Metal/Ferromagnet Nano-Composite Materials, ***R.A. Lukaszew***, *J.R. Skuza, M. Sestak,* University of Toledo, *N. Dushkina*, Millersville University

Magnetic nanoparticles embedded in noble metal thin films exhibit interesting properties that are function of the microstructure and can be used in relevant applications. Some of these materials can be processed further to achieve a particular magnetic anisotropy of interest while others may exhibit plasmonic enhancement of their optical properties that can be used in a variety of sensing applications, in particular biosensing. The optical, magnetic and magneto-optical properties of these nano-composite materials depend on the materials used, the nano-particle size and distribution, the inter-particle distance, etc. We will present our studies on such composite materials in thin film form. In particular, we will show that ion-implantation of ferromagnetic metal ions onto noble metal thin films is a powerful tool for nano-fabrication of embedded nano-clusters with controlled geomety, i.e. size and distribution. We will present our studies applied to two such systems: FePt and AuCo. In the former case, we have also used thermal treatments to achieve the L10 phase of interest in new generation perpendicular magneto-recording media. In the latter case, we were particularly interested in the enhancement of the surface plasmon resonance (SPR) of the noble metal when combined with a ferromagnetic one, i.e. a magneto-plasmonic material. We will compare the SPR response of a Au/Co/Au trilayer in which the optical response can be tailored varying the thickness of the Co layers, with a nano-composite material made with Co magnetic nano-clusters embedded on a Au thin film matrix. In this latter case, the Co clusters are ion-implanted onto the Au matrix and their size and penetration depth can be tailored by choosing the ion-implantation conditions. We will show our field dependent SPR data on this nanocomposite material.

PL-TuP10 Nanopatterned Polypyrrole Based Surfaces for Enhanced Surface Plasmon Resonance Detection, ***P. Lisboa***, European Commission, Italy, *M.B. Villiers, C. Brakha, S. Cortes,* INSERM U823, Institut Albert Bonniot Grenoble, France, *A. Valsesia, P. Colpo,* European Commission, Italy, *P. Marche,* INSERM U823, Institut Albert Bonniot Grenoble, France, *F. Rossi*, European Commission, Italy

The interaction between biomolecules and materials is regulated by the chemical properties of the surfaces and by their micro and nano-morphologies. An accurate control of chemical contrasted motives is highly required for the improvement of the sensitivity and the specificity of biosensing devices.[1,2] Polypyrrole (PPy) is a preferential material for bio-analytical sensors thanks to its good environmental stability and excellent biocompatibility, together with the possibility of being functionalised with biological relevant functional groups.@foontote 3@ In this work the gold surface of Surface Plasmon Resonance (SPR) chip was nanostructured to create gold nano-areas over a SiOx matrix by using colloidal lithography. Then, micro spots of modified PPy with ovalbumin (recognition element) and with casein (control) have been created on the nano-structured surfaces and non nanostructured surfaces by electrochemical copolymerization using a microarrayer in potentiostatic conditions. The growth of the modified PPy in the nanostructures takes place only in the gold nano-areas since the surrounded matrix of SiOx presents electrically insulating properties. The effect of the nano-structured PPy surface on the immunoreaction efficiency was evaluated using SPR imaging device. The SPR signals related to the recognition of ovalbumin by different concentrations of anti-Ovalbumin have been measured. The results were compared with a chip with micro spots of uniformly (non nanostructured) modified PPy. Even if the active area of PPy containing Ovalbumin represents only 3% of the area of non nanostructured PPy, the absolute SPR signals resultant from the ovalbumin/anti-ovalbumin reaction was higher by only a factor of 2 in the case of the uniform PPy than in the case of nanostructured surfaces. Nevertheless at lower concentrations, the SPR signal is similar showing that the nanostructured surface improves the biorecognition efficiency at these concentrations. Furthermore, the SPR signals normalised to the active PPy area were higher by a factor of 14 in the nanostructure surfaces for all the antibody concentrations. These results indicate that the nanostructured surfaces improve the immunoreaction efficiency. This is a very promising result regarding the increase of detection sensitivity in analytical devices.

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[2] A. Valsesia, et al, Langmuir 2006, 22, 1763.,

[3] L. Grosjean et al., Analytical Biochemistry 2005, 347, 193-200.

Plasma Science and Technology

Room: 4C - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Selective Etching of SiO_2 over Si_3N_4 in Triple Frequency Capacitively Coupled Plasma System, ***H.-G. Lee****, S.-O. Lee, M.-S. Lee, S.-H. Cho, S.-K. Lee, S.-C. Moon, J.-W. Kim*, HYNIX Semiconductor Inc., Republic of Korea

It has been reported that the triple frequency (60MHz, 27MHz, 2MHz) capacitively coupled plasma (CCP) system provides more advanced process performance and wider process window for etching dielectric films compared to conventional dual frequncy (60MHz, 2MHz) CCP system. In this study, the effect of triple frequency with the bottom electrode in $C_4F_6/O_2/Ar$ gas plasma on the selective etching of SiO_2 over Si_3N_4 is considered as a function of the power applied to each frequencies. To understand the characteristics of triple frequncy concerning etch selectivity of SiO_2 over Si_3N_4, we considered the chemical species such as CF_2 radicals and other radicals that have influence on polymerization using optical emission spectroscopy (OES). The thickness of deposited polymers and components in this triple frequency CCP system were investigated by high resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS).

PS-TuP2 Etching Characteristics of V_2O_5 Thin Films using by Cl_2/Ar Inductively Coupled Plasma, ***C.M. Kang****, C.I. Kim*, Chungang University, Korea

Recently, the technology of microelectronic systems has attracted global attention for applications such as medical devices, communication systems, sensors and actuators. Vanadium oxide has a high capacity for ion storage, it is stable under a cyclic voltage and provides a particular (mixed) type of coloration complementary to that exhibited by the tungsten oxide (WO_3), allowing the production of high performances smart windows. Also vanadium oxides, with unique characteristic structures, comprise a particularly interesting group of inorganic 3d-transition metal oxide compounds due to their diverse, electronic, opto-electronic, electrochromic, and magnetic properties, which makes them potential candidates for important technological applications. Research and development of V_2O_5 have been rapidly accelerated to improve materials for the last decades. But, etch properties of V_2O_5 have not established yet. In this study, we investigated etch characteristics of dry etching of the V_2O_5 thin films in the inductively coupled plasma etch system with (Cl_2/Ar) gas mixture. The etching characteristics of V_2O_5 thin films were investigated in terms of etch rates and selectivity as a function of (Cl_2/Ar) gas mixing ratio, rf power, dc bias voltage and chamber pressure. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) was used to investigate the etching profile.

PS-TuP3 Advanced Gate Stack Processes for sub-70nm CMOS Technology, ***G.H. Kim****, K.T. Kim, C.I. Kim*, Chung-Ang University, Korea

The continued evolution of MOS (metal-oxide-semiconductor) transistor beyond the 90nm technology node will most likely be driven by advances in materials engineering and process integration. Fundamental changes in the materials used in the MOSFET (MOS field effect transistor) gate stack will become necessary as will novel processing techniques. High-k dielectrics can potentially extend scaling to thinner equivalent oxide thickness. However, in the production of very small size devices, the fine patterning technology is very important in order to manufacture the detailed device design based on the principle of the device operation. In this work, the dry etchings of new materials studied for the future CMOS devices are described. TiN as the metal gate electrode material and high-k gate insulators such as HfO_2 and Al_2O_3 are investigated. Etch rates and etch selectivity of TiN/high-k dielectrics gate-stack structures on Si substrate were investigated by varying the process parameters such as gas mixing ratio, source RF power, DC bias voltage, and process pressure. Plasma diagnostics were performed by quadrupole mass spectrometer (QMS) measurements and optical emission spectroscopy analysis. To investigate the etch residues of the high-K dielectric is generated by $BCl_3/Cl_2/O_2$ plasmas, the surface analysis on the dielectrics was performed using x-ray photoelectron spectroscopy (XPS).

PS-TuP4 Etching Characteristics of High-k Dielectric Materials in Inductively Coupled $Ar/CF_4/C_4F_8$ Plasma, ***S.W. Kim****, B.J. Park*, Sungkyunkwan University, Korea, *S.-K. Kang*, SKKU Advanced Institute of Nano Technology, Korea, *K.S. Min, S.D. Park, G.Y. Yeom*, Sungkyunkwan University, Korea

For the next generation metal oxide semiconductor field effect transistor (MOSFET), high-k materials such as HfO_2, ZrO_2, BST, etc. are required as gate dielectric materials which replace SiO_2/Si_3N_4. To apply these high-k materials to the next generation devices, the etch characteristics needs to be satisfied in addition to the adequate materials characteristics. For these materials, precise etch rate is required instead of high etch rate due to the low thickness of the material and extremely high etch selectivity over underlayer material is required. Also, no damage or residue remaining on the etched surface is tolerable. In this study, the etch characteristics of high-k materials such as HfO_2 and ZrO_2 were investigated as a function of gas mixture composed of $Ar/CF_4/C_4F_8$ using an inductively coupled plasma etcher, and the effect of gas mixture on the etch rate, etch selectivity to silicon, the remaining C-F polymer on the silicon surface, and the damage to the MOSFET device were investigated. In the presentation, the change of materials physical, chemical, and electrical properties etched by $Ar/CF_4/C_4F_8$ using an inductively coupled plasma etcher will be shown in details with the properties of MOSFET devices fabricated by $Ar/CF_4/C_4F_8$ ICP.

PS-TuP5 The Etching Mechanism of Zinc Oxide Thin Films for Optoelectronics Device Application using Inductively Coupled Plasma, ***J.C. Woo****, K.T. Kim, G.H. Kim, C.I. Kim*, Chung-Ang University, Korea

Zinc oxide (ZnO) exhibits an interesting combination of multifunctional properties, including optical, piezoelectric, and optoelectronic properties, and in thin film form ZnO films find immense applications in many electronic devices including sensors, transducers, and high frequency surface acoustic wave (SAW) devices. It has advantage relative to GaN because of its availability in bulk, single-crystal form, and wide bandgap energy of 3.4 eV, which makes it transparent to visible light. The excition binding energy is ~60 mV for ZnO, as compared to GaN, ~25meV; the higher excition binding energy enhances the luminescence efficiency of light emission. Research and development of ZnO have been rapidly accelerated to improve materials for the last decades. But, etch properties of ZnO have not established yet. Accordingly for many application optoelectronic devices, the etching mechanism of ZnO thin films during the etching process must be understood. However, few of etching mechanism was examined in our previous works and it can be hardly etched. So it is very important to improve the high etch rate, vertical etch profile, smooth etch surface, high mask selectivity and smooth sidewalls for developing ZnO thin films. In this study, we investigated etch characteristics of the ZnO thin films in the inductively coupled plasma system. The etching characteristics of ZnO thin films were investigated in terms of etch rates and selectivity as a function of additive gas mixing ratio. The plasmas were characterized by optical emission spectroscopy analysis and quadrupole mass spectrometer measurements. The chemical reaction on the surface of the etched ZnO thin film was investigated with X-ray photoelectron spectroscopy. Scanning electron microscopy was used to investigate the etching profile.

PS-TuP6 Study of the Amorphous Silicon Etching using Pin to Plate Dielectric Barrier Discharge in Atmospheric Pressure Plasma, ***S.J. Kyung****, J.B. Park, J.H. Lee, G.Y. Yeom*, Sungkyunkwan University, Korea

In this study, atmospheric pressure plasmas were generated with a modified dielectric barrier discharge (pin-to-plate DBD) having the power electrode composed of multi-pins instead of a conventional blank planar plate and their characteristics of discharge were investigated. The effect of CF_4 in the N_2/NF_3 gas mixture on the characteristics of the pin to plate dielectric barrier discharge (DBD) having the size of 170 x 100 mm have been investigated for the application to thin film transistor liquid crystal display (TFT-LCD) processing such as amorphous silicon(a:Si) and silicon nitride(Si_3N_4) etching. The result showed that the selectivity of a:Si/ Si_3N_4) was increased with CF_4 flow rate in N_2/ NF_3 up to 250 sccm, however, the further increase of CF_4 flow rate decreased the selectivity of a:Si/ Si_3N_4). A maximum etch rate of a:Si of 110 nm/sec with the selectivity of a:Si/ Si_3N_4) of 5.1 could be obtained with a gas mixture of 250 sccm CF_4 in N_2 (50 slm)/ NF_3 (300 sccm) and at 8.5 kV of AC rms voltage.

PS-TuP7 Effect of Gate Processing on Line edge Roughness in 45nm, *P.K. Subramanian,* ***I. Matthew****, T. Wallow,* Advanced Micro Devices, *L. Tsou*, IBM Corporation

As gate lengths shrink in 45nm technology node and beyond, the variation contributed by Line Edge Roughness(LER) becomes a larger proportion of the total CD variation Therefore, a reduction in the LER is one way of reducing the total variability of gate dimensions across a chip. In this paper we study evolution of the LER through the various process steps that end with the formation of a gate on the wafer. We examine the frequency components of the roughness as the wafer processed through various (lithography and etch) steps and examine the effects of each of these processes on the roughness spectrum. The advent of the immersion lithography and the attendant higher Numerical Aperture(NA) has led to the adoption of new schemes to reduce reflectivity. The impact of the new lithographic schemes on LER evolution is also examined. We also examine the effects of modifying etch process parameters and chemistry on the roughness spectrum. The effect of HBr plasma curing during etch processing on the LER is studied.

PS-TuP8 Directional Oxidation of Silicon Trench in Surface Wave Oxygen Negative Ion Plasma, *H. Shindo, T. Mitomi, M. Suzuki, **K. Kusaba***, Tokai University, Japan

A low temperature and low damage silicon oxidation technique is highly required in various ULSI processes. In particular for trench isolation of a memory cell to realize further integrations, the oxidation should be ion-assisted for directionality but with low damage. Additionally, a new type of MOS transistor with a trench gate has recently been proposed for the next generation of ULSI. For this purpose, a new method of negative ion assisted silicon oxidation has been proposed employing microwave oxygen plasmas. In this work, a new method of negative ion assisted silicon oxidation is proposed employing microwave oxygen plasma, and a directional and low temperature silicon trench oxidation will be demonstrated. The oxidation characteristics were intensively studied in silicon trench to form a shallow trench insulation layer for cell isolation of MOS transistor. The plasma was produced in an aluminum chamber 240 mm in diameter. At the one end of the chamber, a microwave of 2.45 GHz was introduced through a high permittivity material of AlN (permittivity: 10.9) window of disc plate. The oxidation characteristics were precisely examined in a silicon trench of 0.15 um width and 0.2 um depths. The oxidation was made in the condition of 400 degree C and the bias frequency of 1900 kHz. The oxidation depth at the three positions of the trench was determined from SEM photograph. These three positions are labeled as “Top, Side and Bottom” The oxidation depth at all positions was at first decreased with an increase in the axial distance from the microwave window, but it was increased again in the downstream. Particularly, the oxidation depth at the trench bottom showed a maximum in a very downstream of 18 cm from the window, and thus the step coverage of the trench oxidation, defined as the depth ratio of the trench bottom to the top, reached as high as 0.8. Since the axial distance at which the oxidation depth begins to increase again is just coincident with the region where the electron energy is rapidly decreased, this directional oxidation feature is ascribable to the negative oxygen ions. It is concluded that the oxidation by high density oxygen surface-wave plasma with high permittivity window is innovative.

PS-TuP9 Dry Etching Technology of Cobalt Silicide for sub-60nm Gate Patterning using ICP Source with High Temperature ESC, ***H. Lee***, Samsung Electronics, Korea, *J.I. Shin, H.S. Lee,* Applied Materials, *D.H. Kim*, Samsung Electronics, Korea, *T.W. Kim,* Applied Materials, *K. Shin, M.C. Kim, G.J. Min, C.J. Kang, J.T. Moon*, Samsung Electronics, Korea

Dry etching of $CoSi_2$ gate in sub-60nm design rule is successfully done using ICP (Inductively Coupled Plasma) source with high temperature ESC (Electro-Static Chuck). Vertical profile is achieved by forming a volatile Co byproduct reacted with Cl_2/Ar based plasma at 250°C of ESC temperature under relatively low DC bias voltage (~300V). Since Cl_2/Ar based plasma has low etch selectivity to polycrystalline Si (poly-Si) and gate oxide, O_2 and N_2 were added to reduce the recess of poly-Si layer which is remained beneath $CoSi_2$ layer during silicidation process. $CoSi_2$ layer used in this experiment was formed by sintering of sputtered Co layer on poly-Si layer. Dry etching of poly-Si is followed with both low temperature(~80°C) and high temperature (~250°C) ESC after $CoSi_2$ etching. For the poly-Si etching, $HBr/O_2/He$ plasma was used to maintain high selectivity to gate oxide. However, even though poly-Si layer is recessed more than 200Å during $CoSi_2$ etching process, it was not possible to remove remaining poly-Si completely with $HBr/O_2/He$ plasma. TEM and EDX are used to analyze surface of poly-Si, and thin metal layer containing Co is observed on the surface of polycrystalline Si layer. It is believed that this thin metal layer blocks etching of poly-Si. Therefore, removing the thin metal layer or preventing re-deposition of Co byproduct on polycrystalline Si layer during $CoSi_2$ etching will be necessary. Co as a barrier metal of bit line is also etched with vertical profile on high temperature (~300°C) ESC with Cl_2/Ar plasma. In this case, there was no remaining Co by-product since enough amount of Co OE is possible, resulting in complete removing of Co byproduct on ILD.

PS-TuP10 Stripe and Hole Shape Contacts Etch for Power Amplifier BICMOS Devices, ***J.P. Oddou***, *D. Ristoiu, J. Mourier*, STMicroelectronics, France

Power amplifier applications of BICMOS devices need a specific contact module in order to support high current density and temperature. In order to achieve such performances, stripe-shaped contacts are designed for the bipolar transistor, while classic hole contacts are used for CMOS and the contact depth is increased to 1.5µm. Therefore, taking into account the topography of the bipolar and MOS structures, 5 different types of contacts must be opened. To fulfill these specifications, contacts etch process requires: - sharp profile to achieve high depth contacts; - high selectivity of oxide to nitride to safely land on emitter, gate and active areas; - low loading effects to achieve both stripe and hole contacts having the same critical dimension (CD). In this paper we focus on oxide etch process for contact opening developed on a MERIE industrial etcher using C5F8/ O2/ Ar chemistries. In a first time we characterize the oxide to nitride selectivity and the profile slope as a function of the C5F8/O2 ratio. Higher C5F8/O2 ratio favors selectivity, but degrades slope and CD, while lower C5F8/O2 ratio leads to sharp profile in the detriment of selectivity, therefore our approach consists in using a sequence of etching steps having different C5F8/O2 ratio. We demonstrate that this process solution enables us to achieve the above mentioned morphological constraints. Moreover, electrical tests performed on contact chains show that the resistivity and leakage results are in line with technology specifications.

PS-TuP11 Sidewall Passivation Effect during $C_4F_8 + N_2$ Etch Process for SiOCH Low-k Films, ***S.-K. Yang***, *H.-S. Yoo,* Inha University, Korea, *H.-Y. Song,* Samsung Electro-Mechanics Co. LTD., Korea, *J.-G. Lee,* Bucheon College, Korea, *S.-G. Lee, B.-H. O, I.-H. Lee, S.-G. Park*, Inha University, Korea

Plasma induced damage to low k dielectric layer is one of key issues in developing the multi-level interconnection technology based on Copper and low k dielectrics. Change in chemical bonds and contents of carbon or fluoride often results in higher dielectric constant. In this work, etching of SiOCH low k films was studied by $C_4F_8 + N_2$ plasma in Inductively coupled plasma etcher. X-ray photoelectron spectroscopy showed C-F and C-N bondings on the sidewall of patterned low k dielectric layer, which indicated the formation of passivation film. This passivation layer remained after photoresist removal by N_2 plasma and even after dipping in 1% HF solution. It is shown that patterning of SiOCH layer by $C_4F_8 + N_2$ plasma caused the increase in dielectric constant k by forming C-F passivation films.

PS-TuP12 Critical Dimension Shrink and Control with Different Frequency Source Powers in Dielectric Etch Chamber for 45nm Technology and Beyond, ***J. Wang***, Applied Materials

The Critical Dimension (CD) shrink from BARC was invested by using the capacitive coupled plasma etcher with high frequency source due to BARC open step is the most critical in dielectric etch. Two frequencies (<100MHz vs >100 MHz) source power with different plasma densities were compared. It was found that the CD shrink was related to the CF2 species that were excited from source and>100 MHz source power showed the strong control knob on CD shrink comparing to <100MHz. Chemistry selection and process control knobs have been evaluated and it was found that the CD shrink was basically controlled by pressure, polymer gas, and source power. And a maximum >60nm CD shrink bias was obtained when profile and final CD range was maintained in the spec. (1) CD bias comparison on the BARC open with and without source power indicated source power strong effect on CD shrink. The CF2 radical emission in etching plasma were collected by the optical emission spectroscopy (OES) as shown to evaluate the difference on the CD shrink when other process parameters changed . It was found that the >100 MHz source provided the efficient generation of CF2 radical density that resulted in more CD shrink. The CD shrink varied with different source power for both frequencies and it showed the more CD shrinks with high source power. The CF2 species density without source power showed lowest signal and the strongest emission with the high source power, which was pretty much consistent with the wafer results. (2) CHF3 flow on BARC open was tested at different pressure and the high CHF3 gas flow and low pressure were showing strong knobs on CD shrink control with source power. It was known that CF2 was one of many species from CHF3 dissociation during the plasma etch and more CF2 has been generated with high frequency power, which deposited on the sidewall to protect the isotropic etch and therefore made the top CD shrink. With the low CHF3, the CD shrink range was much bigger than high CHF3 flow with pressure change. The CF2 species density explained why high source power and low pressure as the knobs on CD shrink control. (3) The production-like runs on customerâ?Ts wafers were tested with two source powers and both showed CD shrink consistently repeatable. The high frequency source power provided the high plasma density as the strong knob for CD shrink and meantime allowed the high efficiency wafer-less dry clean, which benefited APF etch clean mode requirement.

PS-TuP13 Analysis of High Aspect Ratio Contact Etch using High Flow Concept, ***S.-J. Park**, S.-C. Park, Y.-J. Kim, W.-S. Han*, Samsung Electronics Co. Ltd., Korea

As contact sizes scale down below 100nm, high aspect ratio contacts (HARC) encounter the limits such as the low selectivity of the resist material, etch stopping mechanism, the profile distortion, and so on. The high flow concept is a widely used scheme for RIE (reactive ion etching) technology. The rapid movement of reactive ion sources affect on the dissociation mechanism of the etching chemistry. The carbofluoride (CxFy) chemical sources show different behaviors, while the flow rate changes at the same pressure. The QMS (quadrapole mass spectroscopy) method enables the analysis of the dissociated chemicals and the byproducts during HARC etch. The ratio of carbofluoride and fluorine seem to be the major factor which determines the profile of HARCs and the resist selectivity. The contact patterns with an aspect ratio of 30 are used to identify the high flow concept in this experiment. The flow rate of carbofluoride chemistry changed up to 2.8 times higher than the normal reference flow rate in a CCP (capatively coupled plasma) chamber. The higher flow rate improves in terms of the resist selectivity. However, the profile distortion between the top opening and the bottom opening is worse than the profiles under the normal condition. The HARC etch study at the high flow condition will be shown in terms of the profile distortion and the real time chemistry monitoring using QMS method.

Keywords : RIE, HARC, high flow.

PS-TuP14 Improvement of Sputter Deposited Mo-based Barrier Films by Insertion of a Thin Al Interlayer for Copper Metallization, ***P. Majumder**, C.G. Takoudis*, University of Illinois at Chicago

Copper is used as interconnects in advanced ultra large scale integration microelectronic devices due to its low electrical resistivity and superior resistance to electromigration compare to Al. However, Cu diffuses easily into Si and SiO_2, and forms copper silicide compounds at temperatures as low as 200 °C, resulting in degradation of Si devices at low temperature. Therefore, the use of diffusion barriers between Cu and Si becomes essential in order to successfully implement copper as an interconnecting metal. Sputter-deposited refractory metals, like W, Ta, Mo, and Ti and their nitrides have been recognized as diffusion barriers due to their high thermal stability, low resistivity and excellent capability of suppressing reactions between Cu and Si. In recent years, Mo-based diffusion barriers have been investigated for copper metallization. Many studies show that sputtered deposited Mo and MoN_x barrier layers are polycrystalline in nature and thus failed after annealing at relatively lower temperatures due to the diffusion of copper through the grain boundaries of the polycrystalline films. In this work, we investigate the barrier performance of sputtered deposited Mo and MoN_x due to the insertion of ultrathin Al interlayer. Al is used to stuff the grain boundaries of Mo and MoN_x thereby increasing the breakdown temperature of the barrier films. Mo and MoN_x films are sputtered deposited using Ar and Ar/N_2 mixture, respectively, under a 4.5 mtorr total sputtering pressure. The formation of crystallites takes place on the surface of the copper layer at the barrier failure temperature. The quantitative analysis of these crystallites is done using energy-dispersive spectroscopy. The thermal stability of Mo-based barrier layers are evaluated after annealing at wide range of temperatures in the presence of N_2 using four probe measurements for sheet resistance, X-ray diffraction analysis for phase identification and scanning electron microscopy for surface morphology. The interaction of different layers due to high temperature annealing is evaluated by depth profiling using X-ray photoelectron spectroscopy.

PS-TuP15 Ar Ion and Ammonia Modification of OSG Surfaces: A Novel Route to Nanoscale Diffusion Barriers, *J. Wilks, **J.A. Kelber***, University of North Texas

The continued scaling of barriers to < 4 nm thickness drives the quest for a practical single step deposition process, in contrast to the current TaN/Ta two step standard. Pure Ta deposition has been considered, but Ta deposition on OSG and related materials results in a Ta-O-C "interphase" 2-4 nm thick which inhibits Cu adhesion and prevents barrier scaling to sub-4 nm length scales. We present in-situ XPS and ex-situ AFM data indicating that 500 eV Ar ion bombardment in the presence of ammonia results in a self-limiting process involving carbon depletion and nitrogen addition to the surface region. No significant change in surface rougness is observed. The surface nitridation results in a qualitatively different response to Ta deposition: an abrupt interface with initial Ta2N formation, with subsequent Ta formation at longer deposition times. These results suggest a new direction in plasma pretreatment of OSG surfaces prior to metallization--a self-limiting surface nitridation, followed by a single step Ta PVD process resulting in a Ta2N/Ta nanoscale barrier. Further, the results observed for the ion bombardment process mimic in major respects results observed for low pressure plasma treatments--including enhanced carbon depletion due to the presence of ammonia, the self-limiting nature of the process, and nitrogen incorporation. The usefulness of such UHV-based processes as models for low-pressure plasma processing will also be discussed.

PS-TuP16 Size Distribution Factor of Platinum Nanoparticles Synthesized by Plasma in Aqueous Solution, ***T. Nishigaki**, T. Ishizaki, N. Saito, O. Takai*, Nagoya University, Japan

Well-defined platinum nanoparticles activate of photo catalysis, decompose harmful component in exhaust gas of automobile, lead to high potential of fuel cell. Platinum nanoparticles have been synthesized by various techniques including chemical reduction, photo reduction and electrochemical technique. However, in these techniques, it takes few hours to synthesize the nanoparticles or chemically toxic substances leave in a product. Now, it is required to develop a green process rapidly to synthesize nanoparticles. We have developed 'Solution Plasma', which is defined as plasma in aqueous solution. Solution plasma has attracted much attention as a novel chemical reaction field. As solution plasma generates UV light, electrons, and radicals, higher reaction rate would be achieved. In this study, we aimed to synthesize platinum nanoparticles by solution plasma. In addition, we investigated influence of solution pH on the sizes of the platinum nanoparticles. Optical absorption of nanocolloidal platinum was measured by UV-vis spectrometer. The nanoparticles were observed by transmission electron microscopy (TEM). $H_2PtCl_6?6H_2O$ (1.44mM) and PVP (Polyvinylpyrrolidone, 12.1mM) were used as row materials. The pH of solution was varied from 2.5 to 4.5. The electrical conductivity was adjusted to 1.5mS/cm by the addition of KCl. A pulsed power supply was utilized to generate plasma. Pulsed voltage of 1.6kV was applied between the tungsten electrodes in the solution. Pulse width and frequency were varied from 2.0 to 3.0μs, respectively. Solution color changed from orange to dark brown at discharge times of more than 40 min. An absorption peak at 262 nm originated from $PtCl_6^{2-}$ became weaker with the increases of the discharge time, while baselines in the spectra became higher in all the range. These results indicate the formation of platinum particles. TEM image shows that the mean diameter of the nanoparticles was 10nm. Debye rings by (111), (200), (220), (311) were also observed by diffraction patterns. The effects of pulse width, frequency and pH on the particle size distribution were also discussed.

PS-TuP17 Effects of Ions and Radicals on the Growth of Single-Walled Carbon Nanotubes Produced by Diffusion-Plasma CVD, ***T. Kato**, R. Hatakeyama*, Tohoku University, Japan

Individual single-walled carbon nanotubes (SWNTs) have attracted a great deal of attentions since the discoveries of their prominent electrical and optical characteristics. Recent progresses in a synthesis stage of the isolated SWNTs provide outstanding opportunities to efficiently study the basic science of ideal one-dimensional materials. A plasma CVD is well-known as a nanotube formation method including outstanding benefits in the vertical growth of individual multi-walled carbon nanotubes. Up to now, our group firstly demonstrated that those benefits in the plasma CVD can be also applied to the SWNT growth stage, and the freestanding individual SWNT growth on a flat substrate has been achieved with a diffusion plasma CVD method. These progresses of a plasma technology in the nanotube fabrication field can strongly accelerate industrial application of SWNTs. Unfortunately, however, any quantitative discussion about effects of plasmas on the growth of SWNT has not been realized at all so far, and it is one of inevitable issues to fully utilize potential abilities of plasmas for a realistic use of SWNT-device applications. These backgrounds motivate us to investigate the detailed effects of plasmas on the growth of SWNTs. In our study, the effects of ion energy and radicals are mainly focused with a precisely parameter- controlled diffusion plasma CVD system. Derived from the carefully investigated experimental results about the time evolution of SWNT growth, the simple equation is established to describe the growth kinetics of SWNTs during the plasma CVD. Based on the fitting of the experimental result with the equation, remarkable effects of ions and radicals are uncovered. There are clear threshold energies of ions for the destruction of the tube structure. It is conjectured that those threshold energies correspond to that of the bond breaking between carbon in the nanotube and the displacement of the carbon atom from a graphite network in the nanotube. In the case of the radicals, the etching rate during the SWNT growth is found to be strongly influenced by the amount of atomic hydrogen in the plasma. Furthermore, a unique correlation is also identified between the incubation time of the SWNT growth and density of ions in the plasma. These discoveries of the interesting correlations between the detailed growth parameters of SWNTs and key elements in plasmas could contribute to the further advance for the perfect structure control of SWNTs.

PS-TuP18 Structure and Properties of Tungsten Carbide / Amorphous Hydrogenated Carbon Composite Films Prepared by Plasma Immersion Ion Immersion and Deposition, *M. Xu,* Shanghai Jiaotong University and City University of Hong Kong*, Z.W. Wu, S.H. Pu,* City University of Hong Kong*, X. Cai,* Shanghai Jiaotong University, Hong Kong*, **P.K. Chu***, City University of Hong Kong

Amorphous carbon films have excellent properties including high hardness, low friction coefficient, high chemical inertness, and good corrosion resistance. Metal-containing hydrogenated carbon films have recently attracted attention as nanocomposite films with microstructures comprising nanocrystalline grains in an amorphous matrix. These composite films have properties intermediate between a-C:H films and metal carbides and their mechanical and tribological properties and suitable for some applications. A variety of methods such as plasma-assisted chemical vapor deposition (CVD), magnetron sputtering and ion beam assisted deposition (IBAD) have been developed to produce MeC/a-C:H films. Acetylene (C2H2) plasma ion immersion implantation and deposition (PIII&D) was used in this work to fabricate carbon films with better adhesion to the substrate. Tungsten ion implantation was subsequently conducted without breaking vacuum to produce WC/a-C:H films in which there is a gradual transition region between the WC and a-C:H. The composition and structure of the films were evaluated by X-ray photoelectron spectroscopy and glancing angle X-ray diffraction. High resolution transmission microcopy was adopted to investigate the structure transformation. The surface morphology was observed by atomic force microscope and the hardness by nanoindentation measurements. Our results indicate that in addition to the formation of WC nanocrystalline grains in the amorphous structure, high energy W ion implantation reduces the sp2 contents and consequently enhancesm the mechanical properties.

PS-TuP20 Effect of Multi-polar Magnetic Field on Properties of Nano-crystalline Silicon Thin Film Deposited by Large-area Internal ICP-PECVD, ***H.B. Kim***, *H.C. Lee, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Nano-crystalline silicon films have broadly been studied due to their applications to the thin-film-silicon solar cells and the TFT(Thin Film transistor) for the elimination of light induced degradation, the enhancement of long wave length response, and high electric mobility by comparison to amorphous silicon films. Especially, the deposition of nano-crystalline with a high deposition rate at the low temperature below 200°C is important. In other to realize the nano-crystalline silicon at a low temperature, a high density plasma such as inductively coupled plasma (ICP) is required. The conventional high density plasma sources have mainly been focused on the external ICP types, however, these sources show some problems in extending to a large area due to the very thick dielectric windows and standing wave effect. On the other hand, the use of an internal type antenna where the ICP antenna is inserted into the plasma gives more feasibility in depositing nano-crystalline silicon on the large area uniformly. And the application of multi-polar magnetic field is believed to improve the properties of the deposited film. In this study, as an internal type large-area plasma source, U-type internal linear ICP source using multi-polar magnetic field utilized to deposit nano-crystalline silicon on the glass substrate (370mm x 470mm) at the temperature below 200°C using H_2/SiH_4. ICP power of 13.56 MHz is in the rage of 100 W - 4000 W and the working pressure was varied from 10 to 60 mTorr. In this presentation, the variation of physical, chemical, and electrical properties of the nano-crystalline silicon deposited by the large area internal ICP with multi-polar magnetic field will be presented as compared to the source without multi-polar magnetic field.

PS-TuP21 Study on Plasma Assisted Metal-Organic Chemical Vapor Deposition of Ti(C,N) and Zr(C,N) Thin Films and In-Situ Plasma Diagnostics with Optical Emission Spectroscopy, *J.-H. Boo, C.-K. Jung, D.C. Lim, M.C. Kim, **S.J. Cho**, J.G. Han*, Sungkyunkwan University, Korea

Ti(C,N), Zr(C,N) films were synthesized by pulsed D.C. plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) using metal-organic compounds of tetrakis diethylamido titanium and tetrakis diethylamido zirconium at 200 °C to 300 °C. H_2 and $He+H_2$ gases were used as the carrier gases to compare plasma parameter. The effect of N_2 and NH_3 gases as reactive gas was also evaluated in reduction of C content of the films. Radical formation and ionization behaviors in plasma were analyzed by optical emission spectroscopy (OES) at various pulsed bias and gas conditions. He and H_2 mixture as carrier gas was very effective in enhancing ionization of radicals, especially N_2 resulting is high hardness. However, NH_3 as reactive gas highly reduced the formation of CN radical, there by decreasing C content of Ti(C,N) and Zr(C,N) films in a great deal. The hardness of film is obtained to be 1400 HK to 1700 HK depending on gas species and bias voltage. Higher hardness can be obtained for H_2 and N_2 gas atmosphere and bias voltage of 600 V. Plasma surface cleaning using N_2 gas prior to deposition appeared to increase adhesion of films on cold forming steel. The changes of plasma including radicals and film properties are illustrated in terms of carrier and reactive gases as well as pulsed power variation.

Keywords: Ti(C,N) and Zr(C,N) films, Low temperature pulse DC-PAMOCVD, Optical emission spectroscopy, High hardness

Advanced Surface Engineering

Room: 4C - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 Protective Coatings of Extensible Biofibers, ***N. Holten-Andersen***, *F. Zok, J.H. Waite*, University of California, Santa Barbara

As thin film coatings are increasingly finding their way in engineering and biomedical applications, the demand for unique combinations of their material properties is increasing as well. A coatings protection of the underlying substrate against wear relies on its resistance to penetration, i.e. its hardness. Increasing hardness of the coating however, significantly lowers its extensibility. Protecting substrates undergoing large strains against wear is therefore a challenge beyond the reach of current engineering coating applications. By investigating natural coating materials adapted to high- and low-stress environments we have studied nature's solution to this problem. In the protective cuticles of mussel holdfast threads (self-assembled biological fibers), high wear resistance have in wave-exposed species been combined with high extensibility. Here, we demonstrate that the inclusion of deformable micro-particles within a stiff protein matrix allows the cuticle of these holdfast threads to exhibit sufficient hardness against wear without encumbering the elasticity of the thread. This unique composite design results in an impressive damage tolerance by arresting developing micro-cracks thereby preventing catastrophic failure of the coating up until an astounding 70% strain. Cuticles from mussel species in deeper and calmer habitats lack these deformable particles and fracture below 30% strain. This increase in extensibility of the granular composite cuticle parallels the behavior observed with rubber toughened polymers such as High Impact Poly-Styrene. However, whereas the inclusion of rubber particles significantly compromises the hardness of these synthetic composites, our study shows that only a small reduction in hardness is observed in the biological coating composite. Interestingly, the interior morphology of the micro-particles in the cuticle shares a striking similarity with the bi-continuous network morphologies observed in polymer micro-emulsions and block copolymer systems. The superior mechanical properties together with the self-assembling nature of the material, makes this study significant for the broad materials community.

SE-TuP2 Optimization of Process Parameters using Matrix Assisted Pulsed Laser Evaporation (MAPLE) for Deposition of Carbon Nanoparticles, ***M.H. Check***, University of Dayton, *A.A. Voevodin, C.N. Hunter*, Air Force Research Laboratory, *J.J. Hu*, University of Dayton Research Institute

Matrix Assisted Pulsed Laser Evaporation (MAPLE) is a thin film deposition technique that can be applied to a large range of polymeric and biological substances. The advantage of using MAPLE compared to other laser techniques is that deposition can be accomplished with little or no damage to the transported material. The technology was explored for preparation of tribological coatings with carbon nanopearls (~150 nm in size) encapsulated in metal (Au and Ag) and ceramic (TiN) matrices. The focus was placed on understanding how to control transport and uniformity of nanopearls on the deposition surface. The controlling parameters included laser fluence (200-800 mJ), repetition rate (1-30 Hz), solvent material (methanol and isopropanol), and background gas composition and pressure (5-30 mTorr of Ar and N2 mix). The characteristics of the synthesized 1-2 micron thick carbon/metal and carbon/ceramic composite films were correlated with area fraction of the nanoparticles, degree of dispersion of the nanoparticles and effect of the transport process on the properties of the nanoparticles. Results from electron microscopy, optical profilometry, and XPS are discussed.

SE-TuP3 High Rate Deposition of Photocatalytic TiO_2 Films with High Activity by Hollow Cathode Gas-Flow Sputtering, ***Y. Kubo***, Aoyama Gakuin University, Japan, *Y. Iwabuchi, M. Yoshikawa,* Bridgestone Co., Japan, *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Titanium dioxide (TiO_2) has been well known as a photocatalyst because of the strong oxidizing power of photo-generated holes. Reactive sputter depositions using a Ti metal target should be one of the most promising techniques for uniform coatings in large area with high packing density and strong adhesion. However, the deposition rate is very small of 2~5 nm/min for the conventional reactive magnetron sputtering to deposit fully oxidized TiO$_2$ films because the films should be deposited at the "oxide mode" where the target surface is oxidized and the sputtering yield is very smal.[1] In order for the high deposition rate of 30~90 nm/min, we have been reported on dual cathode sputtering system[2] or unipolor pulsing system[3] with plasma emission control systems[2-3]. As the much simpler and lower cost system, TiO$_2$ films were deposited on unheated alkali-free glass substrates by gas-flow sputtering using two Ti metal targets which were mounted parallel with each other. Ar (sputtering gas) was supplied between these two targets.O$_2$ (reactive gas) was supplied in the vicinity of the substrate. Ar and O$_2$ flows were 3.0 SLM and 10~50 sccm, respectively, and total gas pressure during the depositions was maintained at 45 Pa. In such pressure mean free path of gas atoms is very small and a gas flow is in viscous regime, that is why the process has been named gas-flow sputtering.[4] The photocatalytic activity was evaluated by photo-decomposition of acetaldehyde and contact angle for water after UV illumination (black light lamp, 0.4 mW/cm^2). Both of the as-deposited films and the post-annealed films at 300 °C in air performed the photocatalytic decomposition. Especially the post-annealed films performed extremely high photocatalytic activities. The highest deposition rate to deposit such photocatalytic TiO$_2$ films were 162 nm/min.

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SE-TuP4 High Rate Deposition of Photocatalytic WO$_3$ Thin Films with Visible Light Activity by Gas-Flow Sputtering, ***M. Fukuyama***, *M. Kikuchi*, Aoyama Gakuin University, Japan, *Y. Iwabuchi*, *M. Yoshikawa*, Bridgestone Corporation, Japan, *Y. Sato*, *Y. Shigesato*, Aoyama Gakuin University, Japan

In recent years, we have been reported on the visible-light induced photocatalytic properties on polycrystalline WO$_3$ films deposited by reactive dc magnetron sputtering on heated glass substrate at around 600 oC.[1,2] However deposition rate was very low of about 10 nm/min for the conventional reactive magnetron sputtering to deposit fully oxidized WO$_3$ films because the films should be deposited at the "oxide mode" where the target surface is oxidized and the sputtering yield is very small. In this study, polycrystalline WO$_3$ films were deposited by on fused quartz glass substrate by gas flow sputtering using two W metal target which were mounted parallel with each other. Ar was used as sputtering gas and O$_2$ was used as reactive gas, which were supplied between these two targets. Total gas pressure was maintained at 70Pa. Ar and O$_2$ gas flows were 5.0 SLM and 50 sccm, respectively. WO3 films were deposited on the substrate without heating or heated upto 500 oC, 600 oC or 700 oC. The films deposited on the unheated substrate were post-annealed at 500 oC, 600 oC or 700 oC for an hour in the air. The crystal structure of the WO$_3$ films were analyzed by X-ray diffraction (XRD). The transmittance and reflectance of the films in UV-VIS region were measured using spectrophotometer in order to estimate absorption coefficient by Newton-Raphson's method. The photocatalytic activity was evaluated by decomposition of acetaldehyde and contact angle for water after UV (black light lamp : 0.4mW /cm^2, center wavelength : 352 nm) light and VIS (Xe lamp with a 410-500 nm band pass filter : 1.0, 7.0 mW/cm^2 respectively, center wavelength : 450 nm) light irradiation. Both of the films deposited at 500-700 oC and the films post-annealed at 500-700 oC performed the visible-light induced photocatalytic activity. The highest deposition rate to deposit such photocatalytic WO$_3$ films was 230nm/min.

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SE-TuP5 Photocatalysis of Dense and Porous Bilayers of Cuprite and Titania, ***M.H. Wu***, *M.S. Wong*, National Dong Hwa University, Taiwan

Titanium dioxide with anatase phase couples with different materials contributing better or worse photocatalysis. Transferring of electrons and holes in junction is caused by the different energy levels of conduction band and valence band. Dense and porous bilayers of cuprous oxide and titanium dioxide with various microstructures and thickness were prepared by magnetron sputtering and electron beam evaporation with glancing-angle deposition technique. The photocatalysis of the films was tested via photo-degradation of methylene blue. Porous columnar titania films covered with Cu2O layer allow good carrier transfer and high specific surface area, where the photo-generated electrons and holes can be separated and function at different area of the columnar structure, resulting better photocatalytic performance.

SE-TuP6 Preparation of TiO$_2$ Thin Films by Laser Ablation for Photocatalytic Applications, *W.-T. Chang*, ***J.-Y. Ciou***, National Dong Hwa University, Taiwan, *S.-J. Wang*, National Taipei University of Technology, Taiwan, *M.-K. Wei*, *M.S. Wong*, National Dong Hwa University, Taiwan

Thin titanium dioxide (TiO2) films were deposited by KrF excimer laser ablation deposition system using a titanium oxide target. The effects of substrate temperature and oxygen partial pressure on the phase formations of various microstructures were investigated by X-Ray diffraction (XRD), scanning electron microscopy (SEM), Raman scattering spectroscopy and UV-Vis spectrophotometer, respectively. Increasing the substrate temperature can improve the quality of anatase phase of crystalline TiO2 films that were obtained from the amorphous structure hybridized with rutile and anatase phases. However, the oxygen pressure in the range between 15 to 60 mTorr shows a single anatase phase in TiO2 films that the rutile and anatase phases were observed elsewhere. The bandgap of TiO2 films varied from 2.72eV to 3.27 eV with more oxygen partial pressure in the film deposition indicates the phase changed from rutile phase to anatase phase. The surface area of TiO2 films was increased as more oxygen partial pressure involved in the fabrication. The photocatalytic effect measured by exposing the methylene blue in UV light that was distinguishable in the TiO2 films with high anatase phases and surface area.

SE-TuP7 Effect of Internal Pressures for TiO$_2$ based Colloidal Sols during Hydrothermal Process, ***C.R. Yoon***, *H.J. Oh*, *N.H. Lee*, *Y. Guo*, *S.J. Kim*, Sejong University, Korea

Transparent TiO$_2$ sols were prepared by hydrothermal synthesis to heat Ti precursor solutions, from Ti hydroxides obtained with neutralizing aqueous TiOCl$_2$ solutions having various concentrations of NaCl by aqueous NaOH solution, in the autoclave at 120°C, and then their photocatalytic abilities using glass beads coated with the sol for gaseous benzene were evaluated. Because it was possible to prepare brookite phase TiO$_2$ sol by external pressurization into the autoclave during the synthesis, the internal pressure in the autoclave was controlled using a technique with capturing Na ions in the lattice of Ti hydroxide. As a result, it was found that due to the increase of brookite phase in TiO$_2$ by controlling the concentration of Na ion the optical absorption of TiO$_2$ increases toward long wavelength but that in the range of short wavelength becomes relatively low and consequently the photocatalytic performance of TiO$_2$ thin film for benzene gas rather decreases, compared to that of composite film of anatase and brookite phases. These results suggest that in order for coated TiO$_2$ thin film to have high dissociation performance for benzene gas it is effective to form anatase and brookite phases compositely in TiO$_2$.

SE-TuP8 Photoinduced Friction Force Variation of Polycrystalline Anatase Thin Films, ***N. Arimitsu***, *A. Nakajima*, *Y. Kameshima*, *K. Okada*, Tokyo Institute of Technology, Japan

Titanium dioxide (TiO$_2$) thin film has attracted much attention as a photocatalyst. TiO$_2$ surface exhibits conventional photocatalytic oxidation reactions and photoinduced highly hydrophilic conversion. These reactions result in useful properties such as antibacterial functions, self-cleaning, and antifogging. The photoinduced reaction on TiO$_2$ surface has been well studied by various techniques. According to a friction force microscopy (FFM) study using a Si$_3$N$_4$ cantilever, it was revealed that rutile single crystal produce a unique microdomain structure in the surface with a contrast difference by UV illumination.[1] Since the tip of the cantilever is hydrophilic, the image contrast implies the difference in hydrophilicity on the surface. Recently, it is reported that the contrast difference after UV illumination was also obtainable on polycrystalline anatase thin film as in the case of rutile single crystal.[2] In the present study, we prepared polycrystalline anatase thin films on Si substrates using sol-gel process and O$_2$ plasma treatment[3] and investigated the relationship between photoinduced friction force change and photoinduced hydrophilicity of the film. The photoinduced friction force change was evaluated by FFM with a Si$_3$N$_4$ cantilever. Upon UV illumination, the average friction force decreased gradually with decreasing water contact angle until it reached the lower limit. Then, the friction force began to increase with increasing UV illumination time. Detailed relationship among contact angle change, UV illumination period, and friction force change will be discussed.

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SE-TuP9 Pretreatment by High Power Impulse Magnetron Sputtering - Interface Structure and Stress Evolution, ***D. Jädernäs***, *M. Lattemann*, *U. Helmersson*, Linköping University, Sweden

Substrate pretreatment using metal ion bombardment is an effective way of promoting film-substrate adhesion. In this work we have used high power impulse magnetron sputtering (HIPIMS) to produce the Cr-ions that are bombarding the high speed steel substrates with an applied negative substrate bias, U_b, between 200 and 1100 V. During pretreatment and subsequent film growth, the stress evolution was measured and the adhesion of the films was evaluated using scratch testing. Some samples were also post-annealed at a temperature of 900 K. The results showed that all pretreatment conditions result in a compressive stress that can be correlated to U_b. The stress induced during pretreatment was also shown to affect the growth of the subsequently grown film. For U_b below 600 V significant etching did not occur and a Cr-layer was formed. In this case, the native oxide on the steel remained. For higher U_b values the oxide layer was removed. For the non-annealed films a strong correlation between U_b and adhesion was observed. Substrates with the oxide layer intact showed low film adhesion. After annealing all samples showed an increased adhesion and no clear trend between different pretreatments and adhesion could be observed. The interfacial chemistry and structure were examined in order to find the correlation between structure, chemistry and adhesion. The results show that strong interfaces, capable of resisting an applied force, can be produced even though an oxide is still present.

SE-TuP10 Nanostructure and Properties of TiAlN/a-C Composite Coatings, ***M. Nose***, *T. Kawabata*, University of Toyama, Japan, *S. Khamthe*, Graduate School of Science and Engineering, Japan, *K. Matsuda*, *T. Nagae*, *S. Ikeno*, University of Toyama, Japan, *K. Nogi*, Osaka University, Japan

Aluminum/magnesium pressure die-casting needs protective coatings to the molding dies in order to extend die life. When applied to cast liquid aluminum or magnesium alloy into molding parts, die surface faced harsh conditions such as soldering and erosion at temperatures over 600 ºC. DLC (diamond like carbon) or a-C (amorphous carbon) coating has been widely applied to machine-tools for aluminum, due to enhanced tribological properties in terms of low friction, high hardness and non-affinity to aluminum. However, DLC or a-C becomes thermally unstable at temperatures higher than 300 ºC when coating hardness drastically drops with temperature. Nanocomposite coatings consisting of transition metal nitride/carbide and amorphous carbon are expected to be stable at higher temperatures and to reduce adhesion of nonferrous alloy. In this study, TiAlN/C nano-composite coatings synthesized by PVD process were examined the effects of sputtering conditions on the microstructure and mechanical properties, and evaluated as potential applications in molding dies. Coating films were synthesized by the co-sputtering of TiAl (pulsed-d.c. sputtering) and C (d.c. sputtering) targets using a Facing Target-type Sputtering system (FTR-2, Osaka Vacuum Co., Ltd.) under an environment with a mixture of Ar and N_2 on square plates of Si and high speed steel (ANSI M2). The structure of the films was investigated by means of XRD, XPS and HRTEM with GIF (Gatan Imaging Filter). Mechanical properties of coating films were measured in detail by a submicron indentation system (H-100, Fischer). Although TiAlN or a-C films showed hardness of about 30 or 10 GPa, one of TiAlN/a-C films containing several % of a-C showed higher hardness of 43 GPa. The Zero-loss image indicated that a change of contrast accompanies the change of composition of Ti and Al. Nanometer-size of Al agglomerates were observed and Ti distribution corresponded to that of Al. XPS analysis of C1s spectrum revealed that carbon in the films bound almost as C-C with a few bondings of Ti-C or Al-C and C-N. Ti2p and Al2p spectrum indicated that these transition metals bound mostly with nitrogen. These results indicated that nano-composite structure consisting of complicated mixture of nanocrystalline Ti-Al-N phase and a-C phase (with a small amount of C:N phase and metal carbide phase) existed in the TiAlN/a-C films.

SE-TuP11 Wear Behavior of Unbalanced Magnetron Sputtered Multilayer CrN/TiAlYN Coatings Deposited on Plasma Nitrided Steels, ***M. Flores***, *E. Rodriguez*, Universidad de Guadalajara, México, *E. De las Heras*, *P. Corengia*, Instituto Nacional de Tecnología Industrial, Argentina, *L. Huerta*, Universidad Nacional Autonoma de México

The influence of pretreatment on the wear behavior of tool steels coated with TiN, CrN and CrN/TiAlYN multilayers were experimentally investigated. The substrate materials were nitrided using plasma nitriding. The thin films were deposited using unbalanced magnetron sputtering technique. A comparison between the wear resistances of nitrided, coated, nitrided and coated samples were made. The nitrided coatings and CrN/TiAlYN multilayer grown on pulse plasma nitriding steels have been characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM), micro-indentation and abrasive wear tests. The depth profiles were studied by X-ray photoelectron spectroscopy (XPS) and Rutherford Backscattering spectroscopy (RBS). The duplex coatings showed a low wear respect to the coated samples. The out-performance of the prenitrided TiN, CrN and CrN/TiAlYN coatings can be attributed to the presence of a nitrided subsurface.

SE-TuP12 Power Supplies to Enable High Power Impulse Magnetron Sputtering, ***D. Ochs***, HÜTTINGER Elektronik GmbH, Freiburg, Germany, *R. Spencer*, Alacritas Consultancy Ltd., Leicestershire, U.K.

High Power Impulse Sputtering (HIPIMS or HPPMS) receives more and more attention as a technique to produce very dense films. It relies on the creation of high density plasma in front of the sputtering source and by that way a large fraction of the sputtered atoms are ionized. These ionized atoms can be used for surface pretreatment and deposition as well. The interfaces and layers so produced show superior properties in many applications. Currently the most investigated and promising application is use for hard coatings as wear and corrosion protection. Popular layers are for example CrN and TiN. To enable the HIPIMS process a specially designed power supply for powering the magnetron cathode is needed. This power supply consists of 3 modules. The DC module contains a converter which charges a capacitor bank in the pulse module. A semiconductor switch is activated by the pulse control unit. The third module is an impedance matching circuit to shape the output current pulse in order to match the requirements of the cathode. Several power supply configurations have been realized in order to fulfill the different process needs. HIPIMS power supplies with a max. pulse power of up to 18MW, a voltage of 1kV to 3kV and a current of 1kA to 6kA will be presented with practical results from industrial coating applications.

Surface Science

Room: 4C - Session SS-TuP

Surface Science Poster Session

SS-TuP1 Size-Selected Deposition of $Mo_6S_8^+$ on Au(111), ***M.J. Patterson***, Stony Brook University, *M.G. White*, Brookhaven National Laboratory

Nanoscale MoS_2 has a layered assembly that shows a high propensity towards folding, forming hollow nanotube and fullerene structures which display a wide range of catalytic, photovoltaic, and lubricant properties.[1-3] Supported MoS_2 nanoparticles are known for their ability to catalyze a wide array of heterogenous reactions, in particular hydrodesulfurization (HDS).[4-5] However, understanding the role of size, structure, and overall composition of the MoS_2 particles in HDS has not yet been resolved due to the inhomogeneity of these commercial catalysts. Work done in our laboratory is geared towards preparing homogenous samples in ultra high vacuum (UHV) that can serve as model systems for these types of catalytic reactions. We are currently investigating the reactivity of size-selected transition metal clusters generated in the gas-phase and deposited on a Au(111) surface. Using a magnetron cluster source, we are able to produce a wide range of nanoparticle stoichiometries including the metal sulfide core of the superconducting Chevrel phase[6], $Mo_6S_8^+$. The work presented here focuses on characterization of the $Mo_6S_8^+$ cluster deposited on a Au(111) single crystal using surface science techniques such as TPD, AES, XPS, and UPS.

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SS-TuP2 Preparation and Characterization of Au Nanoparticle, ***G. Kutluk***, Hiroshima University, Japan, *S. Yagi*, Nagoya University, Japan, *H. Sumida*, Mazda Motor Co., Japan, *H. Namatame*, *M. Taniguchi*, Hiroshima University, Japan

Gold highly dispersed on metal oxide supports has unexpectedly been found to be highly active for a number of catalytic reactions. However, the electronic nature of the gold species in active catalysts has not been fully elucidated. We have applied a modified version of the gas phase condensation combined with Arc plasma method for the metal nanoparticle synthesis. Which is not only convenient in synthesizing highly dispersive metal nanoparticle with cleaner surface but also is suitable for the size controlling. In addition, this method also shows advantage in synthesizing metal nanoparticle with simple shape on a supporting material (Si Ta, TaN). The performance of the gas phase condensation and Arc plasma method for the size control has been confirmed in the earlier work.[1] In this study, we report the investigations of the thermal stabilities, crystallographic structure and the size dependence of electronic structures of Au nanoparticle in range of 1.5 ~ 5nm in diameter. The Au nanoparticle were characterized by the TEM, AFM, XPS and UPS. Drastic change have observed in the 4f level photoemission spectrum when the size of Au particle down to 1.5nm. The spectrum is characterized by component of an oxidized doublet states of Au_2O_3 coexisting with the doublet states of pure Au. The vanishing of component of Au_2O_3 doublets has been observed with increasing the annealing temperature of the sample in the reduction atmosphere.

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SS-TuP3 Surface Reaction of $(CH_3S)_2$ /Rh(100) Depending on Adsorption Coverage Studied by XPS and NEXAFS

O. Sumi*, T. Nomoto, S. Yagi, K. Soda,* Nagoya University, Japan*, H. Namatame, M. Taniguchi*, Hiroshima University, Japan

The automobile exhaust catalysts oxidize and/or reduce the exhaust gases, such as CO, C_xH_y and NO_x. As know as Sulfur Poisoning, the sulfur-containing molecules that originate from fuels affect the reactivity of noble metals (Rh, Pt and Pd), which are capital components of the catalysts. There are some reports that Rh has the highest resistance to the Sulfur Poisoning among those noble metals. However there are a few reports that have an interest in adsorption reaction of sulfur-containing molecules at low temperature. Therefore it is important to investigate the reaction mechanism. In this report, we reveal the surface reaction of dimethyl disulfide (DMDS) on the Rh(100) surface using XPS and NEXAFS techniques. The clean Rh(100) single crystal was cooled down to 90 K and subsequently exposed to DMDS. DMDS coverage was controlled to 0.44 ML, 0.32 ML and multilayer. As a result of the XPS spectra at 0.44 ML, DMDS molecules are decomposed into methanethiolate and atomic S at 90 K. Methanethiolate is generated by the dissociation of S-S bond and partial methanthiolate dissociates into atomic S and methyl. After heating up to 170 K, XPS results indicate that some of methanethiolate desorbs. At 0.32 ML, DMDS molecules are also decomposed into methanethiolate and atomic S at 90 K. However the ratio of atomic S has increased and methanethiolate does not desorb but dissociates into atomic S at 170 K. These results indicate that the surface reaction depends on initial DMDS coverage. Polarization dependent S K-edge NEXAFS spectra for submonolayer at 90 K show that the peak intensity of σ*(S-C) at 90° is larger than that of 20°. This results indicates that the coordination angle of σ*(S-C) should be almost lying on Rh(100) surface.

SS-TuP4 XPS and NEXAFS Studies for Co-Adsorption Reaction of Dimethyl-Disulfide and Water on Rh(100)

S. Yagi*, O. Sumi, T. Nomoto, K. Soda,* Nagoya University, Japan*, H. Namatame, M. Taniguchi*, Hiroshima University, Japan

It is an important reaction that water molecule plays some interaction in the bio-body. There are many sulfur-including molecules in the bio-body, such as L-cysteine amino acid. Is there any interaction between the sulfur-including molecule and water? We have pay attention to the interaction of the co-adsorption system, the sulfur-including molecule and water, on the transition metal surface. For the bio amino molecule of L-cysteine, it is reported that the L-cysteine molecule has an interaction with water molecule on transition metal surface.[1] For the adsorbate of L-cysteine on NI and Cu surfaces, the S-H bond dissociates and becomes thiolate form. It is found that the oo-adsorbed water molecule has a new bonding with the sulfur of the thiolate. Because the Sulfur K-edge Near-edge X-ray Absorption Fine Structure (NEXAFS) shows sigma*(S-O) peak at 2482 eV. It seems that there are bondings of three or four water molecules at the sulfur part of the thiolate. The adsorption systems of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) on Rh(100) surface have been investigated by T. Nomoto[2,3] and O. Sumi[4] by XPS and NEXAFS. For both adsorption systems, the adsorption molecules partly dissociates and becomes thiolate and atomic sulfur on the surface at 90 K. In this paper, the aim is to reveal the co-adsorption reaction of DMDS and water molecules on Rh(100) at 90 K by means of XPS and Sulfur K-edge NEXAFS techniques. Judging from the spectral results of XPS and NEXAFS, it is found that DMDS molecules partly dissociate and the adsorbates are the thiolate and atomic sulfur. In case of the co-adsorption with water, it is cleared that water molecule does not have an interaction with the atomic sulfur, but has a bonding with the thiolate.

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SS-TuP5 Illuminating Analysis of Observed Low-Dimensional Plasmons in an Array of Metallic Quantum Wires

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Using self-assembly of adsorbed Au atoms on vicinal surfaces of Si(111) with regular step rows, one can form a regular array of Au atom chains at interval of 1.91 nm on a Si(557) surface. Each atom chain of alternating Au and Si atoms embedded in the topmost Si layer of the terrace creates a one-dimensional (1D) surface-state band of metallic character. Conduction electrons in this band are confined in a narrow region one-atom wide. This array of metallic quantum wires sustains low-dimensional plasmons (PL's), namely, 1D PL's interacting with one another, and strong 1D confinement enhances the exchange-correlation (XC) effect on the PL's. In our previous work, by means of electron energy-loss spectroscopy (EELS) with a high wave-number resolution, we measured the low-dimensional PL's in the quantum-wire array.[1] In the present work, taking account of the interwire interaction and the XC effect, we investigate the dynamical response of the wire array to a probe electron in EELS. To consider the XC effect, we apply a self-consistent local-field-correction (LFC) theory to the wire array.[2] Although the interwire interaction is so significant as to produce a considerable distribution of the PL-mode energy, the calculated PL energy dispersion in EELS agrees with the dispersion of a single isolated wire. This paradox can be ascribed to the fact that the external potential generated by the probe electron is localized so sharply as to act and to produce substantial induced charges only on one or two wires. The calculated dispersion gives a complete explanation of the observed sound-wave character. By comparing the results of the LFC calculation with those of the Random-phase-approximation calculation, we evaluate the XC effect. This effect is found to operate to lower the PL energy and to heighten the energy-loss intensity in EELS. Our analysis can reproduce quantitatively the observed energy dispersion and energy-loss intensity.

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SS-TuP6 STM Study of Temperature Effect on Electron Induced Hopping Motion of CO/Cu(110)

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Scanning tunneling microscope (STM) enabled the observation and manipulation of the single isolated molecule, and we can follow the molecular motion precisely with its high spatial resolution (~ 0.1 nm).[1] In this study, we investigated hopping motion of carbon monoxide (CO) on metal surface, which is one of the most simple and fundamental molecular motions at surfaces. Same as thermal diffusion, vibrations of the adsorbates are important because some vibrations couple with surface motions strongly. For example, a study using STM has revealed that internal stretching vibration of CO on Pd(110) (~ 250 meV) plays an important role.[2] We can control the energy of innelasticaly tunneled electrons from the tip of STM precisely, and those electrons can excite the vibration of aimed molecule. And recently, time resolved SFG study on Pt(553) has revealed that hindered rotation mode of CO (~ 51 meV) also contributes to hopping motion.[3] They performed the experiment at 100 K where hindered translation mode (~ 4 meV) is thermally excited enough. We took notice of this temperature effect. We performed the experiments at 4.8 ~ 45 K using STM (LT-STM, Omicron GmbH) equipped in an ultrahigh-vacuum chamber ($< 3\times10^{-9}$ Pa). The Cu(110) surface was cleaned by cycles of Ar ion sputtering and annealing cycles, and exposed to CO molecules below 50 K. First, by Inelastic Electron Tunneling Spectroscopy (STM-IETS) on CO/Cu(110) obtained at 4.8 K, the vibrational peaks of two surface parallel vibrations (hindered translation and hindered rotation) are clearly observed. Then, I tried Action spectroscopy on single CO molecule at various temperatures. In that spectra, the sudden change of the yields of hopping motion which corresponds to the internal stretching vibration of CO was observed. It means that anharmonic coupling between vibrations enables hopping motion of CO on Cu(110) surface easily. And temperature dependence of the yields of hopping motion does not obey the simple Arrhenius law. In the presentation, I will discuss the coupling between vibrations and molecular motions from these results.

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SS-TuP7 Effects of Interadsorbate Interactions on Surface Resistivity: Oxygen on Sulfur-Predosed Epitaxial Cu(100)

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Measurements of surface resistivity for oxygen absorbed on sulfur-predosed epitaxial Cu(100) reveal the existence and properties of two types of interadsorbate interactions between sulfur and oxygen: S-O repulsion and scattering suppression. The repulsive interaction causes oxygen atoms to first occupy adsorption sites far from the sulfur atoms. As a result the low-coverage variation of surface resistivity with oxygen coverage is unaffected by predosed sulfur, showing the linear dependence previously observed for oxygen on clean Cu(100).[1] As the oxygen coverage increases, oxygen begins to occupy sites near the sulfur atoms. At these sites the resistivity effect of the oxygen atoms is strongly suppressed, so that the sample resistance levels off, remaining unchanged even as oxygen continues to adsorb on the surface. With increasing sulfur precoverage both the maximum resistivity change and the oxygen coverage at which the leveling occurs decrease, because the number of sites unaffected by sulfur is reduced. Both the S-O repulsion and the scattering suppression have an effective range on the order of about 1.4 lattice spacings, with a rather sharp boundary. Both interactions presumably arise from a through-metal coupling involving the metal's local density of states.

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SS-TuP8 Wettability and Chemical Bonding of Water and Hydroxyl at Metal Surfaces, ***T. Schiros,*** Stanford Synchrotron Radiation Laboratory, *O. Takahashi,* Hiroshima University, Japan, *K. Andersson,* DTU/Center for Individual Nanoparticle Functions, Denmark, *H. Öström,* Stockholm University, Sweden, *S. Yamamoto, L.-Å Näslund,* Stanford Synchrotron Radiation Laboratory, *L.G.M. Pettersson,* Stockholm University, Sweden, *A. Nilsson, H. Ogasawara*, Stanford Synchrotron Radiation Laboratory

The nature of the chemical bonding and structure of water and water co-adsorbed with hydroxyl at metal surfaces is of immense relevance to a number of important reactions in heterogeneous catalysis, including the water gas shift reaction over Cu and the fuel cell reaction over Pt and related alloys. We have combined core level x-ray spectroscopy, in both UHV and near-ambient conditions, with density functional theory to derive a detailed picture and comparison of the interaction of water and water plus hydroxyl with different metal surfaces, including Cu(110), Cu(111) and Pt(111). We demonstrate that the ability to form water-metal bonds, or wettability, is controlled by the degree of Pauli repulsion, which is influenced by both the electronic and geometric structure of substrates. At near ambient conditions, formation of OH groups by pre-adsorbed oxygen significantly modifies the ability to form water-metal bonds and plays a decisive role in the wetting of metal surfaces.

SS-TuP9 Low Temperature Microcalorimetry to Measure the Heat of Adsorption of Cyclohexene, Cis and Trans 2-Butene on Pt(111), *O. Lytken,* ***W. Lew****, J.W. Harris, E.K. Vestergaard, C.T. Campbell*, University of Washington

The hydrogenation and dehydrogenation of cyclic hydrocarbons and short chain alkenes on platinum catalysts are important petrochemical reactions. We have used low temperature microcalorimetry measurements to determine their enthalpy of adsorption and sticking probability on Pt(111) at 100 K. Cyclohexene adsorbs intact at surface temperatures below 180 K, but decomposes at higher temperatures via several intermediates, including benzene and hydrogen starting at ~300 K. Trans-butene adsorbs intact below 200 K and cis butane adsorbs intact below 230 K. The difference between the heat of adsorption energy of the two isomers is compared with results from Zaera et al.[1] Since cyclohexene and butene both adsorb irreversibly on platinum, the traditional method to measure adsorption enthalpies, Temperature Programmed Desorption (TPD), cannot be used. Low temperature microcalorimetry makes it possible to measure the heats of formation of important reaction intermediates that are frequently unstable at room temperature. One of the major challenges of conducting low temperature calorimetric studies for small heats of adsorption is getting the microcalorimeter to detect small temperature changes on the order of 10 milliKelvins with minimal noise. This study explores modifications to the microcalorimetry apparatus to detect small adsorption energies.

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SS-TuP10 Electron Correlation Effects in Co Nano-Islands on a Nitrogen Covered Cu(001) Surface, ***Y. Takagi,*** RIKEN, SPring-8 Center, Japan, *K. Nakatsuji, Y. Yoshimoto, D. Sekiba,* University of Tokyo, Japan, *Y. Harada,* RIKEN, SPring-8 Center, Japan, *K. Amemiya,* University of Tokyo, Japan, *Y. Takata,* RIKEN, SPring-8 Center, Japan, *T. Ohta,* University of Tokyo, Japan, *S. Shin,* RIKEN, SPring-8 Center and University of Tokyo, Japan, *F. Komori*, University of Tokyo, Japan

Recently, the atomic and electronic structures of magnetic nano-structure on surfaces have been intensively studied. We have investigated the initial growth of Co nano-islands on a nitrogen saturated Cu(001) c(2x2)-N surface by scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy and found that the nitrogen segregates on top of the Co islands and form Co-c(2x2)N structure.[1] In the present study, we discuss the electronic structure of this system in terms of electron correlation effect investigated by x-ray absorption spectroscopy (XAS) at both Co 2p and N 1s absorption edges comparing with the growth process studied by STM. N 1s XAS spectrum shows gradual increase of the absorption intensity just above the Fermi level with the increase of Co coverage. This indicates that the bonding of N 2p with Cu 3d changed into that with Co 3d which has smaller number of d electrons than Cu. The result strongly supports the segregation of N atoms. In the Co 2p XAS spectrum, a shoulder-like structure was found at 3 eV higher energy side of the main peak both at L_3 and L_2 absorption edges. Its relative intensity of this "3 eV satellite" to the main peak gradually decreases with Co coverage below 2 ML on average. In the case of Ni thin film, the origin of 3 eV and 6 eV satellites in the Ni 2p XAS spectrum are attributed to the configuration interaction of correlated electrons (CI) and multiple scattering in absorption process (MS), respectively.[2] We simulated XAS spectrum including the MS effect by FEFF code with the optimized atomic structure parameters obtained from first-principles calculation. However, the experimental results were not reproduced. Therefore, the origin of 3 eV satellites in our case is considered to be CI, indicating the presence of d^7 configuration as well as d^8. Comparing with the STM observation, the satellite is attributed to the mono-atomic height isolated Co-N islands. In such small islands, the charge transfer between Co and N would be different from that in the larger islands possibly by lattice compression.

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SS-TuP11 LEED and XPS Investigations of Surface Alloying of Ir on Cu(110), *P.F. Lyman,* ***S.S. Parihar***, University of Wisconsin-Milwaukee

Subsurface alloying is an interesting phenomenon that has been observed for several transition metals deposited on noble-metal surfaces, even where there is no bulk solubility of the two metals. In particular, while the bulk phase diagram of Ir-Cu has a large miscibility gap, subsurface alloying has been observed for Ir/Cu(100).[1,2] The Ir atoms appear to occupy ordered subsurface sites, forming a (2x1) reconstruction, with the required atomic place exchange taking place even for deposition at 200 K.[1] In the second layer, Ir and Cu atoms form Ir-Ir and Cu-Cu chains along every other close-packed direction. We evaporated submonolayer to monolayer Ir films on clean Cu(110) surfaces, and investigated the Ir-induced reconstruction using low energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). The (1x1) LEED pattern changes into a (2x1) pattern for Ir coverages of close to half a monolayer. We expect that the Ir will still be confined to the near-surface region by the lack of bulk solubility, and we hypothesize that the Ir atoms will occupy subsurface sites based on their behavior on Cu(100). Based on LEED and XPS results, we propose that Cu and Ir form Ir-Cu-Ir-Cu chains along the close-packed direction for Ir/Cu(110)-(2x1), in contrast to the finding for Ir/Cu(100)-(2x1).

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SS-TuP12 Surface Diffusion of Hydrogen Atoms on Cu(111) Studied by Optical Diffraction from Hydrogen Density Patterns formed on Removable Templates of Xenon Monolayers, ***Y.Y. Fei,*** *X.D. Zhu*, University of California at Davis

We formed grating-like patterns of hydrogen adatom density on Cu(111) by using complementary patterns of xenon adatom density as the template. The template was pre-formed by laser-induced thermal desorption of a Xe monolayer on Cu(111) using the interference pattern of two coherent laser pulses. By following the evolution of hydrogen density gratings on Cu(111) from 153 to 183 K with linear optical diffraction, we found that the diffusion of hydrogen atoms on Cu(111) in this temperature range is the classical over-barrier hopping characterized by an activation energy barrier $E_{diff} = 6.4$ kcal/mol (or 279 meV) and a pre-exponential factor $D_0 = 2.0 \times 10^{-3}$ cm^2/sec. Based on the potential model proposed by Basdescu and coworkers for hydrogen on Ni(111), the WKB tunneling coefficient between the first vibrational excited states of a hydrogen adatom on Cu(111) is expected to be at least one order of magnitude smaller than that on Ni(111), indicating that the classical over-barrier hopping of hydrogen atoms could directly cross-over to under-barrier tunneling between ground-states on Cu(111).

SS-TuP13 Surface Temperature Dependence of Methane Dissociation on Ni, ***V.L. Campbell,*** *A.L. Utz*, Tufts University

The past decade has seen major groundbreaking work in the understanding of the role vibrational energy plays in the dissociation of methane on nickel surfaces. Yet, little work has been done on developing an understanding of the effect of surface temperature on this reaction. Two questions remain regarding the energy contained in the surface: First, how does the thermal bath of the surface atoms couple to the reaction coordinate? Second, does dislocation of the surface atoms alter the distribution of barriers to dissociation? Recent theoretical work suggests that the system is able to access lower barriers when the surface atoms are displaced above the plane of the surface. A change in the location of the Ni surface atom below the incident methane molecule could result in a lower energetic barrier making the reaction much more probable. As the surface temperature is increased, the probability of the incident methane molecule impacting on a displaced Ni atom increases. Experimentally, the biggest hurdle in understanding the dynamics that surface temperature plays in reactivity is deconvolting the gas-phase dynamics from the surface temperature dynamics. In thermal bulb experiments, it is not possible to discern the role of energy in the gas-phase comparatively to that of energy of the surface. Supersonic molecular beam experiments allow independent control of both the surface temperature, the impact energy and the average vibrational energy of the incident gas-phase molecules. Additionally, we use a narrow-bandwidth IR laser to prepare a non-equilibrium distribution of vibrational states, which allows us to determine the reactivity of select rovibrational eigenstates of the methane molecules over a range of incident kinetic energies and surface temperatures. The overall goal of these experiments is to determine the coupling of the vibrationally excited methane molecules to the phonon bath of the surface atoms and see what impact different surface temperatures have on reactivity.

SS-TuP14 Vibrational Effects on Precursor Mediated Surface Reactions, ***D.F. Del Sesto***, *C.R. Thomas, N. Chen, A.L. Utz*, Tufts University

At high translational energies, methane dissociation on metal surfaces is generally shown to be dominated by a direct mechanism. The majority of methane molecules in a steam-reforming reactor have little translational energy, but are vibrationally excited. The vibrational energy content of these molecules is significant relative to the barrier to dissociation. In contrast, low translational energy molecules in conventional beam surface experiments are predominantly in the vibrational ground state. We propose experiments to explore the possibility that a precursor mechanism involving vibrationally excited molecules may be an important contributor to methane activation on metal surfaces at the high temperatures characteristic of industrial steam reforming reactors.

SS-TuP15 XPS Study of the Early-stage Oxidation Behavior of (Pt, Ni)$_3$Al(111) Surfaces in Air, ***F. Qin***, Iowa State University and Ames Laboratory, *J.W. Anderegg, C.J. Jenks,* Ames Laboratory, *B. Glesson,* Iowa State University, *D.J. Sordelet,* Ames Laboratory, *P.A. Thiel*, Iowa State University and Ames Laboratory

We have studied the early stage of oxide formation on (111) oriented (Pt, Ni)$_3$Al single crystals in air. From X-ray photoelectron spectroscopy (XPS), the predominant surface oxide changed from NiO to Al$_2$O$_3$, as oxidation temperature increased from 900 to 1300 K. Some NiAl$_2$O$_4$(spinel) also formed at the higher temperatures. Under conditions where NiO and/or NiAl$_2$O$_4$ was present, it resided atop a layer of aluminum oxide, mixed in some cases with metallic Ni. By comparing samples that contained 0, 10 and 20 at. % Pt in the bulk, we found that the effects of Pt were to (1) promote the preferential formation of aluminum oxide over nickel oxide(s) in the top layer at all temperatures studied, (2) suppress the amount of metallic Ni mixed with Al$_2$O$_3$ in the underlying oxide region, (3) reduce the total oxide layer thickness, and (4) sharpen the interface between the oxide and the metallic alloy. The effects of Pt probably arise from a combination of sources: The non-oxidizing nature of Pt relative to Ni or Al; the substitution of Pt for Ni that occurs in the Ni$_3$Al lattice structure; and the increase in Al activity that is induced by Pt.

SS-TuP16 Ion Beam-Induced Formation and Interrogation of Metal Nanoclusters, ***J.A. Yarmoff,*** *A.B. Arjad, P. Karmakar, G.F. Liu,* University of California, Riverside, *Z. Sroubek*, Czech Academy of Sciences

Metal nanoclusters are important systems that display quantum size effects and have remarkable catalytic activity. We utilize low energy (0.5-5 keV) ion beams as a simple, but efficient means for both the controlled production and the characterization of nanoclusters. Low energy Ar$^+$ beams enable control of the size and shape of nanoclusters because of the curvature dependence of ion sputtering. The neutralization of scattered low energy alkali ions provides a sensitive measure of the localized electronic states. It was previously shown that scattered alkalis couple to atomic-like states specific to Au nanoclusters grown by deposition, and the neutralization probability is a function of the cluster size.[1] We further showed that sputtering a thin Au film on TiO$_2$(110) with Ar$^+$ forms self-organized nanoclusters that display quantum size effects.[2] The scattered alkali neutral fractions increase as the cluster dimensions decrease, indicative of the quantum size effects, and the data shows that the electronic structure of clusters grown by deposition and by sputtering are similar. In this work, Li$^+$, Na$^+$ and K$^+$ ions are employed to probe metal nanoclusters formed by both deposition and sputtering, and the dependence of neutralization on cluster size is compared. Au or Ag is first deposited on an insulating or semiconducting substrate, and self-organized clusters are produced either during the deposition, or by Ar$^+$ sputtering a thin film. The ion scattering NF's have different dependences with respect to cluster size for each alkali projectile. The microscopic mechanisms responsible for the formation of the nanoclusters, and for the charge exchange between scattered alkali ions and the nanoclusters, will be discussed.

[1] G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 92, 216801 (2004).

[2] P. Karmakar, G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 98, 215502 (2007).

SS-TuP17 The Formation of Iron Oxide Nanoparticles and Thin Films on Au(111), ***N.A. Khan***, *C. Matranga*, National Energy Technology Laboratory (NETL)

Iron-based catalysts, including iron oxides, are an important class of materials with relevance to Fischer-Tropsch catalysis and gas-sensing applications. The controlled growth of nanoparticles and atomically thin films on single crystal surfaces allows for systematic studies of how size, shape, and atomic structure affect the chemical reactivity of these materials. We have studied the formation of monolayer thick iron oxide nanoparticles and thin films on the reconstructed Au(111) surface. STM, XPS, ISS, and LEED were used to evaluate the structure and composition of the iron oxide nanoparticles and films as a function of growth conditions. Iron oxide growth was achieved by first depositing iron nanoparticles on Au(111) at room temperature. At coverages of 0.2-0.5 monolayer (ML), Fe forms triangular islands at the elbows of the Au(111) herringbone reconstruction. At higher coverages, the particles begin to coalesce and the second and third layers of Fe start to form before the first layer is complete. The oxidation of Fe was performed by exposing the nanoparticles to molecular oxygen at 323 K and 423 K, followed by annealing to 500-700 K. XPS results indicate that the Fe is oxidized, with a shift of the Fe 2p peak to a higher binding energy. Atomically-resolved STM images show the formation of iron oxide particles that are hexagonal in shape and one monolayer high with a diameter of 10-20 nm. STM images at higher iron oxide coverages also show evidence of a non-coincidence overlayer lattice with a short periodicity of 0.25-0.3 nm modulated by a larger periodicity of approximately 3.5 nm. The larger periodicity results from a moiré pattern formed between the iron oxide overlayer and the underlying Au(111) surface.

SS-TuP18 Binding Character for a Xe Adatom on Nb (110), ***C.Y. Fong***, *M.C. Qian, X.D. Zhu,* University of California at Davis, *L.H. Yang,* Lawrence Livermore National Laboratory, *S. Dag*, Oak Ridge National Laboratory

We determined the binding characteristics of a Xe adatom on Nb (110) using density functional theory within the local density approximation. The on-top site is the most favorable for adsorption with a binding energy of 271 meV. Although the preference for the on-top site is the same as on the (111) surface of Pt and a number of other fcc metals, there is a discernable charge accumulation showing a weak covalency between Xe and its nearest-neighboring Nb atom. Compared to the Xe on Pt case, the differences are manifested by (i) the hybridization of Xe p-state with nearly half-filled Nb d-states causes the energy levels of Xe p-states to shift downward by 1.2 eV with the p$_z$-state splitting off from the p$_x$- and p$_y$-states, and (ii) the shifted Xe p-states have relatively narrow bandwidths due to the off-resonant condition between the p-states of an isolated Xe and the Nb d-states. They can be attributed to the less than half filled d shell of the Nb atom inducing stronger hybridization with the p-states of the Xe atom. †Work done at Lawrence Livermore National Laboratory under the auspices of the US Department of Energy under Contract No. W-7405-Eng-48.

SS-TuP19 Coverage and Temperature Dependence of LEED Streak Intensity on Li adsorbed on Cu(001) Surface at Lower Coverage, ***H.M. Mitani***, Fukuoka University of Education, Japan

Arced shape streaks, which connect four fold spots are observed in LEED experiment, in Li adsorbed system on Cu (001) surface, where the four fold spots correspond to c(2x2) structure of adsorbed Li atoms. The streaks originate from second neighbor pair (d=2a) of Li atoms in the c(2x2) structure sites. Especially, there are two types of adatoms in terms (y-)component of wave number of the streak ($k_y = \pi /a$). Both types of the sub-lattices give an anti-phase relation on the streak. If Li atoms are fully occupied on the c(2x2) sites at a coverage 0.5, the intensity is vanished. While, if the coverage is less than 0.5, a deviation of the number of atoms in the two types of sub-lattices gives a certain intensity of the streak; it becomes strongest at coverage 0.25 (H.Mitani et al. J.Phys.Soc.Jpn. 2005). In this paper, using Monte Carlo simulation, we obtain arrangements of Li atoms on adsorption sites on Cu (001) surface, as a lattice gas model, in a range of coverage (0-0.5), and a certain temperature width. By Fourier transforming of the arrangement of the atoms, we obtain almost square type streaks, which correspond to the arced shape steaks in the experiment. The reason of change from the line streaks in the square to the arced one, as shown in the experiment has already been clarified (H.Mitani et al. J.Phys. Cond.Matt. 2006). It is not a matter in the present paper. We also obtain coverage and temperature dependence of an intensity of the streak and also the four fold spots. Especially the coverage dependence of the intensity, reproduces a result of experiment; it increase along the coverage (0-0.25), and decrease in coverage (0.25-0.5). We also obtain the coverage-dependence of the intensity of the four fold spots. In terms of temperature-dependence, there is no result in experiment now. We obtain that the intensity of the streaks, broadly speaking, increases as temperature. Especially at coverage 0.5, it shows as Shottkey type behavior. On the other hand, the intensity of the four fold spots, shows second order transition, which has a certain phase transition point.

SS-TuP20 Thickness Dependence of the Interaction of NO$_2$ with Thin MgO(100) Films Grown on Ag(100) as Studied Photoemission Spectroscopy, *D.E. Starr, Ch.D. Weiss,* Lawrence Berkeley National Laboratory, *S. Yamamoto, A. Nilsson,* Stanford Synchrotron Radiation Laboratory, *M. Salmeron,* ***H. Bluhm***, Lawrence Berkeley National Laboratory

The adsorption of NOx compounds onto alkaline-earth metal-oxide surfaces has recently received a great deal of attention due to the use of alkaline-earth metal-oxides as NOx storage compounds for controlling emissions during combustion under fuel lean conditions. In this work we have studied the adsorption of NO2 onto MgO(100) thin films grown on Ag(100) ranging from 2 ML to over 8 ML in thickness and NO2 exposures from a few hundred Langmuir up to twenty thousand Langmuir at 300 K. We have used the Ambient Pressure Photoemission Spectroscopy experiment at beamline 11.0.2 of the Advanced Light Source to characterize this system using both core level and valence band photoemission as well as Auger-yield Near Edge X-ray Adsorption Spectroscopy. On thin films (~ 2 ML thick) we observe exclusively the adsorption of NO2 with coverages of ~ 0.5 ML for all exposures. As the film thickness increases the initial amount of NO2 adsorbed onto the surface decreases (~0.05 ML on films with thicknesses greater than ~5 ML) and we observe the formation of NO3 with increasing exposures. The final amount of NO3 on the surface of films thicker than 5 ML is ~ 0.3 ML. This indicates that the adsorption and reaction of NO2 on the surfaces of MgO(100) can, to some extent, be controlled by growing MgO(100) films of specific thicknesses. The mechanism of NO2 stabilization on the surfaces of thin MgO(100) films on Ag(100) will also be presented.

SS-TuP21 Comparative Study of the Electronic Structure of ZrB$_2$ and ZrB$_{12}$, ***L. Huerta***, *R. Escamilla, E. Regalado,* Universidad Nacional Autónoma de México, *M. Flores*, Universidad de Guadalajara, México

X-ray photoemission spectroscopy (XPS) and Ultraviolet photoemission spectroscopy (UPS) are used to compare the electronic structures of ZrB$_2$ and ZrB$_{12}$. The Zr 3d and B 1s core levels associated with the chemical states of ZrB$_2$ and ZrB$_{12}$ were identified, the Zr 3d core level shows a spin-orbit split 3d$_{5/2}$ and 3d$_{3/2}$ while that the B 1s core levels exhibit a single asymmetric peak typical of a metallic boride. Comparing with Zr metallic, boron and ZrO$_2$ reference materials, for ZrB$_2$ we observed a positive chemical shift for B 1s and a negative chemical shift for Zr 3d$_{3/2}$ while that in ZrB$_{12}$ the chemical shift in B 1s and Zr 3d$_{3/2}$ is inverse, suggesting that a some charge transfer occurred from the Zr atoms to the B atoms in the ZrB$_2$ and from the B atoms to the Zr atoms in ZrB$_{12}$. The measured valence bands using UPS and XPS are consistent with band-structure calculations indicating a higher density of states (DOS) at E$_F$ for ZrB$_{12}$ compared to ZrB$_2$. That's suggesting that the T$_c$ in ZrB$_{12}$ is due to B 2p and Zr 4d-derived DOS at E$_F$.

SS-TuP22 Reactivity of Model Iron and Iron Oxide Surfaces and Nanoparticles with Chlorinated Hydrocarbons, ***G.S. Parkinson***, *Z. Dohnalek, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

Iron and iron oxide surfaces and nanoparticles have been shown to be catalytically active in the destruction of chlorinated hydrocarbons in environmental remediation applications. We employ a combination of molecular beam and surface analytical techniques to synthesize and characterize model iron and iron oxide thin films grown on Pt(111) and supported nanoparticles deposited on FeO(111)/Pt(111). The chemical activity of these model catalysts is explored using temperature programmed desorption and X-ray photoelectron spectroscopy. The reactivity of a series of chlorinated methanes is explored both anhydrously and in the presence of coadsorbed water. The experimental methods, results, and their mechanistic implications will be presented.

The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

SS-TuP23 High Temperature Scanning Tunneling Microscopy on the Ion Conducting Material YSZ(111), *A.J. Carter, J. Lahiri,* ***M. Batzill***, University of South Florida

Most STM studies are performed on samples with good electron conductivity. Here we demonstrate STM measurements on the ion conductor yttrium stabilized zirconia (YSZ) at elevated temperatures. YSZ is the prototypical solid electrolyte that finds applications as an ion conductor for solid fuel cells and in gas sensing applications. In spite of these important technological applications the fundamental surface properties of ZrO2 are not well investigated. The wide band gap (>5eV) of zirconia and its poor electron conductivity hamper surface studies. Here we show that at elevated temperatures of about 600 K the ion conductivity is high enough to enable scanning tunneling microscopy investigations of this material and thus open the door for the investigation of the surface and defect structure at the atomic scale.

SS-TuP24 Nature of Photoactive Species on the TiO$_2$ Nanotube Thin Films, *T.-L. Hsiung, Y.Y. Hsu,* ***H.P. Wang***, National Cheng Kung University, Taiwan

The TiO$_2$ nanotube thin films were synthesized using ZnO nanorods as a template on the silica substances. By scanning electron microscopy (SEM), the TiO$_2$ nanotube thin films having a pore opening of about 200 nm were observed. Experimentally, the TiO$_2$ nanotube thin films have a very high activity in photocatalytic degradation of 2-chlorophenl (2CP) (220 mg/gTiO$_2$ hr) under UV/Uis irradiation. By pre-edge X-ray absorption near edge spectroscopy (XANES), the photoactive species may be distinguished in three titanium structures such as A$_1$ (TiO$_4$), A$_2$ ((TiO$_4$)=O), and A$_3$ (TiO$_6$). Interestingly, the A$_2$ species with a Ti=O and four Ti-O bonds to form a polyhedron in the TiO$_2$ nanotube thin films might be the main active sites involved in the photocatalytic degradation of 2CP. The TiO$_2$ nanotube thin films were also used in photocatalytic degradation of toxic pollutants such spill oils in the harbor or seashores.

SS-TuP25 Reaction Properties of NO over the Rh/Al$_2$O$_3$/NiAl(110) Model Catalyst, ***I. Nakamura***, *A. Takahashi, T. Fujitani*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of the noble metal content in the three-way automotive catalyst is currently required. In order to reduce noble metal loading, the enhancement of atomic efficiency of noble metal is an important subject. In this study, we investigated the NO reaction properties using Rh supported model catalyst. The model catalyst was prepared by deposition of Rh onto the Al$_2$O$_3$ thin film. It was shown that the NO dissociation activity on Rh deposited on Al$_2$O$_3$ is higher than that on Rh(111). Furthermore, we found that the NO dissociation activity on the Rh supported model catalyst increased by annealing treatment, where the activity increased with increasing heating temperature up to 500 K, and then decreased above 600 K. These results indicate that the atomic efficiency of Rh for NO dissociation is enhanced by supporting on Al$_2$O$_3$. To clarify the effect of Al$_2$O$_3$ support on Rh, we examined the NO adsorption state on the Rh supported model catalyst using IRAS. The IRA peak due to NO adsorbed on hollow site was observed at 1615 cm^{-1} for the surface without heating, which agreed with the frequency observed for Rh(111). In contrast, the peak due to NO adsorbed on bridge site was newly observed at 1645 cm^{-1} for the surface annealed to 500 K. Thus, we considered that the Rh surface structure changes from (111) face to (100) face by heating to 500 K. We previously found that the NO dissociation activity on Ir(100) was about twice of that on Ir(111), which was consistent with the relationship between the Rh supported model catalyst annealed to 500 K and Rh(111). Therefore, the enhancement of atomic efficiency of Rh is due to a change of the Rh surface structure to (100) face with a high NO dissociation ability. We concluded that the effect of Al$_2$O$_3$ support on NO dissociation is not electronic effect on Rh, but stabilization of (100) Rh surface structure.

SS-TuP26 Quantum-Resolved Photodesorption and Photodissociation Studies of Organic Nitrates and Halides on Ice, ***B. Olanrewaju***, *T.M. Orlando*, Georgia Institute of Technology

Several mechanisms have been proposed for the release of reactive species from organic halides and nitrates on ice during tropospheric ozone depletion episodes at polar sunrise. However, the description of the initial reactions that lead to the formation of precursors for these species remains incomplete because the surface enhanced catalytic effect of ice/snow interfaces is not well understood. Since the photochemical processing of interfaces involving these systems may be an important source of reactive species; we have carried out state resolved studies of photochemical production and release of Br and NO$_x$ from selected organic halides and nitrates adsorbed on ice. Specifically, we utilized resonance enhanced multiphoton ionization to detect the 300 nm photoproduced and desorbed NO and Br (Br*) from photoexcitation of bromoform and isopropyl nitrate adsorbed on crystalline and amorphous ice. We report cross sections and discuss the potential atmospheric relevance.

SS-TuP27 Antirelaxation Surface Coatings for High-Density Alkali-Metal Magnetometers, ***D.M. Rampulla***, *S.J. Seltzer, M. Romalis, S.L. Bernasek*, Princeton University

Atomic magnetometers containing spin-polarized alkali-metal atoms are capable of detecting magnetic fields with a sensitivity superior to that found in SQUIDs; however, a current issue with atomic magnetometers are depolarizing collisions between alkali-metal atoms and the cell walls. An inert buffer gas can be used to slow diffusion of spin-polarized alkali-metal atoms to cell walls, but a preferable solution would be a high-quality antirelaxation surface coating that would diminish the depolarization events that lead to the loss of spin-coherence and reduce the need for buffer gas. Although some coatings have been proven effective, paraffin and others presently in use typically can not operate at the relatively high temperatures (T > 100°C) for cesium and (T > 150°C) for potassium required for high-density magnetometers; therefore, it is desirable to find an effective antirelaxation coating suitable for these temperatures. In previous work, we have found that a coating of octadecyltrichlorosilane (OTS) at T > 150°C can allow a potassium atom to collide more than 2000 times with the walls of a spherical borosilicate glass cell before depolarizing. However, spherical glass cells are not easily studied with surface science techniques (X-ray photoelectron spectroscopy and reflection-absorption infrared spectroscopy), thus we constructed a reusable alkali vapor cell for measuring antirelaxation properties of multiple flat surfaces coated with various monolayers (chlorosilanes and phosphonic acids). In addition to antirelaxation properties, the coatings were tested for reactivity toward alkali metals and temperature stability.

SS-TuP28 Co-deposited $BaTiO_3$ Nanocomposites in Polymer and LiF Host for Embedded Capacitor Applications, ***A. Biswas***, *I.S. Bayer, P.C. Karulkar*, University of Alaska, Fairbanks

Embedding capacitors has become a critical system need for high performance miniaturized electronic systems. Fabrication and performance constraints make developing materials, processes, structures, and devices for embedded capacitor technology a great challenge. Nanocomposites comprising metal or ceramic nanoparticles in polymer have recently emerged as promising candidates. They offer potential for attaining high capacitance value, high frequency performance, process compatibility, and reliability, while being lightweight, volume-efficient, flexible and low-cost. Among other materials, barium titanate is considered one of the most promising dielectric materials due to its high dielectric constant to blend with polymers to develop high-value capacitors. However, the existing techniques that are mostly based on chemical synthesis and high temperature (>1000°C) sintering followed by blending with the polymers. This makes implementation difficult. In this paper, we present a single-step method based on electron-beam assisted vapor-phase codeposition in vacuum that allows ambient temperature fabrication of nanocomposites (~0.5 µm thick) comprising ferroelectric barium titanate nanoparticles in polymer (polymethyl methacrylate and polyurethane/polyaniline block copolymer) as well as inorganic matrices (LiF). Ferroelectric properties of barium titanate can be achieved without post deposition annealing. Preliminary capacitance-frequency results exhibit flat capacitance densities around 12-15 nF/cm^2 in most of the devices with a low tangent loss (~ 0.03) and leakage current of about 70 nA/cm^2 in the -20 V to +20 V bias region over a frequency region of 10-100 MHz. Exposing the capacitors to prolonged heating at 125°C for several days to investigate the effects of thermal stress on the device capacitance resulted in a slight reduction in the capacitance density which may be due to the possible transition from ferroelectric to paraelectric phase in barium titanate. However, overall high-frequency response improved significantly due to minimized ferroelectric loss that resulted in self-resonance frequencies occurring beyond 250 MHz. The paper will describe the novel application of vacuum codeposition technique, very encouraging physical and electrical characterization results, and their potential for embedded technology.[1]

[1] Financial support of the Defense Microelectronics Activity is acknowledged.

SS-TuP29 Heats of Adsorption and Growth Mode of Lithium on MgO(100), ***N. Ruzycki***, *J. Farmer, J.H. Baricuatro, C.T. Campbell*, University of Washington

MgO(100) is a very well studied model oxide surface in model oxide-supported metal catalysis. Lithium-promoted MgO is an active catalyst for the partial oxidation of methane. Inherent surface defects change the surface reactivity and act as anchors for catalytically active metal nanoparticles. This study explored the adsorption energetics and growth mode of lithium atoms on stochiometric and defected MgO(100) surfaces, in a unique UHV chamber designed for sensitive adsorption calorimetry measurements, electron and ion spectroscopies and LEED. The MgO(100) thin films (4 nm thick) were grown on a Mo(100) single crystal. The lithium was vapor deposited onto the MgO(100) film under UHV conditions using a pulsed metal atom source. The sticking probability of lithium was near unity. The heat of adsorption for lithium on MgO(100) was 260 kJ/mol initially, dropping with coverage to reach the heat of sublimation of pure lithium metal (159 kJ/mol) above 0.5 ML. Low energy He+ ion scattering (LEIS) revealed the growth mode for Li adsorption: Li initially wets the surface as adatoms up to ~0.5 ML, after which 3D islands of Li grow. Work function measurements yielded a change with coverage typical for alkali metal adsorption on late transition metals, with a 2.2 eV initial decrease associated with cationic Li adatoms, followed by an increase back to the value for bulk Li metal as the Li depolarizes at higher coverages due to dipole-dipole repulsions in the Li adlayer. Argon ion beam damage created defects which adsorb Li more strongly than MgO(100) terraces (up to 370 kJ/mol or more).

SS-TuP30 Strong Interaction between BaO and Al_2O_3 in NO_x Storage Materials: Correlation between Model and High Surface Area Catalysts, ***C.-W. Yi***, *J.H. Kwak, C.H.F. Peden, C.M. Wang, J. Szanyi*, Pacific Northwest National Laboratory

A series of Ba-containing NO_x storage reduction (NSR) model catalysts were prepared by reactive layer-assisted deposition (RLAD) of Ba onto Al_2O_3/NiAl(110) and investigated with surface science techniques. Upon NO_2 exposure the model catalysts demonstrated corresponding properties to the high surface area ones. Initially nitrite species form, and then Ba ions are pulled out from the surface at higher NO_2 exposures, resulting in the formation of ionic barium nitrates. The formation and agglomeration of $Ba(NO_3)_2$ clusters were observed by infrared reflection absorption (IRA) and x-ray photoelectron spectroscopies (XPS) for the model systems, and by Fourier transform infrared (FT-IR), time-resolved synchrotron x-ray diffraction (TR-XRD), and high resolution scanning transmission electron microscopy (HR-STEM) for the high surface area catalysts. The correlation between the model and real catalysts shown here for NO_2 adsorption and reaction strongly emphasizes the value of well-designed surface science studies aimed at understanding practical catalytic systems, and this approach ultimately can allow us to develop NSR catalysts with better performances.

SS-TuP31 Substitution of Carbon for Oxygen in TiO_2 for Photocatalysis Applications, ***P. Nachimuthu***, *S. Andrews, V. Shutthanandan, M.H. Engelhard,* Pacific Northwest National Laboratory*, T. Tyliszczak, D.K. Shuh,* Lawrence Berkeley National Laboratory*, S. Thevuthasan, M.A. Henderson*, Pacific Northwest National Laboratory

In semiconductor photochemistry, the redox potential of a photocatalyst is strongly modified by its band gap, which in turn dictates the energy separation of the electron-hole (e^-/h^+) pairs. The position of the bands relative to the band gap with respect to the electron donor and acceptor orbitals in the reactants determines the degree of overlap between adsorbate molecular orbitals and the electronic states associated with the e^-/h^+ pairs. TiO_2 is one of a few candidate materials with promising photocatalytic properties although the optical absorption spectrum of pure TiO_2 has poor overlap with the solar spectrum and high e^-/h^+ pair recombination rates. However, anion doping of TiO_2 is known to red-shift its optical absorption spectrum into the visible region and as a result, visible light phtotoactivity has been observed for N-doped TiO_2. Recently, we have investigated C-doped TiO_2(110) rutile using ion beam implantation as a function of temperature and dopant concentrations. Subsequent high temperature annealing was carried out on selected samples to heal the implantation damage as well as to understand the location and mobility of the dopants in the rutile lattice. Following implantation and annealing, the samples were characterized using several surface and bulk sensitive techniques such as x-ray photoelectron spectroscopy (XPS), near-edge x-ray absorption fine structure (NEXAFS), Rutherford backscattering spectrometry (RBS) (both random and channeling), and nuclear reaction analysis (NRA). NRA measurements along the channeling and random geometries clearly indicate the substitution of carbon for oxygen in the TiO_2 lattice under certain conditions. XPS data on sputter cleaned samples show the presence of carbon in two different environments with binding energies of 282.4 eV (carbide; Ti-C interaction) and 284 eV (C-C and/or C-O interactions). However, sputter cleaning followed by annealing in oxygen, eliminates the higher binding energy features suggesting that sputtering effects play a role in modifying the carbon environment in the rutile lattice. Carbon K-edge NEXAFS data are consistent with the XPS findings. Both XPS and NEXAFS show that non-carbidic interactions were significantly developed following annealing at high temperatures, although no evidence of carbon release was found from these C-doped samples.

SS-TuP32 Formation and Surface Chemistry of TiO_2 Nanoparticles on Au(111), ***Y.Z. Le***, *N. Stojilovic, R.M. Osgood,* Columbia University*, J. Hrbek*, Brookhaven National Laboratory

Titania (TiO_2) nanoparticles are formed on Au(111) surfaces under ultrahigh vacuum conditions using the method of reactive-layer-assisted deposition (RLAD). In this method, physical-vapor deposited Ti on H_2O/Au(111) reacts with oxygen from water to produce TiO_2 nanoparticles. During heating of the substrate unreacted water molecules and its fragments desorb leaving the TiO_2 nanoparticles on Au(111) surfaces. Characterization of the nanoparticles is performed using Auger electron spectroscopy (AES) whereas temperature programmed desorption (TPD) experiments are used to probe the surface chemistry of water and halogenated alkanes on these nanoparticles. Effect of titania coverage and particle size on subsequent desorption kinetics and surface chemistry is investigated. In particular, we have probed the reactive formation of these particles as a function of surface annealing temperature and observed changes in desorbed species. This formation chemistry is aided by a separate scanning tunneling microscopy (STM) study of the particle morphology, which reveals nanoparticles of 1-5 nm in size.

SS-TuP33 Characterization of Ceria-Titania Nanostructures: Insights into the Catalytic Performance, ***A.S. Karaoti***, *S.V.N.T. Kuchibhatla, T. Spalding, K. Suresh babu, S. Seal*, University of Central Florida

Oxide based semiconductors such as ceria and titania are used prolifically for a host of catalytic applications. Recently there has been an upsurge in the research, marrying the two materials for enhanced catalytic applications. A marked increase in the catalytic performance of the mixed ceria-titania oxides have been reported by various groups. However, a clear understanding of the underlying mechanisms is still at large. The present work focuses on the characterization of ceria mixed titania using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC) and Photoluminescence (PL) experiments. The retention of more catalytic anatase phase at higher temperature upon mixing with ceria and the electronic properties which result in enhancing the catalytic behavior are critically analyzed. Influence of increasing ceria concentration on phase stability, particle size and electronic properties of titania will also be discussed.

SS-TuP34 Surface Structure of $BaTiO_3$ (001), ***D.B. Li***, *R. Shao, A. Kolpak, A. Rappe, D.A. Bonnell*, University of Pennsylvania

Although oxide surfaces have been extensively studied over the last 2 decades, the atomic structure of $BaTiO_3$ (001) has received relatively little attention as a consequence of a variety of experimental challenges. The fundamental aspects of reactions on ferroelectric surfaces are critical to a range of device applications and $BaTiO_3$ (001) is the prototypical model surface. On overcoming these challenges we have used STM, nc-AFM, LEED and AES, to show that this surface adopts a family of reconstructions depending on thermo-chemical history. Most of these structures have not been observed previously. Some of the reconstructions are reminiscent of those that occur on $SrTiO_3$ (001) but the details differ significantly. Using a combination of density functional theory and ab initio thermodynamics, we compute the surface phase diagrams with oxygen potential as a dependent variable, since this is a critical variable in the experiment. The stabilities of reconstructions with Ba-adatoms, O-vacancies and Ti-O clusters are compared for different thermo-chemical conditions. Comparisons of the results of the calculations with the STM and nc-AFM results are used to construct atomic models for the reconstructed surfaces.

SS-TuP35 Water Dissociation on TiO_2(110) Supported Au Catalyst: A DFT Study, ***G. Wang***, *J. Jiao*, Nankai University, China

The present DFT calculations have clearly reproduced the experimental phenomena for H2O dissociation on TiO2(110) supported Au catalyst (including both Au cluster and scattered Au-atoms). Our results indicate that the Au-atom scattered on TiO2 strongly interacted with the supported TiO2, and compared with the supported metallic Au particle, is the most active site for the H2O dissociation reaction to occur due to the low activation energy (0.80eV). Second, the neighboring supported metallic Au particles have no effect on the catalysis activity of scattered Au-atoms for adsorbed H2O dissociation; Third, the supporting TiO2(110) has positive effect as regard to the scattered Au-atom-catalyzed H2O dissociation reaction, because it could reduce the reaction activation energy by about 0.37eV; on contrast, it has little effect on the activity of metallic Au particles; Fourth, the calculations also indicated that the active site for molecular decomposition reaction is just opposite to that of its reverse reaction, that is, as the reverse reaction of H2O dissociation, H(a)+OH(a)=H2O(a), has a less activation energy on supported metallic Au particles than on scattered Au-atoms.

SS-TuP36 Preparation and Chemical Modification of Nanoparticle Layers by Plasma Treatments, *B. Gehl*, University Bremen, Germany, *A. Frömsdorf, V. Aleksandrovic*, University Hamburg, Germany, *T. Schmidt, J. Falta*, University Bremen, Germany, *H. Weller*, University Hamburg, Germany, ***M. Baeumer***, University Bremen, Germany

Nanoparticles deposited as thin films on oxidic substrates represent a highly interesting class of materials systems not only for physical (e.g. magnetic) but also chemical applications, such as heterogeneous catalysis for example. A flexible and relatively simple way to prepare such layers is to wet-chemically synthesize nanoparticles in colloidal solution and deposit them onto a flat substrate by spincoating or a comparable method. In most cases the as-prepared particles are surrounded by a shell of organic molecules stabilizing the colloidal suspended state. To freely access the properties of the metallic particle surface for measurement or application, it is necessary to remove this shell of physically obstructing and chemically passivating ligands. It is important that the method used to strip the particles of their organic sheath neither disturbs the particle material, the substrate nor the structure of the layer. This can be achieved by exposing the deposited nanoparticles to a mild plasma removing the ligand shell through a combination of sputtering and etching processes with free radicals. It will be demonstrated that both reducing and oxidizing plasmas can be used for this purpose. Moreover, by varying plasma gasses and parameters, it is also possible to modify the chemical state of the particles selectively but leaving the lateral arrangement on the surface undisturbed. The contribution will shed light on the possibilities and limits of the approach also comparing the results to experiments where the ligand shell was removed by thermal treatment. Another aspect that will be addressed is the risk of chemical interactions with the support material induced by the plasma treatment.

SS-TuP37 Behavior of Deuterated Ethanol on Zircaloy-4 Surfaces, *Y.C. Kang*, ***J.Y. Park***, Pukyong National University, S. Korea

The surface chemistry of deuterated ethanol on the zircaloy-4 surfaces was investigated by means of temperature programmed desorption(TPD) and Auger electron spectroscopy (AES) techinques. The cleanliness of the zircaloy-4 was checked by AES and the purity of deuterated ethanol was checked by quadruple mass spectrometer (QMS) after several cycles of freeze-pump-thaw method. Depending on the adsorption temperatue, water evolution was changed as peak maximum position and absolute peak intensity. Even highly pure deuterated ethanol was used, hydrogen exchange was observed in this experiment. As the amount of exposed deuterated ethanol increased, the oxidation state of zirconium was changed from metallic to zirconia form. During linear heating of the deuterated ethanol dosed zircaloy-4 surfaces, hydrogen evolution was observed. This implys that this system has potential of production of hydrogen.

SS-TuP38 Design and Construction of a Batch Microreactor for Investigations of Heterogeneous Catalysts Deposited on Flat Supports, ***M. Sushchikh***, *J. Colby, L. Cameron, W. Tang, A. Kleiman-Shwarsctein, J.N. Park, H. Metiu, E. McFarland*, University of California, Santa Barbara

A five microliter volume batch microreactor system has been developed for the investigations of the reaction kinetics over low surface area catalysts deposited on flat supports including submonolayers of metals on single crystals. The main features of the reactor are: micro-probing capability using principle of variable leak valves (minimal altering of the amount of gases in the reactor volume); direct probing of the gases into ultra-high vacuum (UHV) mass-spectrometer volume (high sensitivity); enclosure of the reactor volume in larger tank (leak-proof by design). The reactor is made of UHV compatible components and is ready to be attached to an UHV chamber equipped with linear stage sample transfer. The reactor has been tested at initial total pressure 500 Torr, but both, lower and higher pressures are possible. The temperature is controlled over the range of 20°C to 250°C. The reactor allows monitoring of the reactions over time from tens of minutes to hours. The performance of the reactor has been demonstrated for CO oxidation reaction over Pd foil.

SS-TuP39 Growth and Physical Properties of Epitaxial Metastable $Hf_{1-x}Al_xN$ Alloys Deposited on MgO(001) by Ultrahigh Vacuum Reactive Magnetron Sputtering, ***B.M. Howe***, *J. Bareño*, University of Illinois at Urbana-Champaign, *M. Stoehr*, Université de Haute Alsace, France, *M. Sardela, J.G. Wen, J.E. Greene*, University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden, *A.A. Voevodin*, Air Force Research Laboratory, *I. Petrov*, University of Illinois at Urbana-Champaign

Epitaxial metastable $Hf_{1-x}Al_xN$ alloys with 0 = x = 0.50 were grown on MgO(001)substrates at 600°C by ultrahigh vacuum reactive magnetron sputtering from Hf and Al targets in 90 % Ar + 10 % N2 discharges at 7 mTorr. X-Ray diffraction and crosssectional transmission electron microscopy show that $Hf_{1-x}Al_xN$ alloys are single crystals with the B1-NaCl structure. Rutherford backscattering spectroscopy investigations reveal that all films are slightly overstochiometric with N/(Hf+Al) = 1.05 ± 0.05. The relaxed lattice parameter decreased linearly from 0.4519 nm with x = 0 to 0.4438 nm with x = 0.50, compared to 0.4320 nm expected from the linear Vegard's rule. We find a metastable single phase field that is remarkably broad given the large lattice mismatch (~ 9 %) between the two alloy components. Alloying HfN with AlN leads to an increase in hardness (~ 30% to 32.4 ± 0.7 GPa), as well as nanostructured compositional modulations due to the onset of spinodal decomposition.

SS-TuP40 Effect of Water Vapor on Monolayer Features Produced by Pulsed 248-nm Irradiation of Cleaved Alkali Halide Surfaces[1], ***K. Kimura***, *S.C. Langford, J.T. Dickinson*, Washington State University

Low doses of energetic electrons can produce monolayer etch pits on alkali halide cleavage surfaces.[2] Similarly, UV laser radiation can roughen steps and produce monolayer islands and pits on NaCl at fluences well below the macroscopic damage threshold.[3] Step edges on NaCl are highly vulnerable to erosion due to high densities of kinks. In NaCl, step erosion is dramatically accelerated in the presence of 10^{-5} Pa water vapor.[4] In this work, we compare atomic force microscopy (AFM) images of NaCl, KCl, and KBr cleavage surfaces exposed to pulsed 248-nm laser radiation in vacuum. Since atmospheric water vapor affects all these surfaces, AFM was performed under dry nitrogen. Prior to laser exposure, the principal features are straight, monatomic cleavage steps. Fifty 248-nm pulses at 100 mJ/cm^2 are sufficient to produce monolayer islands and to roughen cleavage steps in ultrahigh vacuum on all three materials. Island-free zones are observed on both the upper and lower terraces along cleavage steps. The island densities and the width of the island free-zones vary significantly with laser fluence. Islands appear to be formed from material eroded from the steps. Similar laser exposures in the presence of 10^{-5} Pa water vapor produce monolayer etch pits, rather than islands, on KBr and KCl. Higher laser fluences are required to produce pits on NaCl. Calibrated quadrupole mass spectrometry on the products emitted during laser irradiation shows emission intensities consistent with that required to form the etch pits. In the presence of 10^{-5} Pa water vapor, the detected intensities are typically several times higher than in ultrahigh vacuum. Islands and etch pits are also observed on surfaces exposed to low doses of 2 keV electrons; again, these features are dramatically affected by the presence of water vapor. Although mechanism for the effect of water vapor is not clear, the dissociative adsorption of water at surface halogen vacancies is expected to play a role.

[1] This work was supported by the U.S. Department of Energy-under Grant DE-FG02-04ER-15618.

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Thin Film

Room: 4C - Session TF-TuP

Aspects of Thin Films Poster Session

TF-TuP1 A Polymer-Based Process for Substrate Transfer or Conformal Coating of Carbon Nanosheets, ***R.A. Quinlan****, B.C. Holloway, M.Y. Zhu, K. Hou*, The College of William and Mary

Carbon nanostructures such as chemically vapor deposited carbon nanotubes have shown remarkable thermal, mechanical and electrical properties, making them an area of intense scientific interest. However, their actual use in new technology has been limited by both the extreme nature of efficient growth conditions and the difficulty of conformally coating the structure while maintaining the original morphology. Carbon nanosheets - vertically oriented nanostructures of 1-5 graphene layers - have shown promise as a more robust alternative carbon nanostructure. Previous reports have detailed the synthesis of carbon nanosheets via RF PECVD on metallic, insulating and semiconducting substrates, their characterization via Raman, XRD, SEM, TEM, FTIR, PIXE, ERDA, and TDS. Of interest, previous BET measurements yielded an effective surface area of ~1,300 m^2/g, which is comparable to that of the theoretical limit for carbon nanotubes (1315 m^2/g) and much higher than that of activated charcoal. Here we report, that utilizing a customized polymer incorporation technique, nanosheets have been transferred to alternative substrates while maintaining their original morphology. The ability to transfer nanosheets to a substrate that need not take on the thermal budget of the carbon nanostructure synthesis combined with the ability to pattern nanosheets using standard photoresist techniques offers the potential for an enabling technology for more realistic nanosheet-based devices and sensors. In addition the conformal coatings of nanosheets with an industrial silicone, standard photo resist, and two photoactive polymers via a tailored spin-casting or drop-casting procedure of the polymers will also be discussed. SEM shows that, at low loadings, a conformal coating of polymer on the nanosheets is produced; thicker loadings cause intercalation of the polymer between the nanosheets and a complete incorporation of the nanosheets into a solid polymer film. Tuning the deposition conditions allows for air release and eliminates void formation and thereby minimizes undercutting when patterning the nanosheets via photoresist-based techniques.

TF-TuP2 Carbon Nanotube (CNT) Growth and Substrate Adhesion for CNT-based Materials, ***M.J. Bronikowski***, Jet Propulsion Laboratory

Growth of Carbon Nanotubes (CNTs) by chemical vapor deposition (CVD) on various substrates has been studied as various CVD process parameters are varied, and CNT up to several millimeters long have been grown in both continuous dense mats and as patterned CNT bundle arrays. The adhesion of these CNT mats to their substrate surfaces has also been investigated as a function of processing conditions, and various methods to improve CNT-substrate adhesion have been investigated. Recent results will be presented from these studies, which have as their long-term goal the incorporation of as-grown, aligned CNT mats into composite materials, so that CNTs' outstanding mechanical, thermal and electrical properties can be exhibited by the resulting materials.

TF-TuP3 Vacuum Phase Deposition of Thin Films of poly(2,6-dimethyl-1,4-phenylene oxide)/Polystyrene/Silver Nanostructured Composites and Their Electrical and Surface Adhesion Characteristics, ***I.S. Bayer****, A. Biswas, P.C. Karulkar*, University of Alaska, Fairbanks

Thin nanocomposite films comprising Poly(2,6-dimethyl-1,4-oxyphenylene)/Polystyrene and Poly(2,6-dimethyl-1,4-oxyphenylene)/Silver were fabricated using an electron beam assisted physical vapor co-deposition technique. The fabrication process is a one step novel vapor phase co-deposition of polymers and metal on substrates maintained at room temperature in a vacuum chamber. Glass, Polyethylene terephtalate, aluminum and gold were used as substrates during experiments. Nanocomposite film topologies were studied with various techniques including AFM, X-Ray diffraction, Raman Spectroscopy, Scanning Electron Microscopy and finally static contact angle measurements to estimate surface adhesion properties as a function of silver volume filling. Fabrication of the thin film structures involved evaporation and subsequent condensation of materials from specially designed tungsten crucibles. The crucibles were heated in a controlled manner by bombarding with electrons generated by applying high voltage to tungsten filaments. The deposition system had four crucibles allowing four different components to be co-deposited simultaneously. Before deposition of nanocomposites, preliminary and separate experiments were conducted in order to establish evaporation rates of Polystyrene and Poly(2,6-dimethyl-1,4-oxyphenylene) (a.k.a PPO). Different metal volume filling ratios in the thin film nanocomposites were achieved by adjusting relative evaporation rates of polymers and silver. AFM and electron micrographs of the deposited nanocomposites featured a nanoporous surface morphology. Using a multi-fluid contact angle technique (Kaeble plots) surface energy of the nanocomposites was estimated as a function of metal filling. Composite surface energy polarity increased as a function of increasing silver filling. Above a critical metal filling the composites were conductive, on the other hand particularly below this critical metal filling, based on forward bias I-V measurements, nanocomposite film-metal interfaces displayed Schottky barrier type characteristics. In addition, a number of thin film capacitors were also made by co-deposition of PPO and metal on Aluminum substrates. The thin film capacitors exhibited capacitance densities of about 4-7 nF/cm^2 up to 80 MHz frequency.

TF-TuP4 Influence of Glancing Angle Deposition (GLAD) Technique on Mechanical, Structural and Optical Properties of CuInS2 Thin Films, ***F. Chaffar Akkari***, Photovoltaics and Semiconductor Materials Laboratory, Tunisia

Porous films of CuInS2 nanostructures were grown on glass substrate by Glancing Angle Deposition (GLAD) technique and the substrate motion in order to sculpt a typical columnar microstructure into desired shapes. The deposition angle θ with respect to the surface normal was varied from 0 degree to 80degree in order to directly probe the effect of atomic shadowing on the surface morphological evolution. By changing the direction of the incident flux of the species impinging on the substrate surface, deposited films form columns that are tilted with respect to the substrate normal. The growth mechanisms and the morphology of such films were studied by scanning electron microscopy and X-ray diffraction. The influence of the flux angle was investigated. Optical properties of these coatings were also measured and discussed.

TF-TuP5 Role of Carbon Nanotube and Water in Photoconductivity of Polythiophne Based Water Soluble Polymer, *J. Choi,* ***D.Y. Kim***, Wayne State Univ.

Polythiophene based water soluble polymer, Sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate)] (PTEBS) is attractive as a strong candidate for photovoltaic devices and humidity sensor. PTBS is water soluble, processable using conventional solvents, and shows high response to visible light. However, the higher energy band gap and the low conductivity of the polymer are obstacles for the full utilization of full visible light spectrum range and efficient charge separation, which are critical to the efficiency of photovoltaic devices. In order to develop an efficient solar cell, understanding conduction mechanism of polymer is essential. To overcome the obstacles related to the intrinsic properties of PTEBS, we studied the photo-response as a function of voltage, polymer concentration, carbon nanotube, phase and wavelength of light. In result, we found out the photo-response depends on the applied bias voltages, carbon nanotube incorporation, wavelength of light, phase of polymer and humidity. These results can be directly applicable to design efficient photovoltaic devices for the practical applications.

TF-TuP6 Study of Point Defects in Uranium Oxide by Ab-Initio and Semi-Empirical Calculations

***P.V. Nerikar**, S.B. Sinnott*, University of Florida

Uranium oxide is used as the standard nuclear fuel in pressurized water reactors. Point defects have an important effect on the physical properties of the fuel as they can cause swelling of the material and change the crystal structure thereby reducing the fuel performance. The aim is to understand the stability of these defects while including their correct electronic structure. Here, density functional theory calculations using the local spin density approximation with the Hubbard U correction term, or the L(S)DA+U method, is used in combination with thermodynamic approaches to calculate the formation energy of point defects present in UO_2. The nudged elastic band method is used to calculate the migration energies. These calculations are supported by semi-empirical simulations using two different potentials and larger supercells. We have been able to predict the correct electronic structure of UO_2 which allows us to consider charged defects. We predict the defect formation energies of neutral uranium vacancy and interstitial to be 4.2 eV and 7.29 eV respectively. For the oxygen vacancy and interstitial, we predict the values to be 6.33 eV and -2.71 eV respectively. The calculations thus predict that the oxygen Frenkel pair complex is the dominant defect in UO_2, which is also what is observed experimentally. We observe a similar trend with our semi-empirical calculations. We will discuss the effect of temperature, pressure and microstructural features, such as grain boundaries, on the defect formation energies.

TF-TuP7 Chemical, Optical and Electrical Properties and Radiation Effects of ZrO2/Si and HfO2/Si

***J.M. Burst**, B.W. Schmidt, N.D. Vora, R.D. Geil, S.K. Dixit, R. Schrimpf, B.R. Rogers*, Vanderbilt University

HfO2 and ZrO2 ceramics find use in many diverse applications. Hafnia has broad usefulness in protective coatings, optical thin films, and the technologically important MOS gate dielectric. Zirconia is studied for its thermal barrier, catalytic, optical and electronic applications. Much previous work has either focused on measuring a specific material property as a function of processing, or measured radiation-induced effects without much accountability given towards material processing. Here we report on the chemical, physical, optical and electrical properties of MOCVD-grown thin hafnia and zirconia films and relate their performance to their surface, interfacial and processing conditions. We combine fundamental and application-specific analyses such as in situ Spectroscopic Ellipsometry, X-Ray Photoelectron Spectroscopy (XPS), Medium Energy Backscattering Spectrometry (MEBS) and electron microscopy with surface roughness and Capacitance-Voltage measurements both before and after radiation exposure.

TF-TuP8 PL and EL from Eu-Activated $CaAl_2O_4$-Based Multicomponent Oxide Thin-Film Phosphors

***H. Fukada**, S. Matsui, T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

In this paper, we describe the photoluminescent (PL) and electroluminescent (EL) characteristics from Eu-activated $CaAl_2O_4$-based multicomponent oxide thin-film phosphors. Various Eu-activated $CaAl_2O_4$-based thin-film phosphors were developed using multicomponent oxides composed of $CaAl_2O_4$ with $CaGa_2O_4$ or $CaIn_2O_4$ as the host material. The phosphor thin films were prepared on thick $BaTiO_3$ ceramic sheets by either a conventional or a combinatorial r.f. magnetron sputtering deposition (rf-MSD) using a powder target. In $((CaAl_2O_4)_{1-X}$-$(CaGa_2O_4)_X)$:Eu phosphor thin film preparation, a powder mixture of CaO, Al_2O_3 and Eu_2O_3 and/or CaO, Ga_2O_3 and Eu_2O_3 calcined at a temperature range of 1000-1300°C in either a pure Ar gas or air was used as the target. The sputter depositions were carried out under the following conditions: atmosphere, either a pure Ar or an $Ar+O_2$ (2%), pressure, 6 Pa; r.f. power, 140 W; and substrate temperature, 100-350°C. Some deposited thin films were postannealed in either air or an $Ar+H_2$ (5%) gas atmosphere for 30-300 minutes at 500-1000°C. It was found that PL characteristics of $CaAl_2O_4$:Eu phosphor thin films were significantly affected by the deposition and postannealing conditions. Intense yellow-green (Y-GL) PL emission was observed from as-deposited $CaAl_2O_4$:Eu thin films prepared in a pure Ar sputter gas atmosphere using a powder target calcined at 1000°C in air. In addition, blue (B) PL emission was observed in $CaAl_2O_4$:Eu thin films postannealed in an $Ar+H_2$(5%) gas atmosphere at a temperature above approximately 800°C, and the intensity of the B emission increased as postannealing temperature was increased. The EL device fabricated using a postannealed $CaAl_2O_4$:Eu thin film as the emitting layer exhibited red EL emission. In addition, in the $((CaAl_2O_4)_{1-X}$-$(CaGa_2O_4)_X)$:Eu multicomponent oxide phosphor thin films were prepared by the combinatorial rf-MSD method. The obtained PL and EL characteristics from these multi-component oxide phosphor thin films were considerably affected by the postannealing conditions as well as the chemical composition ($CaGa_2O_4$ content or Ga/(Al+Ga) atomic ratio; X

TF-TuP9 Macroscale Surface Morphology in KMC Simulations of Growth on Surfaces with Negative Ehrlich-Schwoebel Barriers

***A.K. Jones**, A. Ballestad, S. Cheng,* University of British Columbia, Canada, *T. Li,* University of Illinois, Urbana, *J. Rottler, T. Tiedje*, University of British Columbia, Canada

In order to understand which atom scale processes are important in controlling macroscopic shapes in epitaxial crystal growth, we have simulated the epitaxial growth process numerically, using a kinetic Monte Carlo (kMC) simulation of a restricted solid-on-solid model. Step edge potential barriers (Ehrlich-Schwoebel or ES barriers) are a well-known example of an atomistic property which has an important effect on macroscopic surface morphology. Most theoretical work has concentrated on the effects of positive ES barriers, which are commonly found in metals, and which lead to spontaneous mound formation. In the case of GaAs and probably other III-V semiconductors, epitaxial growth is found to be stable, suggesting a negative ES barrier. In this paper we consider epitaxial growth dynamics for vicinal surfaces with negative ES barriers. In kMC simulations as a function of surface slope we find a "magic slope" with a step density minimum. The step density minimum is caused by the fact that linear arrays of steps are more efficient at capturing adatoms than step edges in the form of loops, thereby reducing island nucleation and step density for small vicinal angles. We show that the step density minimum produces a preferred macroscopic slope similar to a crystal facet but with a different physical origin, in the smoothing of patterned substrates during epitaxial growth. Conventional wisdom[1] suggests that in the absence of nucleation, negative ES barriers lead to unstable step edges (step bunching) for 1D vicinal 'surfaces' and positive ES barriers lead to stable step edges (equally spaced steps). In kMC simulations on 2D vicinal surfaces we find a contrary result. In the case of negative ES barriers the steps become evenly spaced and the growth is stable, with or without nucleation. For 2D vicinal surfaces with positive ES barriers, at low temperatures nucleation on top of monolayer islands eventually leads to mounds and unstable growth. If nucleation is turned off, above a critical value of the ES barrier, step edge wandering eventually produces enclosed regions (pits) which do not fill in, which also leads to unstable growth.

[1] J. Villain, J. de Physique, 1 1991.

TF-TuP10 Detection of H_2 at High Temperature by Nickel Oxide (NiO) Based Gas Sensors

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Stricter restrictions in exhaust gas emissions are creating a need for gas sensors that can operate in harsh environments and high temperatures (> 500 °C). NiO is one of the few stable p-type oxide-based gas sensitive semiconductors. Being exposed to reducing gases like H_2 or NH_3 decreases the charge carrier concentration. The sensitivity of ~50 nm thick NiO films with and without 5 nm thick gold, platinum or titanium promoter layers were compared to each other. Promoters are used to increase the gas sensitivity of metal oxides. H_2 sensitivities between 3 and 7.5 were measured from NiO films with Ti promoter layers at an operating temperature of 600 °C. NiO thin film were deposited by radio frequency (RF) sputtering with an 8" ceramic NiO target in a pure argon atmosphere (10 mTorr, 500 W, 2.48 nm/min). The films were deposited on inter-digitated electrodes (IDE) with 100 µm finger spacing to measure the change in resistance during test gas exposure. Promoter layers were deposited in a separate sputtering system. The gas sensing films were annealed for 5 hours at 900 °C in synthetic air (80% N_2, 20% O_2), nitrogen or oxygen in order to achieve stable films. As deposited and annealed films were characterized by Atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to measure the surface morphology, composition and grain size. The grain size was calculated by the Scherrer equation to be ~22 nm for the (200) NiO, Bunsenite peak, for all annealing conditions. Particle size measured from AFM micrograph were consistently near 100 nm from all annealing conditions. The gas sensitivity of these films was investigated using H_2 in synthetic air (80% N_2, 20 % O_2) or nitrogen as a carrier gas. The carrier gas composition has a strong effect on sensitivity of NiO gas sensors, with higher sensitivity in synthetic air. Pure NiO films without promoters showed gas sensitivity (S) ~1 to 4700 ppm H_2 at an operating temperature of 600 °C in synthetic air (80% N_2, 20 % O_2) carrier gas. Using the same testing conditions, promoted NiO sensitive layers with Pt and Au promoter layers showed reduction in sensitivity (S<1). Using Ti promoter layers increased the sensitivity up to 7.5 at these conditions.

TF-TuP11 Effects of Annealing Gas on Characteristics of High-k Oxide Films (HfO2) Deposited by ALD for MIM Capacitors

***S.W. Jeong**, B.K. Kim, E.T. Lee, Y.H. Roh*, Sungkyunkwan University, Korea

Research on the insulating films in metal-insulator-metal (MIM) capacitors has focused on ways to increase the dielectric constant of insulator to improve the packing density of integrated RF capacitors. High-k oxide (e.g., Ta_2O_5) has been suggested as an alternative material to replace SiO_2 and

Si_3N_4. However, reliability problem caused by leakage current may limit the application of Ta_2O_5. Properties of HfO_2 grown on the Si substrate shows a dielectric constant which is comparable to that of Ta_2O_5. Further, the characteristics of HfO_2 more stable than those obtained from Ta_2O_5, suggesting that we may use HfO_2 film as insulator in MIM capacitor. In this work, we report the physical and electrical properties of ALD-deposited HfO_2 film (11-12 nm) annealed at various gases (N_2, O_2, N_2O). HfO_2 films were annealed at 400, 600, 800°C using a rapid thermal processor for 1 min. Top and bottom metal electrodes were Pt and Pd, respectively. The electrical characterization indicates that HfO_2 MIM capacitors fabricated at 800 °C under O_2 ambient show the most desirable electrical properties, such as a high capacitance density of ~16.9 fF/μm^2, a low leakage current of 2.7×10-4 A/cm^2 at -5 V, low-voltage coefficients of capacitance, and good-frequency dispersion properties. In addition, better properties were obtained from the samples annealed using N_2O than those of samples treated using N_2. These results indicate that oxygen content has certain role(s) on the electrical properties of ALD-deposited HfO_2 film. These results, as well as further investigation of physical properties of the samples using XPS, will be presented at the conference.

TF-TuP12 Transparent Multi-Layer Diffusion Barrier Coating on PES Substrate by Low-Temperature PECVD, ***S.M. Park***, *Y.B. Yun, D.J. Kim, N.-E. Lee*, Sungkyunkwan University, Korea

Recently, transparent barrier coatings on polymer substrate have received much attention for liquid crystal displays, organic light-emitting-diode (OLEDs) displays, solar modules, and food packing applications. In this work, SiO_xN_y and methylcyclohexane (MCH) plasma polymer films as transparent diffusion barrier coating were deposited by a low temperature plasma enhanced chemical vapor deposition (PECVD) on polyether sulfone (PES) substrate using hexamethyldisilazane (HMDSN)/N_2O/O_2/Ar gas and methylcyclohexane/Ar gas mixtures, respectively. Effects of source flow rates, plasma power and chamber pressure were investigated. The deposition rate, chemical bonding states, transparency, surface morphology and WVTR were characterized by FE-SEM, fourier transform-infrared (FT-IR) spectroscopy, UV-visible, atomic force microscope (AFM) and permeability measurement system. Multilayer structures were also fabricated in one PECVD system. Transparent multilayer of SiO_xN_y/plasma polymer with the optical transparency larger than 90%.

TF-TuP13 Fabrication of Silver Oxide Films using Reactive Bias Sputter-Deposition, ***T. Ichinohe***, Tokyo National College of Technology, Japan, *M. Iwase*, Tokai University, Japan, *S. Masaki, K. Kawasaki*, TDY Co, Ltd., Japan

Silver suboxide (Ag_2O) is known to be a p-type semiconductor with a narrow band gap (1.2 eV). Lower temperature processes are needed to form the oxide films because the oxide is reduced by heat-treatment over 200 ^oC by dissociating the oxygen. This report describes fabrication of silver oxide films at lower temperatures using a reactive sputtering system by applying a substrate bias voltage (V_s). According to XRD analyses, silver films have been deposited by bias free sputtering with a lower oxygen partial pressure while AgO films have been fabricated with a high oxygen partial pressure. In the lower oxygen partial pressure environment, applying a substrate bias made silver react to oxidize such that Ag_2O_3 and Ag_2O films were fabricated by applying a V_s = 20 V, and Ag_2O_3 being formed at V_s = 40 V. Ag_2O_3 films showed very high resistivity. Ag_2O films showing p-type characteristics and lower resistivity were fabricated at V_s = 40 V after bias free sputter-deposition, that is, combining with and without substrate bias resulted in the fabrication of Ag_2O. The negative oxygen ions accelerated by the substrate bias can contribute to fabricate silver oxide in the lower oxygen partial pressure environment.

TF-TuP14 Photoluminescence Excitation Spectroscopy of Cu(In,Ga)Se_2 Thin Films, ***D.N. Hebert***, *A.J. Hall, A. Rockett*, University of Illinois at Urbana-Champaign

Cu(In,Ga)Se_2 (CIGS) and related materials yield the highest performance thin film solar cells and show excellent promise for very high efficiency multijunction devices if adequate single junction devices can be produced. However, intrinsic defect chemistry and the origin of band edge fluctuations are not understood and are likely responsible for limited device performance. Low-temperature, long-wavelength photoluminescence excitation (PLE) spectra of films with varying composition, growth temperature, substrate orientation and crystallinity are presented. Despite low excitation power, low-temperature, long-wavelength PLE measurements allow for the detection of luminescence by selective wavelength excitation and reveal sub-gap absorption bands. Position-dependent photoluminescence spectra acquired from epitaxial bicrystals and apertured photoluminescence spectra on device-grade polycrystals are also presented. Local area scanning tunneling microscopy band edge measurements on in situ cleaved and sputtered CIGS are used to interpret PL results.

TF-TuP15 Phase Formation Control of Sputtered Ta(N) Films, ***R.L. Kinder***, *N. Mackie, A. Pradhan*, Novellus Systems, Inc.

High quality Ta(N) barrier is required for the 65 nm node and beyond. Not only must this Ta(N) barrier be dense and conformal, it must have the correct phase and orientation in order to minimize electromigration (EM) and stress migration (SM) of dual damascene Cu structures. Two phases of Ta barrier can be observed after sputter deposition: a-Ta, which is body centered cubic (bcc), and beta-Ta which is distorted tetragonal. These two phases have different properties: alpha-Ta has lower bulk resistivity (15 - 30 μW cm vs. 150 - 200 μW cm) higher temperature coefficient of resistivity, and slightly higher density. Furthermore, a-Ta has a higher potential for driving <111> Cu orientation for better EM reliability. The formation of alpha-Ta by sputter deposition processes can occur through several methods. i) Small additives, such as N or O, into the Ta film can lead to a change in the crystalline structure from tetragonal beta-Ta to distorted a-Ta. ii) deposition temperature exceeding 400 °C. iii) using a base layer of TaN between the dielectric and deposited Ta film can drive the formation of alpha-Ta. More recently it has been observed that phase of deposited Ta(N) grown films largely depends on the combination of ion kinetic energy and ion-to-neutral flux ratio. Previous work has shown that low kinetic energy (< 20 eV) and high ion-to-neutral ratio (> 15) are essential to synthesizing low resistivity alpha-Ta. In this study, it was observed using selective area diffraction (SAED), that, under normal sputter deposition conditions, beta-Ta tends to form preferentially on the field, while weak alpha-Ta tends to form along feature sidewalls. Several studies various TaN underlayers to promote alpha-Ta formation throughout the feature have been conducted. Experimental and modeling studies to characterize process regimes necessary to synthesizing low resistivity alpha-Ta film will be discussed. Overall, the ability to deposit a TaN/Ta barrier and seed layer with the correct phase and orientation throughout the feature is essential in order to improve reliability of dual damascene Cu structures. Although, a TaN underlayer does promote alpha-Ta phase, as the TaN barrier size shrinks, the ability to deposit sputtered alpha-Ta throughout the feature is critical. It was demonstrated that the high ionization efficiency of the Inova HCM allows for the deposition of alpha-Ta at the feature sidewall.

TF-TuP16 An EIES Flux Sensor for Monitoring Deposition Rate at High Background Gas Pressure with Improved Accuracy, *C. Lu*, C. Lu Laboratory, ***C.D. Blissett***, *G. Diehl*, Sigma Instruments

Electron impact emission spectroscopy (EIES) has been proven to be a critical tool for film composition control during co-deposition processes for the fabrication of multi-component thin film materials including the high-efficiency CIGS (copper-indium-gallium-diselenide) photovoltaic cells. This technique is highly specific to atomic species because the emission spectrum of each element is unique, and the typical width of atomic emission lines is very narrow. Non-interfering emission lines can generally be allocated to different atomic species. However, the electron impact emission spectra of many molecular species are often broadband in nature. When the optical emission from an EIES sensor is measured by using a wavelength selection device with a modest resolution, such as an optical filter or monochromator, the emissions from common residual gases may interfere with that from the vapor flux and cause erroneous flux measurement. The interference is most pronounced when measuring low flux density with the presence of gases such as in reactive deposition processes. This problem is solved by using a novel EIES sensor that has two electron impact excitation sources in separate compartments but with one common port for optical output. The vapor flux is allowed to pass through one compartment only. Using a tri-state excitation scheme and appropriate signal processing technique, the interfering signals from residual gases can be completerly eliminated from the output signal of the EIES monitor for process control. Data obtained from Cu and Ga evaporations with the presence of common residual gases such as CO_2 and H_2O are shown to demonstrate the improvement in sensor performance. The new EIES sensor is capable of eliminating the effect of interfering residual gases with pressure as high as in the upper 10^{-5} Torr range.

TF-TuP17 Top-emitting Organic Light-emitting Diodes with Ba/Ag/ITO Cathode and Built-in potential Analyses in these Devices, *G.Y. Yeom*, ***J.T. Lim***, Sungkyunkwan University, Korea

The top-emitting organic light-emitting diodes (TEOLEDs) have generated considerable interest in recent years, owing to their use in active matrix displays. Significant progress has been made in the development of thin semitransparent conducting cathodes (STCCs), semi-transparent conducting cathode (STCC) thin film composed of Ba (x nm)/Ag (10 nm)/ITO (100 nm) (x: 0,, 1, 2 and 3 nm) were fabricated by thermal evaporation. The optical properties of STCCs at the wavelength of 535 nm showed the transmittance of about 77 % and the reflectance of about 13 %, respectively. The TEOLED which is consisted of glass/Ag (100 nm)/tin-doped indium oxide (125 nm)/4,4',4''-tris[2-naphthylphenyl-1-phenylamino]triphenylamine (2-TNATA, 30 nm)/ 4,4'-bis[N-(1-napthyl)-

N-phenyl- amino]-biphenyl (NPB, 15 nm)/tris(8-quinolinolato) aluminum (III) (Alq3, 55 nm)/Ba (x nm)/Ag (20 nm)/ITO (100 nm) showed the highest driving performance when the deposition thickness of Ba is 1 nm. The effect reducing the barrier height for an electron-injection from Ba to Alq3 can explain a driving performance of these devices. We proved these results by measuring a built-in potential in the devices. Meanwhile, in the case of the top-emitting device with the Ba (1 nm)/Ag (20 nm)/ITO (100 nm) cathode, the maximum luminance was about 80,000 cd/m2 and an external quantum efficiency at about 100 cd/m2 was 1.5 %.

TF-TuP18 Novel Method to Fabricate BLT/CeO2/Si MFIS Structure by One-Step Chemical Mechanical Polishing Process, ***S.-H. Shin****, P.-G. Jung, Y.-K. Jun, P.-J. Ko,* Chosun Univ., Korea, *N.-H. Kim,* Sungkyunkwan Univ., Korea, *W.-S. Lee*, Chosun Univ., Korea

Metal-ferroelectric-insulator-silicon field-effect-transistors (MFISFETs) have attracted much attention as promising non-volatile memory devices due to their nondestructive read operation possible. Both the ferroelectric and insulator materials are generally known not to be etched well with plasma etching system. Plasma damage on sloped sidewall of the ferroelectric materials and integration problem by the sloped sidewall were also reported in plasma etching process. In this study, BLT/CeO2/silicon structure was fabricated by damascene process of chemical mechanical polishing (CMP) with one-step polishing process. The process parameters of CMP were optimized for one-step CMP process for BLT/CeO2 films. This novel method to fabricate the MFIS structure could reduce the many process steps. Vertical sidewall of the BLT/CeO2 structure was also obtained, which led to densify the devices without the plasma damage. The C-V and I-V characteristics of the BLT/CeO2/Si structures were measured for MFISFET devices. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

TF-TuP19 Dielectric and Piezoelectric Properties of Polished PZT Ceramics for MEMS Applications, ***P.-J. Ko****, P.-G. Jung, Y.-K. Jun,* Chosun University, Korea, *N.-H. Kim,* Sungkyunkwan University, Korea, *W.-S. Lee*, Chosun University, Korea

Piezoelectric actuators and sensors are main applications of micro-electro-mechanical system (MEMS). The perovskite lead zirconate titanate (PZT) piezoelectric ceramic is one of the most commonly used piezoelectric materials due to its high dielectric constant and piezoelectric coupling coefficient. The piezoelectric PZT films have been successfully fabricated and processed by using various semiconductor technologies in manufacture of MEMS applications. Some investigations on PZT-chemical mechanical polishing (CMP) process were also carried out for the patterning and the improvement of surface morphology. In this study, dielectric and piezoelectric properties of the polished PZT films were investigated for the application of CMP process to the piezoelectric MEMS applications. The crystal structure and the microstructure of PZT films were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively before and after CMP process. The P-E hysteresis loops of the polished PZT films were analyzed and compared to the as-deposited samples. Consequently, the CMP process parameters were optimized for the sufficient piezoelectric coefficient of PZT films. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2006-005-J00902).

TF-TuP20 Nitrogen-dope Effect for Photofunctional Properties of Titanium Dioxide Films Prepared by Magnetron Sputtering, ***J. Hamaguchi****, I. Takano, M. Sato*, Kogakuin University, Japan

Titanium dioxide is anticipated as one of materials which are alternative for existing solar cell technology based on silicon. Silicon has a wide wavelength range including visible light, while titanium dioxide has a shorter wavelength range under ultraviolet light, according to each band gap. Hence, many researchers have studied about improvement of absorbance band in titanium dioxide, such as doping of nitrogen using plasma,[1] doping of chromium using ion implantation,[2] or dye sensitization of titanium dioxide. In this study, photofunctional properties of nitrogen-doped titanium dioxide were investigated about the films prepared by each method of ion implantation to titanium dioxide and reactive magnetron sputtering. In the former, nitrogen ion implantation was performed after preparing titanium dioxide by reactive magnetron sputtering. In the latter, nitrogen doping was performed during formation of titanium dioxide by reactive magnetron sputtering in nitrogen gas atmosphere. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic change of methylene blue solution was applied to photocatalytic property. Light irradiation to titanium dioxide in a methylene blue solution was carried out using a commercial sterilizing lamp as ultraviolet light and a commercial fluorescent lamp as visible light. Transmittance of a methylene blue solution was measured by a spectro photometer. Furthermore, photocurrent between titanium dioxide and platinum electrode were measured in a potassium hydrogencarbonate solution using an unresisted ammeter. In the case of nitrogen doping during film formation, photofunctional property using a fluorescent lamp showed lower photocatalytic effect and photocurrent as compared with the case of a sterilization lamp. The higher photocatalytic effect and photocurrent using a sterilization lamp were obtained at N_2 gas flow rate of 0.6 sccm and 0.4-0.5 sccm respectively, while both properties using a fluorescent lamp also showed the same behavior as a sterilization lamp.

[1] R.Asahi, et al.; Science, 293(2001)269.

[2] S.Anpo, et al.; Surface Science Society of Japan, 20(1999)60.

TF-TuP21 Formation of Nitrogen-doped Diamond like Carbon Films in a C_7H_8 Gas Atmosphere by the Ion Beam Assist Method, ***K. Harada****, I. Takano*, Kogakuin University, Japan

DLC (Diamond Like Carbon) constituting a class of new materials is an amorphous carbon including hydrogen and has similar properties of matter with a diamond. DLC film was formed by the ion beam evaporation method in the early 1970's,[1] and after that has been manufactured by various methods such as CVD (Chemical Vapor Deposition) or PVD (Physical Vapor Deposition). Because representative mechanical properties of DLC is to show the high hardness and low friction coefficient, DLC is applied in various filed such as motor parts or tools. Also the electric properties of DLC are anticipated as field emission source. In this study, mechanical properties were investigated about the DLC films prepared by the ion beam assist method. The ion beam assist method of present study was applied for formation of nitrogen-doped DLC films using irradiation of nitrogen ion in a C_7H_8 gas atmosphere. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and Raman spectroscopy. The mechanical properties were evaluated by the hardness and a friction coefficient. The hardness was measured from size of an indentation with a Knoop indenter. The friction coefficient was measured for a SUJ2 ball with a constant load 0.98N until the sliding distance reaches a length of 10m. On mechanical properties, the film prepared at an acceleration voltage of 12 kV obtained the highest hardness in spite of very thin carbon layer, while the friction coefficient of this film showed the high value close to that of stainless steel. Conversely, the hardness of the film prepared at a voltage of 1 kV showed the low value, while the friction coefficient of this film obtained the lowest value. The ware track of the film prepared at a voltage of 1 kV had a small thrust in a depth as the film showed the low friction coefficient compared with the film of 12 kV. The concentration of nitrogen was around 7% at an acceleration voltage of 1 kV and was not an enough value for leading the drastic change of physical matters.

[1] S. Aisenberg , R. Chabot : J. Appl. Phys., 42, 2953 (1971).

TF-TuP22 Effects of Annealing on the Characteristics of SnO2:Sb Films Prepared by RF Magnetron Sputtering Method for Transparent Electrodes, ***S.U. Lee****, W.S. Choi, B. Hong*, Sungkyunkwan University, Korea

Tin oxide (SnO2) have been widely used as transparent conducting thin film material for application in various fields such as liquid crystal displays, optoelectronic devices, solar cells, heat mirrors and gas sensors, etc.[1] Recently the increased utilization of many transparent electrodes has accelerated the development of inexpensive transparent conducting oxide (TCO) materials. Antimony-doped tin oxide films (ATO) show the best thermal and chemical stability than other TCO films such as Al-doped zinc oxide (ZnO) and tin-doped In2O3 (ITO). Moreover, the production cost of ATO films is cheaper than other TCO materials. However its resistivity is still unsatisfactory. So, in this work, we investigated the effect of annealing treatment on the resistivity variation of the ATO films. Tin oxide films doped with antimony (Sb) of 6 wt% were deposited on 7059 corning glass by RF magnetron sputtering methods for the application to transparent electrodes. The synthesized ATO films were annealed at temperatures ranging from 300 to 600 oC in steps of 100 oC using RTA equipment in oxygen and nitrogen ambient, respectively. We measured and compared the properties of the post annealed ATO films using structural, electrical and optical methods as a function of the annealing temperature.

[1] A.V. Tadeev, G. Delabouglise, M. Labeau, Thin Solid Films 337 (1999) 163.

TF-TuP23 Self-Assembly of Organic Thiocyanates on Gold: An Alternative to Thiols?, ***C. Shen****, M. Buck,* University of St Andrews, UK, *T. Weidner, M. Zharnikov*, Universität Heidelberg, Germany

Adsorption of organothiols is a standard way to form self-assembled monolayers (SAM) on coinage metals, in particular on gold and it is the ease of preparation and flexibility in the design of the molecular structure which enables the tailoring of surface properties for a diversity of applications in (bio)sensors, electronics, or electrochemistry. However, thiols are prone to oxidation to disulfides which can seriously impede the formation of SAMs. This becomes particularly apparent in the case of dithiols where poorly ordered multilayers can form rather than well-defined monolayers with one thiol binding to the substrate and the other thiol moiety forming the SAM surface. A viable alternative to protected or unprotected thiols has recently been reported by Ciszek et al.[1] who demonstrated that thiocyanates form thiolate SAMs through cleavage of the S-CN bond. While SAMs formed from thiocyanates are, therefore, chemically identical to thiol SAMs, there are structural differences between the respective SAMs with organothiocyanates resulting in layers of inferior quality.[1,2] Since the structural quality of SAMs is a decisive factor in some applications such as those related to electrochemistry we have investigated possibilities of how to improve the quality of thiocyanate based SAMs. Applying spectroscopic and electrochemical characterisation and scanning tunneling microscopy it is shown that high quality films from isocyanate precursors can be formed. However, the quality is critically dependent on the preparation parameters such as temperature, concentration, or exposure time.

[1] Ciszek, J. W.; Stewart, M. P.; Tour, J. M. J. Am. Chem. Soc. 2004, 126, 13172.

[2] Dreesen, L.; Volcke, C.; Sartenaer, Y.; Peremans, A.; Thiry, P. A.; Humbert, C.; Grugier, J.; Marchand-Brynaert, J. Surf. Sci. 2006, 600, 4052.

TF-TuP24 Effect of Substrate Temperatures on Amorphous Carbon Nitride Films Prepared by Reactive Sputtering*, M. Aono, H. Akiyoshi, N. Kitazawa,* ***Y. Watanabe***, National Defense Academy, Japan

Amorphous carbon nitride (a-CNx) thin films were deposited on silicon single crystal and fused silica substrates by rf-reactive sputtering method using a graphite target and the effect of the substrate temperatures on film properties has been studied. The substrate temperature was varied from room temperature to 873 K. Film composition and their chemical bonding states were analyzed by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR). Film hardness was measured by nano-indentation method using a Berkovich diamond tip and the maximum load was kept at 1 mN. XPS studies show that the decreasing tendency in the composition ratio of carbon to nitrogen in a-CNx films with the substrate temperature is observed, but the bonding fraction of nitrogen and sp3-carbon increases with the substrate temperature. The D-peak position obtained from Raman spectroscopy shifts to high wave number with the substrate temperature. The nano-indentation tests reveal that the film hardness increases from 2 to 12 GPa as the substrate temperature increases from RT to 823 K. These results suggest that the film hardness is closely related to the bonding states between carbon and nitrogen. The effect of the substrate temperature on other properties will be discussed.

TF-TuP25 Investigating the Surface Morphology of Polymer Thin Films Grown by Matrix-Assisted Pulsed Laser Evaporation*,* ***J.M Fitz-Gerald****, A.T. Sellinger, E.M. Leveugle, L.V. Zhigilei*, University of Virginia

The ability to achieve controlled growth of polymer and polymer nanocomposite thin films in a dry-processing environment is of significant interest to both the microelectronics and biomedical communities. While matrix-assisted pulsed laser evaporation (MAPLE) has been successfully utilized to deposit thin films spanning several classes of polymer, films often possess excessive surface roughness due to the ejection of matrix-polymer clusters from the irradiated target. Research has shown that as an ejected cluster travels through the laser-generated plume, internal polymer molecules are pushed towards the boundaries of the cluster, forming a balloon-like structure that is subsequently deposited onto the substrate surface. The deposition of these clusters results in numerous surface features exhibiting a range of geometries. In order to investigate the structural origin of these features in greater detail, coarse-grained molecular dynamics simulations were conducted to model the behavior of these clusters upon deposition onto the substrate at incident velocities of 100, 500, and 1000 m/s. The results of these simulations suggest that the structural range of surface formations observed experimentally can be partially attributed to the velocities of incident clusters prior to deposition. Previous experimental work has shown that the presence of these features can be reduced in pure polymer films by either decreasing the polymer concentration in the targets, or through substrate heating. Similar experiments were therefore performed for polymer/carbon-nanotube (CNT) composite thin film growth in an effort to both alleviate surface roughness, and enhance the dispersion of CNTs in deposited films. Characterization included the use of high-resolution electron microscopy, high-speed imaging, and infrared spectroscopy.

Applied Surface Science

Room: 610 - Session AS-WeM

Chemical Imaging at High Spatial Resolution and Nanoscale Materials

Moderator: K.G. Lloyd, DuPont

8:00am **AS-WeM1 Local Chemical Measurements with the Scanning Tunneling Microscope**, ***P.S. Weiss***, The Pennsylvania State University **INVITED**

Interactions within and between molecules can be designed, directed, measured, understood and exploited at unprecedented scales. We look at how these interactions influence the chemistry, dynamics, structure, electronic function and other properties. Such interactions can be used to advantage to form precise molecular assemblies, nanostructures, and patterns, and to control and to stabilize function. These nanostructures can be taken all the way down to atomic-scale precision or can be used at larger scales. We measure these interactions and the electronic perturbations that underly them using scanning tunneling microscopy. In these and other measurements, we collect substantial data sets in order to generate distributions with the statistics of ensemble-averaging techniques, while still retaining all the single-molecule and environmental information. This requires new automated tools for acquisition and analyses. We use molecular design, tailored syntheses, intermolecular interactions and selective chemistry to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements of single or bundled molecules.

8:40am **AS-WeM3 Chemical Characterisation on the Nanoscale: Imaging XPS and Scanning Auger Microscopy with Ultimate Spatial Resolution**, ***M. Maier***, *T. Berghaus, D. Funneman, K. Winkler,* Omicron NanoTechnology, Germany, *N. Barrett,* CEA-DSM/DRECAM/SPCSI, CEA Saclay, France, *O. Renault*, CEA-Leti, Minatec, France

In this contribution we briefly summarize the current status of Imaging XPS (iXPS) and Scanning Auger Microscopy (SAM). Novel instrument concepts are presented, one in either field achieving ultimate resolution beyond todays limits. In iXPS a great obstacle for higher resolution is the limited X-ray brilliance in the analysis area in combination with the small electron acceptance angle of current spectrometers. Today commercial laboratory instruments are limited to approx. 3 μm resolution at best. Acquisition times as well as time for experiment set up increase unacceptably when the attempt is made to utilise this kind of resolution routinely. In particular with those instruments acquiring each image pixel sequentially by either scanning the X-ray beam or the analysis spot. We present first results of the NanoESCA instrument recently installed at LETI. A new lens concept provides a huge progress for the acceptance angle of photo electrons. This is combined with a patented abberation compensated analyser allowing the acquisition of typically 640x512 image pixels in a single shot. This offers the unique possibility to achieve sub micron image resolution routinely as well as small spot spectra from well defined areas below 1μm diameter, within reasonable acquisition times. In the field of SAM, the spatial resolution depends mainly on the performance of its electron source. Crucial parameters are the probe diameter, the electron energy, and the beam current density. As state of the art a spatial resolution on the order of 10 nm and slightly below has been demonstrated recently on the most advanced commercial instruments, using beam energies as high as 20 keV. However, the Auger cross section increases for lower beam energies and the scattering volume in the sample decreases. Thus operation at lower beam energies is desirable, but the probe diameter still shall not increase to an counteracting extent. We present SAM measurements acquired with a new electron source employing a patented lens system optimised for low beam energies and high current density. This concept enables the highest so far reported SAM resolution of 5 nm (at 10kV). Even at beam energies as low as 1keV more than 1 nA beam current can be focussed into <10nm spotsize. Furthermore we describe the combination of SEM/SAM with complementary techniques, such as STM/AFM, 4 Probe STM, SEMPA, or EBSD to provide information on topography, electronic structure, magnetic domains, or crystal orientation.

9:00am **AS-WeM4 Application of Chemical Imaging in the Pharmaceutical Industry**, ***X. Dong***, *C.A.J. Kemp*, Eli Lilly and Company

Chemical imaging methods have seen increased utilization within the pharmaceutical industry due to their ability to provide insight into the composition and product performance of solid oral dosage forms. The primary imaging tools used for this type of characterization include EDS, NIR, Raman, NMR, and TOF-SIMS. This presentation will focus on the use of imaging tools for studying the detailed composition of dosage forms and packaging materials, and the inhomogeneous discoloration of API stored in USP-approved materials. Additionally, data will show that TOF-SIMS can be a pivotal tool for trouble-shooting by combining high mass resolution spectra with high spatial resolution images. The strengths and limitations of various imaging techniques (chemical and physical) will also be discussed.

9:20am **AS-WeM5 In-situ Surface Analysis by Optical Means**, ***C.M. Eggleston***, University of Wyoming **INVITED**

Understanding natural geochemical systems requires investigating fundamental reactions (adsorption, dissolution/growth, electron transfer, catalysis) at a variety of solid-solution interfaces. The availability of techniques for characterizing solid-liquid interfaces in-situ has made this task simpler. Such techniques include synchrotron-based X-ray absorption spectroscopies (e.g., EXAFS, XANES), scanning probe microscopes (STM, AFM, and their variations), and developments in Raman and IR specroscopies. Here, we explore some perhaps less well-known techniques: Optical second harmonic generation (SHG), optical waveguide lightmode spectroscopy (OWLS), and photocurrent measurements coupled to impedance spectroscopy. SHG is a nonlinear optical technique. Briefly, the interface represents a noncentrosymmetric setting between two centrosymmetric bulk phases. Intense laser light impinging on an interface can produce a few photons of doubled-frequency (second harmonic) whose intensity and polarization can be related to the concentration - and possibly orientation - of adsorbed species. We have used SHG to observe the adsorption of organic molecules to oxide surfaces and to study the structure of water near charged oxide surfaces. OWLS operates on the basis of small changes in the effective refractive index of a waveguide of sub-wavelength thickness as the result of molecular adsorption to the waveguide surface. We are using OWLS to study the adsorption of proteins, particularly outer membrane cytochromes from iron-reducing bacteria, on oxide surfaces. This technique has proven crucial in studying the adsorption of small amounts of protein. Furthermore, comparison of quartz crystal microbalance (QCM) adsorption results (which includes associated water in the adsorbed mass) to OWLS results (which excludes associated water) shows that of the total adsorbed mass, only 27% is protein in these cytochromes. Our work with semiconducting oxide electrodes necessitates electrode charcterization with regard to flatband potential, charge carrier density, and other properties. In addition, these and photocurrent transient techniques allow us to locate electronic states both at the semiconductor surface and within its bulk bandgap. This presentation will briefly show how such states may be located and studied using photocurrent transient spectroscopy and impedance spectroscopy in the case of iron oxide photocatalysts.

10:40am **AS-WeM9 Synchrotron Radiation Induced X-ray Photoelectron Emission Microscopy (SR-XPEEM) with Aberration Corrected Energy Filterin**, ***N. Barrett***, CEA-Saclay, FR, *O. Renault,* CEA LETI Minatec, FR, *L.-F. Zagonel,* CEA Saclay, FR, *A. Bailly,* CEA LETI Minatec, FR, *J. Charlier, J. Leroy,* CEA Saclay, FR, *J.C. Cezar, N. Brookes,* ESRF, FR, *M. Senoner,* Fed. Inst. Mtls Testing, Germany, *J. Maul, T. Berg, F. Schertz, G. Schönhense*, Univ. of Mainz, Germany

The combination of high brightness photon source and aberration corrected energy filtering has allowed new progress in the field of electron emission microscopy for nanoscience and nanotechnology. The first commercially available NanoESCA instrument (OMICRON GmbH) has been recently commissioned and tested at the CEA Nanocharacterization centre (Minatec) in Grenoble and on beamline ID08 at the ESRF. We first present the principles of spectromicroscopy, and in particular the use of an electrostatic PEEM column together with an energy aberration corrected double hemispherical analyzer. The objective immersion lens and the high extraction voltage considerably improve lateral resolutions. The use of a contrast aperture reduces the chromatic aberrations in the PEEM column. The accurate focus tracking of the instrument allows imaging at the secondary electron threshold and across specific core levels at chosen kinetic energies. The resulting lateral resolution better than 150 nm and energy resolution give an imaging capability with full chemical state sensitivity. The principles will be illustrated by several examples. The core level intensity contrast is demonstrated with a multilayer certified standard sample of GaAs/GaxAl1-xAs variable multilayer. The energy resolved chemical mapping will be illustrated via the preferential molecular grafting on a heterogeneous Au-Si substrate. Finally, the depth resolution thanks to the variable photoelectron escape depth is employed to do non-destructive position detection of pre-solar grains coming from a meteorite, prior to nano-SIMS analysis. The perspectives include reaching the ultimate resolution limits using an optimized synchrotron beamline, the development of valence band imaging and the study of single nanodevices.

11:00am **AS-WeM10 Directed Growth of Ordered Metal Nanostructures on Crystalline Cellulose Templates**, ***G.J. Exarhos***, *Y. Shin*, Pacific Northwest National Laboratory

A form of nano-crystalline cellulose, isolated from carbohydrate-derived materials like paper or cotton, serves as a reducing template that drives formation of ordered regions of metal nanoparticles or nanorods when placed in aqueous metal precursor solutions under hydrothermal conditions. Uniform sized gold, silver, palladium, platinum, copper, nickel, selenium and other metal or metal-oxide nanocrystals were observed to rapidly nucleate and preferentially grow along the ordered hydroxyl-rich regions of the substrate. The ordered metals display catalytic, electrical and optical properties that would not normally be present in larger crystals. For example, a marked enhancement in the rate of degradation of organic dyes in water under uv-irradiation has been measured when selenium-decorated templates were immersed in methylene blue solutions. Materials have been characterized by means of XRD, FESEM, TEM, and optical methods. The mechanistics of the growth process will be discussed based upon these structural measurements and the known reducing properties of carbohydrate materials. Prospective uses of these materials for catalysis and in optical applications also will be described.

11:20am **AS-WeM11 Critical Issues Concerning the Use of Nanomaterials In Aerospace Platforms**, ***P.T. Lillehei***, NASA Langley Research Center **INVITED**

Revolutionary aerospace vehicle designs are enabled by the use of lightweight structural composites. These composites must possess structural integrity and multifunctionality features, such as lightning strike protection, for the vehicle to fully realize the weight savings. NASA and the aerospace industry are aggressively pursuing the use of nanomaterials as both structural reinforcements and as an enabler of multifunctionality. Optimal utilization of nanomaterials in multifunctional aerospace platforms will demand an understanding of the fundamental principles that govern their behavior at the nanoscale. For example, NASA has established that a critical factor governing the electrical conductivity characteristics of a nanomaterial or nanocomposite is the degree of dispersion of the nanomodifier in the host matrix. However, before conductive nanomaterials can be considered for use in applications such as lightweight, flexible, surface mountable materials for lightning strike protection, a set of robust, field- ready quality assurance/control (QA/QC) standards must be developed. The research described in this presentation establishes a means of quantifying the dispersion of carbon nanotubes in high-performance, aerospace polymers. Work can now begin on developing the field ready QA/QC implementations of these techniques.

12:00pm **AS-WeM13 Functionalization and Characterization of Gold Nanoparticles**, ***S.D. Techane***, *L.J. Gamble, D.G. Castner*, University of Washington

Gold nanoparticles (AuNPs) are non-toxic and have a high percentage of surface atoms, which gives them special electronic properties and reactivities. Since these properties are dependent on the size, shape and surface chemistries of the AuNPs, one can vary these quantities to achieve desirable applications for AuNPs in biomedicine, microarray and biosensor fields. In this research, AuNPs of different diameters (14nm - 50nm) were synthesized with a citrate reduction method and later functionalized with various chain lengths (3, 6, 8, 11, and 16 carbon chain) of carboxyl terminated alkyl thiol by direct displacement of the citrate ions. To obtain a hydrophobic surface, functionalization with 1-dodecanethiol was tried using a two step functionalization method. The size, shape, and size distribution of the AuNPs were characterized with transmission electron microscopy (TEM) and ImageJ, where the distribution in terms of 3 σ ranged from 2.5 to 20nm, depending on the average diameter of the AuNPs. Surface chemistries of the self assembled monolayer (SAMs) of alkyl thiol were analyzed with X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry. Comparison between SAMs of 16-mercaptohexadecanoic acid (C/O = 8 and C/S = 16) on AuNPs and flat Au surface was done to verify the applicability of XPS data analysis method for curved nanoparticle surfaces. Surface atomic composition ratios: C/S (26 for AuNPs and 42 for flat Au), C/O (5 for AuNPs and 8 for flat Au), C/Au (1.7 for AuNPs and 1.2 for flat Au) exhibited some differences between the two surface types. These differences indicate the need to develop specific XPS data analysis methods to accurately represent the surface chemistries of curved nanoparticles surfaces. XPS results for the two-step functionalization method, which uses thioctic acid as an intermediate, showed 11% oxygen surface composition with 6% carboxyl carbon indicating incomplete displacement of the intermediate carboxyl thiol and a need for a better functionalization method to achieve hydrophobic surface. AuNPs with carboxyl terminated SAMs are being used to investigate adsorption thermodynamics of short chain peptides onto these surfaces. Protein assay, XPS, and NMR are being used to characterize the adsorbed peptides.

Biomaterial Interfaces

Room: 609 - Session BI-WeM

Nano-Engineered Biointerfaces

Moderator: A. Chilkoti, Duke University

8:00am **BI-WeM1 Multifunctional Quantum Dots for Biomedical Detection and Imaging**, ***X. Gao***, University of Washington **INVITED**

Metal and semiconductor nanoparticles in the 1-50 nm size range are of considerable current interest, not only because of their unique size-dependent properties but also their dimensional similarities with biological macromolecules (e.g., nucleic acids and proteins). These similarities could allow an integration of nanotechnology and biology, leading to major advances in medical diagnostics, prognostics, and targeted therapeutics. In this talk, I present recent development of multifunctional nanostructures for biomedical applications, such as bioconjugated nanoparticles for in vitro ultrasensitive detections and in vivo molecular imaging.

8:40am **BI-WeM3 Lateral Bilayer Fusion to Nanofunctional Probes**, *B.D. Almquist*, ***N.A. Melosh***, Stanford University

The cell membrane is one of the most vital components of a cell, and crossing through this barrier is a crucial component of biotechnology. Integration of inorganic structures with the cell membrane is poorly understood, and current techniques involve creating holes in or puncturing cell membranes to control access into the cell. However, functionalized materials with nanoscale hybrophobic layers may be able to directly fuse the lipid membrane edge to an inorganic structure, enabling non-disruptive electrical and chemical access into the cell. We have tested whether nanoscale inorganic probes integrate into the hydrophobic core of a lipid bilayer using an AFM probe with hydrophobically functionalized bands 5-20 nm thick at the end of the tip. We quantitatively measure the adhesion strength between the probe and the lipid bilayer, and correlate this molecule-membrane force with the molecular structure. We find the thickness of the nanoscale band and the identity of the hydrophobic molecules alters the ability to fuse to the membrane.

9:00am **BI-WeM4 GaN Nanowires for DNA-Sensing Applications**, *C.P. Chen, A. Ganguly, C.H. Wang*, ***L.-C. Chen***, National Taiwan University, *C.W. Hsu, Y.-K. Hsu, K.-H. Chen*, Academia Sinica, Taiwan

A novel DNA-sensing system based on GaN nanowires (NWs) is presented coupled with their electrochemical impedance and photoluminescence measurements. GaN is well established now for a variety of optoelectronic applications. However, while its inherent bio-compatibility has also been recognized, its application as bio-sensors has been surprisingly lacking till date. Meanwhile, one-dimensional nanostructures have attracted huge interest as potential building blocks for the future nanoelectronic devices. In this report, GaN NWs are used as a transducer for DNA-sensors, by immobilizing single-strand DNA (ssDNA) molecules through covalent binding using organosilane linker (MPTS). The MPTS-modified GaN NWs exhibited an electrochemical window remarkably wider than those of boron-doped diamond or carbon nanotubes reported to date. The immobilization of ssDNA and the subsequent hybridization to double-strand DNA (dsDNA) were confirmed using confocal microscope. Electrochemical impedance measurement showed that interfacial electron-transfer resistance (Ret), from solution to transducer surface, increased significantly when pristine GaN NWs were immobilized with ssDNA, along with a formation of additional semicircle region at lower frequency in Nyquist plot. The unique appearance of double-semicircle region for ssDNA-immobilized NWs, compared to single-semicircle region for pristine GaN NWs, leads to the idea of formation of double-capacitance layer in series. The phenomenon is more prominent by the appearance of double peaks in the plot of phase angle vs. frequency (Bode plot), the second peak, formed after ssDNA-immobilization, showed further increase under the hybridization to dsDNA, and consequently reduces the overall impedance. Moreover, quenching behavior in photoluminescence of the GaN NWs was distinguishable for the ones immobilized with ssDNA and the same hybridized to dsDNA. Both the technique implies the ability of oligonucleotides, immobilized on the NW-surface, to interact with other biomolecules. The dual and label-free sensing capability in impedance and photoluminescence of GaN NWs makes them effective DNA transducers.

9:20am **BI-WeM5 Functional Protein Chip Nano-Templates by Chemical Lithography and Multivalent Chelator Techniques***, **A. Turchanin**, M. El-Desawy, M. Schnietz, A. Gölzhäuser,* University of Bielefeld, Germany*, A. Tinazli, H. Großmann, R. Tampé,* Johann Wolfgang Goethe-University, Germany*, H.H. Solak*, Paul Scherrer Institut, Switzerland

To study protein function and interaction, there is a high demand for specific, stable, highly parallel, and functional protein arrays on solid substrates. To implement this, we propose a protein chip approach based on the combination of electron induced chemical lithography[1] with aromatic self-assembled monolayers (SAMs) and multivalent chelators[2] for high-affinity capturing of His-tagged proteins. Templates for functional and switchable His-tagged protein architectures were created by electron induced changes in 4'-nitro-1,1'-biphenyl-4-thiol SAMs on gold (NBPT). Chemical nanopatterns were generated in SAMs by both electron beam lithography (EBL) and extreme UV interference lithography (EUV-IL). As a model system carboxy derivative tris-NTA chelators were studied. Different steps of the protein chip assembly (fabrication of amino terminated cross-linked areas, generation of protein repellent EG3-OH thiols matrix, grafting of tris-NTA chelators, and chelating efficiency of Ni(II) ions) were characterized in detail by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The functionality of the generated protein chips was shown in situ, under physiological conditions by AFM and scanning fluorescence microscopy measurements via specific, homogeneous, oriented and reversible immobilization of His_6-tagged 20S proteasome and fluorescence labelled His_{10}-tagged maltose binding proteins (MBP). We will present highly parallel large area (~10 mm^2) protein arrays with the lateral dimensions of periodic features ranging from 1000 nm to 50 nm.

[1] A. Gölzhäuser, W. Eck, W. Geyer, V. Stadler, T.Weimann, P. Hinze, M. Grunze, Adv. Mat. 13 (2001) 806

[2] A. Tinazli, J. Tang, R.Valiokas, S. Picuric, S. Lata, J. Piehler, B. Liedberg, R. Tampé, Chemistry 11 (2005) 5249.

9:40am **BI-WeM6 Protein Patterning by Scanning Near-Field Photolithography***, **G.J. Leggett**, R.E. Ducker, M. Montague, K.S.L. Chong*, University of Sheffield, UK

Photolithography is a convenient and rapid route to the fabrication of patterned self-assembled monolayers for the control of biological organisation. Alkanethiols may be photo-oxidised by exposure to light with a wavelength of 244 nm to yield soluble sulfonates which may be displaced by complementary thiols to yield clean, well-defined chemical patterns. Protein patterning is complicated by the problems of non-specific adsorption. Most proteins adhere to most surfaces, rendering protein patterning difficult. Oligo(ethylene glycol) (OEG) terminated self-assembled monolayers are attractive because they resist protein adsorption very effectively. Here we have explored the possibility of patterning OEG-terminated SAMs using photolithography. Rates of photo-oxidation of OEG-terminated thiols have been measured using contact angle goniometry, static SIMS and friction force microscopy. The kinetics observed appear to be different from those observed for other thiols. The mechanism appears to be complex. Over longer exposures, photo-oxidation of the head group occurs. Subsequent patterning through a mask yields well-defined structures that consist of either methyl or carboxylic acid terminated thiols in regions exposed to UV light, to which proteins may, respectively, be adsorbed or covalently bound, and protein-resistant OEG-terminated adsorbates over the rest of the surface. Exposure using a near-field scanning optical microscope (scanning near-field photolithography, SNP) yields nanometre scale structures. At short exposures, photodegradation of the OEG chain occurs leading to the formation of aldehyde groups that covalently bind proteins with high efficiency. This provides a very convenient single-step route to the introduction of a reactive functional group, in a spatially selective fashion, to a protein resistant OEG monolayer. The amount of streptavidin bound to such a photo-modified monolayer is nearly as great as that bound using well-established carbodiimide-based methods on carboxylic acid terminated monolayers. Significantly, the photodegradation of the OEG terminal groups in this process is much more rapid than the oxidation of the thiol head-group and is, moreover, capable of excitation at longer wavelengths, where photo-oxidation of the thiol sulfur atom is no longer a possibility. Photopatterning thus appears to be a simple and versatile route to protein patterning.

10:40am **BI-WeM9 Multicomponent Nanoparticles for Controlled Intracellular Delivery to Targeted Cells***, J.M. Bergen, I.K. Park, E. Kwon, **S.H. Pun***, University of Washington **INVITED**

Gene therapy offers the possibility of treating diseases by altering the protein expression profiles of affected cells. Nucleic acids can be condensed by complexation with cationic polymers to nanoparticle structures called "polyplexes". These synthetic vehicles can be used to accomplish gene delivery but are usually limited in their applications due to poor delivery efficiencies in non-dividing cells. I will describe our work on developing multicomponent polyplexes that incorporate biologically-derived peptides that facilitate delivery. Peptides that mediate neuron-specific uptake and endosomal release were incorporated into polyplexes. The intracellular trafficking of these materials was also investigated by live cell imaging in compartmented chambers. Incorporation of functional peptides improves delivery efficiency to cultured, neuron-like PC-12 cells.

11:20am **BI-WeM11 Femtosecond Laser Ablation to Create Nanometer-Scaled Cell Adhesion Ligand Patterns***, **R.C. Schmidt***, UC Berkeley/UC San Francisco Joint Graduate Group in Bioengineering*, D.H. Hwang, C.P. Grigoropoulos,* UC Berkeley*, K.E. Healy*, UC Berkeley/UC San Francisco Joint Graduate Group in Bioengineering

The goal of our project is to fabricate interfaces for mammalian cell culture that control cell fate via the spatial distribution of the individual focal adhesions cells use to interrogate the interface. To create nano-scale cell adhesion sites on a surface, a thin protein adsorption resistant polyethylene glycol (PEG) brush layer was synthesized via surface initiated atom transfer radical polymerization (SI-ATRP). The surface chemistry was verified with XPS, showing strong oxygen and carbon peaks consistent with a PEG film, and thickness of the dry film in air was calculated to be 10nm using a quartz crystal microbalance with dissipation (QCMD). The film was selectively ablated using focused femtosecond laser pulses, exposing the underlying quartz substrate as centers for adsorption or grafting of cell-adhesive molecules. Preliminary results at a wavelength of 400nm with a 50X objective demonstrated spatial resolution approaching 200nm based on atomic force microscopy (AFM) scanning of the ablated features. The practical resolution limit can be further improved (~10-100nm) by utilizing higher magnification lenses at shorter wavelengths or processing in the optical near-field. This technique allows us to generate arbitrary nanoscale protein patterns on the benchtop without specialized processing environments. These nanostructured surfaces will eventually allow us to decouple the effects of cell size and shape, focal adhesion placement, and ligand density on cell fate decision by directly controlling the number and area of focal adhesion complexes formed. Each variable can be modulated independently to determine the effects on cellular function and fate determination.

11:40am **BI-WeM12 Neuron Pathfinding on Functionalized Patterned, Gradient, and Fiber Biomaterial Surfaces***, W.M. Theilacker, M.E. Boggs, S.K. Mbugua, S.P. Sullivan,* Univ. of Delaware*, D.E. Willis,* Nemours Biomedical Res. of Alfred I duPont Hospital for Children*, K.W. Dabney,* Alfred I duPont Hospital for Children*, J.L. Twiss,* Nemours Biomedical Res. of Alfred I duPont Hospital for Children*, **T.P. Beebe, Jr.***, Univ. of Delaware

This paper will present the recent results from a collaborative study that is aimed at developing novel growth-promoting substrates for injured and damaged neurons, with an emphasis on understanding the mechanisms of substrate-neuron interactions and the resulting modulation of intra-axonal signal transduction. Axons regenerating in vivo must traverse from a permissive into a non-permissive environment. We use the permissive environment of novel surface-grafted 2-D and 3-D materials to increase the capacity for axons to traverse into a non-permissive growth environment. We have generated novel patterned and well characterized 2-D and 3-D biomaterial growth substrates that mimic the environment encountered by the regenerating axons in the injured spinal cord. This is accomplished by engineered patterns and gradients with tailored composition of growth-promoting extracellular matrix molecules. We will also describe the results of studies aimed to observe and mimic how permissive growth substrates directly modulate axonal-substrate interactions and intra-axonal signal transduction. The program incorporates elements of surface chemistry, surface analysis, cell culture, optical microscopy, and neuroscience.

12:00pm **BI-WeM13 XPS, ToF-SIMS, NEXAFS and SPR Characterization of Nitrilotriacetic Acid-Terminated Self-Assembled Monolayers For Controllable Immobilization of Proteins***, **F. Cheng**, L.J. Gamble, D.G. Castner*, University of Washington

For immobilization of proteins onto surfaces in a specific and controlled manner it is important to start with a well-defined surface that contains specific binding sites surrounded by a nonfouling background. For immobilizing histidine-tagged (histagged) proteins, surfaces containing nitrilotriacetic acid (NTA) headgroups and oligo(ethylene glycol) (OEG) moieties are a widely used model system. The surface composition, structure and reactivity of mixed NTA/OEG self-assembled monolayers (SAMs) on Au substrates were characterized in detail using X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and surface plasmon resonance (SPR) biosensing. XPS results for sequentially adsorbed NTA thiols followed by OEG thiols showed that OEG molecules were incorporated into a incompletely formed NTA monolayer until a complete mixed SAM was formed. Surface concentration of NTA headgroups was estimated to be 0.9 molecule / nm^2 from XPS results. Angle-resolved XPS and polarization-dependent NEXAFS results both indicated NTA headgroups were slightly reoriented toward an upright position upon OEG incorporation. Nitrogen-containing and OEG-related secondary ion fragments from the ToF-SIMS experiments confirmed the presence of NTA headgroups and OEG moieties in the monolayer. These fragments along with secondary ion amino acid fragments are being used to investigate the orientation and conformation of histagged proteins immobilized onto the NTA/OEG SAMs. SPR measurements of a histagged, humanized anti-lysozyme variable fragment (HuLys Fv) immobilized onto Ni(II) -treated mixed NTA/OEG SAMs demonstrated the reversible, site-specific immobilization of histagged HuLys Fv (170 ± 7 ng / cm^2) with strong binding affinity (approximately 43 nM). The mixed NTA/OEG SAMs without Ni(II) treatment exhibited good resistance to nonspecific adsorption of histagged HuLys Fv (< 2 ng / cm^2).

Electronic Materials and Processing

Room: 612 - Session EM-WeM

Contacts, Interfaces and Defects in Semiconductors

Moderator: L.M. Porter, Carnegie Mellon University

8:00am **EM-WeM1 Role of Hydrogen Bonding Environment in Amorphous Silicon Films for Passivation of Crystalline Silicon Based Photovoltaic Devices**, *M.Z. Burrows, U.K. Das,* ***R.L. Opila****, R.W. Birkmire,* University of Delaware

The search for an ideal surface passivation layer of crystalline silicon (c-Si) to be employed in the silicon heterojunction photovoltaic device has garnered much attention. The leading candidate is a few nanometers thick amorphous silicon (a-Si:H) film. This is due to the fact high open circuit voltages above 700mV, key to 20% power conversion efficiencies, are only possible with low surface recombination velocities at the passivated c-Si / a-Si interface. Our approach involves a concentrated effort to link the deposition parameters to the thin a-Si:H material properties as revealed with Fourier transform infrared spectroscopy (FTIR) and match observed changes in H bonding to passivation quality as determined by effective minority carrier lifetime measurements. Reported dependencies of film surface passivation quality on substrate preparation, orientation, and deposition temperature have been extended in this work to include H to SiH_4 dilution ratio and post-deposition annealing. Marked differences have been observed with carrier lifetimes ranging from few microseconds to few milliseconds. A simple yet extremely sensitive FTIR procedure based on Brewster angle transmission measurements enables the probing of films of just 5-10nm thickness. By cataloguing the changes in H content and bonding environment as hydrogen dilution or annealing conditions were varied a comprehensive picture of material quality as related to passivation quality has emerged. Simple avoidance of the growth regimes that lead to epitaxial growth of Si on the c-Si substrate produces decent lifetimes on the order of 500µsec can be achieved. However this often entails harsh deposition conditions that lead to defective films of primarily bulk SiH_2 bonding. Subsequent low temperature anneals, presumed to only relax the amorphous lattice, are shown to not only cause unexpected bulk hydrogen evolution but also involve various complex reactions. Annealing in atmosphere changes surface SiH_2 to chainlike $(SiH_2)_n$ as well as oxygen back-bonding to create surface oxides like $SiH(O_3)$. Annealing in vacuum causes minimal surface SiH_2 disturbance but rather surface SiH and SiH_3 evolution. Finally it is concluded that the best passivation layer consists of primarily well ordered mono-hydride bonding in purely amorphous phase. Sub-optimal amorphous phase films can be improved by post-deposition anneal.

8:20am **EM-WeM2 Impact of Intrinsic Vacancies on Phase Change and Epitaxial Growth of In_2Se_3 on Si(111)**, ***C.Y. Lu****, E.N. Yitamben, T.C. Lovejoy,* University of Washington, *K.M. Beck, A.G. Joly,* Pacific Northwest National Laboratory, *M.A. Olmstead, F.S. Ohuchi*, University of Washington

The strong change in optical reflectivity during the amorphous-crystalline phase transition in ternary chalcogenides is the basis of re-writeable compact disc and digital video disk technology. The binary, group-III-chalcogenide semiconductor, In_2Se_3 has recently been proposed as a resistance-based phase-change random access memory (PRAM) material due to its large (10^5) resistance change between the crystalline and amorphous phases.[1] The intrinsic vacancies and structural variability characterizing crystalline In_2Se_3 likely play an important role in controlling phase-change characteristics. We have investigated growth of amorphous and epitaxial In_2Se_3 films on Si(111), as well as the crystallization of amorphous In_2Se_3 films through resistive annealing using a combination of scanning tunneling microscopy, photoemission spectroscopy, and X-ray diffraction. Amorphization of crystalline In_2Se_3 films by laser annealing was studied using photo electron emission microscopy. Despite the 7.3% lattice mismatch, we are able to grow laminar, epitaxial films of γ- In_2Se_3 (0001) up to at least 3 nm in thickness that exhibit a surface reconstruction associated with the ordered vacancy structure; we attribute this ability to grow laminar films to the flexibility provided by the intrinsic vacancy structure. A minimum thickness of 2 bilayers (0.64 nm) is required to undergo the phase change and a minimum thickness of 3 bilayers (0.96 nm) is required for the ordered-vacancy reconstruction characteristic of the epitaxially grown material during phase change. Annealing room-temperature-deposited films can transform amorphous In_2Se_3 to be highly textured γ- In_2Se_3 with the (0001) plane parallel the substrate surface. A buffer layer of epitaxial In_2Se_3 before deposition of the amorphous film lowers the crystallization temperature and improves the uniformity of the crystalline In_2Se_3 phase. This work was supported by NSF grant DMR 0605601. TCL acknowledges support from NSF/NCI IGERT DGE-0504573. Some of the research was pursued at the Advanced Light Source, which is supported by the DOE under contract DE-AC02-05CH11231. KMB acknowledges the support from U.S. Department of Energy by Battelle Corporation.

[1] H. Lee, D-H. Kang, and L. Tran, Mat. Sci. Eng. B 119 (2004) 196.

8:40am **EM-WeM3 Reliability of Electrical Contacts to Single Crystal SiC**, ***R.S. Okojie***, NASA Glenn Research Center **INVITED**

The utilization of Silicon Carbide (SiC) semiconductor-based microsystems targeted for extreme applications (i.e., high temperature, high power, extreme vibration, and aggressive chemical environments) has largely been hindered by intrinsic material defects and the reliability issues that are associated with the stability of the contact metallization.[1] In this talk, the research efforts at NASA Glenn to resolve the reliability problems of the contact metallization will be presented, which includes the in-depth reliability studies to identify the multilayer metallization that provides stable long-term performance of ohmic contact to SiC. The observation of process-induced stacking faults (SFs) has also been determined to present a reliability problem to 4H-SiC polytype devices. The formation of single and multiple stacking faults that sometimes give rise to 3C-SiC was observed in several doped n-type 4H-SiC epilayer following thermal oxidation. Transmission electron microscopy following oxidation revealed double stacking faults and bands of 3C-SiC in the 4H-SiC epilayer. Depth-resolved cathodoluminescence spectroscopy at 25 oC based on low energy-excited electron nanoscale luminescence revealed a spectral peak at 2.5 eV photon energy that was not present in the sample prior to oxidation. This is in addition to the 3.22 eV photon energy peak corresponding to 4H-SiC.[2] The polytypic transformation is attributed to the motion of Shockley partial dislocations on the (0001) slip planes.[3] Auger electron spectroscopy, Scanning Electron Microscopy, Transmission electron microscopy, and current-voltage measurements that were used to develop an in-depth knowledge of these failure mechanisms will be discussed.

[1] P. G. Neudeck, R. S. Okojie, Liang-Yu Chen, Proceedings of the IEEE, Vol: 90 , Issue: 6 , pp.1065 . 1076. 2004

[2] R.S. Okojie, D. Lukco, L. J. Brillson S. Tumakha, G. Jessen, M. Xhang and P. Pirouz,. Appl. Phys. Lett. 79, 3056 (2001).

[3] Robert. S. Okojie and Ming Zhang, in Silicon Carbide 2004-Materials Processing and Devices, edited by Michael Dudley, Perena Gouma, Tsunenobu Kimoto, Philip G. Neudeck, and Stephen E. Saddow (Mater. Res. Soc. Symp. Proc. 815, Warrendale, PA , 2004).

9:20am **EM-WeM5 Epitaxial CVD of Metallic HfB2 on SiC Substrates**, ***Y. Yang***, University of Illinois at Urbana-Champaign, *V.M. Torres,* Dow Corning Compound Semiconductor, *J.R. Abelson*, University of Illinois at Urbana-Champaign

HfB2 is an attractive candidate for many technological applications owing to its refractory melting temperature (3250°C), high mechanical hardness (29 GPa), low electrical resistivity (15 µΩ-cm), high optical reflectivity, and chemical inertness at high temperatures. The epitaxial growth of HfB2 is particularly interesting because the (0001) plane has a small lattice mismatch with the compound semiconductors GaN (1.5%) and SiC (-2%) and the coefficients of thermal expansion are reasonably close for these three materials. In principle, epitaxial HfB2 could be used as a growth template and/or as an electrical contact in a multilayer compound semiconductor device while maintaining crystallographic continuity. We report that high quality HfB2 thin films can be deposited on SiC(0001) substrates by chemical vapor deposition using the single source precursor Hf(BH4)4. This precursor is a solid which sublimes at room temperature with a vapor pressure of 15 Torr, such that no carrier gas or heated delivery lines are needed; and it contains no organic or halogen groups. The HfB2 microstructure is strongly dependent on temperature. Films deposited at low substrate temperature are (0001) textured and polycrystalline, as indicated by SEM and XRD analysis. An increase of deposition temperature increases the grain size and reduces the mosaic spread. Films deposited under optimal deposition conditions are extremely flat. The (0001) rocking curve has a FWHM of only 0.26°, indicating a very high epitaxial quality. The room temperature resistivity is < 20 μΩ-cm, close to the bulk value. The surface morphology of the epitaxial film is sensitive to the surface finish of the SiC substrate: film coalescence can be delayed by substrate surface imperfections.

9:40am **EM-WeM6 Surface and Grain Boundary Electron Scattering in Encapsulated Cu Thin Films***, **T. Sun**, B. Yao,* University of Central Florida*, V. Kumar,* Carnegie Mellon University*, A.P. Warren, K.R. Coffey,* University of Central Florida*, K. Barmak*, Carnegie Mellon University

Surface and grain boundary electron scattering contribute greatly to resistivity as the dimensions of polycrystalline metal thin films and interconnects are reduced to and below the length of the electron mean free path. A quantitative measurement of the relative contributions of surface and grain boundary scattering to the resistivity is very challenging, requiring not only the preparation of suitably small conductors having independent variation of the two relevant length scales, namely, the sample critical dimension and the grain size, but also independent, experimental quantification of these two length scales. Since for most work to date the sample grain size has been either assumed equal to conductor dimension or measured for only a small number of grains, the quantification of the classical size effect still suffers from an uncertainty in the relative contributions of surface and grain boundary scattering. A methodology is reported to independently evaluate surface and grain boundary scattering in dielectric encapsulated polycrystalline Cu thin films. The film resistivity measured at both room temperature and at 4K is compared for samples having different grain sizes (determined from 400 to 1,500 grains per sample) and film thicknesses. The experimental data is compared to existing and empirical models of surface and grain boundary scattering in thin films. The resistivity measured at room temperature and 4K is observed to follow similar trends. We find that the resistivity contribution from grain boundary scattering to be significantly greater than that of surface scattering for Cu thin films having Cu/SiO_2 surfaces and grain sizes similar to their thickness. We also find that the resistivity at room temperature is not equal to the simple sum of the low temperature resistivity and the room temperature phonon resistivity contribution, suggesting that either Matthiessen's rule can not be applied, or that the grain boundary and/or surface scattering has a temperature dependence.

10:40am **EM-WeM9 Microstructural Evolution of Nickel Germanides in the $Ni_{1-x}Ta_x$/Ge Systems during In-situ Annealing***, **J.W. Lee**, J.H. Bae, M.H. Park, H.B. Kang, H. Kim, C.W. Yang*, Sungkyunkwan University, Korea

It is becoming increasingly difficult to further improve the performance of Si-based complementary metal-oxide-semiconductor (CMOS) using traditional device scaling. Ge-based devices have attracted considerable attention for high-performance logic applications on account their its lower effective mass and high carrier mobility (double for electrons and four times higher for holes compared with those in Si).[1] However, the NiGe shows a poorer thermal stability than NiSi. The limited thermal stability of NiGe may deteriorate the performance improvement of Ge metal-oxide-semiconductor field-effect transistors (MOSFETs). These features of Ge substrate motivated us to investigate the mechanism of the formation and thermal stability of NiGe and the effect of alloying elements, i.e. the tantalum which is the refractory metal. In this study, the formation and morphological evolution of the germanides formed from the $Ni_{1-x}Ta_x$ (~30nm)/Ge (x=0 and 0.1) systems as a function of temperature was investigated by in-situ annealing in the transmission electron microscope (TEM, JEM-3011, JEOL Co. Ltd) with a specimen heating holder. The sheet resistance of the germanides formed in the $Ni_{0.9}Ta_{0.1}$/Ge system was lower at temperatures above 550°C than the Ni/Ge system. Through the addition of Ta atoms, Ni germanide grain growth was retarded and the surface morphology of the Ni germanide layer improved. An approximately 10nm thick Ta-rich layer formed on the top of the germanide layer. Eventually, the agglomeration of Ni germanide was retarded and the thermal stability of the Ni germanide formed from the Ni-Ta alloy became superior to that formed from the pure Ni.

11:00am **EM-WeM10 Probing the Effect of Interaction and Thermal Expansion Mismatch between Ge and Templated Mask on Defects during Selective Molecular Beam Epitaxy of Ge on Si***, **D. Leonhardt**, Q. Li, S.M. Han*, University of New Mexico

We have previously demonstrated that high-quality, single-crystalline Ge can be grown on Si by epitaxial lateral overgrowth (ELO) as well as by touchdown where nanoscale windows (~7 nm in diameter) are created through a thin chemical SiO_2 layer. These techniques have been successfully used to reduce threading dislocations in the Ge-Si lattice mismatched system. Despite the improvement, dislocations are generated in the epilayer above the templated mask. To test the hypothesis that these defects occur due to varying level of epilayer-template interaction energy (e.g., bond strength and diffusion activation barrier) and thermal expansion differences between the epilayer and template, in addition to coalescence events, we have created masks of SiO_2, Al_2O_3, and Ta having thermal expansion coefficients smaller, larger, and equal to Ge epilayers selectively grown on Si in the mask openings. The windows in the masks are created by spin-coating a disperse layer of polystyrene spheres on the Si substrate followed by mask deposition and lift-off. Ge islands are selectively grown in the mask openings using molecular beam epitaxy (MBE), and further grown laterally over the mask until coalescence occurs. The Ge layers are then characterized by x-ray diffraction, transmission electron microscopy, and etch pit density after chemical-mechanical polishing to determine the effect of interaction energy and thermal expansion differences on the resulting film quality. Furthermore, we quantitatively measure the desorption activation energy of Ge adspecies from the SiO_2, Al_2O_3, and Ta masks to determine the characteristic diffusion lengths of Ge adspecies on the mask surfaces. We will then present the impact of inter-distance of windows in the masks on dislocation density in the Ge epilayer.

11:20am **EM-WeM11 Silver-Bearing Ohmic Contacts for AlGaN/GaN Heterostructures***, **M.A. Miller**, S.E. Mohney*, The Pennsylvania State University

We have investigated the use of Ag in place of Au in V- and Ti-based ohmic contacts to $Al_{0.27}Ga_{0.73}N$/GaN heterostructures for high electron mobility transistors. An optimized V/Al/V/Ag contact provided a specific contact resistance of $1.7x10^{-6}$ Ohm-cm^2 when annealed at 825°C for 60s in N_2. As measured by atomic force microscopy, the contacts had a root-mean-square roughness of 4.5 nm over a 10 x 10 micron area, which was much smoother than the analogous Au-bearing metallizations. An optimized Ti/Al/Ti/Ag contact provided a higher minimum specific contact resistance of $7.4x10^{-6}$ Ohm-cm^2, and the Ti/Al/Ti/Ag contacts were not as smooth as the V/Al/V/Ag contacts, perhaps due to the higher annealing temperatures necessary to minimize the resistance of the Ti-based contacts. The specific contact resistance and morphology of the V/Al/V/Ag contacts were also superior to those of the more conventional Ti/Al/Ti/Au and V/Al/V/Au contacts tested. Transmission electron microscopy revealed a very limited reaction of the annealed V/Al/V/Ag metallization with the semiconductor, leaving the AlGaN layer intact. The majority of the AlGaN interface is contacted by Ag-bearing phases. Silver has a lower work function than Au and may facilitate the formation of a low-resistance ohmic contact.

11:40am **EM-WeM12 Schottky Barrier Characteristics and Interfacial Reactions of Ir and Ti Gate Metallizations on In0.52Al0.48As/In0.53Ga0.47As High Electron Mobility Transistors***, **L. Wang**, I. Adesida*, University of Illinois at Urbana-Champaign

InAlAs/InGaAs HEMTs are promising devices for high speed circuits, millimeter-, and sub-millimeter-wave applications. Selection of gate metallizations plays a significant role in the performance, operation mode, stability, and manufacturability of these devices. Two factors need to be considered in choosing gate metals, namely, work function and reactivity with InAlAs during fabrication and operation. Electrically, metal work function determines Schottky barrier height (φB) which in turn decides key device operation parameters such as threshold voltage, transconductance, gate capacitance, etc. Structurally, reactivities or diffusivities of metals/InAlAs control the final gate-channel distance and thermal stability of the transistors. However, a thorough correlation of electrical and structural characterizations of metal/InAlAs contacts at various annealing conditions is still lacking. In this study, we examined the relationship between the φB characteristics and interfacial reactions of Ti/InAlAs and Ir/InAlAs. I-V characteristics of Schottky diodes were used for φB and ideality factors characterizations. Cross-sectional transmission electron microscopy is utilized to elucidate the microstructural evolution occurred at the metal/semiconductor interfaces. For Ir/InAlAs, φB decreased slightly compared to the as-deposited value when annealed at 250 °C. Beyond that φB increased monotonically until it reached the peak value of 825 meV at 400 - 425 °C. Further increasing the temperature led to φB degradation. Over a wide temperature range from ~375 to 450 °C, φB of over 800 meV could be achieved. XTEM studies showed that enhancement in φB is due to the formation of amorphous layer at the interface. Annealing above 455 °C

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[1] C. O. Chui, S. Ramanathan, B. B. Triplett, P. C. Mclntyre, and K. C. Saraswat, IEEE Electron Dev. Lett. 23, 473 (2002).

led to the nucleation of IrAs2 crystals. For Ti/InAlAs, as-deposited diodes had a typical φB of 668 meV and an ideality factor of 1.0. Two maxima in φB were observed for samples annealed at temperatures above 300 °C. The first set of maxima had values between 748 and 726 meV. The second set of maxima had higher φB of over 760 meV after prolonged annealing. Similar to Ir/InAlAs, an amorphous mixture between Ti and InAlAs formed for samples annealed at short durations. Prolonged thermal treatment resulted in aggressive reaction leading to Kirkendall voids formation, deformation of InAlAs, and TiAs crystal growth. Such aggressive reaction and thus defects formation led to higher diode ideality factors.

12:00pm **EM-WeM13 Improvement of AlGaN/GaN HEMT and GaN Schottky Contact Device Performance by Reduction of Epitaxial Film Dislocation Density**, ***D.J. Ewing***, *M.A. Derenge, P.B. Shah, U. Lee, T.S. Zheleva, K.A. Jones*, Army Research Lab

The electrical characteristics of AlGaN/GaN high electron mobility transistors (HEMTs) and GaN Schottky contacts were correlated with dislocations and other material defects. AlGaN/GaN heterostructures and GaN epitaxial films were grown using conventional MOCVD and pendeo-epitaxy (PE), a lateral growth technique that reduces the dislocation density of the epitaxial films by 2-3 orders of magnitude. Current-voltage (I-V) and capacitance-voltage (C-V) measurements were conducted to determine the quality of the Ni gate (Schottky) contacts to both the conventional and PE films. The Schottky contacts to the PE material all displayed a single, homogeneous Schottky barrier height evidenced by the linearity of the log I-vs-V plot over 4-5 orders of magnitude. Conversely, the Schottky contacts to the conventional material displayed an inhomogeneous Schottky barrier height, with a characteristic "knee" at low voltage indicating the presence of a low Schottky barrier height. The average ideality factor increased from 1.71 for the PE material to 2.29 for the conventionally grown GaN. The average reverse leakage current increased from 7.5×10^{-4} A for the PE GaN to = 4.0×10^{-3} A for the conventionally grown GaN. The electrical properties were then correlated with improved material quality as determined by several microscopy techniques. The conventional GaN epitaxial films were found to have an RMS surface roughness twice as large as that of the PE film. Similarly, cathodoluminescence revealed that the near band edge intensity of the PE films was almost an order of magnitude higher than the conventionally grown material, indicating the presence of fewer defects in the PE material. Devices fabricated on the AlGaN/GaN heterostructure also displayed variations in electrical properties. Variations in the ideality factor, Schottky barrier height, and reverse leakage current density were 1.60-2.60, Φ_B=0.60-0.95 eV, and J=1×10^{-4}-1×10^{1} A/cm^2, respectively. These variations correlated with a variation in local etch pit density directly under the gate contact as determined by SEM. For devices with high leakage-current density, the etch-pit density was found to be twice as high as that of devices with low leakage current density. Determining the relationship between the electrical characteristics and materials defects will facilitate the fabrication of high-power and high-frequency devices with improved performance and reliability.

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-WeM

Catalysis for Hydrogen Storage and the Hydrogen Economy

Moderator: G. Fisher, Delphi

8:00am **EN+SS+TF-WeM1 Catalysts for Hydrogen Production by Sulfur-Iodine Thermochemical Water Splitting Cycle**, ***L.M. Petkovic***, *D.M. Ginosar, K.C. Burch, H.W. Rollins, S.N. Rashkeev, H.H. Farrell*, Idaho National Laboratory

Thermochemical cycles can be used to split water through a series of chemical reactions where the net result is the production of hydrogen and oxygen at much lower temperatures than direct thermal decomposition. When the primary energy source to drive the cycle is nuclear or solar heat, hydrogen can be produced without the need of fossil fuels and without generating gasses considered to be responsible for global warming. The sulfur-iodine (S-I) thermochemical cycle appears promising for producing hydrogen from water. The S-I cycle consists of three simultaneous reactions: the decomposition of hydroiodic acid (HI) to produce hydrogen and generate iodine for recycle, the decomposition of sulfuric acid to produce oxygen and generate sulfur dioxide for recycle, and a main reaction where incoming water and the recycle chemicals react to regenerate HI and sulfuric acid. Both HI and sulfuric acid decomposition reactions are facilitated by heterogeneous catalysts. The high-temperature, harsh chemical reaction conditions of the sulfuric acid decomposition reaction present a significantly challenging environment for catalytic materials. In this work a number of titania (rutile)-supported platinum-group metal (i.e., Pt, Ir, Pd, Ru, and Rh) catalysts were investigated for this reaction. To develop an understanding of the factors that cause catalyst deactivation, density-functional theory-based first-principles calculations and computer simulations for transition metal particles positioned on titania (rutile) were performed. In addition, experimental determination of the activity and stability of activated carbon catalysts for the HI decomposition reaction will also be presented. Results of activated carbon characterization analyses, including surface area, temperature programmed desorption, Boehm's titration results, and contact pH of the activated carbons will be discussed.

8:20am **EN+SS+TF-WeM2 Trends in Hydrogen Splitting on Transition Metals at 1 Bar**, ***M. Johansson***, *O. Lytken, I. Chorkendorff*, Technical University of Denmark

Despite the fact that the interaction of hydrogen with various metal surfaces has been studied extensively under ultra-high vacuum conditions, there is very little data available for the hydrogen dissociation rate on clean surfaces at pressures on the order of 1 bar. Here we investigate the hydrogen splitting rate for a number of transition metals by measuring the rate of the H-D exchange reaction. Experiments are also carried out in the presence of CO, in order to investigate the mechanism behind CO poisoning of the anode catalyst in proton-exchange membrane fuel cells. The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.[1] Model catalysts are prepared by electron-beam evaporation of metal spots onto a highly ordered pyrolytic graphite (HOPG) substrate. Typically, the spots are 1 mm in diameter and 50 Å thick. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The gas is sampled 0.2 mm from the center of the spot, and the sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent D_2 in H_2, with or without the addition of 10 ppm CO. The temperature was varied in the range 40 - 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES) before and after exposure to gases in the high-pressure cell. In order to take the back-reaction (HD splitting) into account, a simple model for the H-D exchange reaction is used. It is assumed that the sticking probability, S, is the same for H_2, HD and D_2. Under the conditions of interest here, S is mainly dependent on the coverage of adsorbed species on the catalyst surface. Once S has been extracted from the experimental data, the dissociative adsorption/desorption rate for pure H_2 at 1 bar can be calculated. So far, the metals Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt have been investigated. The measured values for S are reasonably consistent with data obtained with high hydrogen coverage under vacuum conditions. Metals which bind hydrogen strongly are expected to give lower values for S. However, S is found not to correlate with the heat of adsorption for hydrogen as determined at low coverage under vacuum conditions. The most active metal for hydrogen splitting is Ru, closely followed by Rh. For these metals, S is close to being independent of temperature. Pt and Pd give comparable values for S in the temperature range investigated, but the temperature dependence is stronger for Pd than for Pt. The activity then decreases in the order Ir, Co and Ni. No measurable activity is found for Cu. The addition of 10 ppm CO lowers the splitting rate significantly on all the metals, also at 200 °C. Among the investigated metals, Pt and Ir are the ones most sensitive to CO poisoning.

[1] M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, Rev. Sci. Instrum., 75 (2004) 2082.

8:40am **EN+SS+TF-WeM3 Catalytic Autothermal Reforming of Renewable Fuels at Millisecond Times**, ***L. Schmidt***, University of Minnesota **INVITED**

We compare the reforming of different types of biofuels by autothermal reforming at millisecond contact times to produce synthesis gas, hydrogen, and chemicals. Fuels examined are alcohols, esters, carbohydrates, biodiesel, vegetable oil, and solid biomass. Biofuels generally have higher conversions than fossil fuels because the hydroxyl and ester linkages in these fuels produce higher sticking coefficients than for saturated alkanes. Consequently, conversions of all biofuels in these processes are nearly 100%. Highly oxygenated feedstocks tend to produce mostly syngas with little olefins or oxygenated products because surface reactions dominate, and these larger products are formed predominantly by homogeneous reaction processes after all oxygen is consumed. Recent results on production of syngas by reactive flash volatilization of nonvolatile liquids and solids will also be described. We show that, by impinging cold liquid drops or small solid particles onto the hot catalyst surface, the process can be operated in steady state with no carbon formation for many hours. This occurs because, while pyrolysis of vegetable oils and carbohydrates at low temperatures produces carbon, above ~600oC the equilibrium shifts to produce syngas rather than solid carbon.

9:20am **EN+SS+TF-WeM5 Transient Kinetic Analysis of Intermediates in Steam Reforming on Oxide Supported Cu Catalysts**, ***Y. Yang***, *R. Disselkamp,* Pacific Northwest National Laboratory*, C.T. Campbell,* University of Washington*, C. Mims,* University of Toronto, Canada*, D. Mei, J.H. Kwak, J. Szanyi, C.H.F. Peden*, Pacific Northwest National Laboratory

Formate hydrogenation was proposed to be the surface reaction channel forming methanol through reverse water gas shift by previous investigators [Chorkendorff et al., J. Vac. Sci. Technol. A, 10(4), 2277 (1992)]. The interconversion and decay of copper formates on a Cu/Gamma-Al2O3 catalyst are studied here using an apparatus that combines in-situ transmission-FTIR of adsorbed species and mass spectrometric detection of reactor effluent during transient kinetic analyses (transmission-FTIR/MS/TKA). At 573 K, ~ 2% CO and 0.07% methanol conversions were obtained by sending 2.5 bar H2:CO2 3:1 flow at 10 sccm through the reactor. It is also observed that at lower temperature, 353 K - 433 K, surface formate species are formed with the input feed stream as observed by IR. The kinetics of their transient reactivity (e.g., titration) are examined after switching to either a reducing (H2), oxidizing (2% N2O in He), or inert gas (He, Ar) feed stream. The kinetics of total formate decay at 306, 363, and 433 K under H2, He, or Ar gas exposure are observed to be comparable, suggesting that a thermal unimolecular desorption and not hydrogenation alone, is operative. However upon hydrogen exposure it is observed that within the broad formate IR band(s) there is internal species exchange which indicates two types of different formates are formed. Similar studies are presented for a SiO2 supported polycrystalline Cu sample to help identify the formate species. Methanol steam reforming on both samples were also studied for further understanding of the reverse reaction processes.

9:40am **EN+SS+TF-WeM6 Model Catalysts for Water-Gas Shift Reaction***, S. Ma, X. Zhao, J.A. Rodriguez, P. Liu,* ***J. Hrbek***, Brookhaven National Laboratory

Gold supported on ceria was shown to be very active catalyst for water-gas shift reaction and low temperature CO oxidation. Both reactions are used to purify hydrogen by removing CO, a poison of fuel cell catalysts, and are therefore of importance in the hydrogen economy. In this presentation we will discribe the preparation, characterization and reactivity of an â?oinverseâ? model catalyst, i.e. CeOx nanoparticles supported on the Au(111) surface. Using STM and XPS we found that physical vapor deposition of Ce metal leads to formation of surface intermetallic compounds after annealing. The Ce-Au surface alloys have low reactivity toward oxygen, however, we were able to prepare CeOx by vapor-deposition of Ce in a moderate oxygen pressure (10-7 torr). Elongated flat ceria nanoparticles are 0.5 nm thick, several nanometers long and anchored mostly to steps. Atomically resolved images of the ceria island show well-ordered CeO2 (111) surfaces with few defects. Ce 3d photoelectron spectra were used to identify the oxidation state of Ce in oxides prepared by different methods. In general, oxidation at temperatures below 400 K leads to formation of poorly ordered nanoparticles of Ce2O3 and higher temperature annealing in background oxygen is needed to form CeO2. Individually, neither Au(111) nor CeO2(111) have any activity in the WGS reaction, while both the Au/CeO2(111) model catalyst and the CeOx/Au(111) inverse model catalyst show significant activity in high pressure experiments. Our photoemission data indicate that Ce2O3 nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO2 nanoparticles are inactive. As the water dissociation could be the rate limiting step in the WGS reaction, our ability to identify dissociation products under vacuum conditions and to link them with the structural characterization at the atomic level reinforces reaction models in which the oxide support is not a simple spectator and plays an essential role in the WGS process. Acknowledgement: This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

10:40am **EN+SS+TF-WeM9 Double Role of Water in Fuel Cell Oxygen Reduction Reaction***,* ***H. Ogasawara****, L.-Å Näslund, J.B. MacNaughton, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

A management of appropriate humidity level is necessary for the fuel cell to operate. The oxygen reduction reaction (ORR) occurs at the triple phase boundary where gas, electrolyte containing water and catalytic metal particle contact forms humid and dry region on the surface of the catalyst. Using XPS and XAS, we have demonstrated active site poisoning by water, where the activation of oxygen to the adsorbed atomic phase occurs rapidly in the dry region, but not in the humid region. On the contrary, there is a promoter effect of water on the reduction of adsorbed atomic oxygen in the formation of a water-hydroxyl surface complex.

11:20am **EN+SS+TF-WeM11 Adsorption and Dehydrogenation of Carborane on Pt(111)**, ***A. Tillekaratne****, M. Trenary*, University of Illinois at Chicago

The techniques of reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to explore the dehydrogenation on a Pt(111) surface of 1,2-dicarba-closo-dodecaborane, $C_2B_{10}H_{12}$, also known simply as carborane. Complex hydrides, such as the boranes and carboranes, are of interest as possible hydrogen storage materials because of their high hydrogen content. Many hydrides are quite stable and catalysts are needed to promote the release of hydrogen at low temperatures. The carbon and boron atoms of the $C_2B_{10}H_{12}$ carboranes occupy the vertices of a slightly distorted icosahedron and have a hydrogen weight percentage of 8.3. There are three isomers of these icosahedral carboranes, of which the ortho form (the 1,2 isomer) is the most readily available. The icosahedral structure of the boron-carbon cage structure of carborane is also adopted by the boron-rich solid boron carbide. The similarity in the structures of carborane and boron carbide has led to the successful use of carborane as a precursor gas for the growth of boron carbide thin films. However, the detailed mechanism by which carborane dehydrogenates to form boron carbide has not been previously investigated. At submonolayer coverages at 85 K the RAIRS spectrum of carborane displays strong B-H stretching vibrations near 2600 cm^{-1}, and a weak C-H stretch at 3090 cm^{-1} that indicate molecular adsorption at low temperature. The molecule is stable on the surface up to 250 K, where it is transformed into a new intermediate with a strongly red-shifted B-H stretch vibration at 2507 cm^{-1}. This intermediate is stable up to 400 K, above which no B-H stretch vibrations are observed. Hydrogen is released in stages as the carborane monolayer is heated from 85 to 800 K, which is also indicative of the formation of partially hydrogenated surface intermediates. Further analysis of the data may permit definitive identification of the surface intermediates formed during the course of carborane dehydrogenation on the Pt(111) surface.

11:40am **EN+SS+TF-WeM12 Short Range Order of Ti Dopants in Al(111): Implications for Hydrogen Storage**, ***E.M. Muller***, Brookhaven National Laboratory*, C.V. Ciobanu,* Colorado School of Mines*, P. Zahl, P. Sutter*, Brookhaven National Laboratory

Complex metal hydrides can potentially satisfy the need for lightweight, high-capacity hydrogen storage materials, a key requirement for the Hydrogen Economy. However, for most known complex hydrides the solid-state reactions involved in hydrogen release are not reversible, and their rates are low under moderate ambient conditions. The discovery that small amounts of Ti make the decomposition of sodium alanate ($NaAlH_4$) to NaH and Al reversible at moderate temperatures and pressures[1] has demonstrated doping with catalysts as a promising route to induce reversible hydrogen storage and fast reaction kinetics. A fundamental understanding of the catalytic effect of Ti in $NaAlH_4$ could form the basis for rational strategies to optimize a broader class of complex hydride hydrogen storage materials. We combine experiments on single crystal model surfaces and density-functional theory (DFT) to establish the role of near-surface Ti in the re-hydrogenation of NaH and Al to $NaAlH_4$. A likely primary effect of Ti is the formation of catalytically active surface sites enabling the facile dissociative chemisorption of H_2 on Al, which itself has very low affinity to H_2. Using chemically specific scanning tunneling microscopy and DFT we identify the stable configurations of Ti atoms incorporated into Al(111) surfaces as a first step to identifying potential catalytically active sites. Surprisingly, despite a higher surface energy of Ti (i.e., a driving force for diffusion into sub-surface sites), our observations show a pronounced stabilization of Ti at the Al surface where its catalytic effects are maximized. STM shows a large population of a specific Ti-atom pair complex, which has been predicted to catalyze H_2 dissociation.[2] We discuss the origin of this pairing, and the interaction of atomic and molecular hydrogen interactions with these surface Ti complexes.

[1] B. Bogdanovic and M. Schwickardi. J. Alloys Comp. 253-254, 1 (1997).

[2] E. Muller, E. Sutter, P. Zahl, C.V. Ciobanu and P. Sutter., Appl. Phys. Lett. 90, 151917 (2007).

12:00pm **EN+SS+TF-WeM13 Alane Formation on Al(111) and Ti-doped Al(111)*****, S.C. Chaudhuri,*** Washington State University*, J.-F. Veyan, S.C. Schaäfer,* Rutgers, The State University of New Jersey*, J.T. Muckerman*, Brookhaven National Laboratory*, Y.J. Chabal*, Rutgers, The State University of New Jersey

Complex metal hydrides, such as $NaAlH_4$, are candidates for hydrogen storage because they can reversibly release and recapture hydrogen under near ambient conditions. Surface processes in the hydrogen storage reaction in $NaAlH_4$, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na_3AlH_6 to the hydrogen-rich $NaAlH_4$, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Since metallic Al, particularly when doped with other metals, appear key to H_2 dissociation, we have undertaken a comprehensive study of H interaction with Al(111) and Ti-doped Al(111) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. We have combined in-situ infrared absorption spectroscopy with first principles calculations to investigate the reaction of atomic hydrogen reacts with Al surfaces. As previously observed,[1] IR spectra show that alanes are formed upon H exposure. Alanes are highly mobile species at or near room temperature and desorb from Al(111) surfaces at higher temperatures mainly as AlH, AlH_3 and Al_2H_6.[2] Using FT-IR we show that the size of the alanes formed on Al(111) depend on the temperature of the sample. For low temperatures (Ã90K), small alanes such as AlH_3 and Al_2H_6 are predominant. At higher temperatures (Ã250K), bigger alanes are formed. When the Al(111) surfaces are doped with 5% Ti, the Ti containing sites are reactive, dissociating molecular hydrogen, and thus act as a pump to generate hydride species on Al surfaces that subsequently convert into alanes. LEED is used to test the validity of first principles c alculations predicting that Ti atoms occupy hollow sites on the Al(111) surface. Using TPD, the nature of desorbed species from Al(111) and Ti-doped Al(111) surfaces have been analyzed as a function of the sample temperature after either atomic H or H_2 exposures. This presentation summarizes hydrogen dissociation on Ti/Al(111), and alane formation and mobility on both Al(111) and Ti/Al(111) surfaces.

[1] Eden P. Go, Konrad Thuermer, Janice E. Reutt-Robey, Surf. Sci. 437 (1999) 377

[2] Hara, M.; Domen, K.; Onishi, T.; Nozoye, H., J. Phys. Chem., 95, (1), (1991) 6-7

Magnetic Interfaces and Nanostructures

Room: 619 - Session MI-WeM

Magnetic Thin Films and Nanostructures

Moderator: S.H. Liou, University of Nebraska, Lincoln

8:00am **MI-WeM1 Surface Stability and Electronic Structure of Half-Metallic MnSb,** ***S.J. Jenkins***, University of Cambridge, UK **INVITED**

Half-metallic materials, which exhibit complete spin-polarisation at the Fermi level, hold great promise for device applications in the field of spintronics. Amongst a variety of potential drawbacks, however, one of the most pressing is a lack of knowledge concerning surface and interface properties. In particular, the relationship between the stability of different surface/interface phases and the presence of surface/interface-localised electronic states is of great importance.[1,2] We have performed first-principles density functional calculations aimed at elucidating this relationship for various surfaces of the half-metallic zincblende phase of MnSb, demonstrating that it is essential to account for the possibility of reconstruction in determining whether half-metallicity is retained at the surface.[3]

[1] S.J. Jenkins and D.A. King, Surf. Sci. Lett. 494, L793 (2001).

[2] S.J. Jenkins, Phys. Rev. B 70, 245401 (2005).

[3] S. Mollet and S.J. Jenkins, J. Phys.: Cond. Matter (invited, in press).

8:40am **MI-WeM3 Magnetic and Structural Properties of Epitaxial FeRh Thin Films Grown by MBE,** *Y. Ding, **D.A. Arena**,* Brookhaven National Laboratory, *L.H. Lewis,* Northeastern University, *J. Dvorak,* Montana State University, *C. Kinane, M. Ali, C.H. Marrows, B.J. Hickey*, University of Leeds, UK

Thin films of FeRh alloys with near equiatomic composition and CsCl type ordering exhibit an intriguing antiferromagnetic (AFM) to ferromagnetic (FM) first-order phase transition near 100° C. This easily accessible phase transition has generated interest in using FeRh films as a temperature-tunable AFM pinning layer in exchange-biased magnetic structures.[1] The AFM to FM transition is associated with the dramatic increase of the saturation magnetization M_s, along with temperature hysteresis of M_s, and a variation in the lattice parameter. We have grown high quality, epitaxial FeRh films on MgO(100) via molecular beam epitaxy (MBE); film thickness ranged from ~200 Å to 1000 Å. The films are characterized with a combination of laboratory-based magnetometry and synchrotron-based x-ray diffraction (XRD) and x-ray magnetic circular dichroism (XMCD). Magneto-optic Kerr effect measurements and SQUID magnetometry confirm the AFM to FM transition in the films. Temperature dependent XRD indicates an expansion of the out-of-plane lattice parameter across the phase transition which mirrors the change in M_s. XMCD spectra were collected in conventional total electron yield (TEY) mode, which probes the near-surface region (probe depth ~50 Å - 100 Å) and in indirect transmission mode (ind-trans), where the oxygen K-edge fluorescence from the MgO substrate is monitored as the photon energy is swept through the Fe $L_{2,3}$ core levels. For the Au capped films, TEY scans reveal a FM near-surface region even at room temperature, while the ind-trans mode data are consistent with a bulk AFM state at ambient temperatures which transforms to a FM state above 100° C. The choice of capping layer also affects the room-temperature magnetism in the near-surface region as the MgO capped films do not exhibit an appreciable XMCD signal in TEY mode.

[1] Thiele. et al., Appl. Phys. Lett.,82, 2859 (2003).

9:00am **MI-WeM4 Properties of Epitaxial Co_2MnSi on Vanadium,** ***G.J. Mankey**, M.J. Walock, C.A. Culbert, Z. Lu, M. Pathak, Z.T. Reddy, P. LeClair, S. Gupta, W.H. Butler*, University of Alabama

There is a consensus that read sensors for hard drives will transition from tunnel magnetoresistance based sensors to all metal current perpendicular to the plane giant magnetoresistive sensors. To achieve this goal, a new generation of high spin polarization materials are required. Half-metallic Heusler alloys, combined with carefully chosen spacer materials, are prime candidates for incorporation into these devices. However, robust half-metallic behavior must be established and confirmed. Recently, we have investigated the electronic structure of $L2_1$ full Heusler alloys in detail. We can, theoretically, devise an infinite number of periodic systems that are half-metallic, with the hope that at least a handful will be experimentally accessible. Our preliminary calculations of the electronic structure of these materials suggest that they have a robust half-metallic nature. These theoretical results are combined with an experimental study of the half-metallic compound, Co_2MnSi. Epitaxial films are deposited using magnetron sputtering on low-index, single-crystal vanadium substrates and their crystal structure, electronic structure and magnetic properties are determined. Films processed under different deposition conditions are compared to determine the optimum conditions for producing half-metallic single-crystal films. This work is funded by NSF-DMR 02-31985.

9:20am **MI-WeM5 High Magnetization FeCo/Pd Multilayers,** ***M.J. Walock*,*** The University of Alabama, *H. Ambaye,* Oak Ridge National Laboratory, *M. Chshiev,* The University of Alabama, *F.R. Klose,* Oak Ridge National Laboratory, *W.H. Butler, G.J. Mankey*, The University of Alabama

A high saturation magnetization is advantageous in magnetic recording. For the 3d ferromagnets, the peak of the Slater-Pauling curve corresponds to BCC FeCo, with a saturation magnetization of 2.45 T. Recently, a magnetization of 2.57 T in the FeCo layers of a [40 nm $Fe_{70}Co_{30}$ /1.7 nm Pd]x25 superlattice has been reported.[1,2] This result may be attributed to an enhanced Fe moment due to interfacial strain and an accompanying induced moment in the Pd. We have fabricated multilayer samples with varying superlattice periodicity and interlayer thicknesses to determine the nature of the enhanced moment in this intriguing thin film system. Magnetic characterization experiments show an enhanced magnetic moment in the multilayers as compared to a film containing the same amount of FeCo. However, since the magnetization is defined as the magnetic moment divided by the sample volume, the sample exhibits an overall reduction in the magnetization when the volume of the Pd layers is also taken into account. Our experimental findings are also supported by theoretical calculations which identify the origin of the increased magnetic moment in the multilayer system. Polarized neutron reflectivity experiments will be used to determine the lateral distribution of the magnetization in a number of superlattice samples.[3].

[1] K. Noma, M. Matsuoka, H. Kanai, Y. Uehara, K. Nomura, and N. Awaji. IEEE Trans. Magn. 42, 140 (2006).

[2] ibid. 41, 2920 (2005).

[3] This project was funded by grants from the DOE, the INSIC EHDR Program, and NSF-DMR 0213985 .

9:40am **MI-WeM6 Induced Spin Polarization of Copper Spin 1/2 Molecular Layers,** ***D.S. Wisbey§§**, D. Feng,* University of Nebraska-Lincoln, *A.N. Caruso,* North Dakota State University, *C.M. Silvernail,* University of Minnesota, *J. Belot,* University of Nebraska-Lincoln, *E. Vescovo,* National Synchrotron Light Source, *P.A. Dowben*, University of Nebraska-Lincoln

Substrate induced spin polarization was observed in molecular layers of $C_{24}H_{36}N_2O_4Cu$ ($Cu(CNdpm)_2$) deposited on cobalt (111). Extra molecular interactions between these Cu 1/2 molecules and the ferromagnetic substrate are implicated while the $Cu(CNdpm)_2$ molecular layers have an opposite spin polarization compared to the Co(111) substrate near the Fermi edge. The spin-polarized photoemission results are seen to be consistent with magnetometry and mean field (Ginzburg-Landau) models. The spin asymmetry favors select molecular orbitals, suggesting that the local spin 1/2 moment of copper is enhanced by contributions from select molecular orbitals.

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* Falicov Student Award Finalist

10:40am **MI-WeM9 Controlling Magnetic Anisotropy and Probing Magnetic Structure in Magnetic Nanoparticles and Ferromagnetic/Antiferromagnetic Bilayers**

M.-T. Lin, National Taiwan University **INVITED**

Controlling the magnetic orientation and imaging magnetic structure are two of crucial issues in both aspects of fundamental science and application for magnetic nanomaterials. In particular, tuning perpendicular magnetic anisotropy by the more concise and efficient process draws a lot of attentions due to the possible application for perpendicular medium with high storage density. In this work, an enhanced perpendicular magnetic anisotropy of ferromagnetic thin films is demonstrated by introducing an antiferromagnetic (AF) underlayer. A new kind of spin-reorientation transition is also observed with varying thickness of the AF layer. This finding is shown to be related to the strength of the AF coupling of the AF layer. Controlling the magnetic anisotropy can be also important in the magnetic domain imaging with in-plane sensitivity by spin-polarized scanning tunneling microscopy (SP-STM). A simple method by using a ring-shaped magnetically coated wire as the tip of SP-STM is shown to be able to have the spin contrast easily in the in-plane direction of the film. A well-defined magnetization orientation of magnetic tip is achieved due to controlled anisotropy caused by geometrical asymmetry. Finally, magnetic coupling and magnetic structure in magnetic self-aligned Fe particles grown on the single crystalline oxide layer Al_2O_3/NiAl(100)[1,2] will be also discussed. With help of the technique of scanning electron microscopy with polarization analysis (SEMPA) the magnetic domain is imaged, revealing a vortex structure, which is suggested to be attributed to a dipole-dipole interaction. Furthermore, capping the magnetic particles with non-magnetic metallic layer (Cu) can enhance the magnetic coupling, and in turn the Curie temperature of the system.[3] This finding can also be confirmed in the enhanced spin contrast observed by SEMPA for magnetic particles with capping layer. The magnetic coupling under magnetic particles is shown to be able to propagate through the Cu layer.

[1] W.C. Lin, C. C. Kuo, M.F. Ro, K. J. Song, and Minn-Tsong Lin, Appl. Phys. Lett. 86, 043105 (2005).

[2] W. C. Lin, S. S. Wong, P. C. Huang, C. B. Wu, B. R. Xu, C. T. Chiang, H. Y. Yen, and Minn-Tsong Lin, Appl. Phys. Lett. 89, 153111 (2006).

[3] W. C. Lin, P. C. Huang, K. J. Song, and Minn-Tsong Lin, Appl. Phys. Lett. 88, 153117 (2006) .

11:20am **MI-WeM11 Fabrication and Real Time Characterization of Highly Anisotropic Magnetic Nanostructures**

J.R. Skuza*, *R.A. Lukaszew,* The University of Toledo, *C. Clavero,* Instituto de Microelectrónica de Madrid - IMM (CNM - CSIC), Spain, *D.A. Walko,* Argonne National Laboratory*, R. Clarke*, University of Michigan, Ann Arbor

The FePt binary alloy system exhibits several chemically ordered phases (i.e., $L1_0$ and $L1_2$) depending on the Fe:Pt stoichiometry. This chemical ordering affects the crystallographic structure of the alloy and hence the magnetic anisotropy. For example, in thin films of this alloy, the $L1_0$ phase exhibits strong perpendicular magnetic anisotropy when the ordering axis is in the growth direction ($\sim 10^7$ erg/cc), while the $L1_2$ phase exhibits in-plane magnetic anisotropy. Thus, suitable combinations of these chemically ordered phases have been proposed for the next generation of magnetic recording media with tilted magnetization. A significant challenge for this latter application is to achieve chemically ordered nanostructures that can further push the present super-paramagnetic limit. Here, we report on our recent magnetic and real time thermal annealing studies of nanostructured FePt thin films. FePt nanocomposite thin films were obtained by implanting Fe^+ ions into epitaxial Pt thin films using the Toledo Heavy Ion Accelerator (THIA). The size and penetration depth of the resulting Fe nanoclusters were tailored by modifying the implantation conditions (i.e., ion beam energy and implantation dose). Upon annealing these nanocomposite samples at the Advanced Photon Source at Argonne National Laboratory, we observe within minutes the onset of the $L1_2$ phase at ~400° C with further re-ordering and formation of the $L1_0$ phase at ~500° C. Further data analysis shows that the activation energy of the $L1_0$ phase in these nanocomposite samples is ~1.0 eV. Our magnetic measurements show a strong out-of-plane component of the magnetic anisotropy after the annealing treatment consistent with the formation of the $L1_0$ phase.

This work was partially supported by the National Science Foundation (DMR Grant #0355171), the American Chemical Society (PRF Grant #41319-AC), and the Research Corporation Cottrell Scholar Award. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The authors would like to acknowledge M. S. Brown for his assistance during ion implantation.

11:40am **MI-WeM12 Effects of Preheat Treat on the Anisotropy and Particle Size of Sr(TiMn)2Fe8O19 Magnetic Powders**

H.Y. He, Shaanxi University of Science & Technology, China

The excellent properties of Ti-Mn-substituted ferrite are largely dependent on the characters of multidomain ferrite powders except for Ti-Co-substitution rate. Preheat treatment can influences the formation process of Ba(TiMn)2Fe8O19 powders and further influences the anisotropy of the powders. However this effect has not be reported previously. Ultrafine substituted M-type Sr(TiMn)2Fe8O19 powders were synthesized successfully by sol-gel method. The hydroxide precursor particles were formed in gel solution containing ethanol and water at a ratio of 1:1 and NaOH as coprecipitation agent. The effects of preheat treatment on particle size and c/a value of Sr(TiMn)2Fe8O19 nano powders were studied using XRD and SEM. XRD analysis indicated single phase substituted M-type Sr-ferrite Sr(TiMn)2Fe8O19 were formed by either preheating precursors at 300oC and 400oC respectively for 1h or non-preheating followed by calcining at 900oC for 2h respectively. The particle sizes of powder were changed from 40.8nm to 39.8nm and 41.1nm when the samples were preheated at 300oC and 400oC respectively. Calculation of c/a value with XRD data indicated that the The c/a ratio changed from 3.9145 to 3.9183 and 3.9153 at the preheating temperatures of 300oC and 400oC respectively. A largest c/a value was achieved at preheating temperature of 300oC. SEM analyses revealed that particles were platelet and the decrease in aspect ratio in morphology was accordant to the increase in the c/a ratio with change from non-preheating to preheating at 400oC and to preheating at 300oC.

12:00pm **MI-WeM13 Surface Functionalization of Single Iron Oxide Magnetic Nanoparticles (SPIONs) for Targeted Magnetic Resonance Imaging (MRI)**

E. Amstad*, E. Reimhult, S. Zurcher,* ETH Zurich, Switzerland, *J.A. Hamilton,* Boston University Medical Campus, *J.Y. Wong,* Boston University, *M. Textor*, ETH Zurich, Switzerland

Commercially available negative magnetic resonance (MR) contrast agents often consist of multiple iron oxide cores embedded in a macromolecular matrix such as dextran. An alternative to the reversibly binding dextran is PEG-gallol or PEG-dopamine. The latter two molecules have a considerably higher binding affinity towards iron oxide nanoparticles compared to dextran, leading to enhanced particle stability and smaller particle diameters. Because PEG-gallol and PEG-dopamine adsorb on iron oxide in a well defined way, particles can be stabilized individually. Moreover, surface modifications of such PEGylated particles can be achieved by using PEG-chains that bear functional groups. Superparamagnetic iron oxide nanoparticles have been synthesized by an aqueous precipitation reaction and were stabilized individually using PEG-gallol and PEG-dopamine. Particle size, thermal stability and magnetic properties of these individually stabilized PEGylated particles have been compared with Feridex, a commercially available negative MR-contrast agent. To functionalize the former particles, iron oxide cores were coated with a combination of biotinylated PEG-dopamine and PEG-gallol. Neutravidin, a biotin-binding protein, served as a linker between the PEGylated particles bearing biotin sites and biotinylated functional groups. Neutravidin is an attractive linker for research purposes because any biotinylated ligand can be attached to it. Moreover, the number of ligands bound to one particle can easily be varied if neutravidin is used as an intermediate layer. In a first approach, these neutravidin coated PEGylated nanoparticles were targeted against atherosclerotic sites by attaching a custom-synthesized biotinylated peptide sequence to them.[1] E-selectin is a transmembrane protein expressed on inflamed endothelial cells.[2] It thus is an early marker for atherosclerosis. The blood half-life time of these functionalized superparamagnetic iron oxide nanoparticles has been determined in vivo in rabbits using magnetic resonance imaging (MRI).

[1] Martens, C.L., et al., Peptides Which Bind to E-Selectin and Block Neutrophil Adhesion. Journal of Biological Chemistry, 1995. 270(36): p. 21129-21136.

[2] Choudhury, R.P., V. Fuster, and Z.A. Fayad, Molecular, cellular and functional imaging of atherothrombosis. Nature Reviews Drug Discovery, 2004. 3(11): p. 913-925.

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* Falicov Student Award Finalist

Nanomanufacturing Topical Conference

Room: 615 - Session NM-WeM

Nanomanufacturing for Information Technologies

Moderator: J. Murday, University of Southern California

8:00am **NM-WeM1 Emerging Materials for Nanomanufacturing**, ***D. Herr***, Semiconductor Research Corporation **INVITED**

The emerging nanomaterials era offers novel tool sets that exhibit the potential for addressing the ITRS's concurrent vision for enhancing functional density and driving new waves of market opportunities. Though significant materials challenges remain, new generations of smart patterning materials and assembly methods likely will enable the continued scaling of extreme CMOS, the integration of heterogeneous nanomaterials onto silicon platforms, and functional diversification. However, it remains to be seen whether potential material solutions are identified and matured in time to impact key insertion windows. One key challenge is the extensibility of optical patterning. At the November 1992 Semiconductor Technology Workshop, the demise of optical patterning was projected to occur in 2001, after the 180 nm technology node. This corresponded to nine years or three technology nodes, n+3, out from the then current 500 nm technology node, n. The 1994 and 1997 National Technology Roadmaps for Semiconductors (NTRS) conveyed similar messages that optical lithography would end after the 130 nm and 100 nm generations, respectively, or n+3 nodes out from the current technology nodes. The 1999 and 2003 International Technology Roadmaps for Semiconductors (ITRS) also predicted lithography's end n+3 technology nodes out from the current 180 nm and 90 nm nodes, respectively. The 2003 and 2006 ITRS potential solutions roadmaps for exposure tool technologies suggested that optical lithography would not be viable beyond the 32 nm and 22 nm nodes, respectively. Only the 2001 update of the ITRS conveyed a more near term, n+2, transition to a non-optical lithography technology, after the 65 nm node. Over the last forty years, considerable attention was focused on the exposure tool and mask infrastructure. Cumulative investments in developing exposure tool and mask related technologies are on the order of $10B and $1B, respectively. During this same period, relatively modest investments were made in the development of imaging materials, such as photo resists. However, line edge roughness (LER) and line width roughness (LWR) increasingly challenge our ability to achieve uniform electrical properties in the deep nanometer transistor domain. Additionally, the discussion about the interdependence between LER and dopant nano-roughness and their impact on device properties is just beginning to happen. This talk will consider the limitations of current families of lithographic materials and suggest emerging patterning materials that may satisfy projected nanofabrication requirements, including LER, long range dimensional control, resolution, and functionality. The materials science needed to develop these new generations of robust imaging materials for future information processing technologies represents a relatively unexplored and untapped frontier. Today's convergence difficult nanofabrication challenges, emerging market drivers, and recent breakthroughs in materials technology offers a rare opportunity for chemists, chemical engineers, materials scientists, and others to develop breakthrough material and process insertion options will impact future nanofabrication technology. This research area exhibits the potential for keeping the demise of optical patterning n+3 generations away from current technology, for nodes to come.

8:40am **NM-WeM3 Defect Engineering for Ultrashallow Junctions using Surfaces**, ***E.G. Seebauer***, *C.T.Z. Kwok, R Vaidyanathan,* University of Illinois, Urbana-Champaign, *S.H. Yeong, M.P. Srinivasan,* National University of Singapore, *B. Colombeau, L. Chan*, Chartered Semiconductor Manufacturing, Singapore

Formation of extremely shallow pn junctions with very low electrical resistance is a major stumbling block to the continued down scaling of microelectronic devices. Recent work in our laboratory has shown that the behavior of defects within silicon can be changed significantly by controlling the chemical state at the surface. Certain chemical treatments of the surface induce it to act as an active 'sink' for point defects that removes Si interstitials selectively over impurity interstitials, leading to less dopant diffusion and better electrical activation. The present work demonstrates such effects experimentally for several dopants such as boron, arsenic and phosphorous in both crystalline and Ge pre-amorphized silicon wafers. Moreover, such active surfaces dramatically reduce the number of end-of-range defects observed after annealing. In the case of boron, a continuum model for boron diffusion and activation has been developed to quantify the surface effects under a wide range of annealing protocols ranging from hours to milliseconds in duration. Two-dimensional simulations based on this model indicate that the beneficial effects of active surfaces in the source-drain region extend laterally to the surface toward the channel region of a device as well as perpendicularly to the surface into the bulk. In a separate but parallel mechanism, fixed charges created at surfaces or interfaces can interact with charged defects in the bulk. Simulations suggest that this electrostatic mechanism results in a deeper junction and dopant pile-up near the surface/ interface. The work also discusses possibilities for creating such active surfaces in real RTP conditions.

9:00am **NM-WeM4 Formation of Parallel- and Latticed-Nanostructures by Surface-Patterning Technique**, ***H.J. Kim***, *Y.H. Roh, B. Hong*, Sungkyunkwan University, Korea

Nanowires, semiconducting nanowire, carbon nanotube (CNT) and deoxyribonucleic acid (DNA), have been extensively investigated to obtain highly ordered electronic components for nanocircutitry and/or nanodevices. However, there are difficulties to apply them to nanodevices because of and aligning them with uniform interval on specific location and high contact resistance between metal electrodes and nanowire. We report a new method to carefully control the interval of DNA-templated gold nanowires (AuNWs) using surface-patterning techniques. In this technique, a process to form parallel- and latticed-nanostructures involves three steps: (1) nano-road was generated on oxide surface, chemically treated with (aminopropyl)triethoxysilane (APS) which has a NH3+ terminal group, patterned by electron beam lithography (2) ?-DNA molecules were stretched and aligned on chemical nano-road by tilting techniques. (3) AuNWs were formed by the electrostatic interaction between DNA and gold nanoparticles. By the combination of a tilting technique and surface-patterning technique, we could selectively align ?-DNA molecules and AuNWs by chemical nano-roads of 500 nm interval on Si substrate. We used atomic force microscopy (AFM) to analyze the configuration of AuNWs.

9:20am **NM-WeM5 The Challenges and Rewards of Building a Better Biosensor System: The NRL cBASS®**, ***L.J. Whitman***, Naval Research Laboratory **INVITED**

On December 5, 1995 David Baselt, at the time a postdoctoral researcher at NRL working on a cantilever-based biosensor using magnetic particle labels, wrote in his lab notebook, "Did some reading on magnetoresistive sensors. It may be possible to use these rather than piezolevers to detect magnetic particles." Over the past dozen years, a dynamic team of researchers at NRL has developed this idea into the compact Bead Array Sensor System (cBASS®), a prototype biosensor system that integrates a suite of patented and patent-pending technologies for magnetic labeling and biomolecular detection, biomolecular assay methods, surface chemistry, and microfluidics.[1-9] The current system is capable of multiplexed detection of biomolecules at attomolar concentrations in complex matrices in <20 min with little or no sample preparation. The technology has been licensed for a variety of applications, including food and water testing, environmental analysis, veterinary diagnostics, and biodefense. I will describe the development history of this project, the challenges of moving an idea from concept to advanced development within a government laboratory, and some of the lessons learned along the way.

[1] Baselt et al., Biosens. Bioelectron. 13, 731 (1998).

[2] U.S. Patent 5,981,297.

[3] Edelstein et al., Biosens. Bioelectron. 14, 805 (2000).

[4] Tamanaha et al., J. Micromech. Microeng. 12, N7 (2002).

[5] Sheehan et al., Biosens. Bioelectron. 18, 1455 (2003)

[6] Rife et al., Sensors Actuat. A 107, 209 (2003).

[7] Sheehan and Whitman, Nano Lett. 5, 803 (2005).

[8] Stine et al., Langmuir 23, 4400 (2007).

[9] Mulvaney et al., Biosens. Bioelectron., in press.

10:40am **NM-WeM9 Patterned Medium Substrates for Magnetic Recording Fabricated Using Ion Beam Proximity Lithography**, ***V. Parekh***, *A. Ruiz, Ch. E, P. Ruchhoeft, D. Litvinov*, University of Houston

We describe the fabrication of patterned medium substrates consisting of 50nm diameter Co/Pd multilayer pillars in a densely packed array with 100nm pitch using ion beam proximity lithography (IBPL) to pattern a resist followed by argon ion milling to transfer the pattern into the magnetic stack. These pattern medium samples serve as test structures to develop a fundamental understanding of the switching behavior of isolated magnetic islands and as a test-bed for developing next-generation magnetic recording media. In our fabrication approach, substrates are first coated with a Ta buffer layer, followed by deposition of alternating Co (0.3nm) and Pd (0.7nm) layers (repeated 10 times). Hydrogen silsesquioxane, a negative tone, ion sensitive resist, is deposited onto the multilayer structure and patterned using IBPL, in which an energetic helium ion beam irradiates a stencil mask, placed in front of the resist-coated sample, and ions passing through the stencil openings damage the resist and copy, in a single exposure, the entire mask pattern. After developing the resist, the HSQ pillars are transferred into the multilayers by argon ion milling. In developing this process, we have concentrated on the uniformity of the lithographically defined bits to improve the switching field distribution of the magnetic medium. To this end, we have developed stencil masks fabricated from 250nm thick, 1cm^2 area, free standing silicon nitride membranes. The blank membranes are coated with palladium, silicon dioxide and resist. Electron beam lithography is used to define 100nm circular openings on a 200nm pitch in the resist, which are then transferred into the membrane using a series of reactive ion etching and ion milling steps. A conformal gold coating allows for further reduction of the mask features without significantly increasing the feature size variation. Measurements using scanning electron microscopy reveal a 3nm standard deviation in the sizes of the mask openings over a 1mm^2 area. The standard deviation of the island structures that are formed using this mask have a similar standard deviation in size (4.5nm), indicating that our printing process is primarily limited by our ability to fabricate masks. A six-fold increase in the coercivity of the multilayer samples (from 900Oe for continuous samples to 6kOe for the patterned samples) and a switching field distribution of ~15% in the patterned sample was measured using magneto-optical kerr effect.

11:00am **NM-WeM10 Fabrication of Large-area Magnetic Ring Arrays using Ion Beam Proximity Lithography**, ***A. Ruiz,*** *V. Parekh, J. Rantschler, P. Ruchhoeft, D. Litvinov*, University of Houston

Arrays of 500nm/300nm outer/inner diameter permalloy rings on a 700nm pitch were fabricated to study transitions between the micromagnetic configurations within these structures. The existence of these states, which are both very stable and confine the magnetic flux within the material, is the basis for next-generation, high-density magnetic memory devices. To form these rings, oxidized silicon substrates were first coated with a 5nm thick Ta layer, a 10nm permalloy ($Ni_{80}Fe_{20}$) layer deposited in a magnetic field to induce anisotropy in-plane, and a 5nm thick Ta capping layer. Circular openings were defined in a 200nm thick resist layer, deposited on the magnetic stack, using ion beam proximity lithography (IBP) and a conformal coating of SiO_2 was applied to the surface by reactive sputter deposition. A directional reactive ion etch removed the oxide coating at the base of the opening and on top of the resist but preserved the oxide wall coating. After removing the resist in an oxygen ashing step, a ring-shaped hard mask remained that was transferred into the underlying permalloy using argon ion milling. Our fabrication approach has two distinct advantages over direct-write processes (i.e., electron beam): the patterns can be formed with much higher throughput using the parallel IBP approach (the entire mask pattern was replicated with a single exposure lasting less than 20 sec.) and the pattern of dots is significantly easier to control than the more complex ring structure. Hysteresis loops were measured using a vibrating sample magnetometer and show evidence of the switching sequence observed in micromagnetic simulations of these structures using the OOMMF code. However, the size and shape variation in the patterning process mask used for printing the dots must first be reduced to better understand the switching behavior. The results do suggest that the field required for onion-to-vortex transition and field required for vortex-to-onion transition to be 85Oe and 330Oe, respectively. We are currently reducing the size variation in the rings by fabricating improved IBP masks with more uniform openings to achieve smaller size distributions, which is expected to substantially reduce the switching field distribution. Currently we have fabricated large area masks that contain patterns with a standard deviation in size of less than 3nm.

11:20am **NM-WeM11 Nano-fabrication of Patterned Media**, ***T.-W. Wu***, *M. Best, D. Kercher, E. Dobisz, Z.Z. Bandic, X.C. Guo, M. Mate, T. Karis, H. Yang, T. Albrecht*, Hitachi Global Storage Technologies **INVITED**

The outlook of magnetic storage technology predicts that, with current 40% growth rate, the recording areal density will hit ~700 Gbits/in2 in 2011. However, the magnetic recording physics also predicts that perpendicular magnetic recording (PMR) media will hit the thermal instability limit as the grain size of the magnetic coating scaled down below ~5nm in diameter. Because patterned media (PM) leverages the geometric decoupling magnetic exchange, a magnetic material even with ultra-small (e.g. d<5nm) but strong magnetically coupled grains can still be utilized to constitute the required recording bit (d=10~15nm) and avoid the thermal instability. Furthermore, because of its geometrically defined bit border, PM can achieve both higher track and linear densities than does the continuous media and hence boost the areal density. As a disruptive magnetic recording technology, PM is viewed as one of the most promising routes to extending magnetic data recording to densities of 1 Tbit/in2 and beyond. The fabrication of PM disk starts with the imprint master mold creation followed by pattern replication by nano-imprinting, pattern transfer by reactive ion etch and finished with blank deposition of a magnetic coating. The key challenges in the PM substrate fabrication are how to create those nano-scaled features (e.g. pillars with 20nm in diameter) with acceptable fidelity? How to create them with an incredibly high density (e.g. a square lattice with less than 40nm in period) in a very large area (e.g. ~2 square inches) and also within a reasonable time frame? How to inspect them with a reasonable statistics basis? In addition, those features need to be arranged in a circular array and have a very stringent long range order as well. Although the physical feasibility at each critical stage has been demonstrated to a degree in the recent years, to ensure a manufacturing feasibility for the production of patterned disk substrates, the process robustness and reliability, parts longevity, high throughput tooling and low cost operation, etc. are still far from completion and remain as immense challenges. In order to achieve the goal of PM hard disk drive (HDD) production in 2011 time frame, many scientific innovations and technology advances, such as the r-θ ebeam machine, guided self-assembly patterning, double-side high throughput imprinting and RIE, etc. are critically needed.

12:00pm **NM-WeM13 Direct Integration of Carbon Nanostructure Family into Bimetal Micro-tubular Scroll**, *J. Choi,* ***Y. Song***, Wayne State University

Carbon nanostructures including carbon graphene patches, onions, fibers and nanotubes were directly grown on 120 nm thick freestanding Ti (100 nm)/Ni (20 nm) bimetal structures. During the direct growth of carbon nanostructures, the bimetal layers are scrolled. The interplay between stress driven by the scrolled bimetal and anisotropic carbon nanostructure growth increases the number of turns and induces the transition of carbon nanostructure growth behavior from the lateral to the vertical growth at the growth temperature of 375 oC.

Nanometer-scale Science and Technology

Room: 616 - Session NS+EM-WeM

Nanoscale Devices and Nanowires I

Moderator: S. Pang, University of Michigan, C. Eddy, Naval Research Laboratory

8:00am **NS+EM-WeM1 Self-Organization of SiGe Quantum Dots Grown on Ultrathin Si Nanomembranes**, ***F.S. Flack***, *C.S. Ritz, M.G. Lagally, H.J. Kim, K. Turner,* University of Wisconsin-Madison, *M. Huang, F. Liu*, University of Utah

Self-assembly in nanostructures is a linchpin of the bottom-up design technique essential to the advance of nanoscale fabrication. In particular, the self-assembly demonstrated by quantum dots (QDs) in strain-mismatched systems has potential for applications in lasers, high-density memory, and thermoelectric devices. Self-assembled arrays of QDs have been fabricated by several techniques with varying degrees of success and usability. We demonstrate an entirely new route for investigating the nucleation and ordering of QDs: growth on ultrathin semiconductor nanomembranes, substrates that are so thin, usually on the order of tens of nm, that they allow the strain created by a QD to penetrate the entire structure,. Such freestanding thin films are truly compliant and, when thin enough, regions of high strain will bend. Thus, we must address the effects of both strain and bending on the preferential nucleation of SiGe QDs. Tethered Si nanomembranes (cantilevers, ledges, wires, and ribbons) with thicknesses ranging from 20 nm to 60 nm are fabricated from silicon-on-insulator (SOI) substrates. SiGe QDs are then grown epitaxially by ultrahigh vacuum chemical vapor deposition. To ensure appropriate strain, the QDs are grown to have dimensions of the same order as the membrane thickness - roughly 8 nm in height. CVD allows for QD nucleation simultaneously on both sides of the membrane, so that nucleation of a QD on one side influences nucleation on the other. In addition, the nanomembranes are thin enough to be semi-transparent in an SEM, granting us a direct view of the alignment of QDs on the top surface to those on the bottom. We model this growth system with finite element analysis and see that a SiGe island nucleated on the top creates regions of high strain on the bottom along preferential crystallographic directions. These strained regions act as sites for preferential nucleation for QDs on the bottom, which will then seed the next QDs on the top layer and so on to create highly ordered, anticorrelated, arrays on both the top and bottom of the membrane. We discuss the simulations and observations in the limits of QD nucleation due to substrate bending and strain modulation. Research supported by DOE and AFOSR.

8:20am **NS+EM-WeM2 Synthesis of Si$_{1-x}$Ge$_x$ Nanowire Alloys by Chemical Vapor Deposition**, ***S.G. Choi,*** Los Alamos National Laboratory, *P. Allea,* Arizona State University, *S.B. Chikkannanavar, E. Akhadov, S.T. Picraux*, Los Alamos National Laboratory

There is an increasing interest in semiconductor nanowires (NWs) as a result of their unique physical properties which have resulted in new conceptual devices at the "nano" scale. Among a large number of NWs explored so far, Si and its related NWs have received much attention, in part due to their potential for easy integration into the well-developed Si microelectronics. Recently, attention has been given to SiGe alloy NWs which offer bandgap tuning from 0.7 to 1.1eV and possible applications in various devices. In order to synthesize these SiGe alloy NWs in a controlled manner and to realize nanoscale devices with optimum performance, it is important to understand the nature of alloy NWs growth. Although the two binary endpoints - Si and Ge NWs - have been well investigated, studies of SiGe alloy NWs are still in a formative stage. In this work, we studied effects of growth conditions on the structural characteristics of SiGe alloy NWs. SiGe alloy NWs were grown by chemical vapor deposition (CVD) on Si(111) substrates by the vapor-liquid-solid (VLS) mechanism. Au nanoparticles were used as the catalysts, and SiH$_4$ and GeH$_4$ were used as the source gases. Partial pressures were controlled precisely by mass-flow controllers for the flow rate of individual gases and a pressure controller for the total process pressure. NWs were grown at temperatures between 450 and 600°C. Morphology and composition of the grown NWs were investigated by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS), respectively. The NWs are observed to become more tapered as growth temperature or Ge composition is increased. Also for the same Au nanodot seeding conditions, the epitaxial Ge-rich alloy NWs grow primarily in the four <111> directions with a substantial fraction of these being vertical [111]-directed NWs, whereas the Si-rich alloy NWs exhibit a noticeable amount of the smaller diameter <110> oriented NWs as well as the four <111> NW orientations. In this work, we examined possible dependences of composition on: (1) diameter of NWs, (2) growth orientations, (3) growth temperature, (4) ratio of GeH$_4$ to the total partial pressure (i.e., P[GeH$_4$]/(P[SiH$_4$] + P[GeH$_4$]). In this presentation, we will contrast alloy growth with Si and Ge end point growth, and discuss possible mechanisms for explaining the observed effects of growth parameters on composition, morphology, and structure of SiGe alloy NWs.

8:40am **NS+EM-WeM3 In Situ Kinetic Measurements during the Nucleation and Growth of Si and Ge Nanowires**, ***F.M. Ross***, IBM T. J. Watson Research Center **INVITED**

In this presentation we will discuss the growth of epitaxial nanowires in Si and Ge using Au as the catalyst, focusing on the kinetic processes that influence nucleation and wire shape. We grow wires in an environmental TEM, which has capabilities for evaporating Au onto a clean Si substrate and for introducing the precursor gases while the sample remains under observation. In situ video rate imaging allows us to measure nucleation events and growth kinetics and to observe structures during growth. We will start by showing the nucleation of Si nanowires within the catalyst particles, and will discuss the buildup of supersaturation that leads to nucleation. After nucleation, the variation of growth rate with pressure, temperature and droplet size allows us to determine the rate limiting step and evaluate the relevance of curvature-driven effects to wire growth. For Si wires, the simple picture that results is complicated by some interesting phenomena caused by the high mobility of Au on the wire surface. And for Ge wires, we show that the growth-driven supersaturation can stabilise the droplets and allow growth far below the eutectic temperature. We finally discuss the growth of hybrid nanowires composed of group IV and group III-V components, showing how the balance of interface energies determines the overall structure. Thus we find that nanowires provide a unique window into fundamental crystal growth processes, as well as an opportunity to fabricate precisely controlled structures for novel applications.

9:20am **NS+EM-WeM5 Self-Catalyzed Growth of Defect-Free Indium Phosphide Nanowires on Silicon**, ***R.L. Woo,*** University of California, Los Angeles, *Y. Kobayashi, T. Mallouk,* Penn State University, *R.F. Hicks*, University of California, Los Angeles

Compound semiconductor nanowires exhibit promising properties for high-speed nanoelectronic devices. However, in order to realize their full potential, growth processes must be developed for the precise control of the nanowire shape, density, uniformity, and crystalline quality. In this study, we report on the fabrication of indium phosphide nanowires on silicon (100) and (111) by metalorganic vapor-phase epitaxy. Nanoscale indium droplets were used instead of gold catalyst to nucleate wire deposition. High-resolution transmission electron microscopy with selected area electron diffraction have revealed that the InP nanowires are free of crystal defects and grow along either the <110> or the <113> axis. This may be contrasted to gold catalyze growth, where the preferential orientation is <111>, and there is a relatively high density of stacking faults. Through careful control of the substrate preparation and the MOVPE process conditions, it has been possible to grow vertical InP nanowires of uniform diameter and lengths over 1.0 micron. At the meeting, we will present data on the novel electrical and optical properties of the indium phosphide nanowires.

9:40am **NS+EM-WeM6 Plasma-stimulated Control of Silicon Nanowire Nucleation, Orientation and Growth Kinetics**, *P. Aella, W.T. Petuskey,* Arizona State University, ***S.T. Picraux***, Los Alamos National Laboratory

Plasma-enhanced chemical vapor deposition is shown to significantly alter the nucleation rate and activation energy for vapor-liquid-solid (VLS) growth of silicon nanowires compared to thermal growth, providing new control over nanowire morphologies and new insight into the rate-limiting mechanisms of VLS growth. Initially, catalytic gold films (0.5 - 2 nm thick) were thermally evaporated onto hydrogen terminated Si (100) substrates at room temperature in a UHV deposition system. Subsequently, Si nanowires were grown in a cold wall reactor at 0.5 Torr in atmospheres of 10% SiH4 in H2 between 350 to 510ºC and RF plasma powers of 2.5 to 10 W. SEM images show that thermally grown nanowires on Si (100) substrates nucleate and grow predominantly in <111> directions. In contrast, plasma stimulation significantly enhances the nucleation rate of smaller diameter <110> Si nanowires and also reduces coarsening of Au dots. A two step growth process is demonstrated whereby initial plasma excitation nucleates <110> nanowires followed by thermal growth to preferentially form a high density of small diameter <110> nanowires on Si (100) surfaces, greatly limiting the large diameter <111> nanowire formation found under thermal growth conditions with identical Au seeding. This demonstrates the overall effect of the plasma on shortening nucleation times, favoring thinner wires, and thereby dominating the rest of the growth process. A comparison of the growth rate vs. temperature for both <111> and <110> nanowires shows a large reduction in the activation energy (from 0.74 to 0.26 eV) due to the plasma. The overall growth rate is also greatly enhanced at low temperatures by plasma excitation, with growth rates at 350ºC an order of magnitude greater than for thermal growth. Under our low temperature thermal conditions the predominant source gas is silane, while in the case of plasma stimulation SiH3 radicals are also present. Our results unequivocally demonstrate that the rate limiting step for Si nanowire growth under these conditions is due to the kinetics of silicon incorporation at the vapor-liquid interface and not at the liquid-solid interface as has also been previously proposed in some cases. Based on our measured incorporation coefficients and activation energies under thermal and plasma-enhanced growth we suggest the first model for the rate-limiting kinetic steps for Si nanowire growth by the VLS mechanism.

10:40am **NS+EM-WeM9 Nanowires in Nanoelectronics: Problems and Promise**, ***D.K. Ferry***, Arizona State University **INVITED**

Progress in microelectronics has generally followed the well known scaling rules known as Moore's Law. By the end of this decade, we will approach some well recognized limits in traditional semiconductor devices. Nanowires have been put forward as a new technology with new promise to extend nanoelectronics. For this to be the case, the nanowires must fit into the scaling rules and must offer important new options, primarily in circuit cleverness. In this talk, I will review the scaling rules, and where they have led us, then discuss how the constraints of these rules, particularly Si area cost, dictate how new technologies can be used. These suggest that the impact of nanowires will likely be in providing new options for architectural revolutions, as opposed to merely clever new devices.

11:20am **NS+EM-WeM11 Electrical and Mechanical Characterization of Nanowire Properties using In-Situ SEM**, ***D.F. Ogletree***, Lawrence Berkeley National Laboratory

Nanowires have unique electrical and mechanical properties with a wide range of potential applications in electronics, opto-electronics and nano-mechanics. Local measurements of the electrical and mechanical properties of individual nanowires in controlled environments are required to develop these applications and to optimize nanowire growth conditions. A flexible system for nanowire characterization based on a high-resolution environmental scanning electron microscope (SEM) has been developed combining sample heating in controlled gas environments with nano-positioning of local probes. This system has been used to investigate the evolution of size-dependent nanowire mechanical properties between room temperature and the melting point of the nanowires.

11:40am **NS+EM-WeM12 Four Independent STM Navigated by High Resolution UHV SEM: Transport Measurements on In-Situ Grown Titanium Silicide Nanowires on Si(111)**, ***J. Koeble***, *M. Maier,* Omicron NanoTechnology, Germany, *B. Grandider*, IEMN, Lille, France

A major challenge in Nanotechnology is the incorporation of single nano-devices into larger integrated circuits. Traditional instrumentation suffers from one fundamental issue: How to cover the dimensional range of a fully integrated circuit down to the nanometer range (or even atomic scale) of single devices and have an adequate integrated navigation system. To meet these requirements, we have established and being advancing a new approach to integrating state-of-the-art SPM technology via high resolution electron microscopy and spectroscopy: (1) Bridging dimensions and rapid navigation; (2) Combining different surface analysis methods at the very same sample area to gain complementary information; (3) Integrated position-readout of sample and probe positioning; (4) Pushing each single technology to its inherent limits. The system facilitates four independent Scanning Tunnelling Microscopes and the UHV version of the Zeiss Gemini SEM column with ultimate resolution below 4nm for probe navigation and rapid localisation of sample features or devices. STM imaging is used to pro-actively position and contact the probe(s) on nano-devices. Using STM probe approach technology, a controlled electrical contact is ensured to finally perform a four-point measurement on the nano-scale. We report on electrical measurements on self-assembled titanium silicide nanowires (NWs) in-situ grown on a Si(111) surface. Transport measurements have been taken in 2-point and 4-point configuration. The transport measurements indicate metallic behavior for the silicide nanowires and that the NWs are electronically decoupled from the Si surface and reveal a Schottky barrier between the NWs and the Si surface.

12:00pm **NS+EM-WeM13 Anisotropic Plasmon and Electronic Structure of Ag Nanowires on Cu(110)**, ***P.T. Sprunger**, I. Senevirathne, W. Zhao, B.M. Watson, O. Kizilkaya, A.K. Sekharan, R.L. Kurtz*, Louisiana State University

Epitaxial Ag nanowires have been found to self-assemble on Cu(110) for Ag coverages exceeding 1.2 ML. The electronic and plasmon loss structure of the nanowires have been characterized by ARPES and EELS. STM images reveal that Ag nanowires grown on Cu(110) are approximately 2 nm high and ~12 nm wide. The nanowires grow oriented with the long axis parallel to the $[\bar{1}10]$ substrate direction and they have aspect ratios up to 20:1. The ARPES results show that the valence bands within the Ag nanowire are strongly anisotropic with clear band dispersion in the along-wire direction, but no dispersion in the across-wire direction. This strongly suggests that the valence electrons of Ag behave as quasi-one-D conductors along the wire yet confined with atomic-like states perpendicular. Fermi surface crossings have been observed, confirming that metallic behavior is realized along the wire axis. In accord with the ARPES measurements, EELS reveals that the plasmon excitation is red-shifted at the zone-center and is nearly dispersonless perpendicular to the nanowire direction. These results will be discussed in light of recent band-structure calculations of Ag nanowires and models for plasmon behavior in quasi-1D structures. We would like to acknowledge the support of the LSU CAMD synchrotron light source and the support of and LA-R&D and NSF through DMR-0504654.

Understanding Biointerphases and Magnetism with Neutrons Topical Conference

Room: 618 - Session NT+BI-WeM

Phospholipid Bilayers and Membranes

Moderator: M. Tanaka, University of Heidelberg

8:00am **NT+BI-WeM1 Tethered Bilayer Lipid Membranes in Biomedical Research: Lessons from Neutron Scattering**, ***M. Lösche**, F. Heinrich,* Carnegie Mellon University*, D.J. McGillivray,* The Australian National University*, G. Valincius,* Institute of Biochemistry, Vilnius, Lithuania*, Y. Sokolov, J.E. Hall*, UC Irvine **INVITED**

Tethered bilayer lipid membranes (tBLMs) on solid supports hold potential to mimic biological membranes. Molecular-scale studies of the interactions of peptides and proteins with membranes provide ample opportunities in biophysical and biomedical research. Membrane stabilization by the proximity of a solid substrate provides resilience to the system, but has often at the same time introduced severe problems. A prerequisite, for example, for tBLM characterization by scattering and electrochemical techniques is a low defect density of the membrane. Only then is it possible to quantify minor structural and functional changes induced by, e.g., protein interaction with the membrane. We have optimized a membrane architecture on molecularly flat gold surfaces which meets all these challenges. Different lengths of the hydrophilic poly(ethylene glycol) (PEG) spacer that controls the structure of the inner monolayer leaflet provide highly hydrated sub-membrane spaces between 20 Å and 60 Å in thickness, as determined by neutron reflection. Such tBLMs may be composed of charged or zwitterionic lipids with various chain saturation, and can include cholesterol. The membranes are highly insulating and are routinely probed with electrochemical impedance spectroscopy (EIS). As an example for ongoing biomedical research we will discuss the interaction of soluble prefibrillar β-amyloid oligomers with tBLMs and compare the impact of the peptide on such membranes with that of a pore forming bacterial exotoxin, Staphylococcus aureus α-hemolysin.

8:40am **NT+BI-WeM3 Study of Fluctuation and Destabilization of Single Phospholipidic Bilayer by Neutron and X-ray Scattering**, ***T. Charitat***, CNRS-Université Louis Pasteur, France, *S. Lecuyer*, Harvard University **INVITED**

Supported bilayer are interesting model systems for biologist and present also fascinating physical properties. We investigate experimentally these dynamical properties on floating bilayer. First, the equilibrium structures of single and double bilayers are studied by neutron reflectivity. The submicronic fluctuation spectrum of a floating bilayer is determined by off-specular X-ray scattering: surface tension, bending modulus and, for the first time with this technique, inter-membrane potential. Using fluorescence microscopy, we show that this single bilayer can be completely destabilized leading to well control vesicles formation. Destabilization can occur either at the main gel-fluid transition of the lipids, and can be interpreted in terms of a drop of bending rigidity, or under an AC low-frequency electric field applied in the fluid phase. In that last case we also study the effect of the electric field at the molecular length scale by neutron reflectivity. In both cases, the destabilization leads to the formation of relatively monodisperse vesicles, which could give a better understanding of the formation mechanism.

9:20am **NT+BI-WeM5 Protein-induced Pores in Membranes Detected and Studied by Neutron Scattering**, ***H.W. Huang***, Rice University **INVITED**

Gene encoded antimicrobial peptides kill bacteria by forming pores in the bacterial membranes. Apoptotic protein Bax forms pores in the outer mitochondrial membrane to release the apoptosis-inducing factor cytochrome c from mitochondria. The evidence of pore formation in membranes is usually ion conduction or leakage. The structure of a pore in a fluid membrane is difficult to detect or measure by conventional methods such as electron microscopy. Neutron scattering is uniquely suited for such structural studies. We will show neutron scattering from membrane pores made by antimicrobial peptides, alamethicin, magainin, protegrin as well as by bee venom toxin melittin. Surprisingly, these peptides form two different kinds of transmembrane pores first detected by neutron methods.

10:40am **NT+BI-WeM9 Using Neutron Spectroscopy to Study Collective Dynamics of Biological and Model Membrane Systems**, ***M.C. Rheinstadter***, University of Missouri-Columbia **INVITED**

The spectrum of fluctuations in biomimetic and biological membranes covers a large range of time and length scales, ranging from the long wavelength undulation and bending modes of the bilayer with typical relaxation times of nanoseconds and lateral length scales of several hundred lipid molecules, down to the short-wavelength, picosecond density fluctuations involving neighboring lipid molecules. New developments and improvements in neutron scattering instruments, sample preparation and environments and, eventually, the more and more powerful neutron sources open up the possibility to study collective excitations, i.e. phonons, in artificial and biological membranes. The goal of this project is to seek relationships between collective dynamics on various length scales on the one hand, and macroscopic phenomena such as trans-membrane transport, pore opening, and membrane fusion on the other hand. The combination of various inelastic neutron scattering techniques enlarges the window of accessible momentum and energy transfers - or better: accessible length and time scales - and allows one to study structure and dynamics on length scales ranging from the nearest-neighbor distances of lipid molecules to length scales of more than 100 nm, covering time scales from about 0.1 ps to almost 1 μs. The fluctuations are quantified by measuring the corresponding dispersion relations, i.e. the wave vector-dependence of the excitation frequencies or relaxation rates. Because biological materials lack an overall crystal structure, in order to fully characterize the fluctuations and to compare experimental results with membrane theories, the measurement must cover a very large range of length and time scales. By using multiple instruments, from spin-echo to triple-axis spectrometers, we have successfully probed these fluctuations over the desired range of length and time scales.[1-5]

[1] M.C. Rheinstädter, C. Ollinger, G. Fragneto, F. Demmel and T. Salditt, Phys. Rev. Lett. 93, 108107, 1-4 (2004).

[2] Maikel C. Rheinstädter, Wolfgang Häußler and Tim Salditt, Phys. Rev. Lett. 97, 048103, 1-4 (2006).

[3] Maikel C. Rheinstädter, Tilo Seydel, Franz Demmel and Tim Salditt, Phys. Rev. E 71, 061908, 1-8 (2005).

[4] Maikel C. Rheinstädter, Tilo Seydel and Tim Salditt, Phys. Rev. E 75, 011907, 1-5 (2007)

[5] Maikel C. Rheinstädter, Tilo Seydel, Wolfgang Häußler and Tim Salditt, J. Vac. Soc. Technol. A 24, 1191-1196 (2006).

11:20am **NT+BI-WeM11 The Coupling between Hydration-Water and Protein Dynamics as Studied by Neutron Scattering**, ***M. Weik***, IBS, CEA-CNRS-UJF, France **INVITED**

The dynamics of proteins is influenced by motions of water molecules at the protein-solvent interphase. However, details about the dynamical coupling remain to be elucidated. Neutron scattering is particularly well-adapted to study macromolecular motions on the ns-ps time scale and their coupling to hydration-water dynamics. Indeed, elastic incoherent neutron scattering is sensitive to hydrogen/deuterium isotope labelling with the scattering cross-section of hydrogen being about 40 times larger than that of deuterium. Consequently, studying a completely deuterated protein hydrated in H_2O gives access to the dynamics of hydration water. Conversely, an identically prepared sample of hydrogenated protein hydrated in D_2O yields information on protein dynamics only, thus enabling a direct comparison between hydration water and protein motions. We studied the coupling between hydration-water and protein dynamics in a biological membrane (purple membrane (PM)) and a soluble, globular protein (maltose binding protein (MBP)) by measuring mean square displacements of hydrogen atoms in the temperature range from 20 to 300 K. Hydration-water in both PM and MBP undergoes a dynamical transition at 200 K, evidenced as a break in atomic mean square displacements as a function of temperature (Wood, Frölich, Plazanet, Kessler, Moulin, Härtlein, Gabel, Oesterhelt, Zaccai & Weik, unpublished results). In the case of PM, this dynamical transition corresponds to the onset of long-range translational diffusion of water molecules as evidenced by neutron diffraction.[1] When atomic mean square displacements of hydration-water molecules become as large as those of protein atoms, a dynamical transition appears at 250 K in PM and at 230 K in MBP. Our results shed new light on the coupling between hydration-water and protein motions and suggest that they are coupled at room temperature, yet decoupled at cryo-temperatures.

[1]Weik, M., Lehnert, U. and Zaccai, G. (2005) Liquid-like water confined in stacks of biological membranes at 200 k and its relation to protein dynamics. Biophys J., 89, 3639-3646.

Plasma Science and Technology

Room: 606 - Session PS1+NS-WeM

Plasmas in Nanotechnology

Moderator: S. Kodambaka, University of California, Los Angeles

8:00am **PS1+NS-WeM1 Spectroscopic, Spatial, and Temporal Investigation of Fe Nanoparticle Synthesis by Through Thin Film Ablation**, ***A.R. Waite,*** University of Dayton, Air Force Research Laboratory and UTC, Inc., *P.T. Murray,* University of Dayton, *J.G. Jones,* Air Force Research Laboratory, *E. Shin,* University of Dayton, *A.A. Voevodin*, Air Force Research Laboratory

Nanoparticles of Fe have been formed by the process of Through Thin Film Ablation (TTFA). In the TTFA process, the target consists of a thin film (10-20 nm thick) of material that has been applied to an optically transparent support. The thin film target is ablated in vacuum through the transparent support, and this produces a directional plume of nanoparticles. Optical Emission Spectroscopy (OES), Time-of-Flight (TOF) analysis, and high-speed Intensified Charge Coupled Device (ICCD) imaging are utilized to study the plume dynamics and characteristics. OES measurements indicate the ejected nanoparticles to have a temperature of 2232 K, suggesting they are liquid. TOF analysis indicated that there are two main size constituents in the ablation plume, higher speed atomic species and slower nanoparticles. ICCD imaging is used to further study the plume dynamics in both time and space. Ablation in vacuum and in the presence of a background gas will be discussed.

8:20am **PS1+NS-WeM2 Size Manipulation and Control of Nanoparticles Produced from Atmospheric-Pressure Microplasmas**, ***N.A. Brunelli***, *K.P. Giapis*, California Institute of Technology

Size manipulation and control of nanoparticles produced from atmospheric-pressure microplasmas Atmospheric-pressure microdischarges have been shown to produce silicon nanoparticles between 1-2 nm in diameter, which exhibit intense photoluminescence emission at 420 nm with quantum efficiency of 30%.[1] For imaging applications, it is desirable to have an emission at longer wavelengths which requires larger diameter nanoparticles. However, it has been exceedingly difficult to manipulate the nanoparticle size in a single microdischarge, where perturbations to the growth conditions seem to only influence the number of particles produced while the size remains invariant. We demonstrate here that the combination of a microdischarge with a CVD reactor can overcome this problem by achieving overgrowth of the seed particles produced in the microdischarge. For example, silicon nanoparticles can be enlarged from 2.5 nm to 3.5, 4.5 and 5 nm by mixing an additional 150, 300 and 600 ppm of sila4ne in argon, respectively. In fact, the CVD overgrowth allows not only tuning of the particle size but also permits selection of an alternate overgrowth layer, creating core-shell structures. Examples of Ge and Fe cores overgrown with Si will be shown. We quantify this claim by using a new ultrafine radial differential mobility analyzer immediately after the furnace to monitor in real-time the particle size. We characterize the nanoparticles by AFM, photoluminescence (PL) spectroscopy and transmission electron microscopy. As oxidation has been shown to affect the PL emission,[2] we have encapsulated the particles in thin films to ensure observed light emission is from radiative recombination. Beyond enlarging the seed particle diameter, we demonstrate the synthesis of core-shell structures consisting of an inexpensive metallic core and a thin overlayer of catalytically active material as the shell. Electrochemical measurements demonstrate the catalytic activity and performance of Fe-Pt and Co-Pt core-shell nanoparticles for fuel cell type applications.

[1] Sankaran, R. M., D. Holunga, et al. (2005). "Synthesis of blue luminescent Si nanoparticles using atmospheric-pressure microdischarges." Nano Letters 5(3): 537-541.

[2] Biteen, J. S., N. S. Lewis, et al. (2004). "Size-dependent oxygen-related electronic states in silicon nanocrystals." Applied Physics Letters 84(26): 5389-5391.

8:40am **PS1+NS-WeM3 Ionic Plasmas Yielding Novel-Structured and -Functional Nanocarbons**, ***R. Hatakeyama***, *T. Kaneko, W. Oohara, Y.F. Li*, Tohoku University, Japan **INVITED**

Nanocarbons of carbon allotropes have attracted a great deal of attention due to their high potential for novel properties and a variety of applications. Since fullerenes and carbon nanotubes among them are furnished with hollow inner nanospaces, it is a fascinating challenge to inject various kinds of atoms and molecules into the nanospaces based on plasma nanotechnology, which could lead to innovative functionalization of the pristine ones. For that purpose original approaches using nanoscopic plasma processing mainly in ionic plasmas have been performed in order to develop fullerene-, SWNT(single-walled carbon nanotube)- and DWNT(double-walled carbon nanotube)-based materials with new functions corresponding to electronic and biological applications. Firstly, the encapsulation of charge-exploited alkali atoms inside the fullerene is realized ($Li@C_{60}$ etc.) using alkali-fullerene plasmas as ionic plasmas, which consist of positive alkali ions and negative C_{60} ions. Then the atomic nitrogen as a spin-exploited atom is also encapsulated inside C_{60} ($N@C_{60}$). In relation to the inner nanospace modification of the carbon nanotubes, another ionic plasmas, i.e., alkali-halogen plasma and pair-ion plasma are generated, which consist of positive alkali ions and negative halogen ions, and positive-C_{60} and negative-C_{60} ions with an equal mass, respectively. Furthermore, an electrolyte solution plasma including DNA negative ions is prepared. The substrate bias method is utilized mainly in these plasmas, where positive and negative ions with their energies and fluxes controlled are irradiated to an immersed substrate coated with the pristine carbon nanotubes . In addition, a thermal and plasma combined process is also devised for the treatment of both charge- and spin-exploited atoms. Consequently, we have innovatively created alkali-metals encapsulated SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs), halogen-elements encapsulated SWNTs (I@SWNTs), ferromagnetic-atoms encapsulated SWNTs (Fe@SWNTs), fullerene molecules encapsulated SWNTs and DWNTs (C_{60}@SWNTs, C_{60}@DWNTs, C_{70}@DWNTs, C_{84}@DWNTs), and DNA molecules encapsulated SWNTs (DNA@SWNTs) . Finally, their electronic and magnetic properties are intensively investigated. As a result, we have for the first time succeeded in realizing the continuous transition of air stable electronic transport from p-type to n- type semiconducting property by adjusting an amount of dosed atoms and molecules inside SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs, I@SWNTs, C_{60}@SWNTs, C_{60}@DWNTs), and in forming nano structures of magnetic semiconductor (Fe@SWNTs), nano pn junctions with rectifying characteristic [(Cs/I)@SWNTs)], and nano structures with distinct negative differential resistance of high peak-to-valley ratio (C_{60}@DWNTs, C_{70}@DWNTs, C_{84}@DWNTs) . In the case of DNA@SWNTs an experimental system utilizing an interfacial region between the gas and liquid phases has been constructed in order to enhance the DNA encapsulation rate. Here an ionic liquid consisting of only positive and negative molecules is introduced into the liquid phase, which can be regarded as an ionic plasma, i.e., fully ionized electrolyte plasma.

9:20am **PS1+NS-WeM5 Continuous-Flow Microplasma Synthesis of Metal Nanoparticles for Catalytic Growth of Carbon Nanotubes**, *W.-H. Chiang*, ***R.M. Sankaran***, Case Western Reserve University

Carbon nanotubes (CNTs) have been synthesized in a continuous-flow, gas-phase catalytic process. The synthesis technique consists of two steps: 1) production of well-defined metal nanoparticles in an atmospheric-pressure microplasma and 2) catalytic growth of carbon nanotubes in a tube furnace reactor. In the first step, nanoparticles are generated using a direct-current (dc) hollow cathode microplasma made-up of a stainless steel cathode with a pin-hole (d~180 µm) and an arbitrarily-shaped tube anode. Gaseous precursors are introduced into the microplasma at atmospheric-pressure and decomposed non-thermally by electron impact to generate reactive radical species. Under appropriate precursor saturation conditions, the radicals polymerize to nucleate particles homogenously in the gas phase. Particle growth is limited to the small reactor volume (less than 1 nL) created by the microplasma geometry. As a result of the large concentration gradients and short residence time, the technique is capable of producing very small (1-3 nm diameter) nanoparticles with narrow size distributions. The particle-laden flow is then continuously fed to a second reactor to grow carbon nanotubes in free flight with addition of acetylene and hydrogen and heating at fixed temperatures between 500 and 1000 ^{o}C. Nanotube size and distribution are determined on line using a gas-phase electrophoretic mobility macromolecular analyzer (GEMMA). In situ aerosol classification allows experimental conditions to be directly related to growth parameters. We have recently investigated the catalytic properties of iron and nickel nanoparticles toward growth of carbon nanotubes. Process parameters were optimized to prevent amorphous carbon formation and obtain high-quality CNTs. Ex-situ techniques such as Raman spectroscopy and transmission electron microscope (TEM) were used to characterize the structure of the carbon nanotubes. The combination of continuous-flow synthesis using microplasmas and the GEMMA system opens new possibilities for nanocatalyst synthesis and provides a methodology for enhancing our fundamental understanding of catalytic behavior.

9:40am **PS1+NS-WeM6 Low Temperature Growth of Single-Walled Carbon Nanotubes by Oxygen-Assisted Inductively Coupled Plasma Chemical Vapor Deposition**, ***C.-H. Hsiao***, *C.-H. Weng, Z.-Y. Juang, K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention recently due to their unique physical properties and a wide range of potential applications, in particular, field effect transistors (FET) and nano-photonic devices. It is highly desirable to develop a method compatible with standard semiconductor microfabrication processes for direct synthesis of high quality SWNTs. In this work, we demonstrated a low temperature growth process of SWNTs on silicon substrates by inductively coupled plasma chemical vapor deposition (ICP-CVD) method with CH_4/H_2 gas mixture as base processing gases. A unique Ni/Al/SiO_2 nanocatalysts/support system has also been developed to allow the growth of high quality SWNTs. To further improve the crystalline structure of SWNTs, oxygen was added to the processing gas mixture to remove amorphous carbons during the growth process. Both the scanning electron microscopy and micro-Raman spectra were employed for characterizations of the SWNTs. Parametric experiments were conducted to optimize the O_2 fraction in the gas mixture. The SWNTs were successfully synthesized at a temperature as low as 600°C.

10:40am **PS1+NS-WeM9 Fabrication of Defect-Free and Diameter-Controlled Silicon Nanodisks for Future Quantum Devices by using Neutral Beam Etching**, *T. Hashimoto,* ***T. Kubota****, C.H. Huang,* Tohoku Univ., Japan*, M. Takeguchi,* National Inst. for Mtls Sci., Japan*, K. Nishioka,* Japan Adv. Inst. of Sci. and Tech.*, Y. Uraoka, T. Fuyuki,* Nara Inst. of Sci. and Tech., Japan*, I. Yamashita,* Matsushita Electric Industrial Co., Ltd, Japan*, S. Samukawa*, Tohoku Univ., Japan

Nanometer-scale structures, such as quantum dots, are widely studied because of their possible application in the development of quantum-effect devices, such as quantum-dot lasers and single-electron transistors. To develop practical and robust quantum-effect devices, manufacturers must be able to fabricate selectively arranged, defect-free, sub-10-nm-scale structures of uniform size on substrates. To realize a nanometer-scale structure, we used a ferritin iron core (7 nm in diameter) as a uniform and high-density template and our developed neutral beam (NB) etching process for damage-free etching. We fabricated a "nanodisk,"a nanometer-thick disk-shaped silicon structure by patterning <3.5-nm poly-Si layer / 1.4-nm SiO_2 layer / Si substrate> by using NB etching with a ferritin iron-core mask. To precisely control the diameter of the nanodisk, we must selectively remove the surface native silicon oxide layer before Cl neutral beam etching because the Cl neutral beam has extremely high selectivity to SiO_2 film. SEM and TEM observations revealed that the nanodisk was successfully fabricated and that the buried SiO_2 layer was not damaged during etching. When the nanodisk was only etched by using the Cl neutral beam with the iron core mask, the diameter of the nanodisk was about 13 nm. To shrink the diameter of nanodisk, we developed a dry process to remove native oxide by using NF_3 gas and hydrogen radicals ("NF_3 treatment"). By using the NF_3 treatment to remove the native oxide, we decreased the nanodisk diameter to 10 nm. We found that removing the surface native oxide is very important for controlling the diameter of nanodisk. We then measured the I-V characteristics by using atomic force microscopy (AFM) with a conducting probe. Coulomb staircases were observed from the I-V measurements of the nanodisks at 25 K and at room temperature. These results indicate that the nanodisks we fabricated have a precise quantum-effect structure, and they attained single-electron properties. This research has great potential in the development of practical and robust fabrication processes for future quantum-effect devices. A part of this work was supported by the Nanotechnology Support Project and the Leading Project of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

11:00am **PS1+NS-WeM10 Parallel Writing of Complex Nanofeatures using Nanopantography**, ***L. Xu***, *A. Nasrullah, M. Jain, Z. Chen, V.M. Donnelly, D.J. Economou, P. Ruchhoeft*, University of Houston

Nanopantography is a technique for massively parallel writing of nano-sized features. A broad-area, collimated, monoenergetic ion beam is directed to an array of sub-micron-diameter electrostatic lenses fabricated on a conductive substrate (e.g., doped Si wafer). By applying appropriate voltages to the lens electrodes, each "beamlet" entering the lens is focused to a spot on the wafer surface. The spot size can be up to 100X smaller than the diameter of the lens. With the choice of an Ar^+ beam in the presence of Cl_2 gas, 10 nm-dia holes were etched in Si; while with the choice of a Ni^+ beam, ~10 nm nickel dots were deposited on Si. Nanopantography has the capability to write arbitrary nano-sized features since the focal points can be displaced by tilting the substrate. A second-generation nanopantographic system was built to allow writing of complex nano-features. The improved system design had an ion flux ~ 15X higher than the first generation reactor. A LabView-controlled motorized stage could be tilted in both the X- and Y-axes with an accuracy of 0.011° degrees. This corresponds to translation of the focal point by 1.5 nm on the substrate. The energy distribution of the extracted ion beam was measured to have a spread of 2.2 eV, for a 100 eV beam. By continuously tilting the substrate in one direction, nanotrenches with ~15 nm (FWHM) width and ~40 nm depth were etched in a Si wafer. More complex patterns, such as letters of the alphabet, were also etched into Si in a massively parallel fashion by two-dimensional tilting of the substrate.

11:20am **PS1+NS-WeM11 High Aspect Ratio Deep Trench Chamber and Process Development for Silicon Etch in DRAM Applications below 50 nm**, ***S. Wege****, S. Barth,* Qimonda Dresden, Germany*, A. Kersch,* Qimonda Munich, Germany*, M. Reinicke,* Dresden University of Technology, Germany*, G. Wenig,* Qimonda Munich, Germany*, M. Rudolph, J. Sobe, A. Steinbach*, Qimonda Dresden, Germany

For QimondaÂ´s DRAM Technology the deep trench etched into silicon is the base for the capacitor concept. The shrink of lateral dimensions at approximately constant capacity specifications leads to increased deep trench aspect ratio requirements. Therefore high selectivity to the etch mask and excellent uniformity is needed, especially for technologies below 50nm. In this paper we describe the development of advanced DT plasma etch chamber and process to fulfill these requirements. New process regimes, e.g., RF pulsing and high temperature showed promising results. Simulations were combined with in-situ plasma measurement techniques, e.g., QMS with ion energy analysis, high resolution OES, insitu IR absorption spectroscopy, and technological experiments, to characterize hardware features and process conditions. To achieve high Si etch rate and selectivity, plasma density and electron energy distribution in the plasma bulk, and ion energy distribution on the wafer surface can be optimized through multi frequency cathode excitation. The selectivity is further enhanced by using advanced hard mask materials and combining with RF pulsing. The optimization of the side wall passivation stoichiometry is a key for high aspect ratio silicon etch. In addition, the etch process chamber includes new features for process control, in-situ wafer surface temperature and trench depth measurement. The equipment and process development was accomplished through close cooperation between Qimonda and the tool supplier.

11:40am **PS1+NS-WeM12 Etch Selectivity and Surface Roughening of Polystyrene and Poly(methyl methacrylate) in Plasma Etching of Block Copolymers**, ***Y.-H. Ting***, *S.-M. Park, C.-C. Liu, X. Liu, F.J. Himpsel, P.F. Nealey, A.E. Wendt*, University of Wisconsin-Madison

Polystyrene -block-poly(methyl methacrylate), (PS-b-PMMA) diblock copolymers are a promising lithography alternative for nanometer scale features. The two components segregate into nanoscale domains when the polymer solution is spun on to form a thin film and annealed above the glass transition temperatures of both components. Preferential removal of PMMA domains through plasma etching to leave behind a PS mask for subsequent etching of underlying layers is the focus of this work. The quality of the PS mask is characterized by the thickness and lateral dimension of the PS structures after removal of the PMMA, as well as the smoothness of its surfaces. We have characterized the effects of different plasma chemistries including O2, Ar/O2, Ar, CF4 and CHF3/O2 on etch selectivity and surface/sidewall roughness for PS and PMMA. The surface roughness of PS and PMMA after Ar/O2 plasma etching (which gave the best overall etch performance) was further examined as a function of ion bombardment energy to understand the roughening mechanisms, as the two polymers show different responses to changing plasma conditions. Specifically, the surface roughness of PMMA increases with increasing ion bombardment energy, while that of PS decreases. An oxidation-induced micro-masking process on PS surfaces upon plasma exposure has been proposed to explain the different in roughening of PS and PMMA. Surface chemical analysis using NEXAFS shows that chemical change occurs on the PS surface during exposure to oxygen containing plasmas. Evidence of inhomogeneities in the composition of the PS film suggests that surface inhomogeneities in chemical composition may persist and change chemically upon plasma exposure. Variations in etch resistance associated with the inhomogeneities may in turn be responsible for observed surface roughness. Roughening caused by this "micro-masking" effect is reduced under conditions that minimize selectivity, such as high ion bombardment energies. We acknowledge support from the UW NSF MRSEC for Nanostructured Materials.

12:00pm **PS1+NS-WeM13 Comparison between NF$_3$ and CF$_4$ Chemistries for the Selective Etching of SiGe Sacrificial Layers in a 300mm Chemical Dry Etching Reactor**, ***S. Borel***, CEA-Leti MINATEC, France, *C. Arvet*, STMicroelectronics, *D. Watanabe*, Shibaura Mechatronics Corporation, Japan

The selective removal of a SiGe sacrificial layer is a key step in the realization of several architectures that are based on the SON technology. Such a process has been developed and studied in 200mm, showing very good results in terms of selectivity by using CF$_4$ as an etching gas. This competence has been transferred in 300mm by using a new generation chemical dry etching tool that offers an additional and alternative source of fluorine which consists in NF$_3$. A process based on this environment-friendly molecule has been developed and compared with the CF$_4$ reference in terms of SiGe:Si selectivity while keeping a comparable etch rate. In that aim, a strong dilution (1:10) was necessary because of the high dissociation level of NF$_3$ that results in high etch rates. Morphological analyses clearly show that the selectivity obtained by using NF$_3$ is prohibitive for the realization of advanced devices. Indeed, the selectivity value is around 3, which means that the thinning of the Si cap is only 3 times lower than the SiGe tunnel depth whereas it needs to be higher than 30 (it reaches 70 by using CF$_4$). Surface analyses by XPS reveal that a Si substrate exposed to the CF$_4$ process presents some carbon, which suggests a passivation mechanism that may be involved in the selectivity. With the carbon-free NF$_3$ molecule, this phenomenon does not occur, hence the lack of selectivity we observe. As a conclusion, even if it is possible to etch SiGe faster than Si by using NF$_3$, the reference process made of CF$_4$ remains the best solution for the tunnel etching of advanced devices where a controlled etch rate is necessary and a high SiGe:Si selectivity is mandatory.

Plasma Science and Technology

Room: 607 - Session PS2-WeM

Plasma-Surface Interactions I

Moderator: J.P. Chang, University of California at Los Angeles

8:00am **PS2-WeM1 Measurement of Electron Shading and its Depletion by Ultraviolet Radiation using Scanning Surface Potential Microscopy[1]**, *G.S. Upadhyaya*, ***J.L. Shohet***, University of Wisconsin-Madison, *J.B. Kruger*, Stanford University

Electron Shading, or topography-dependent charging, is believed to occur during plasma exposure when the depth-to-diameter ratio (aspect ratio) of pattern features is greater than 0.5. We present preliminary direct experimental evidence of the existence of electron shading. In addition, we present evidence of removal of the electron shading by exposure of the charged structure to UV radiation produced by a Hg-Ar lamp A patterned test structure was exposed to a d.c. nitrogen plasma operating at a pressure of 120 mTorr. The pattern was composed of a layer of thermally grown oxide with circular pits of 800 nm diameter and 1 micron depth. The pit pitch was 1.6 microns. The structure was placed on the cathode of the discharge to which -500 V was applied to break down the gas and to bombard the surface with ions. The structure was exposed to the plasma for a total of 10 seconds. A Digital Instruments multimode Atomic Force Microscope was modified to operate as a Kelvin probe in order to measure the surface potentials with sufficient spatial resolution to determine the potential inside the pit regions. To enhance the resolution beyond the standard AFM tip dimensions a carbon nanotube was attached to the apex of the AFM tip. Three two dimensional surface potential scans were made. First, a scan of the unexposed test structure showed that the surface potential was less than 10 mV over the surface of the unexposed structure. After plasma exposure, a second scan showed d.c. surface potential of the order of 6 volts over the entire structure. In addition, higher potentials (of the order of 200 mV) were observed directly over the pit regions, thus showing that electron shading appears to be present. The third scan (after UV exposure) shows removal of all surface potentials inside and out of the pit region and returns the structure to the uncharged state before plasma exposure.

[1] Work Supported by NSF under grant DMR-036582 and under grant ECS-9731293.

8:20am **PS2-WeM2 Surface Reaction Enhancement by UV Irradiation during Si Etching with Chlorine Atom Beam**, ***B. Jinnai***, Tohoku University, Japan, *F. Oda, Y. Morimoto,* Ushio Inc., Japan, *S. Samukawa*, Tohoku University, Japan

The surface atomic layer chemical reactions must be accurately controlled in future nanometer scale ULSI devices to enable precise patterning without any irradiation damage being caused during plasma etching processes. Many investigations have been conducted to understand surface reactions during silicon etching in chlorine plasma. Such research has focused on the effects of energetic ion and radical species using high-energy ion beam experiments. However, we recently found that the UV photon irradiation from plasma also plays a very important role in surface reactions during silicon etching in chlorine plasma. In this study, we discuss the effects of UV photon irradiation from chlorine plasma during silicon etching with our developed low-energy chlorine atom beam. A silicon substrate was etched by combining a low-energy chlorine atom beam and UV photon irradiation. When the silicon substrate was irradiated to the UV photons from 200 nm to 380 nm during etching with the chlorine atom beam, the etching rate of silicon was drastically increased. The results suggest that UV photons with wavelengths between 200 nm to 380 nm enhance the silicon surface reactions in the chlorine plasma. Additionally, a total photon irradiation density must be greater than 20 mW/cm^2 to increase the etching rate of silicon. Namely, the silicon surface reactions strongly depend on the wavelength (the energy) of the UV photons and the UV photon flux in the chlorine plasma. Our results are the first to clarify that UV photon irradiation from plasma plays very important roles in silicon surface atomic layer reactions in chlorine plasma.

8:40am **PS2-WeM3 Vacuum-Ultraviolet Radiation-Induced Charge Depletion in Plasma-Charged SiO2/Si by Electron Photoinjection and Fowler-Nordheim Tunneling[1]**, ***G.S. Upadhyaya***, *J.L. Shohet*, University of Wisconsin-Madison

Vacuum-ultraviolet (VUV) radiation emitted from processing plasmas can damage dielectric materials by creating electron-hole pairs. However, the resulting increased dielectric conductivity during VUV irradiation can also be beneficial in either partially or completely depleting previously deposited plasma charge. The underlying mechanisms that can be responsible for VUV-induced charge depletion are determined by exposing plasma-charged SiO2/Si samples to monochromatic-synchrotron radiation with photon energies in the range from 8 to 18 eV. Charge depletion was observed only for photon energies smaller than 13 eV. For photon energies between 8 and 11 eV, photoinjection of electrons from the Si into SiO2 conduction band is identified as the process responsible for charge depletion. For photon energies between 11-13 eV, field emission of electrons from Si into the oxide due to electric-field enhancement at the Si-SiO2 interface is believed to be the charge-depletion mechanism. Qualitative photoinjection and field-emission models convincingly explain all experimental measurements.

This work was supported by the National Science Foundation under grant No. DMR-0306582. The SRC is a national facility, funded by NSF under grant No. DMR-0084402.

9:00am **PS2-WeM4 The Characteristics of a Neutral Beam Angle using a Low Angle Reflected Neutral Beam Etching System**, ***D.H. Lee***, *S.W. Hwang, J.S. Lee, S.H. Oh, Y.H. Lee, Y.-J. Kim, S.W. Choi, W.-S. Han*, Samsung Electronics Co. Ltd., S. Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particles such as positive ions and photons generated in the plasma which causes radiation damage causing physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is a low energy neutral beam etching. The neutral beams recently investigated for the anisotropic etching are generated by a low angle charge exchange collision of an ion beam in the range from 50 to 500eV (hyperthermal ions) with a flat surface. The characteristics of the neutral beam formed after the charge exchange collision such as the neutralization efficiency, neutral beam energy and its distribution, scattering angle of the neutral beam, etc. are the important in the nanoscale device etching characteristics. When an energetic ion collides with the surface, various reactions of the incident ions with the surface are occurred. The collision of ions having a high energy or a high incident angle with the surface increases the possibility of sputtering or implantation, however, the collision of ions having a low energy or a low incident angle with the surface increases the possibility of reflection. The reaction phenomena between the surface and incident ions have been mostly studied with the incident ion energy range from keV to MeV for ion implantation or surface analysis, however, the reactions phenomena with the energy range less than 1 keV, which is important in the application of neutral beam etching, have not been investigated. Therefore, in this study, the variation of angle distributions of neutral beam after the low angle reflection of the low energy (<600eV) ion beam on the flat surface were investigated using double faraday-cup and the etch characteristics for the angle distribution changes were also investigated.

9:20am **PS2-WeM5 Quantitative Characterization of Ions and Si Surface Interactions - Estimation of Plasma-Induced Defect Generation Probability**, ***K. Eriguchi***, *D. Hamada, M. Kamei, H. Fukumoto, K. Ono*, Kyoto University, Japan

The plasma damage induced by ion bombardment has become one of crucial issues from the viewpoints of the physical thickness in scaled devices. Quantitative analysis of the plasma-induced defects is requisite for understanding the mechanism and realizing high performance devices. In this article, ions and Si surface interactions during plasma processing are quantitatively analyzed by novel techniques, providing the defect (charge trapping site) density and defect generation probabilities. Samples were exposed to two different plasma sources, DC and ECR with various biasing, gas mixtures and process time. N-type Si wafers with the low resistivity of 0.02 Ωcm were mounted on the stage and exposed to plasma sources. Combined with plasma diagnostics, two optical analyses, spectroscopic ellipsometry and photoreflectance (a modulation spectroscopy) were conducted to identify the damaged layer thickness with the 4-layer (air/layer-1/layer-2/Si substrate) model, the mechanical strain developing in the vicinity of the surface determined by the Si transition energy change, and the defect density (charge trapping site) by a novel method based on the surface potential change calculation. Also the surface layers were evaluated by a resistivity measurement. We have observed the characteristic structure change in the damaged layers with the relaxed mechanical strain (approximately 0.1 %) and the charge trap site generation with significant densities of 10^{12} cm^{-2}, along with plasma exposure time. Hence we have finally determined the defect generation probabilities per an impinging ion as 10^{-3} - 10^{-5} s^{-1} in the present ion energy and plasma density ranges. The difference is attributed primarily to that in the measured bias voltage (-300 V for DC and -50 V for ECR) dominating the energy of ions accelerated in the sheath, although the ion energy distribution function has to be taken into account for further discussion. This ion energy effect is confirmed from the difference in damage-layer thickness by ellipsometry as well as from the etching simulation. The calculated defect densities in the damaged layer are considered to affect device performances in terms of the increase in power consumption by plasma-induced junction leakage. The obtained defect generation probability is a key parameter for understanding the mechanism of ions and Si surface reactions as well as plasma process designs.

9:40am **PS2-WeM6 Plasma-Catalytic Removal of Nitrogen Oxides**, ***M.M. Morgan***, *E.R. Fisher*, Colorado State University

Nitrogen oxides (NO$_x$), pollutants produced primarily from engine exhaust, contribute significantly to global air pollution. To reduce NO$_x$ emissions, catalysts involved in exhaust treatment must be improved. A greater understanding of fundamental chemical gas-phase and gas-surface processes is, therefore, required. One promising solution is plasma-catalytic processes for removal of pollutants, specifically nitric oxide (NO), from exhaust gases. Our imaging of radicals interacting with surfaces (IRIS) technique allows us to simultaneously examine the gas-phase, perform surface analyses, and probe the gas-surface interface. Here, we have used IRIS to address the fundamental issue of NO$_x$ removal by measuring relative gas-phase densities and by examining the steady-state surface reactivity of plasma-generated species on catalytic surfaces. Data from relative gas phase density studies suggest that increased water content and applied rf powers are required to diminish a majority of NO emissions. Preliminary IRIS data suggest that NO scatters off of surfaces with a high probability. Additional data on the internal temperature of NO in these systems as a function of plasma parameters will also be discussed.

10:40am **PS2-WeM9 New Insight into Fundamental Ion-Surface Interactions**, ***M.J. Gordon***, *X. Qin, K.P. Giapis*, California Institute of Technology **INVITED**

Collisions of ions with surfaces at low energy (<1 keV) are important in reactive ion etching of semiconductors, dielectrics, and metals. For example, ion bombardment can have a strong effect on etch rates, profile anisotropy, and selectivity through physical sputtering, momentum-assisted product removal, and modification of reaction rates. Fundamental understanding of these issues requires detailed information about the scattering processes which occur under different bombardment conditions. To this end, we have conducted scattering experiments involving mass-filtered ions (F$^+$, CF$_x^+$, NF$_x^+$) with tunable energy (50-1000 eV) and high flux (monolayers/s) on several surfaces (Si, Al, Ag) to look critically at collision kinematics, charge exchange processes, and surface reaction products. Topics to be discussed include: (1) electronic excitations in hard collision events (inelastic losses and F^{++} formation); (2) pre-collision fragmentation of CF$_x^+$ ions which result in fast exit products such as C$^+$, F$^-$, and CF$^-$; (3) high yields of fast F$^-$; and (4) bimodal energy distributions of F$^+$ and F$^-$ species leaving Si and Ag surfaces. For instance, energy losses measured for single-scatter events of F$^+$ off Si and Al show that F^{++} can be formed through a double electron promotion mechanism which “turns-on” above a critical collision energy. Velocity analysis of daughter fragments from CF$_3^+$ impact on Si and Ag point to several situations where fast exit species (C$^+$+F$^-$ and F$^+$+CF$^+$ with energies > binary collision predictions) are formed as a result of the projectile ion breaking apart before the hard collision step. Finally, energy analysis of F$^+$ and F$^-$ leaving Si and Ag surfaces shows two distinct scattering channels: one associated with a binary-like, single-scatter elastic event and another narrow, low-energy channel that cannot be explained as simple sputtering. These results illustrate that in many instances, product species can show significant inelastic losses as well as faster-than-SIMS behavior which may have a dramatic impact on profile evolution in plasma etching. In addition, energy analysis of both the positive and negative ion products associated with fluorinated ion scattering provides indispensable clues about the physics of reactive ion etching.

11:20am **PS2-WeM11 Investigating Fundamental Etch Limits: Molecular Dynamics Simulations of Sub-10 nm Feature Fabrication**, ***J.J. Végh***, *D.B. Graves*, University of California, Berkeley

As semiconductor devices are continually scaled down in size, individual device features are approaching the molecular scale. Fundamental knowledge of the mechanisms of the etch process at very small scales will be necessary to effectively design future etch-enabled pattern transfer schemes. Additionally, it is currently unclear how small features can be made using conventional processing methods. Molecular dynamics (MD) simulations have been carried out to examine the fundamental characteristics of etching very small features on silicon and diamond carbon surfaces. These features are created in simulation through bombardment of surfaces by idealized ion and radical beams (i.e. with perfectly controlled confinement, directionality, and energy). For very small beam diameters (less than 2 nm) a novel mode of hole formation is seen in MD in which the substrate atoms are displaced laterally by the ion beam, but not sputtered. This results in uniform holes with high aspect ratios and the formation of a densified, amorphized region laterally surrounding the hole. Lateral densification occurs from atoms that have been displaced from the hole void region during bombardment. As the beam diameter is increased to ~2 nm and beyond, sputtering is seen with yields comparable to those at steady state on bulk flat surfaces. The effects of redeposition on the side walls of the hole in relation to hole uniformity, achievable aspect ratios, and other feature characteristics are discussed. The effects of ion mass, quality of beam confinement, and the dynamics of ion-surface collisions are also addressed. The addition of chemistry to the inert ions (fluorine and fluorocarbon radicals and ions) is also discussed, and its effects on the hole formation processes are illustrated.

11:40am **PS2-WeM12 Fragmentation Dynamics of Energetic Fluorinated Ions on Inert and Reactive Surfaces**, ***X. Qin***, *M.J. Gordon, K.P. Giapis*, California Institute of Technology

Fluorinated ions with energies between 50-1000eV are important in plasma etching and deposition of materials used in the semiconductor industry. However, the scattering dynamics of molecular ions with surfaces are still not well understood in terms of fragmentation and energy transfer. We report results on the collision of mass-selected ions, such as SF$^+$ and SiF$^+$, with Si and Ag surfaces under UHV at impact energies relevant to plasma processing conditions (< 1 keV). Positive and negative products leaving the surface were analyzed in both mass and energy under high flux bombardment conditions (~monolayer/s) to compare with fragmentation of CF$_x^+$. Results show that daughter ions leaving a relatively inert surface (Ag) are much more energetic (not SIMS-like) than those from a reactive surface like Si. Characteristic overlaps in the velocity spectrum of species leaving the target surface suggest that a pre-dissociated projectile scatters nearly elastically off a target atom and breaks apart after the hard collision step. For instance, several daughter ions (S^+, F^+, F^-, SF^+) leave the surface at velocities much larger than expected for an elastic deflection of the molecular ion projectile. Product distributions (chemical identity and energy content) with respect to impact energy for a similar series of projectile ions (i.e., SF_3^+, SiF_3^+, CF_3^+) will be compared to understand the dynamics of how molecular ions fragment upon impact. Detailed reaction channels that lead to the formation of scattered products and etching of the surface will be discussed.

12:00pm **PS2-WeM13 Optical Second-Harmonic Generation to Study Plasma-Surface Interaction in Silicon Materials Processing**, ***J.J.H. Gielis********, *P.M. Gevers, P.J. van den Oever, A.A.E. Stevens, H.C.W. Beijerinck, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Surface and interface properties increasingly govern device performance in microelectronics, therefore, obtaining profound knowledge of these properties in real time during plasma processing is essential. In this respect, the nonlinear optical technique of second-harmonic generation (SHG) is very promising, as it has proven to be an ultra-sensitive probe for surface and interface states such as dangling bonds and strained Si-Si bonds in crystalline Si (c-Si) surface science.[1] In this work the real time and spectroscopic SHG response of amorphous silicon (a-Si) will be addressed in two areas of plasma processing, ion-assisted etching of c-Si and deposition of hydrogenated amorphous silicon (a-Si:H). In addition, spectroscopic ellipsometry was used to deduce linear optical properties. The experiments were carried out under well-defined conditions in high vacuum setups, using ion and radical beams to circumvent the complexity of the plasma.[2] Ion bombardment of c-Si using a low-energy Ar^+-ion gun (70-1000 eV) results in a layer of a-Si with a thickness of several nanometers. For fundamental photon energies from 1.35-1.75 eV, the SHG signal increases with an order of magnitude upon ion bombardment and it is shown that the SHG signal is governed by a two-photon resonance at 3.36 eV, related to modified Si-Si bonds at the a-Si/c-Si interface with an additional a-Si surface contribution. In the 0.8-1.1 eV fundamental photon energy range the increase in SHG signal is even stronger. It is discussed that the time-resolved SHG signal is governed by dangling bond creation and annihilation dynamics at the a-Si surface and a-Si/c-Si interface. Thin films of a-Si:H deposited on c-Si by a SiH_3 dominated beam have been investigated with SHG in the same photon energy ranges. For many applications, such as heterojunction solar cells, the abruptness of the a-Si:H/c-Si interface is crucial. Also in this system the SHG signal displays a strong resonance at ~3.3 eV from the a-Si:H/c-Si interface. It will be demonstrated that real time SHG provides a method to distinguish between direct heterointerface formation and nanometer-level epitaxial growth at a very early stage of film growth.

[1] U. Höfer, Appl. Phys. A 63, 533 (1996).

[2] J. W. Coburn and H. F. Winters, J. Appl. Phys. 50, 3189 (1979).

Advanced Surface Engineering

Room: 617 - Session SE-WeM

Photocatalytic Coatings

Moderator: A. Erdemir, Argonne National Laboratory

8:00am **SE-WeM1 High Rate Deposition of Photocatalytic TiO_2 Films by dc Magnetron Sputtering using a TiO_{2-x} Target**, ***Y. Sato***, *A. Uebayashi, N. Ito,* Aoyama Gakuin University, Japan, *T. Kamiyama,* Asahi Glass Ceramics Co.,Ltd., Japan, *Y. Shigesato*, Aoyama Gakuin University, Japan

Sputter deposition should be the most promising technique for the uniform coatings in large area with very high durability and strong adhesion. However, the deposition rate of TiO_2 films by conventional reactive sputtering using a Ti metal target is very low, because the target surface should be fully oxidized (in "oxide mode") in order to deposit stoichiometric TiO_2 films. Recently, a slightly reduced TiO_{2-x} target (2-x = 1.986, Resistivity: 0.27 Ωcm) has been developed. Using this TiO_{2-x} target TiO_2 film deposition by dc sputtering with rater high rate and high durability should be possible. TiO_2 films were deposited on alkali-free glass substrate at RT-400°C by dc magnetron sputtering using the TiO_{2-x} target under 3.0 Pa. O_2 flow ratio during deposition was controlled from 0 to 100%. The variation in the deposition as a function of O_2 flow ratio did not show hysteresis curve at "transition region" as can be seen in the case of using Ti metal target, indicating that the TiO_{2-x} target surface was gradually oxidized with increasing O_2 flow ratio. The deposition rate using TiO_{2-x} target under 100% Ar gas was about 5 times higher than that using Ti metal target in "oxide mode". XRD patterns of the films deposited at O_2 flow at 0-5% showed entirely amorphous structure. After postannealing in air at higher than 200°C for 1 hour, these films changed to polycrystalline anatase TiO_2 and showed excellent photocatalytic activities such as photo-decomposition of acetaldehyde (CH_3CHO) or photo-induced hydrophilicity. Furthermore, we carried out in-situ analyses on the sputtering processes using the different sputtering target. A quadrupole mass spectrometer (QMS, AQ-360, ANELVA) combined with a specially designed energy analyzer revealed that high-energy O^- ion flux was detected clearly even in the sputtering with 100% Ar gas in the case of using the TiO_{2-x} target. Whereas in the case of using Ti metal target the O^- ion flux was detected only in the "oxide mode". The sputtered fragments mass analyses showed that Ti^+ and TiO^+ existed as sputtered particles in case of using the TiO_{2-x} target under O_2 flow ratio from 0 to 100 %, which was the same result as in the case of using the Ti metal target in the "oxide mode".

8:20am **SE-WeM2 Flat-Flame Chemical Vapor Deposition Synthesis of Nanostructured Titania for Visible Light Photocatalyst**, ***Y.J. Chen***, *J.M. Wu, M.S. Wong*, National Dong Hwa University, Taiwan ROC

Anatase is known as the favorable phase of titania as photocatalyst over rutile. However, several reports suggest that a mixed phase of anatase and rutile possesses even better photocatalytic efficiency. In this paper, we report that a mixed phase of anatase and rutile synthesized by low-pressure flat-flame metalorganic chemical vapor deposition does show such phenomenon that the mixed phase with proper proportion has higher photocatalytic efficiency over single phase anatase. Using acetylene and oxygen as fuel and oxidizer for the flame, the titanium isopropoxide was decomposed and oxidized, and the nanoparticles of titania were formed. The phase of titania powder can be manipulated from almost pure anatase through mixed phases and to pure rutile phase by varying the inert precursor-carrying gas flow rate. The higher the carrier gas flow, the higher the rutile content. From the methylene blue decomposition study we found that the powder with almost pure anatase phase possesses best photocatalytic efficiency under illumination of UV light. However, mixed phase shows best efficiency under visible light illumination. Furthermore, for powder annealed in nitrogen atmosphere at 150 Celsius for 3 hours, the sample of mixed phase further enhanced its methylene blue photodecomposition efficiency. The reaction rate constant is even higher than that of ST-01 titania powder, which is commercially available for photocatalytic applications. While proper annealing process increases the photocatalytic activity of the powder, prolonged or elevated temperature annealing leads to degradation of its power, even the mixed-phase configuration is still retained. It suggest that carbon species play important role in enhancement of mixed-phase photocatalytic activity, since the carbon species will be oxidized during annealing, leaving uncontaminated titania powder, which lose its enhanced catalytic power. Evidence will be provided to show that the carbon species does evolve with annealing, and the presence of carbon species is in coincident with the presence of visible light absorption.

8:40am **SE-WeM3 Preparation and Characterization of TiO2/Ferrite Nanocomposites**, ***K.S. Lin***, *W.R. Chen, C.F. Wu*, Yuan Ze University, Taiwan, R.O.C.

A core-shell structured composite, nanophase titania coated Ni-, or Zn-ferrites nanoparticles, not only reserve the characteristics and advantages of TiO2 but also have the strong ferromagnetism of the ferrites. Therefore, the main objective of this study was to synthesize TiO2/nickel or zinc ferrite nanocomposites with spinel structure. In addition, it focused on the magnetic characteristics of the TiO2 surface-modified Zn or Ni-ferrite nanoparticles, which was expected to prepare a magnetically separable TiO2 photocatalyst. Experimentally, nickel or zinc ferrite core nanoparticles were synthesized under hydrothermal conditions by precipitating from metal nitrates with aqueous ammonia. TiO2 coated on the surface of the nickel or zinc ferrites were then prepared by hydrolysis of titanium chloride in the presence of ferrite nanoparticles. The optimal synthetic conditions included pH values of 8~9 and sintering at 673-773 K. The obtained ferrites or TiO2/Ni-, Zn-ferrites samples were characterized by XRD, FE-SEM, and TEM techniques. The results indicated that the size of nanoshell of TiO2 with anatase structure was 20-50 nm. X-ray absorption near edge structure (XANES) or extended X-ray absorption fine structure (EXAFS) was performed to identify the fine structures and oxidation state of Ni- or Zn-ferrites and anatase-typed TiO2 coated ferrites nanoparticles. By using XANES spectra, Ni- or Zn-ferrites may exhibit an absorbance feature for the 1s to 3d transition can reveal the occupation of tetrahedral sites within the lattice, it showed that Ni ferrite had the same reverse spinel structure

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* PSTD Coburn-Winters Student Award Finalist

with Fe3O4 and the valence of hydrogenated ferrites were between 2 and 3. When the sintered temperature arrive 723 K, the nanoshell of TiO2 would transform from amorphous to anatase, and the nanoshell of TiO2 photocatalysts were all Ti (IV). The EXAFS data revealed that the nanoshell TiO2 photocatalyst had first, second shell of Ti-O, and third shell of Ti-Ti with bond distances of 1.96 ± 0.01, 2.01 ± 0.01, and 3.05 ± 0.01 Å, respectively.

9:00am SE-WeM4 The Substrate Effect on the TiO2 Photocatalytic Thin Films

*J.-Y. Ciou, S.-J. Lin, **M.-K. Wei**, M.S. Wong*, National Dong Hwa University, Taiwan

Titanium dioxide thin films were deposited on two different substrates of p-typed Si (100) and LaAlO3 (001) single-crystal in a pulsed laser deposition system via KrF excimer laser ablation of a pure titania target of 99.95% purity. The substrate temperature and oxygen partial pressure were varied at 400-600?C and 0-9.3 Pa, respectively. The mismatch of lattice constant between anatase TiO2 and LaAlO3 (001) is less than 0.2%, but that between anatase TiO2 and Si (100) is much larger. TiO2 films deposited on LaAlO3 have much better crystallinity than those deposited on Si. The films on LaAlO3 also revealed strong preferred orientation, but the films on Si did not. At all substrate temperatures the films on LaAlO3 compose of only a single anatase phase, while the film on Si composes of mixed phases of anatase and rutile at 600?C, but the crystallinity of the films on both substrates increases with rising substrate temperature. For the surface morphology, the films on LaAlO3 show mosaic structures of epitaxial growth, but the films on Si are polycrystalline in nature with smaller random grains. The photocatalytic performance is determined by the relative amounts of precipitated silver aggregates on the deposited films from AgNO3 aqueous solution under illumination of ultraviolet or visible light. The most precipitated silver aggregates were found at the steps or grain edges on the film surfaces. At lower substrate temperatures, the film deposited on Si has better catalytic performance than those deposited on LaAlO3. It may be due to much more grain edges of the films on Si. At higher substrate temperatures, however, the film deposited on LaAlO3 has better performance than the film on Si, which may be due to pure anatase phase with better crystallinity in the film on LaAlO3.

9:20am SE-WeM5 Structuring Highly Active, Nano-scale Photocatalytic Films using Reactive Sputtering

***K.A. Gray**, L. Chen, M.E. Graham, G. Li*, Northwestern University **INVITED**

Since Fujishima and Honda developed the photoelectrochemical cell for H_2O splitting in 1972, heterogeneous photocatalysis has attracted much attention. TiO_2 is among the most extensively studied semiconductor photocatalysts. It is chemically and biologically inert, photocatalytically stable, commercially available, and inexpensive. In the past three 30 years, most of the effort in the photocatalytic field has been focused on energy and environmental applications, which require materials with the following properties: (1) hindered charge recombination and improved photocatalytic efficiency; (2) targeted reactivity and selectivity that match band energies to the desired reaction, and (3) extended photoresponse into the visible light region. Masakazu Anpo first introduced the notion of "second-generation" TiO_2 photocatalysts, which can absorb visible light and also operate effectively as photocatalysts. We hypothesize that the solid-solid interface in TiO_2-based nanocomposites is key to overcoming these three challenges and are a promising candidates for 2nd-generation photocatalysts. Recent findings in our laboratory and others throughout the world reveal a number of surprising insights as to why TiO_2 nanocomposites tend to display higher photoactivity than pure-phases and point to the critical role of the solid-solid interface as the location of catalytic "hot spots". Yet, efforts to probe the role of the solid-solid interface in photocatalytic activity are stymied by an inability to synthesize under sufficiently controlled conditions and in sufficient quantities the "interface", which would then allow structural characterization and functional interrogation. Advances in photocatalyst synthesis using sputtering technologies promise to revolutionize our ability to engineer the solid-solid interface at the molecular level and thus, to fabricate photoactive nanostructured composite materials having high densities of "defects" designed for energy harvesting and storage. We prepare highly active TiO_2 nanocomposites using chemical and physical methods in our laboratory. By varying key fabrication conditions (target power, substrate bias, oxygen partial pressure, and deposition angle) in reactive DC magnetron sputtering, we synthesize TiO_2 thin films with different microstructures. This paper will report the synthesis and characterization of photocatalytic films and their use to generate solar fuels and oxidize gas phase contaminants.

10:40am SE-WeM9 Photocatalytic Coating: Present Situation and Future Direction

A. Fujishima, Kanagawa Academy of Science and Technology, Japan **INVITED**

The recent decade has witnessed the birth and development of photocatalytic coatings.[1] In the early 1990s, we proposed the concept of photocatalytic thin film coatings for deodorizing, self-cleaning, and antibacterial uses.[2] In 1997, we reported the photo-induced superhydrophilic effect of TiO_2 surface,[3] and proposed the concept of antifogging surface, and the concept of self-cleaning based on the photocatalytic and superhydrophilic actions of TiO_2.[4] Nowadays, these concepts have all born out real products. In Japan, self-cleaning building materials have covered tiles, glass, coatings, polymer films, aluminum sidewalls, and so on. Air-cleaners, equipped with photocatalytic filters, have got recognition of consumers. Antibacterial tiles have been used in hospitals, hotels, and restaurants. Recent news is the carriage of high-speed railway system of Japan will be coated with photocatalytic self-cleaning coating. Besides these matured techniques, we are now studying new applications of photocatalytic coatings; these include anticorrosion coatings,[5] multichromic coatings,[6] low reflection self-cleaning coatings,[7] and heat-transfer applications,[2] etc. We are also thinking of the development visible-light responsive photocatalytic coatings and the standardization of photocatalytic coatings.[1] Our photocatalyst museum, which started three years ago, provides exhibition for companies' products as well as information service for consumers and researchers.

[1] A. Fujishima, X. Zhang, C. R. Chimie 9 (2006) 750.

[2] K. Hashimoto, H. Irie, A. Fujishima, Japn. J. Appl. Phys. 44(2005) 8269.

[3] R. Wang, K. Hashimoto, A. Fujishima, et al. Nature 388 (1997) 431.

[4] R. Wang, K. Hashimoto, A. Fujishima, et al. Adv. Mater. 10 (1998) 135.

[5] T. Tatsuma, S. Saitoh, Y. Ohko, A. Fujishima, Chem. Mater. 13 (2001) 2838.

[6] Y. Ohko, T. Tatsuma, A. Fujishima et al., Nature Mater. 2 (2003) 29.

[7] X.-T. Zhang, A. Fujishima et al., J. Phys. Chem. B 110 (2006) 25142.

11:20am SE-WeM11 Composition-Spread Carbon-Incorporated Titania Films for Visible Light Photocatalysis

*C.W. Weng, P.W. Chou, K.K. Rao, **M.S. Wong***, National Dong Hwa University, Taiwan

We adopted a combinatorial approach to develop a series of carbon-incorporated titania (TiOxCy) films titania films with composition spread up to 40 at.% of carbon. The films were deposited on silicon and quartz substrates by co-sputtering a metallic titanium target and a graphite target simultaneously onto a stationary long-strip of substrate in a gas mixture of argon and oxygen. The location of substrates in relation to targets and the power of targets are found to be very crucial for the desired result. As the carbon content increases, the film structure and crystallinity transform from anatase to amorphous-liked phase and its morphologies and microstructures change from rough surface of columnar grains to smooth surface of nanocomposite. The carbon is present both in the form of substituted Ti-C bonds in anatase grains as well as free graphitic along grain boundaries or in matrix. With increasing carbon content, the film optical absorption in visible region decreases first and then increase, while the film optical bandgap energy varies from 2.6 up to 3.2, and then descends to 2.5 eV. On photocatalysis under visible light, the film with about ~10% carbon exhibits the largest photoreduction of silver-ions to form Ag particles and nano-wires, while the film of the best anatase crystallinity with about 3 at% of carbon has the most degradation of methylene blue. The content and the nature of carbon as well as the titania crystallinity dominate the visible-light induced photocatalytic activity of the TiOxCy films.

11:40am SE-WeM12 High Rate Deposition of TiO_2 Films by using Two Sputtering Sources

***Y. Hoshi**, O. Kamiya, T. Sakai*, Tokyo Polytechnic University, Japan

Deposition of TiO_2 films by reactive sputtering of titanium metal target has been reported by many researchers. However, it is very difficult to realize the high rate deposition of TiO_2 films by conventional reactive sputtering, since the surface of the target is covered with titanium oxide layer, which leads to a significant reduction of the sputtering yield of titanium atoms. If we can suppress the formation of titanium oxide layer on the target surface and promote the oxidization of titanium atoms on the film surface during sputtering, high rate deposition of titanium oxide films can be realized by using the reactive sputtering method. In this point of view, we designed a new sputter-deposition system with two sputtering sources. One source, 33mm diameter magnetron sputtering source, is used as the source of titanium atom, and works at the metal mode sputtering condition and supplies the titanium atoms to the substrate. The other source of 100 mm in diameter works as an oxygen radical source and supplies oxygen radicals to the substrate surface to promote the oxidization of the titanium atoms during film deposition. Each sputtering sources are separated from deposition chamber and Ar gas and oxygen gas was introduced through the 33mm sputtering source and 100mm source, respectively. When Ar gas flow rate is fixed at 50 sccm and oxygen gas flow rate was below 8mTorr, the 33mm titanium sputtering source works in metal mode at a discharge current of 1 A. Whereas, the 100 mm oxygen radical source works in an oxide mode at an oxygen gas flow rate below 8 sccm and the sputtering current below 1.5 A. In this deposition method, most of the titanium atoms deposited on the substrate are supplied from the 33 mm sputtering source, and oxygen radicals supplied from 100mm source promote the oxidization of titanium atoms on the substrate. As a result, deposition rate more than 30 nm/min can be easily realized for the deposition of transparent TiO_2 film with transmittance above 90%. These results indicate that the reactive sputtering method with two sputtering sources is effective to realize a high rate deposition of TiO_2 films.

12:00pm **SE-WeM13 Enhancement of Hydrophilicity and Photo Catalytic Activities of Nanocrystalline TiO_2 Thin Film Doped with Ruthenium**, ***R.R. Pandey***, *K.K. Saini, M. Dhayal, Chanderkant, S.C. Jain,* National Physical Laboratory, India, *M. Singh*, University of Delhi, India

In this study Ru^{+3} ion doped nanocrystalline TiO_2 thin films has been fabricated using dip-coating technique on glass substrates. Surface structure and chemistry of the films was characterized using X-ray diffraction, transmission / scanning electron microscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy and FTIR. The Ru^{+3} ion doping in the film have significant influence on the morphology and surface chemistry. These nanocrystalline films have shown improved activity on the oxidation of organic pollutants possibly due to enhanced surface area with more active site in presence of Ru^{+3}.

Surface Science

Room: 608 - Session SS1-WeM

Oxide Surface Reactivity

Moderator: V.M. Bermudez, Naval Research Laboratory

8:00am **SS1-WeM1 Influence of Ferroelectric Polarization on Adsorption on $BaTiO_3$**, *D.B. Li,* ***M. He****, J. Garra, D.A. Bonnell, J.M. Vohs*, University of Pennsylvania

Many perovskite oxides such as $BaTiO_3$ undergo a phase transition from a ferroelectric tetragonal phase to a paraelectric cubic phase at readily accessible temperatures. In the ferroelectric state the material is polar and has a bulk electric dipole whose orientation can be controlled via application of an external electric field. While it has been suggested that the orientation of the ferroelectric dipole on the surface may affect adsorption and reaction of species from the gas phase, examples demonstrating the ferroelectric control of surface reactivity have to date been elusive. In this talk we will present what we believe are the first definitive examples of the influence of ferroelectric polarization on the surface reactivity of $BaTiO_3$. In the first example, demonstrates the effect of ferroelectric polarization on the adsorption of CO_2 on oxygen vacancies on the surface of a $BaTiO_3(001)$ single crystal. Sub-micron sized out-of-plane domains with the polarization oriented perpendicularly inward (c$^-$) or outward (c$^+$) from the surface were produced on the BaTiO3(001) sample using an AFM tip. Frequency modulation, scanning surface potential microscopy (FM-SSPM) was then employed to measure the potential change of the ferroelectric domains before and after exposure of the poled surface to CO_2. It was observed that CO_2 caused a larger decrease in the surface potential for c$^-$ domains relative to the c$^+$ domains, indicating a difference in the amount of CO_2 adsorbing on each domain. In the second example, the amount of methanol that adsorbed on an oriented, $BaTiO_3$ thin film supported on $TiO_2(110)$ under UHV conditions was found to be dependent on the orientation of the ferroelectric dipole. In this case the sample was poled by heating above Tc and then placing it in contact with an electrode to which a small + or - voltage was applied. For a constant exposure, the amount of CH_3OH that adsorbed at 300 K was found to increase in the following order c$^-$ > unpoled > c$^+$. This result has been attributed to a polarization dependent interaction of weakly bound CH_3OH molecules prior to dissociative adsorption at defect sites.

8:20am **SS1-WeM2 Effect of Poling Direction on the Reactivity of Ferroelectric Oxide Surfaces**, *Y. Yun, M. Li,* Yale University, *L. Kampschulte,* Ludwig Maximilians Universität, Germany, *D. Liao, B. Lukanov,* ***E.I. Altman***, Yale University

Ferroelectric polarization creates high energy surfaces that are expected to reduce their surface energy by reconstructing or strongly adsorbing polar molecules. Because opposite charges must be screened on opposite surfaces, different reactivities are expected on positively and negatively poled surfaces. We have studied the surface atomic composition, structure and reactivity of $LiNbO_3(0001)$ surfaces. The surfaces appeared nearly indistinguishable in spectroscopic and diffraction measurements: both surfaces were (1x1) and appeared almost fully oxygen terminated in low energy ion scattering spectra. Despite the structural similarities, differences in reactivity between positively and negatively poled surfaces were observed using TPD. Polar molecules including 2-propanol and acetic acid adsorbed much more strongly on the positive surfaces as evidenced by desorption peak temperatures over 100 K higher. Further, the TPD curves were found to depend unusually strongly on the heating rate. This efect could be attributed to the change in polarization with temperature - the pyroelectric effect- creating a temperature-dependent heat of adsorption. Including this effect, an 11 kJ/mole higher 2-propanol heat of adsorption was estimated for the positive surface. These results will be compared with adsorption of non-polar molecules where the polarization changing with temperature is not expected to affect the strength of the adsorbate-surface interaction. The results for $LiNbO_3$ will also be compared with $PbZr_xTi_{1-x}O_3$ thin films to determine the generality of the observed phenomena.

8:40am **SS1-WeM3 The Interaction of NO_2 with MgO(100) Studied with Photoemission Spectroscopy**, ***D.E. Starr***, *Ch.D. Weiss,* Lawrence Berkeley National Laboratory, *S. Yamamoto, A. Nilsson,* Stanford Synchrotron Radiation Laboratory, *M. Salmeron, H. Bluhm*, Lawrence Berkeley National Laboratory

NOx compounds are very harmful environmental contaminants commonly formed in combustion processes. Their adsorption onto the surfaces of alkaline-earth metal-oxides has recently received a great deal of attention due to the use of alkaline-earth metal-oxides as NOx storage compounds for controlling emissions during combustion under fuel-lean conditions. In this work we have studied the adsorption of NO2 on MgO(100) films grown on Ag(100) using photoemission spectroscopy. Many of the previous experimental studies of this system were performed at low temperatures with subsequent thermal heating under Ultra-High Vacuum conditions. In this study we have used the Ambient Pressure Photoemission Spectroscopy experiment at Beamline 11.0.2 of the Advanced Light Source to study the adsorption and reaction of NO2 onto MgO(100) at 300 K and 10-6 torr NO2 pressures for exposures ranging from a few Langmuir up to twenty thousand Langmuir. At these conditions, we find that the NO2 initially adsorbs as NO2 with low coverage (~0.05 ML). Upon increasing exposure, we observe a reduction in the coverage of NO2 and the presence of adsorbed NO3. Further, at high exposure we find increasing coverage of NO3 (~0.30 ML) without the presence of NO2 on the surface. This indicates that the production of NO3 on the surface likely occurs via initial NO2 dissociation which produces adsorbed O which then oxidizes NO2 to form NO3.

9:00am **SS1-WeM4 The Interaction of NO_2 with BaO: From Cooperative Adsorption to $Ba(NO_3)_2$ Formation**, ***J. Szanyi***, *C.-W. Yi, J.H. Kwak*, Pacific Northwest National Laboratory

The adsorption and reaction of NO2 on a thick (> 30 ML), pure BaO film deposited onto an Al2O3/NiAl(110) substrate at 90 K and the higher temperatures were investigated with surface science techniques such as temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and x-ray photoelectron spectroscopy (XPS) techniques. For the first time, it was clearly demonstrated that BaO readily reacts with NO2 to initially form nitrite-nitrate ion pairs by the cooperative adsorption mechanism predicted by theoretical calculation. These nitrite/nitrate pairs readily form even at 90 K. In the decomposition process of these pairs first the nitrite species release an NO molecule, and nitrate species decompose in two steps: at lower temperature as NO2 only, then, at higher temperature, as NO + O2. The results of NO2 adsorption/reaction on this model system are identical to those we have found on a high surface area 20 wt.% BaO/Î^3-Al2O3 sample with the exception of surface nitrates that were only observed on the high surface area material.

9:20am **SS1-WeM5 Reactivity of Low-dimensional Oxide Nanostructures**[*], ***F.P. Netzer***, Karl-Franzens University Graz, Austria **INVITED**

Oxide materials in nanostructured layers exhibit physical and chemical properties that are significantly different from their respective properties in macroscopic bulk phases. This novel behaviour forms the basis for many potential applications of oxide nanostructures in diverse areas of the emerging nanotechnologies. Here we discuss the physico-chemical properties of ultrathin oxide overlayers (nanolayers = thickness ≤ 10 ML), grown on metal single crystal surfaces, in terms of their novel structural concepts, their modified electronic behaviour and their sensitivity to changes in the chemical environment. A multitude of experimental techniques (STM, SPA-LEED, XPS, NEXAFS, UPS, HREELS) in conjunction with ab initio DFT model calculations has been applied to characterise the oxide nanolayers deposited on Pd and Rh substrate surfaces. The oxide materials considered comprise nickel, manganese and cobalt oxide phases. Specifically, we will discuss chemical and structural aspects of phase transformations of Mn-oxide overlayers in the 1-10 ML range on Pd(100). Emphasis will be put on the structural transition from the MnO(100) to the MnO(111) orientation as a function of the chemical potential of oxygen and on the oxidation of MnO to Mn_3O_4 surface phases. The chemical interaction of NiO(100) surfaces, epitaxially grown on

Pd(100), with metallic cobalt and Co-oxide overlayers is addressed from the viewpoint of generating sharp antiferromagnetic-(anti)ferromagnetic interfaces. It is shown that CoO(100) can be grown epitaxially on NiO(100) and that a 1-2 ML CoO buffer layer can inhibit the oxidation reaction of Co metal overlayers, thus forming a sharp AFM-FM interface. The oxidation of metallic quasi-one-dimensional (1-D) Ni nanowires, formed on the stepped Rh(15 15 13) surface, to 1-D Ni-oxide phases is illustrated. The latter are compared to the 2-D Ni-oxide phases that develop by reactive physical vapour deposition on the same stepped Rh surface, in order to assess the dimensionality aspects in the formation of oxide nanostructures.

*Supported by the Austrian Science Funds (FWF) and the EU STREP programme GSOMEN.

10:40am **SS1-WeM9 Adsorption Energetics of Ag on CeO_2(111)**, ***J.H. Baricuatro***, *J. Farmer, C.T. Campbell*, University of Washington

The energetics of Ag deposition on well-defined films of CeO_2(111) were investigated using adsorption microcalorimetry. Thin films of CeO_2(111) were grown on Pt(111) at 700 °C by thermal evaporation of Ce under a reactive atmosphere of O_2. Ag was evaporated from an effusive vapor source and the resultant surface structures were probed using a combination of low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and low-energy He^+ ion scattering spectroscopy (LEIS). The adsorption of Ag exhibited a sticking coefficient that is close to unity (0.98), independent of coverage. The enthalpy of adsorption of Ag was initially low (ca. 200 kJ/mol) but increased with Ag coverage up to the sublimation enthalpy of bulk Ag. The effect of surface oxygen vacancies on the adsorption energy of Ag was also investigated.

11:00am **SS1-WeM10 Redox Properties of HCOOH over CeO_2 Surfaces: Pathways to Surface Oxidation and Reduction**, ***S.D. Senanayake***, *D.R. Mullins*, Oak Ridge National Laboratory

This study undertakes a close scrutiny of the reaction of HCOOH, the simplest C-1 carboxylic acid, with the surfaces of CeO_2, a well defined (111) oriented lanthanide oxide system. HCOOH is an important precursor to the formation of CO_2 and H_2 in the water-gas-shift (WGS) reaction, in which ceria (in combination with nobel metal particles) is also used as a stable support rich in oxygen storage capacity. The HCOOH is observed to adsorb by way of a formate intermediate species ($HCOO^-$) through the dissociation of the acidic H over both CeO_2 (Ce^{+4}) and CeO_x (Ce^{+4}/Ce^{+3}) surfaces. This species will be compared to other C1 adsorbates observed such as methanol[1] and formaldehyde[2] reacting over ceria, which yield methoxy (CH_3O) and dioxymethelene (CH_2O_2) species, respectively. The dissociated H species recombines with surface O and desorbs as H_2O <300K. At 300K polarization dependent C K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) data suggest that the formate is adsorbed in a bi-dentate structure with the O-C-O plane oriented normal to the surface. In addition to water, Temperature Programmed Desorption (TPD) spectra indicate the evolution of CO_2 (m/z 44) and H_2 (m/z 2) around 350-400K followed by only CO desorption in two regimes at 450 and 525K. The net result is a slight reduction of the ceria substrate. In a reversal of roles, formic acid oxidizes the reduced CeO_x surface. No H_2O or CO_2 desorbs at lower temperatures but is replaced with desorption of only CO and H_2 between 450-600K. Soft X-ray Photoelectron Spectroscopy (sXPS) indicates that formate is again the only surface intermediate. With the introduction of Rh nanoparticles to the reduced and oxidized Ceria surfaces the formate decomposition is observed over ceria. Furthermore, sXPS also shows CO adsorption on Rh (C1s ~286eV) that decomposes further to give Rh-C species (284.5eV) which can be compared to CO reaction over Rh / CeO_x surfaces.[3]

[1] J. Phys. Chem. B., 110 (32) 15994 (2006).

[2] Surf. Sci., 600 1540 (2006).

[3] J. Catal., 188 340 (1999).

*Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

11:20am **SS1-WeM11 Hydrogen Diffusion on TiO_2(110) at Elevated Temperatures**, ***S.-C. Li***, *J.M. White,* University of Texas at Austin, *Z. Zhang, B.D. Kay, Z. Dohnálek*, Pacific Northwest National Laboratory

The TiO_2 chemistry has been widely investigated in both fundamental science and technical applications, due to its intriguing chemical properties. One of the important applications is the photochemical hydrogen production from H_2O. On a prototypical TiO_2(110) surface, the bridge-bonded oxygen (BBO) vacancies have been shown to be the primary reactive sites for H_2O dissociation yielding geminate pairs of OH groups. In this study we use variable temperature Scanning Tunneling Microscopy (STM) to investigate intrinsic hydrogen diffusion along the BBO rows as a function of temperature. The hopping rates deduced from the consecutively collected STM images at temperatures ranging from 320K to 420K are analyzed. The prefactors and activation barriers are extracted as a function of OH-OH separation using the Arrhenius analysis. A comparison of the hopping rates for hydrogen and deuterium shows a strong isotope effect.

The research described in this presentation was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

11:40am **SS1-WeM12 The Adsorption of Cysteine and Co-Adsorption of Cysteine and Gold on TiO_2(110)**, *E. Ataman, C. Isvoranu, J.N. Andersen,* ***J. Schnadt***, Lund University, Sweden

The bonding of organic molecules to transition metal oxide surfaces such as TiO_2 is a concern central to the construction and optimization of molecule-based devices. Organic–inorganic interfaces are presently receiving increasing attention due to both fundamental and application interests. Interest also derives from the role of TiO_2 as a support for metal catalyst particles such as Au nanoclusters, which act as an excellent catalyst for, e.g., the low temperature CO oxidation reaction. The cluster size of the Au particles has to remain within an optimum range for the catalyst to preserve its activity. However, the Au clusters are prone to coalescence as a function of temperature and gas exposure. In order to retain the catalytic activity it is important to hinder this growth process. The idea developed here is to use L-cysteine as a spacer between the clusters, since it strongly binds to the TiO_2 surface via its carboxylic group. It is well-known that the thiol group of cysteine interacts with gold, which then might establish the missing link between the gold clusters and the spacer molecules. We have investigated the adsorption of L-cysteine as well as the co-adsorption of L-cysteine and gold on rutile TiO_2(110) by means of x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and scanning tunneling microscopy (STM). The spectroscopy results clearly show that the notion of a molecule-TiO_2 substrate bond via the carboxylic group of the molecule is correct. This finding receives further support from the STM measurements. The basic geometry characterized by the oxide-carboxylate bond is retained even for the co-deposition case; however, the S 2p spectra indicate an additional interaction between the gold clusters and molecules. An interesting additional feature of the spectroscopy experiments was the observation of very rapid beam damage, which we attribute to a facile change in the protonation status of the amino and thiol functional groups.

12:00pm **SS1-WeM13 Density Functional Theory Study of Hydrogen Cyanide and Formamide over Rutile TiO_2 (110) and (011) Surfaces**, ***P.R. McGill***, *H. Idriss*, The University of Auckland, New Zealand

Formamide is a compound of considerable interest, owing to its ability to yield nucleobases during photoreaction over TiO_2 in both aqueous[1] and ultrahigh vacuum conditions.[2] The mechanisms for this synthesis have been postulated to involve the generation and subsequent decomposition of HCN polymers on the surface. While a number of experimental studies have investigated formamide and HCN adsorption to the surfaces of TiO_2,[2,3,4] computational work has focused on their interaction with metal surfaces.[5] In this study, a series of periodic DFT calculations are conducted on formamide and HCN adsorption to the (110) and (011) bulk terminated surfaces of rutile TiO_2, employing plane wave basis sets and the PBE exchange correlation functional. Dissociative adsorption appears favoured for formamide on both investigated surfaces; the formamide molecule binding in a bridging manner across two surface Ti sites analogous to that of formic acid on the rutile TiO_2 (110) surface. Molecular adsorption through the carbonyl oxygen's interaction with the surface Ti is also found to be energetically favourable, though to a lesser extent. No stable interaction mode is observed for molecular adsorption through the N atom to the surface Ti species, in agreement with IR studies[3] conducted on formamide over polycrystalline TiO_2. HCN was found to strongly preference toward molecular adsorption in an orientation perpendicular to the surface, with the nitrogen binding to a surface Ti. Dissociative adsorption is found to be less favourable than molecular adsorption, with dissociative adsorption through the C atom yielding a greater stability than through the N atom. Adsorption modes parallel to the surface (which are reported on metal surfaces[5]) do not appear to represent energy minima, and convert back to perpendicular configurations on geometry optimisation.

[1] Saladino, R., Cresti, C., Costanzo, G. DiMauro, E. (2004) Curr.Org.Chem. 8, 1425.

[2] Senanayake, S.D., Idriss, H. (2006) Pro. Nat. Acad. Sci. USA. 103, 1194.

[3] Wu, W.C., Liao, LF, Chuang, C.C., Lin, J.L. (2000) J.Catal. 195, 416.

[4] Raskó, J., Bánsági, T., Solymosi, F. (2002) Phys.Chem.Chem.Phys. 4, 3509.

[5] Oliva, C., van den Berg, C., Niemantsverdriet, J.W.H., Curulla-Ferre, D. (2007) J. Catal. 245, 436.

Surface Science

Room: 611 - Session SS2+EM+TF-WeM

SAMs and Organic Films I

Moderator: H. Fairbrother, Johns Hopkins University

8:00am **SS2+EM+TF-WeM1 Scanning Tunneling Microscopy Growth Study of a Columnar Liquid Crystalline Hexaazatriphenylene Derivative on Au(111)**, ***S.D. Ha***, Princeton University, *Q. Zhang, S. Barlow, S.R. Marder,* Georgia Institute of Technology, *A. Kahn*, Princeton University

The growth of a discotic liquid crystal derivative of tris(thieno)hexaazatriphenylene (THAP) is studied with scanning tunneling microscopy (STM). An electron transport material with relatively high electron affinity (4.59eV), THAP is expected to form columnar stacks in a thick bulk film. It is shown with STM that on Au(111), the first four monolayers of THAP molecules order in such columnar mesophases. The first monolayer forms a square 10.1Å x 10.1Å unit cell with one molecule per cell. However, this is much smaller than expected, and it may be due to buckling caused by the substrate interaction or in-plane molecule-molecule interaction. The second monolayer, at partial coverage, grows commensurate to the first monolayer in a rectangular herringbone with two molecules per 15.7Å x 14.0Å unit cell. The molecules tilt in order to conform to the packing of the first layer and the interlayer interaction controls the molecular orientation. Yet upon full coverage of the second monolayer, the intralayer interaction prevails and the molecules reorganize into a hexagonal close-packed (HCP) structure without obvious tilt. The unit cell is rhomboidal with dimensions 21.0Å x 22.2Å and one molecule per cell. Moreover, the rotational orientation of the molecules forms a herringbone pattern, with alternating rows of the HCP structure switching between two opposite orientations. As for the third and fourth monolayers, STM images indicate that they have HCP geometry with the same dimensions as the second layer. Given the tendency of molecules similar to THAP to stack into columns, it is likely that because the third and fourth layers have the same in-plane structure as the second layer, they are commensurate to the latter. Thus, on Au(111), THAP readily grows in the expected columnar liquid crystal fashion directly from the interface layer, and the columns are hexagonal close-packed with negligible molecular tilt.

8:20am **SS2+EM+TF-WeM2 UHV-STM Studies of DNA Bases on Au(111)**, ***W. Xu***, *R. Otero, M. Schock,* Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark, *R. Kelly, L. Kantorovich,* King's College London, UK, *F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

The self-assembly of Nucleic Acid (NA) base molecules on solid surfaces has recently attracted much attention as on one hand, such studies provide invaluable insight into fundamental interactions between these molecules. On the other hand, NA base molecules and DNA molecules are particularly interesting as promising building blocks for the bottom-up fabrication of functional supramolecular nanostructures on surfaces within the emerging area of nanotechnology. From a biological point of view, the self-assembly processes in DNA and RNA molecules are controlled by i) cross-strand interactions between NA base molecules, which are dominated by hydrogen bonds (H-bonds), ii) stacking interactions between NA base molecules along the strand, and iii) the interactions of NA base molecules with water molecules and metal ions, such as Na+, K+. Among these interactions, the hydrogen bonding between NA base molecules plays a crucial role in determining the conformation and biochemical properties of DNA and RNA molecules. Hence, it is important and interesting to study the fundamental interactions between NA base molecules at the single molecule level to reveal the exact physicochemical nature of the biological systems. Here we will show our recent experimental progress on four individual NA base molecules (guanine, adenine, cytosine, thymine) that are adsorbed on Au(111) surface under Ultrahigh Vacuum (UHV) conditions. We demonstrate by variable-temperature scanning tunnelling microscopy (VT-STM) experiments that guanine and adenine form 2D island with well-ordered structures through hydrogen bonds, and the so-called guanine quartet structure is found to be stabilized by the cooperative hydrogen bonds. Interestingly, cytosine only forms disordered 1D filamentary structure by fast cooling the sample, whose behavior could be described as a 2D organic glass. Thymine in the first stage (low surface coverage) also forms 1D filamentary structure steered by hydrogen bonds. However, when the surface coverage is increased, the filaments could merge into 2D well-ordered islands by van der Waals (vdW) interactions. Moreover, we have also investigated that the thymine 2D island can be broken back into the 1D hydrogen bonded filaments by STM manipulation, which further confirm that we are able to directly probe the hierarchy of bond-strengths involved in the surface self-assembly of multifunctional organic molecules with highly anisotropic interactions.

8:40am **SS2+EM+TF-WeM3 Understanding Molecular Exchange on Surfaces: Controlling and Elucidating the Mechanism of 1-Adamantathiolate Monolayer Displacement**, ***H.M. Saavedra***, *T.J. Mullen, C.M. Barbu*, The Pennsylvania State University, *A.A. Dameron*, University of Colorado, *V.H. Crespi, P.S. Weiss*, The Pennsylvania State University

We have investigated the solution-phase displacement kinetics of 1-adamantanethiolate self-assembled monolayers on Au{111} by n-dodecanethiol molecules using infrared spectroscopy, scanning tunneling microscopy, x-ray photoelectron spectroscopy and electrochemical desorption. The displacement reaction can be described by the fast insertion of n-dodecanethiolate at defects in the original 1-adamantanethiolate monolayer, which nucleates island growth and is followed by eventual slow ordering of the n-dodecanethiolate domains. Langmuir-based kinetics, which describe alkanethiolate adsorption on bare Au{111}, fail to describe this displacement reaction. Instead, a Johnson-Mehl-Avrami-Kolmogorov model of perimeter-dependent island growth yields good agreement with kinetic data obtained over a hundred-fold variation in n-dodecanethiol concentration. Analysis on a model-free basis suggests that displacement is a scale-free process within this concentration regime. The crucial role of the adsorbate lattice, along with the thermodynamic driving forces, rationalizes the rapid and complete displacement of 1-adamantanethiolate monolayers and explains why other monolayers reach kinetic traps that result in slow and incomplete displacement.

9:00am **SS2+EM+TF-WeM4 Thermal Treatment of Glutamic Acid Etched Ni Nanoclusters on Au{111} Leads to the Formation of 1-D Metal Organic Co-Ordination Networks**, *A.G. Trant, T.E. Jones,* ***C.J. Baddeley***, University of St Andrews, UK

The adsorption of glutamic acid onto 2-D Ni clusters on Au{111} has been investigated using reflection absorption infrared spectroscopy (RAIRS) and scanning tunnelling microscopy (STM). Adsorption at 300 K leads to two distinct adsorbate species which we conclude are zwitterionic species adsorbed either at Ni-like sites in the centre of the clusters or at interfacial sites at the edges of clusters. Adsorption of (S)-glutamic acid causes the complete destruction of clusters of initial diameter <3 nm. We conclude that the Ni islands have been corroded resulting in the formation of a Ni salt - presumably nickel (II) glutamate. On annealing to 350 K, chains of 1-D molecular features are observed in STM experiments. We discuss the possible composition and structure of this salt and conclude that the chains most likely consist of nickel (II) pyroglutamate. Metal pyroglutamate salts are known to be produced by heating glutamate salts. The intermolecular bonding and azimuthal alignment of the 1-D chains are discussed. We also report the formation of analogous networks from Ni + (R)-glutamic acid and discuss the influence of stereochemistry on the structure of the networks.

9:20am **SS2+EM+TF-WeM5 Crossover from Site-Sensitive to Site-Insensitive Adsorption of the Fullerene Derivative PCBM on Au(111) due to Hydrogen-Bond Formation**, ***D. Ecija***, *R. Otero,* Univ. Autonoma de Madrid, Spain, *L. Sanchez,* Univ. Complutense de Madrid, Spain, *J.M. Gallego,* Inst. de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *Y. Wang, M. Alcami, F. Martin,* Univ. Autonoma de Madrid, Spain, *N. Martin,* Univ. Complutense de Madrid, Spain, *R. Miranda*, Univ. Autonoma de Madrid, Spain

The 2D arrangement of organic adsorbates at solid surfaces results from a combination of non-covalent intermolecular forces with molecule-substrate interactions. It is generally thought that molecule-substrate interactions determine adsorption geometry and conformation in first place, while intermolecular interactions affect the subsequent self-assembly of the adsorbates. Only when the molecules can form strong directional bonds, like hydrogen bonds or coordination bonds, and the corrugation of the adsorption potential energy is small, the supramolecular structure is dominated by intermolecular interactions. On the other end of the spectrum, vicinal or heterogeneous surfaces show a strong selectivity in the adsorption site of the adsorbates, leading to a final morphology which is almost exclusively substrate-controlled (templated growth). Usually, the role of molecule-substrate interactions on self-assembly is discussed at the single-molecule level, but this is strictly speaking just an approximation, since the formation of intermolecular bonds might modify the adsorption geometry and thus molecule-substrate interactions. For systems showing site-selective adsorption, the modification of the adsorption geometry upon intermolecular bond formation might result in the removal of the site-selectivity. By means of variable-temperature Scanning Tunneling Microscopy (STM) experiments and Density Functional Theory (DFT) calculations, here we investigate the crossover from site-selective to site-insensitive adsorption of PCBM, a C60 derivative, on the herringbone-reconstructed Au(111) surface as a function of the coverage. Whereas at low coverages PCBM self-assembly is dictated almost exclusively by the substrate-related preference for nucleating at the fcc sites of the reconstruction, with a selectivity close to 100%, at higher coverages intermolecular interactions take over the substrate influence, giving rise to PCBM islands that extend through fcc, hcp and dislocations of the herringbone reconstruction. Comparison with theoretical calculations offers the following picture of this crossover: at high-enough coverages hydrogen bonds between double rows are formed that modify the adsorption geometry of PCBM molecules, which in turn removes site-selectivity. The phenomenon of intermolecular interaction-driven modification of the adsorption geometry might thus be crucial to optimize the templating effect of surface nano-scale patterns on adsorbed organic overlayers.

9:40am **SS2+EM+TF-WeM6 Nanostructured Binary Molecular Films: Lessons from ACA:C_{60} Mixtures**, ***J.E. Reutt-Robey,*** University of Maryland, *B. Xu,* Yanshan University, China, *C.G. Tao,* University of Maryland, *D.B. Dougherty,* National Institute of Standards and Technology, *W. Jin*, University of Maryland

Multi-component aromatic molecular films are of increasing interest in photovoltaic technologies and other organic electronic applications. Binary organic films offer the potential to tailor film structure on the nanoscale to optimize device performance through phase selection, domain size, distribution and orientation. A basic understanding of the factors that control structure in binary molecular films is thus important to advance these materials technologies. We report STM-studies of structure evolution in model donor-acceptor systems, such as ACA:C_{60} and Pentacene:C_{60}. Films prepared by sequential physical vapor deposition onto Ag(111) substrates under UHV are monitored directly with an integrated UHV-STM. We demonstrate how ACA:C_{60} film growth conditions can be adjusted to selectively fabricate films that range from phase-separated hexagonal -C_{60} and chain-phase [4 0, 2]-ACA domains to intermixed co-crystalline chiral domains comprised of C_{60}-terminated ACA pinwheels. Films produced with arbitrary composition generally lead to complex multi-phase structures. Predeposited ACA films with single phase structures provide the most effective pathway to single phases of intermixed structures. For example, the intermixed chiral phase is only accessible from the 2-D ACA molecular gas, whereas extended C_{60} chain structures may be accessed only from the dimer-phase [12 2, 6 5]-ACA domains. We apply lessons from the ACA:C_{60} system to Pentacene:C_{60}, mixtures, utilizing the 2-D pentacene gas to access an intermixed honeycomb Pentacene:C_{60} phase.

10:40am **SS2+EM+TF-WeM9 Detection of Gaseous Nitric Oxide Using X-ray Photoelectron Spectroscopy**, ***M. Dubey***, *J. Schwartz, S.L. Bernasek*, Princeton University

Detection of gaseous nitric oxide (NO) in biological systems has attracted significant attention since the identification of NO as the endothelial-derived relaxing factor (EDRF).[1] NO also acts as a signal molecule in the nervous system, and is associated with the presence of infection and Alzheimer's and other diseases. Apart from biological systems, NO is a main product released on the pyrolysis of nitro-organic explosives. For these reasons, much work has been done in the field of NO detection, and the need for a sensitive detector is evident. In this study, we report a direct and a highly sensitive technique to detect gaseous NO using X-ray Photoelectron Spectroscopy (XPS). The binding of NO by heme proteins is well understood,[2] and we have utilized it for detection. We have developed a reliable method to grow Self-Assembled Monolayers (SAMs) of alkylphosphonic acids on oxide surfaces.[3] This platform is used to covalently attach a uniform layer of an iron heme-like molecule, which was synthesized separately. Differential charging in XPS has been used to ascertain the uniformity of the organic film.[4] The N1s signal from the heme ligand was measured by XPS before and after exposure to NO. Before NO binds to the iron, a single nitrogen peak is present, attributed to the nitrogens of the porphyrin ring. After reaction with NO, a new, distinct peak was observed in the high resolution N1s spectrum. This peak is at a higher binding energy (approx 5.5 eV), and is attributed to the NO bound to the iron. An estimate of the bound NO was calculated using XPS and QCM to be about 40 picomoles.

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11:00am **SS2+EM+TF-WeM10 An In Situ EC-STM Study of the Restructuring of Self-Assembled Monolayers upon Metal Deposition**, ***C. Silien***, *M. Buck*, University of St Andrews, UK

The combination of electrochemistry and self-assembled monolayers offers interesting opportunities for nanotechnology due to high resolution defined by patterned SAMs and simplicity and scalability afforded by electrochemistry. However, control of processes such as electrochemical metal deposition on the nanometer length scale requires exact knowledge of the mutual influence of a SAM structure and electrochemical processes. Aiming for an understanding at the molecular level we report an investigation of the underpotential deposition of copper on Au(111) electrodes modified by ω-(4'-methyl-biphenyl-4-yl)-alkanethiols (H_3C-(C_6H_4)-(C_6H_4)-$(CH_2)_nSH$, BPn). As reported recently, this class of molecules gives rise to pronounced structural variations with length n of the alkane spacer and, for n = even, exhibits polymorphism.[1,2] Furthermore they can be prepared to an exceptionally high structural perfection. These properties make SAMs of BPn thiols an attractive basis for further tailoring of properties of functionalized electrodes and the electrochemical generation of nanometer-scaled structures. A decisive step in SAM controlled electrometallisation is the deposition of the first layer of metal which takes place in the underpotential region. Its understanding is of crucial importance as this layer forms at the SAM-substrate interface and, therefore, affects the properties of the system. Our in situ STM investigations of the underpotential deposition reveal, firstly, pronounced differences between BPn SAMs and alkane thiols and, secondly, a pronounced influence of the length of the alkane spacer in the BPn SAMs, i.e., whether n = odd or even. The molecular resolution achieved in this study combined with time resolved monitoring of the events occurring in the course of the copper deposition allows us to highlight the relationship between the SAM structure and its influence on the generation of nanometer scaled structures by electrochemical metal deposition.

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11:20am **SS2+EM+TF-WeM11 Irradiation-Promoted Exchange Reaction: A New Approach to the Fabrication of Heterogeneous Self-Assembled Monolayers and Chemical Lithography**, ***N. Ballav***, *T. Weidner, M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can undergo an exchange reaction with the molecules capable of building a SAM on the same substrate upon the immersion into the respective solution. However, for most systems, the exchange reaction is very slow and incomplete at normal conditions, taking from days to weeks and occurring to a limited extent only. Using several different model systems, we show that the rate and extent of the exchange reaction can be significantly enhanced and even precisely tuned by either electron irradiation with a small dose or exposure to UV light. We assume that both electron and UV irradiation result in the appearance of structural and chemical defects in the target SAM, which promote the molecular exchange. The effect of irradiation and the parameters of the exchange reaction were monitored in detail and correlated with each other using several complementary experimental techniques. The developed approach, irradiation-promoted exchange reaction, can be considered as a platform for the preparation of heterogeneous mixed SAMs. Also, in combination with e-beam or UV-lithography, this method can be used for the fabrication of chemical patterns, including gradient ones. In this regard, the approach is similar to conventional photography: a desired pattern is initially written by electron or UV beam and later "developed" upon its immersion into the solution of a molecular substituent. There are no principal limitations for the form of the fabricated features while the characteristic length scale can be varied in a broad range from centimetres to several tens of nanometers.

11:40am **SS2+EM+TF-WeM12 Calcium Adsorption on Regioregular Poly(3-hexylthiophene): Synchrotron Radiation Photoemission and Microcalorimetric Studies**, ***J.F. Zhu***, *W. Zhao, W.H. Zhang,* University of Science and Techonology of China, *J. Farmer, C.T. Campbell*, University of Washington

The adsorption of Ca on the regioregular poly(3-hexylthiophene) (rr-P3HT) thin film surfaces at 300 K has been studied using synchrotron radiation photoemission spectroscopy, adsorption microcalorimetry and atomic beam/surface scattering. The polymer films were spin-coated on the Si wafers with typical thickness of > 100 nm and were free of oxygen contamination as clarified by both X-ray photoelectron spectroscopy and Auger electron spectroscopy. Synchrotron radiation photoemission spectroscopy provides precise experimental information on the alteration of the Ca/polymer interfacial energy level line-up and the chemical nature at this interface. The deposition of calcium on the rr-P3HT film at room temperature induced a decrease of the work function, indicating Ca donates electron density to the polymer substrate. Moreover, Ca adsorption led to the depression of the bands of the rr-P3HT. The strength of interaction between Ca and the rr-P3HT is probed by both microcalorimetric heats of adsorption and sticking probability measurements.

12:00pm **SS2+EM+TF-WeM13 Supramolecular Coordination Networks at Surfaces: Self-selection and Error Correction in Multi-ligand Nanopore Arrays***, **S.L. Tait**, A. Langner, N. Lin,* Max Planck Institute for Solid State Research, Germany*, C. Rajadurai, M. Ruben,* Research Center Karlsruhe, Germany*, K. Kern*, Max Planck Institute for Solid State Research, Germany and Ecole Polytechnique Fédérale de Lausanne, Switzerland

Supramolecular self-assembly of organic ligands and metal centers is a topic of growing interest for efficient molecular-scale patterning of surfaces. Molecular networks can be designed to self-organize in regular, 2D nanopore lattices, whose dimensions and properties can be controlled by selection of the organic ligands. This approach offers a natural alternative to current nano-fabrication methods, allowing atomic and molecular building blocks to organize themselves into useful nanostructures, and is a model system for supramolecular and biomolecular assembly in general. We present recent results of self-assembled supramolecular networks on the Cu(100) surface, which demonstrate multi-ligand construction of 2D arrays of compartments with tunable shape and size. These binary combinations of complementary ligands represent a significant step in complexity over previous studies. Of technological interest is the capability for modular replacement of either of the two ligands to produce a range of nanopore lattice sizes and shapes in a very predictable and programmable way. Of more fundamental interest in these systems is molecular level resolution imaging using scanning tunneling microscopy, which allows an unprecented perspective of fundamental steps to supramolecular assembly, such as structural error correction achieved by efficient molecule self-selection. Non-covalent metal—organic coordination provides room temperature stability and high structural ordering through directional and selective interactions, but also allows for bonding reversibility, enabling error correction during assembly. By selection of molecular building blocks with specific properties, we can "program" these systems to pattern a surface with homogenous networks of specific size, structure, and physical and chemical properties. The ability to tailor the size and functionality of nanometer-scale arrays produced by molecular self-assembly represents a unique opportunity for molecular recognition, heterogeneous catalysis, thin film growth, and other fields.

Thin Film

Room: 613/614 - Session TF-WeM

Thin Film and Nanoparticle Growth and Characterization

Moderator: J.M Fitz-Gerald, University of Virginia

8:00am **TF-WeM1 Dependence of Fiber Texture on Connectivity in Composite Thin Films***, **J.M.E. Harper**, D. Carlson, A.M. Brown, D.I. Filoti*, University of New Hampshire

The connectivity of metal-insulator composite thin films varies with composition from a continuous metal phase surrounding insulating islands, through a variety of interconnected networks, to disconnected metal islands within a continuous insulating phase. We show that the strength of the metal fiber texture correlates with the degree of metal connectivity. Composite thin films of Au-SiO$_2$ and Ag-Si were deposited using dual-source magnetron sputtering and the crystallographic texture was determined using x-ray pole figure measurements. For metal-rich compositions, we observe strong 111 Au or Ag fiber texture perpendicular to the substrate plane, similar to the fiber texture of pure fcc metal films. As the volume fraction of SiO$_2$ or Si is increased, the strength of the 111 fiber texture decreases monotonically until a random texture is observed. The composition at which the fiber texture is lost correlates well with the composition at which the metal component becomes discontinuous, as determined by resistivity and transmission electron microscopy measurements. We conclude that x-ray pole figure measurements of fiber texture can be used for non-contact determination of the connectivity of phases in composite thin films.

8:20am **TF-WeM2 Morphology Evolution during Growth of Epitaxial Ti$_{1-x}$Al$_x$N and Cr$_{1-x}$Al$_x$N Films onto MgO(100) and MgO(111)***, **M. Beckers**, H. Willmann, J. Birch,* Linköping University, Sweden*, J. v. Borany,* ROBL-CRG at ESRF, France*, P.H. Mayrhofer, C. Mitterer,* University of Leoben, Austria*, L. Hultman*, Linköping University, Sweden

Metastable Ti$_{1-x}$Al$_x$N has found widespread industrial use as hard coating for cutting and forming applications, while the knowledge base for Cr$_{1-x}$Al$_x$N on structure-property relations still evolves. Here, we report on growth studies of epitaxial Ti$_{1-x}$Al$_x$N and Cr$_{1-x}$Al$_x$N films deposited onto MgO(100) and MgO(111) substrates by reactive magnetron sputter epitaxy. Both orientations promote cube-on-cube epitaxial growth. However, transmission electron microscopy reveals a smooth single-crystal morphology for the MgO(100) and a facetted columnar morphology for the MgO(111) substrate. This can be ascribed to the highly anisotropic step energies for the corresponding nitride growth surfaces, resulting in a switch between layer-by-layer and island growth mode as characterized by in-situ x-ray diffraction experiments. High-resolution x-ray reciprocal space maps display that films deposited onto MgO(111) grow fully relaxed with lattice parameters that correspond well to literature values at the given compositions. The growth mode on MgO(100) substrates depends on the Al fraction. Ti$_{1-x}$Al$_x$N films at low Al fractions that are well lattice-matched to MgO show pseudomorphic strained growth with a small percentage of in-plane strain relaxation due to interfacial misfit dislocations, and exhibit almost defect-free single-crystal morphology. On the contrary, less lattice-matched (Ti,Cr)$_{1-x}$Al$_x$N films with x close to the AlN precipitation threshold show an initial pseudomorphic strained layer that relaxes for increasing film thickness. The relaxation starts with interfacial misfit dislocations that gradually evolve into a dislocation network along the {111}<110> slip system. For Cr$_{1-x}$Al$_x$N films with an Al fraction of 0.6, this dislocation network is superimposed by crystals of first-order twins about [111] with the orientation relationship Cr$_{1-x}$Al$_x$N (122) // MgO (100). The twins overgrow the primary (100) orientated film, likely due to the angular vicinity of fast growing (111) planes. These diverse relaxation mechanisms might be attributed to changed stacking fault energies for different Al fractions. Since polycrystalline Ti$_{1-x}$Al$_x$N and Cr$_{1-x}$Al$_x$N show AlN precipitation at grain boundaries during annealing, the observed morphology changes for different substrate orientation and stoichiometries have impact for the understanding of age hardening in these systems.

8:40am **TF-WeM3 A Mesoscopic View on Complex, Stress-Governed Phenomena in Submonolayer Ag-films on Pt(111) at High Temperature***, **B. Poelsema**, E. Van Vroonhoven*, University of Twente, The Netherlands

The growth of ultrathin silver films at 750 K on Pt(111) has been studied with LEEM. The STM-based previous reports on surface confined alloying in this bulk immiscible system are confirmed. This information is inferred from the evolution of the electron reflectivity as well as indirectly from the distribution of adatom islands indicative of highly unconventional nucleation behavior extending to extremely high coverages. De-alloying as previously reported is also confirmed basically. The in-situ mesoscopic data, however, reveal a number of previously unnoticed features. For instance de-alloying is accompanied by strong segregation effects. Platinum-rich disks evolve during de-alloying, showing up as persistent "dark spots" in a bright field measurement, irrespective of the energy of the probing electrons. Also no additional diffraction features spots are observed, indicative of the Pt-disks being highly disordered, amorphous or possibly liquid. In a very narrow coverage window around 85% of a monolayer µ-LEED measurements demonstrate a sudden stress relieve. At this point the de-alloying reaches a summit and the film temporarily releases stress by expansion. This goes together with enhanced segregation. Further along the route to monolayer completion we observe reentrant alloying which actually persists during the growth of a few more layers. Also the film quickly resumes its pseudomorphic structure.

9:00am **TF-WeM4 Field Emission Suppression from Stainless Steel Using Silicon Oxynitride Coatings***, **N.D. Theodore**, B.C. Holloway,* The College of William and Mary*, C. Hernandez-Garcia, H.F. Dylla,* Jefferson Lab*, D. Manos,* The College of William and Mary

We have developed a new RF inductively-coupled, plasma-based, reactive sputtering procedure to deposit high-purity silicon oxynitride (SiO$_X$N$_Y$) films. Oxynitride formation was verified using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Using profilometry, we determined that increasing the nitrogen plasma pressure or the RF power raises the deposition rate. However, FTIR results show that adjusting the plasma pressure also altered the amount of bound nitrogen in the silicon oxynitride layer. The resulting silicon oxynitride coatings have also been characterized with Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS), and elastic recoil detection analysis (ERDA) to determine their elemental composition and density. This silicon oxynitride coating drastically reduced field emission from large area, stainless steel electrodes. High voltage tests showed that a polished, 180 cm^2, stainless steel electrode exhibited 27 μA of field-emitted current at 15 MV/m; however, by applying a silicon oxynitride coating to a similarly polished electrode, emission current was drastically reduced to less than 300 pA at 30 MV/m. The field emission from these silicon oxynitride coatings seems to follow the electron emission mechanisms proposed by Schottky and Poole-Frenkel. Both of their emission equations predict that increasing the band gap, dielectric constant, and electron affinity of the silicon oxynitride coatings could further reduce field emission. Our most recent high voltage tests of two polished electrodes coated with a 'graded' silicon oxynitride layer supports these predictions; at 30 MV/m, the field emitted current was below 4 pA, the detection limit of our high voltage test system.

9:20am **TF-WeM5 A Study of Tungsten Silicon Nitride Films Used for Thermal Inkjet Printheads**, ***J. Wonnacott***, *E. Whittaker, G.S. Long, B. Risch*, Hewlett-Packard Company

Thin ternary films of tungsten and silicon nitride (WSiN) have been studied for use as heater resistors in thermal inkjet printheads. Product applications require films with the appropriate bulk resistivity and thermal stability at process and performance temperatures. A typical resistor may be required to heat and eject several billion ink drops over the lifetime of the printhead. The heating of the WSiN causes changes in film properties that adversely effect ink drop ejection and the subsequent print quality. Specific electrical annealing procedures have been used to stabilize the as deposited WSiN film for resistor firing conditions during printing. Various analytical techniques including X-Ray Diffraction (XRD), X-Ray Reflectance (XRR), X-Ray Fluorescence (XRF), X-Ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM) have been used to study the WSiN film characteristics after the initial Physical Vapor Deposition (PVD), after actual use in printheads, and after simulated use by rapid thermal processing on blanket deposited films. The PVD processing parameters and WSiN target composition have been varied to study the impact the resulting performance of the resistor film. Employing these analytical techniques optimized resistor films have been explored for high temperature stability characteristics.

9:40am **TF-WeM6 Ti as an Interface Stabilizer for Fe-Al Interfaces***, ***W. Priyantha***, *A. Comouth, A. Kayani, M. Finsterbusch, H. Chen, M. Kopczyk, D. Tonn, R.J. Smith,* Montana State University*, D.E. McCready, P. Nachimuthu*, Pacific Northwest National Laboratory

The use of ultra-thin metal interlayers to stabilize metal-metal interfaces and to limit interdiffusion has drawn much attention over the past few years, driven by a variety of technological applications. Earlier, we reported using a Ti monolayer as an interlayer to promote epitaxial growth and to minimize diffusion at the Fe/Al(001) interface. These findings encouraged us to explore the use of interlayer structures for thin films of technological interest deposited on Si wafers using RF sputtering. AlFe and FeAl metal bi-layers, with and without a Ti stabilizing interlayer, were studied using Rutherford backscattering (RBS) and X-ray reflectivity (XRR). Analysis revealed that FeAl and AlFe films without a Ti interlayer on SiO2/Si wafers showed considerable Fe-Al intermixing, especially when the Fe layer was deposited on top of the Al layer. With a Ti interlayer present the interfaces exhibited less interdiffusion.

* This work was supported by the National Science Foundation, NSF Grant DMR 0516603.

10:40am **TF-WeM9 Size-Selected Clusters: From 3D Atomic Structure to Applications in Biochips**, ***R.E. Palmer***, The University of Birmingham, UK **INVITED**

In this talk I will address both atomic-scale characterisation and biological applications of size-selected atomic clusters. Today's advancements in nanotechnology present new challenges for the quality, speed and precision of nanostructure characterization. Here we show that the new generation of aberration-corrected scanning transmission electron microscopes (STEM), coupled with simple imaging simulation, is capable of providing three-dimensional structural information[1] with atomic resolution in a single shot, revealing not only the size but also the shape, orientation and atomic arrangement, for size-selected gold nanoclusters that are preformed in the gas phase and soft-landed on an amorphous carbon substrate. The structures of gold nanoclusters containing 309 (@+=@5%) atoms can be identified with either decahedral, cuboctahedral or icosahedral geometries. The work illustrates a new and efficient means to study the atomic structure and the stability of supported, ultra-small metal clusters in the nanometre range, e.g. catalyst and extracellular particles, with single atom sensitivity. The controlled deposition of such size-selected Au clusters, of size 1-10nm, also provides a route to the fabrication of novel surface binding sites for individual biological molecules, notably proteins. We report the pinning[2,3] of size-selected Au_N clusters (N = 1-100) to the (hydrophobic) graphite surface to create films of arbitrary, sub-monolayer density. Gold presents an attractive binding site for sulphur and thus for cysteine residues in protein molecules. AFM measurements in buffer solution[4,5] show that GroEL chaperonin molecules (15 nm rings), which contain free cysteines, bind to the clusters and are immobilised.[5]. Peroxidase[6] and oncostatin molecules behave similarly. By contrast, green fluorescent protein (GFP) does not bind, consistent with detailed analysis of the protein surface; the cysteine residues lie in the interior of the folded protein. The results provide "ground rules" for residue-specific protein immobilisation by clusters. The extension of the approach to optical surfaces is enabling the production of prototype biochips (microrarrays) for protein analysis, e.g., early stage cancer-marker detection.

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11:20am **TF-WeM11 Formation of Robust, Freestanding Tantalum Oxide Films with Controlled Morphology**, ***P. Kruse***, *S. Singh*, McMaster University, Canada

We have previously shown that electropolishing of tantalum in concentrated acid mixtures can reproducibly lead to very flat surfaces with dimples tens of nanometers in diameter, regular in shape, monodispersed in size and arranged in highly ordered arrays which even transverse grain boundaries. In this work, we are demonstrating the anodic growth of nanometer thick, detachable, amorphous tantalum oxide films with tuneable morphology (porosity) on these surfaces. Large (sqcm) sections of these flexible tantalum oxide films can be separated as sheets from the base tantalum surface by a Lift- Off-Float-On technique. The sheets can then be transferred to a wide variety of substrates, like Si wafers, glass slides, TEM grids etc. We have thoroughly characterised the films and are studying their growth conditions with the intention of gaining even better control over their morphology. Potential applications include nanotechnology, photonics and catalysis.

11:40am **TF-WeM12 Fabrication of Poly-Crystalline Silicon Thin Film by Using a Neutral Beam Deposition Method at a Low Temperature**, ***S.-K. Kang***, SKKU Advanvced Institute of Nano Technology (SAINT), Korea*, B.J. Park, S.W. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Poly-crystalline silicon (p-Si) thin films are generally applied to electronic and optoelectronic devices because of its higher carrier mobility than that of amorphous silicon (a-Si) film and excellent potential in fabricating higher speed, higher resolution and brighter TFT-LCD. Currently, p-Si film is fabricated by re-crystallizing an a-Si film with post-treatment method such as excimer laser annealing (ELA), solid phase crystallization (SPC), metal-induced crystallization (MIC), etc. However, these troublesome post-treatment requires high processing temperature (500~600 °C) which is higher than glass transition temperature. Furthermore, throughput and cost issues will become more critical as the substrate size is increased. Therefore, to simplify process steps and increase production throughput, direct p-Si deposition at a low temperature is definitely required. Chemical assisted neutral beam deposition (CANBD) is investigated as a new approach to fabricate and develop p-Si which has more excellent properties in this study. The difference of CANBD to the conventional PECVD is that the p-Si thin film formation energy of CANBD is supplied by controlled neutral beam energies. Decomposition of source gas (SiH_4) is enhanced by assisted neutral beam which is generated by low energy Ar neutral beam, resulting in the formation of low temperature p-Si. The p-Si made by the neutral beam deposition method shows better electrical property compared to silicon deposited by other processes at low temperature. Resistivity of grown silicon film is measured by 4-point probe measurement. Carrier concentration and carrier mobility are evaluated by Hall measurement. Film crystallinity is investigated by HRTEM, Raman spectroscopy, and X-ray diffraction analysis.

12:00pm **TF-WeM13 Properties of Nano-Crystalline Silicon Grown by Internal Linear Antenna-Inductively Coupled Plasma-type Plasma-Enhanced Chemical Vapor Deposition**, ***H.C. Lee****, H.B. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Considerable attentions have been paid to hydrogenated nano-crystalline silicon film deposited a low temperature because of its promising application to stable high efficient solar cell, thin film transistors, and color sensors. In particular, the development of nano-crystalline silicon film is one of the key issues in developing active matrix liquid crystal displays (AMLCD) and active matrix organic light emitting displays (AMOLED). For this purpose, good field effect mobility in the range of 2~5cm^2/Vs is required to have high quality resolution displays along with higher stability than amorphous silicon thin films due to the less hydrogen bonded to silicon in the film. In this study, nano-crystalline silicon was deposited using an internal-type inductively coupled plasma (ICP) source, and the properties of the nano-crystalline silicon were investigated as a function of operating pressure, SiH_4/H_2 gas mixture, additive gas, etc. Especially, the effect of initial nucleation condition by controlling gas combination on the crystalline size and crystalline percentage was investigated. The crystallinity and orientation of the deposited hydrogenated silicon thin film was estimated by using micro-Raman spectroscopy (Invia Basic Renisaw) and a high-resolution X-ray diffraction (HRXRD, D8 Discover Bruker).

The dark conductivity was calculated by using the I-V characteristics of the films. Field effect mobilities were measured by the fabricated thin film trasnsistors. At the temperature lower than 200°C, nano-crystalline having the size of 30nm could be deposited and the volume fraction of the crystalline calculated by the Raman spectroscopy was higher than 40%. In the presentation, more detailed characteristics of nano-crystalline film deposited by the internal linear ICP film will be discussed.

Exhibitor Workshops

Room: Exhibit Hall - Session EW-WeB

Exhibitor Workshops

Moderator: R. Childs, Consultant

10:00am **EW-WeB1 Thiol Applications: Model Surfaces, Cutting Edge Technologies and Educational Platforms*, D.J. Graham***, Asemblon, Inc.

In this workshop we will highlight the use of alkanethiols in biomaterials, nanotechnology and molecular electronics. For decades, thiols have been used to control surface chemistry and study surface interactions in a wide range of fields. Thiols have again come into the forefront of research with the new developments in nanoparticles and increased interest in self-assembling systems. Come learn about how thiols are being used today and see a new educational kit developed by Asemblon for teaching about nanotechnology and surface modification

10:20am **EW-WeB2 Electronic and Magnetic Transport Measurements with Probe Stations*, J.R. Lindemuth***, Lake Shore Cryotronics

Electronic and magnetic transport based on tunneling is an extremely important technology area of nanotechnology and mesocopic devices. Tunneling of unpolarized electrons is the phenomena responsible for tunnel diodes and negative differential resistivity (NDR). NDR devices are one on the leading candidates for high speed, low power consumption switching devices required by ITRS. Tunneling of spin polarized electrons in magnetic tunnel junctions create large room temperature tunneling magnetoresistance that will be used in the next generation of magnetic read heads. Measurement of tunneling transport requires a stable controlled environment for both the temperature of the device and the magnetic field of the device. For convenience of measurement, a manipulated probes station with fast sample turn around is required. Using probes, instead of attached wires, is a very convenient method for doing electrical measurements. However, the probes can influence the electrical, temperature and magnetic environment of the sample. I will discus the impact of using probes and describe some of the systematic and random errors this technique can introduce into the measurement as well as methods to mitigate these effects. There are many different mechanisms and applications for tunneling. Each mechanism requires understanding and a careful design of the measurement system. Although there are many design criteria common to all tunneling experiments, each mechanism has its own special requirements. This presentation will show results of a variety of tunneling transport measurement, including NDR and TMR, with emphasis on methods and instrumentation for optimal results.

Wednesday Lunch, October 17, 2007

Exhibitor Workshops

Room: Exhibit Hall - Session EW-WeL

Exhibitor Workshops

Moderator: R. Childs, Consultant

12:40pm **EW-WeL2 How to Avoid a Failure During Shutdown or Start-up Events**, ***M. Silva***, FMG Enterprises

Participants will learn how to maximize their uptime success rate, and minimize downtime at shut down and start up events (cold and hot). Both facility and production line levels. We will review the preparatory steps and tasks needed to ensure avoidance of failure during these events. Importantly, participants will share their experiences and lessons. Other tasks such as PM Programs, Base line characterization of pumps, and Inventory Control will also be reviewed. Course outline Shutdown cold: define Example of event: facility shutdown. Shared experience Shutdown hot: define Example of event: facility running, production shutdown. Shared experience Start-up event: Start-up cold: define Example of event: coming up from cold shutdown. Shared experience Star-up hot: define Example of event: turning on of a production line. Shared experience Review preparatory steps of how to ensure avoidance of failure during shutdown or start-up events. Discuss other tasks that can be done during shutdown or start-up events: 1) PM programs. 2) Base line charactering of pumps. 3) Inventory control. All are programs that FMG provides, along with practical training methods for their in-house technicians.

1:00pm **EW-WeL3 Sputter Target Bonding Technology**, ***J.R. Gaines***, Kurt J. Lesker Company

LeskerBond^{TM} Services offers the patented NanoBond® process technology and patented NanoFoil® under license from RNT. NanoFoil® is a free-standing foil capable of generating heat. NanoFoil® is comprised of hundreds, or even thousands, of fine, nanoscale size layers of aluminum and nickel which, when placed between two prepared materials and energized, creates an extremely effective bond. In this presentation we will describe how NanoFoil® is made and we'll explore the various applications of NanoFoil®. Specifically, we will examine the application of NanoFoil® for bonding sputtering targets. We will also present case studies that compare and contrast bonding with NanoFoil® versus traditional bonding methods.

1:20pm **EW-WeL4 Ion Energy and Ion Flux Measurements at an RF Biased Surface**, ***M. Hopkins***, Impedans Ltd.

Impedans is introducing the first floating Retarding Field Energy Analyzer which will allow measurement of the Ion Energy Distribution Function on an RF biased substrate. RFEAs are used in research laboratories to measure ion energy distribution functions. Their use in practise is limited by the need to ground the analyser, whereas most interesting applications are in RF biased substrates. The IEDF is important in understanding the role of ions in processes such as etch. Deviations in ion energy can lead to charging effects on a substrate or wafer and variations in flux can effect etch uniformity. A transition from a high frequency (single peak distribution) to a low frequency (bimodal distribution) sheath is often observed in RF plasma sources. The energy difference between the two peaks of the bimodal distribution is related to the RF modulation of the plasma potential and to the ratio between the ion transit time in the sheath and the RF period. A change in ion mass can result in changes in bi-modal structure and impact the average energy of ions arriving at the substrate or wafer. Due to the complexity of modelling the ion energy profiles, measurements are often necessary to validate the behaviour of a new source design in etch applications. The Impedans RFEA is unique in that it uses the technology developed to float RF Langmuir probes in order to isolate the RFEA from electrical ground. The analyser is built into a dummy wafer and placed on the chuck or wafer holder. The RFEA sensor does not disturb the RF bias and the measured Ion Flux and Ion Energy are similar to that seen by a wafer. By placing multiple sensors on a dummy wafer a spatial scan of the ion energy distribution and flux can be achieved. This is invaluable data to understand the plasma process and its effects on the surface of interest. The Impedans RFEA is designed to operate in hostile environments and can withstand temperatures of several hundred degrees centigrade.

1:40pm **EW-WeL5 Recent Developments: STM 150 Aarhus and FE-LEEM P90**, ***O. Schaff***, Specs, Germany

SPECS has developed a new temperature design for the original STM 150 Aarhus system. Excellent performance in terms of mechanical stability and thermal control could be demonstrated for LN2 temperatures and temperatures exceeding 1000°C up to 1200°C. The high temperature performance of the new design is demonstrated using first results of a Si(111) sample in a FE-LEEM P90 sample holder. Atomically resolved phase transitions of the (7x7) <-> (1x1) surface reconstruction could be observed easily. The FE-LEEM P90 is a next generation Low Energy Electron Microscope with unsurpassed resolution for dynamic LEEM microscopy experiments. With this instrument, based on the design of Dr. Rudolf Tromp, nanometer scale processes on surfaces can be observed in real-time. The instrument can be upgraded with an electron mirror for aberration correction, The design resolution for the corrected FE-LEEM P90 is below 2nm.

Applied Surface Science

Room: 610 - Session AS+BI+NS-WeA

Fabrication and Characterization of Functional Soft Material Surfaces

Moderator: R.T. Haasch, University of Illinois at Urbana Champaign

1:40pm **AS+BI+NS-WeA1 UPS Work Function Measurements on Polymers Combined with C60 Depth Profiling**, ***S. Raman***, *J. Moulder*, *J.S. Hammond*, Physical Electronics, *N. Sanada*, *M. Suzuki*, ULVAC-PHI, Inc.

The performance of ultra thin organic films in organic LED's (OLED) is dependent on the work functions of the electrodes and polymers forming the OLED junctions. Historically, the work functions have frequently been derived from the secondary electron emission edges measured with UPS. The recent applications of C60 ion beams for the sputter removal of a surface layer of many organic materials, leaving the remaining surface with minimal chemical damage, have offered a new tool for studying surface modified polymers. By combining these two techniques, the work function and composition as a function of depth of polymers targeted for OLED applications can be characterized by XPS and UPS. The surface characterization of OLED component polymers exposed to deleterious environments will also be discussed. The possible chemical surface damage induced by the C60 ion beams will be examined by both XPS and UPS spectra and secondary electron emission edge spectra.

2:00pm **AS+BI+NS-WeA2 Patterning and Bonding of Poly(dimethylsiloxane) A Simple New Method for Creating Optically Transparent Biocompatible Surfaces and Robust Microfluidic Devices**, ***P.R. Norton***, *N. Patrito*, *J. McLachlan*, *J. Chan*, *S. Faria*, *S. Tadayyon*, University of Western Ontario, Canada

Our group has developed a simple protocol to prepare inexpensive, single-component substrates capable of confining cell attachment and growth. In the presence of an argon plasma, thin metal films are deposited onto poly(dimethylsiloxane) (PDMS). Removal of the metal layer exposes regions of the polymer surface that are enriched in oxygen and promote the adhesion of fibroblast, epithelial and myoblast cells. This method produces bioactive arrays of controlled size (down to scales in the order of µm), shape, pitch and symmetry on which cells can be grown to confluency. The treated material is storable and can be activated just before use; this eliminates stability problems inherent in a number of previously reported PDMS surface treatments, most notably oxygen plasma modification. The patterned arrays offer highly adaptable means to probe cell-cell interactions, cell motility and cell signaling in response to varied spatial or geometric organization and they are being incorporated into microfluidic channels for combined optical and proximal probe studies of live cells. Serendipitously, this surface treatment alters the mechanical properties of PDMS, rendering the modified material sensitive to tensile stresses imposed by cells. Cellular traction forces generate nanoscale ripples in the elastic substrata which extend outward from the cell bodies and which can be imaged by dark-field microscopy and AFM. Detailed analyses of these ripples can potentially provide a direct measure of cellular traction forces and mechanical signaling. In related experiments, we have also developed a novel means of bonding PDMS to a host of materials relevant to microfluidic device fabrication, including glass, Si, SiO2 and polystyrene. To quantify the adhesive strength, closed PDMS-glass and PDMS-PDMS microfluidic devices were fabricated and subjected to tensile and leakage testing. The data indicate a significant improvement in performance over previously reported bonding technologies, resulting in the production of more robust, longer-lasting microfluidic devices and the concomitant possibility of using higher pressures and flow-rates.

2:20pm **AS+BI+NS-WeA3 Interfacial Structure of Polymer Brush and Gel Investigated by Sum Frequency Generation Spectroscopy**, ***K. Uosaki***, *H. Noguchi*, *S. Nihonyanagi*, *H. Minowa*, *R. Yamamoto*, Hokkaido University, Japan

Polymer brush and gel plays very important roles in biological systems. Information on the interfacial structure is essential to understand the function of these materials. Here we employed sum frequency generation (SFG) spectroscopy, which is known to possess high surface specificity, to investigate the molecular orientation/conformation of polymer brush under various environment and water structure at PVA gel/solid interface. SFG spectra of alkylated poly (vinyl pyridine) in contact with dry nitrogen, water vapor, and liquid water were obtained. The peaks due to CH vibration of CH3 dominated in nitrogen, showing that the side chains are highly ordered. When the polymer layer is in contact with water vapor, in addition to the two peaks due to CH3 group, two peaks of CH2 group were observed, indicating that many gauche defects existed. The SFG spectrum of the polymer brush in contact with liquid water showed no peaks in CH stretching region except for small shoulder due to the ring CH modes, indicating the alkyl side chain was completely disordered. SFG spectra of the polymer brush in OH stretching region were also obtained. A broad band assigned to the OH stretching was observed in water vapor. Two bands corresponding to the OH stretching of the interfacial water molecules at 3200 cm-1 due to "ice-like water" and at 3400 cm-1 due to "liquid-like water" dominated in liquid water. Poly vinyl alcohol (PVA) gel is considered to be one of the possible candidates for an artificial articular cartilage in artificial joints because of very low friction between PVA gel and solid. SFG measurement proved that while the fractions of the "ice-like" and "liquid-like" water were almost equal at water/quartz interface, the fraction of the "liquid-like" water became much higher when the PVA gel was pressed against the quartz surface, showing that the weakly hydrogen bonded water dominate at PVA gel/quartz interface where friction is very low. SFG measurement in Ar showed only weakly hydrogen bonded water was present at the PVA gel/quartz interface. The effect of PVA gel contact was less obvious at the octadecyltrichlorosilane (OTS) coated quartz, where the friction is much higher. These results suggest the important role of weakly hydrogen bonded water for very small friction at PVA gel/solid interface. In conclusion, SFG is demonstrated to be a very useful technique to characterize molecular structure at solid/liquid interfaces including biological interfaces.

2:40pm **AS+BI+NS-WeA4 Multiphoton Patterning of Planar and Topographically Complex Surfaces for Control of Photon, Electron, and Chemical Transport**, ***P.V. Braun***, University of Illinois at Urbana-Champaign **INVITED**

Multiphoton patterning enables fabrication of complex structures with minimum feature sizes on the order of the volume of the focal point. Using a pulsed laser source coupled to a laser scanning confocal microscope, we have concurrently written and imaged various complex structures and patterns. Recently, along with formation of complex structures, we have initiated efforts to locally modify the surface chemistry of both planar and topographically complex (three-dimensional) surfaces to create pathways for photon, electron, and chemical transport. A series of organic chemistries have been developed to enable this patterning, which revolve around the grafting of photoswitchable molecules or polymer brushes to the various surfaces. Once the local chemistry of the surface has been modulated, this chemistry can be amplified through quantum dot attachment, electroless plating, or surface initiated polymerization to create two and three-dimensional patterns for control of photon, electron, and chemical transport. Colloidal crystals and porous glasses are used as model three-dimensional substrates; standard materials are used for two-dimensional structures.

4:00pm **AS+BI+NS-WeA8 Chemical Modification of Self-Assembled Monolayer Surfaces using Soft-Landing of Mass-Selected Ions**, ***P. Wang***, *O. Hadjar*, *J. Laskin*, Pacific Northwest National Laboratory

Stable immobilization of peptides on solid supports plays an important role in biochemistry. Existing techniques for linking peptides to surfaces are based on a variety of solution-phase synthetic strategies and require relatively large quantities of purified material. Here, we report a novel approach for preparation of peptide arrays on self-assembled monolayer (SAM) surfaces using soft-landing (SL) of mass-selected ions. This approach takes advantage of the exceptional selectivity in preparation of projectile ions by mass spectrometry. We demonstrate efficient reactive landing (RL) of several model peptides onto the SAM of N-hydroxysuccinimidyl ester terminated alkylthiol on gold (NHS-SAM). This method introduces unprecedented selectivity and specificity into the surface preparation step by eliminating the effect of solvent and sample impurities on the quality of the film. Peptide ions produced by electrospray ionization are mass-selected and deposited onto SAM surfaces using a novel ion deposition chamber designed and constructed in our laboratory. NHS-SAM, which readily reacts with accessible primary amino groups in proteins or peptides by forming amide bonds, is used as a target for soft-landing experiments. Freshly prepared SAMs and modified surfaces are characterized ex situ using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and infrared reflection absorption spectroscopy (IRRAS). Mass-selected ions of model peptides including cyclo(-RGDfK-), GRGDSPK and RGDGG were soft-landed onto the NHS-SAM surface.

ToF-SIMS and IRRAS characterization suggested efficient covalent binding between the two lysine-containing peptides and the NHS-SAM by the formation of an amide bond through the lysine side chain. Systematic studies were carried out to understand the factors that affect the efficiency of reactive landing. We found that the reaction takes place upon collision and is promoted by the kinetic energy of the ion. The reaction yield is independent of the charge state of the projectile ion suggesting efficient neutralization of peptide ions upon collision. Chemical reactivity and physical properties of the SAM surface are also important factors that affect the outcome of RL. RL of mass- and energy-selected peptide ions on surfaces provides a highly specific approach for covalent immobilization of biological molecules onto SAM surfaces.

4:20pm **AS+BI+NS-WeA9 TOF-SIMS Analysis of Polypropylene Films Modified by Isotopically Labeled Methane Flames**, ***S.J. Pachuta***, *M.A. Strobel*, 3M Company

Flame treatment is a common industrial process for modifying polymer surfaces. Surfaces exposed to flames are known to oxidize, but studies of the oxidation mechanism have been largely confined to correlating simple surface properties with models of the flame composition due to the lack of direct experimental data on the flame-surface interaction. In this work, polypropylene film surfaces were oxidized by exposure to a flame fueled by isotopically-labeled methane (CD_4). The isotopic sensitivity of time-of-flight secondary ion mass spectrometry (TOF-SIMS) was then used to gain new insights into the mechanism of flame treatment. TOF-SIMS analysis indicates that much of the oxidation of polypropylene occurring in fuel-lean flames is not accompanied by deuteration, while for polypropylene treated in fuel-rich flames, deuteration is extensive, and some of the affixed oxygen is deuterated. These observations imply that O_2 is the primary source of affixed surface oxygen in fuel-lean flame treatments, but that OH may be a significant source of affixed oxygen in fuel-rich flame treatments. Application of principal component analysis (PCA) and multivariate curve resolution (MCR) to the TOF-SIMS data was found to provide information beyond that which could be obtained by traditional peak-ratio methodology.

4:40pm **AS+BI+NS-WeA10 The Analysis of Oxidation Profiles in Elastomers Using ToF-SIMS**, ***J.A. Ohlhausen***, *M.C. Celina, M.R. Keenan*, Sandia National Laboratories

As elastomeric materials age, their mechanical properties can change such that they do not perform their desired function. It is important to understand the aging behaviour of such elastomers, so that predictive aging models can be developed. In that light, much work has been done to understand oxygen diffusion limited aging processes under accelerated aging conditions for a range of elastomers.[1-2] In these studies, mechanical properties as a function of depth were determined under differing temperature/time conditions. In addition, chemical changes were measured by analyzing microtomed sections using FTIR. Unfortunately, these measurements were difficult to perform on carbon-black filled samples and were also relatively time consuming. Ideally, an alternative method is needed to measure the chemical oxidation profiles of commercial o-rings containing fillers in a quick and efficient manner. In this talk, the usefulness of ToF-SIMS as a technique to measure the position-dependent extent of oxidation in filled elastomers will be discussed. Accelerated aging in 18O is used to demonstrate the ability of SIMS to directly measure the extent of oxidation. Examples of 18O- cross section line scans in aged elastomers will be discussed and compared to known diffusion limited degradation mechanical profiles. It will be shown that filled elastomers can be analysed using these methods. Additionally, the ability to measure oxidation profiles in air-aged samples will also be shown. Thus, ToF-SIMS is seen as a rapid evaluation tool for the measurement of elastomer oxidation for engineered elastomers. The benefits and limitations of the technique will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

[1] M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, Polymer Degradation and Stability 60 (1998) 493-504

[2] M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, Polymer Degradation and Stability 68 (2000) 171-184 .

5:00pm **AS+BI+NS-WeA11 Surface Chemical Analysis of Nano-Scaled r.f. Plasma Polymer and Co-Polymer Films by using a Combination of "In-Situ"and Ex-Situ Characterization Tools: Hydroxylated and Aminated Surfaces by XPS, ToF-SIMS and NEXAFS Spectroscopy**, ***W.E.S. Unger***, *A. Lippitz, S. Swaraj, E. Yegen*, Federal Institute for Materials Research and Testing (BAM), Germany

The formation of plasma-polymerized materials made from organic molecules is a technologically highly attractive way to obtain films with unique properties. Surface properties like bio-compatibility, wettability, etc., can be adjusted by tailoring the chemical functionalization. A controlled deposition of those films requires the development of surface analytical procedures which are able to derive useful information on relevant parameters. This can be a hard job for an analyst because plasma-polymerized or plasma-modified materials are extremely complex samples. Their complexity is caused by the co-existence of a relatively high number of chemical species. This leads to a kind of mixture analysis at surfaces but without the possibility of a separation step as it is possible, e.g., by using GC-MS techniques in the analysis of organic mixtures. Relevant parameters for film characterization are primarily (1) qualitative and (2) quantitative determination of functional groups. However there are other important parameters as for instance (3) the cross-linking and branching within the films or even the concentrations of (4) radicals and (5) unsaturated species in the films. It is well known that plasma-polymerized materials may undergo ageing processes. It is assumed that many of them will be initiated by radicals in the films. These radicals are inherently produced by plasma processing. Approaches have to be developed enabling a study of ageing processes on the molecular level including the respective reaction kinetics. So-called "in-situ" techniques of surface chemical analysis are required to investigate the real fresh state of samples. Using a selection of hydroxylated or aminated model plasma polymers and co-polymers it will be demonstrated how analytical approaches based on a combination of photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and x-ray absorption spectroscopy (XAS) may provide solutions for the analytical challenges summarized above.

Biomaterial Interfaces

Room: 609 - Session BI-WeA

Nucleic Acid Sequencing and Technology

Moderator: L.J. Gamble, University of Washington

1:40pm **BI-WeA1 Surface Initiated Enzymatic Polymerization of DNA**, ***A. Chilkoti***, *D. Chow, S. Zauscher*, Duke University

We demonstrate a technique to synthesize DNA homopolymers on a surface using surface-initiated enzymatic polymerization (SIEP) with terminal deoxynucleotidyl transferase (TdTase), an enzyme that repetitively adds mononucleotides to the 3' end of oligonucleotides. The thickness of the synthesized DNA layer was found to depend on the deoxymononucleotide monomer, in the order of dATP > dTTP >> dGTP - dCTP. In addition, the composition and the surface density of oligonucleotide initiators were also important in controlling the extent of DNA polymerization. Poly(dTTP) synthesized by SIEP was capable of binding to antibodies specific to oligomers of dTTP, indicating that the DNA homolayer is fully functional. TdTase-mediated SIEP can also be used to grow spatially defined three-dimensional DNA structures by soft-lithography and by E-beam nanolithography, and is a new tool for bioinspired fabrication at the micro- and nano-scale.

2:00pm **BI-WeA2 Genome Sequencing with Polony Technology**, ***J.S. Edwards***, University of New Mexico **INVITED**

The resounding success of the Human Genome Project (HGP) clearly illustrates how early investments in developing cost-effective methods of biological data acquisition can have tremendous payoffs for the biomedical community. Over the course of a decade, through refinement, parallelization, and automation of established sequencing technologies, the HGP motivated a 100-fold reduction of sequencing costs, from $10 per finished base to $0.10 per finished base. The relevance and utility of sequencing and sequencing centers in the wake of the HGP has been a subject of recent debate, however, I maintain that the completion of the human genome marks the end-of-the-beginning, rather than the beginning-of-the-end, of the era of DNA sequencing and, more generally, the era of nucleic-acid (NA) technologies. For a wide range of biomedical goals, a strong need is evolving for low-cost NA technology, and I will describe our progress in using polony technology to cheaply and rapidly re-sequence a human genome. The list of realized and potential applications for this type of high-throughput sequencing technology is rich and growing.

2:40pm **BI-WeA4 In Situ Study of Ionic Strength and Probe Coverage Influences on DNA Hybridization using Cyclic Voltammetry**, ***P. Gong***, *K.L. Shepard*, Columbia University, *R. Levicky*, Columbia University and Polytechnic University

Solid-phase hybridization underpins modern microarray and biosensor technologies. While the underlying molecular process, namely sequence-specific recognition between complementary probe and target molecules, is fairly well-understood in bulk solution, this knowledge proves insufficient to adequately understand solid-phase hybridization. Using self-assembled DNA monolayers as a model system for hybridization assays, the influence of ionic strength and probe coverage and their cross-correlation are studied systematically on mm-sized gold electrodes. Electroactive ferrocene and ruthenium compounds were employed to quantify the surface DNA probe and target densities independently. The use of electrochemical labels enables in situ monitoring of the hybridization process as well as quantification of nonspecific versus sequence-specific attachments of targets. Results of these experiments can be summarized in a hybridization "map" as a function of ionic strength and probe coverage. Optimum probe densities that lead to maximum target binding or, alternately, maximum hybridization efficiency under a given set of conditions have been identified. The objective is to obtain better understanding of the physical characteristics of solid-phase hybridization at a more fundamental level and to subsequently use this knowledge to guide DNA microarray and other surface hybridization applications.

3:00pm **BI-WeA5 Hybridization with DNA Probes Bound to Gold by Adenine Nucleotides***, **A. Opdahl**, D.F. Shudy,* University of Wisconsin, La Crosse*, L.J. Whitman,* Naval Research Laboratory*, D.Y. Petrovykh,* University of Maryland, College Park, and Naval Research Laboratory

The surface density of immobilized nucleotide probes is a key variable in most applications of DNA-functionalized surfaces because the inter-molecular spacing has a strong impact on subsequent hybridization. In an earlier work, it was demonstrated that probe spacing can be controlled by exploiting the strong and preferential interaction between oligo(dA) and gold.[1] Using a model set of d(T_m-A_n) oligos, the lateral spacing between DNA molecules was found to be largely determined by the number of nucleotides, n, in the (dA) component; e.g. increasing the number of dA nucleotides in the sequence increased the spacing between probe strands. Here, we use both in situ (SPR) and ex situ (XPS) methods to demonstrate that the surface density of realistic DNA probe sequences can be controlled on gold by incorporating a d(T_m-A_n) 'tail' in the sequence. We find that surfaces functionalized in this fashion possess many desirable properties, including simplicity in fabrication, highly reproducible hybridization kinetics, and stability over multiple hybridization/melting cycles. The unique feature of our strategy is the relationship between the probe spacing and the length of the dA component in the probe. We find that an even wider range of probe-to-probe spacing can be achieved by co-immobilizing the probe DNA with unmodified oligo(dA), which acts as a lateral spacer. Altering either the length or mole fraction of this spacer systematically changes the probe DNA surface coverage, and thereby systematically modulates the hybridization response. Finally, we will discuss how hybridization with probes immobilized via our approach compares with DNA probes on gold prepared by more conventional strategies.

[1] Opdahl et al., Proc. Nat. Acad. Sci., 104, 9, (2007).

4:00pm **BI-WeA8 Novel Materials and Strategies for DNA Sequencing and Genotyping in Microfluidic Devices***, **A.E. Barron**,* Stanford University*, C.P. Fredlake,* Northwestern University*, J.A. Coyne,* Stanford University*, J.S. Lin, R.J. Meagher*, Northwestern University **INVITED**

High-resolution DNA separations are necessary for electrophoretic DNA sequencing and genotyping, which remains an extremely important workhorse technology even in the present, so-called "post-genomic era". In currently used capillary electrophoresis instruments, polymer networks provide the required molecular sieving of DNA fragments. Electrophoresis in sieving matrices has intrinsic physical limitations in read length, shows reduced performance under high electric fields, and requires capillary loading with viscous polymer solutions. There is an ongoing push toward performing DNA sequencing in miniaturized "lab-on-a-chip" devices, which promise higher throughput and lower cost. We are developing "End-Labeled Free-Solution Electrophoresis" (ELFSE) as way to separate DNA according to size without the need for a sieving matrix. In ELFSE, each DNA molecule in a sample is covalently modified with a unique frictional modifier or "drag-tag" that modifies DNA electrophoretic mobility in a size-dependent fashion. We have designed and synthesized a series of non-natural polypeptide and polypeptoid drag-tags, and conjugated them to DNA for free-solution separations by microchannel electrophoresis. In one approach, artificial genes encoding repetitive polypeptides are constructed by controlled cloning, expressed in E. Coli, and purified. These protein drag-tags have so far have been used to demonstrate 4-color sequencing of ~ 180 bases of DNA by capillary electrophoresis, in the absence of a sieving matrix. The obtainment of longer drag-tags, so that we can get longer reads, is ongoing, and sequencing separations are now being carried out in glass microfluidic chips. The application of hydrophilic polymer wall coatings are a critical element of making this technology work, and this will be discussed in some detail. ELFSE may be the a breakthrough that enables rapid, high-throughput sequencing in integrated microfluidic devices, with all of the accompanying advantages that chips offer.

4:40pm **BI-WeA10 Multivariate Analysis Methods Applied to ToF-SIMS Images of DNA Microarrays***, **P.-C. Nguyen**, L.J. Gamble,* University of Washington*, C.-Y. Lee,* 3M Corporate Research Analytical Laboratory*, G.M. Harbers, B.J. Tyler, D.W. Grainger,* University of Utah*, D.G. Castner*, University of Washington

The printing process for preparing DNA microarrays introduces variability in microspots, as observed with fluorescence detection commonly used to analyze these arrays. The nanolitre drops of solution printed onto the microarray surface dries within seconds. During this rapid drying the solution ionic strength and solute concentrations increase dramatically. Interspot variations and non-uniform distribution of probe molecules within spots are major sources of experimental uncertainty in microarray analysis. Various primary ion sources (Bi^+, Bi_3^+, Bi_3^{++}, C_{60}^+, C_{60}^{++} and C_{60}^{+++}) were used in imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study this non-uniformity. The type of information gained from using different primary ion beams is compared. Principal component analysis (PCA) and maximum autocorrelation factors (MAF) were used to analyze the image results and determine which masses were the main causes of the observed variability. Amine-modified single-stranded DNA was immobilized on commercial slides containing NHS groups. Spots containing 0 to 100% of fluorescent Cy3 labeled DNA were examined. Different percentages of Cy3 label resulted in variations in spot size and shape as well as differences in fluorescence distribution within spots. Imaging ToF-SIMS showed that additives in the print solution (sodium dodecyl sulfate, N-lauroyl sarcosine, salts, etc.) as well as the Cy3 labeled DNA were non-uniformly distributed within the microspots. These non-uniformities were more apparent in images acquired with Bi_3^+ and Bi_3^{++} compared to images acquired with Bi^+. Compared to univariate analysis (i.e., examination of individual masses), both PCA and MAF methods more readily highlighted the distributions of chemical non-uniformities present in the DNA microspots. Results thus far indicate that most detail about types and distribution of chemical species in DNA microspots have been obtained from MAF analysis of the Bi_3^{++} images. However, C_{60}^{++}, C_{60}^{+++} data is providing additional information that is been examined.

5:00pm **BI-WeA11 Quantitative Analysis of Block-oligonucleotide Brushes on Gold***, **D.Y. Petrovykh**,* University of Maryland, College Park, and Naval Research Laboratory*, A. Opdahl,* University of Wisconsin*, L.J. Whitman*, Naval Research Laboratory

DNA brushes with unique properties can be prepared using a new immobilization method that is based on the intrinsic affinity of blocks of adenine nucleotides for gold.[1] Block-oligonucleotides are single-stranded DNA (ssDNA) with sequences that follow, for example, a d(A_k-T_m-N_n) pattern: a block of k adenine nucleotides [d(A_k)], followed by a block of m thymine nucleotides [d(T_m)], and a short sequence of n (arbitrary) nucleotides [d(N_n)]. Brushes formed by the d(A_k-T_m-N_n) block-oligonucleotides are particularly interesting, because they attach to gold via the d(A) blocks and present the d(N) "probe" sequence for hybridization with complementary nucleotides. We are quantitatively characterizing these DNA brushes before, after, and during the hybridization experiments using a combination of x-ray photoelectron spectroscopy (XPS) and surface plasmon resonance (SPR) imaging. Characterizing these systems presents several analytical challenges. First, unambiguous deconvolution of XPS spectral features is not possible for these chemically non-uniform brushes. Second, the low surface density of the d(N) probe sequences, which is required to maintain high hybridization efficiency, results in low XPS intensities. Finally, DNA hybridization is carried out in an aqueous environment, so comprehensive analysis of these experiments requires establishing quantitative correlations between the in situ SPR imaging and ex situ XPS measurements. We addressed these challenges by taking advantage of the high degree of control over the composition and grafting density of ssDNA brushes immobilized via adenine blocks. The resulting sets of samples having systematically varied properties allowed us to observe and quantify by both XPS and SPR the effects of the surface density of ssDNA probes on the resulting hybridization efficiencies. Developing such quantitative methods that combine results of in situ and ex situ analysis is critical for extending well-developed surface analysis techniques to complex biological surfaces and interfaces.

[1] Opdahl, et al., Proc. Natl. Acad. Sci. USA 104, 9 (2007).

Electronic Materials and Processing

Room: 612 - Session EM-WeA

Growth and Characterization of Complex Oxides

Moderator: C.H. Swartz, University of Canterbury, New Zealand

1:40pm **EM-WeA1 Spatially and Energy Resolved Imaging of Nucleation Centers in Ferroelectrics***, **S.V. Kalinin**, S. Jesse, B.J. Rodriguez,* Oak Ridge National Laboratory*, I. Vrejoiu, D. Hesse, M. Alexe,* Max Planck Institute of Microstructure Physics, Germany*, Y.H. Chu, R. Ramesh,* University of California, Berkeley*, S. Choudhury, L.Q. Chen,* Pennsylvania State University*, E.A. Eliseev, A.N. Morozovska*, National Academy of Science of Ukraine

Ferroelectric polarization switching in non-volatile memory and high density data storage devices is governed by a number of nucleation centers that account for the experimentally observed low values of coercive fields. Despite 50 years of research, the microstructural origins of the Landauer paradox (switching fields corresponding to implausibly large nucleation activation energies) are still a mystery. Here, Switching Spectroscopy Piezoresponse Force Microscopy (SS-PFM) is developed as a quantitative tool for real-space mapping of polarization dynamics in ferroelectrics. SS-PFM is an extension of PFM spectroscopy that involves the acquisition and analysis of multiple hysteresis curves at every point in an image to extract maps of parameters describing the local switching properties. In nanodots, the non-uniform work of switching was imaged with ~10 nm resolution within 50 nm ferroelectric nanoparticles. In epitaxial lead zirconate-titanate thin film, the spatial distribution of the switching centers is obtained and the components of thermal (variation in depolarization energy of domain wall energy) and field (built-in polarization) disorder are extracted independently. Phase-field modeling of PFM switching yields nearly quantitative agreement between experimentally measured and calculated nucleation biases on the free surfaces and in the vicinity of the in-plane domains. This indicates that switching in PFM is close to the intrinsic thermodynamic limit. Further prospects of SS-PFM studies of ferroelectric devices and nanostructures for information technology are discussed. Research supported by the Division of Materials Science and Engineering, Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, which is managed by UT-Battelle, LLC.

2:00pm **EM-WeA2 Strain-Enhanced Ferroelectrics and Multiferroics Grown by MBE****, ***D.G. Schlom***, Penn State University **INVITED**

Aided by theoretical predictions, we have used epitaxy and the misfit strain imposed by an underlying substrate to enhance the ferroelectric properties of $SrTiO_3$, $BaTiO_3$, and $BaTiO_3/SrTiO_3$ superlattices grown by MBE. The enhancements include shifting the paraelectric-to-ferroelectric transition temperature by hundreds of degrees and maintaining ferroelectricity in $BaTiO_3$ layers as thin as one unit cell in $BaTiO_3/SrTiO_3$ superlattices. The effect of strain on $EuTiO_3$ will also be presented.

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2:40pm **EM-WeA4 Molten Salt Synthesis and Luminescence Properties of Rare-Earth Doped Yttrium Oxide and Rare-Earth Zirconate/Hafnate***, Y. Mao, **J. Dorman**, J.P. Chang*, University of California at Los Angeles

A molten salt synthetic method is described in this work for synthesizing rare-earth doped yttrium oxide ($RE:Y_2O_3$) and rare-earth zirconate/hafnate ($RE_2(Zr_xHf_{1-x})_2O_7$) ($0 \le x \le 1$), since it is one of the simplest, most versatile, and cost-effective approaches available for obtaining crystalline, chemically purified, single-phase powders at lower temperatures and often in overall shorter reaction times with little residual impurities as compared with conventional solid-state reactions. $RE:Y_2O_3$ are promising rare-earth-ion-activated phosphor materials with wide applications including amplifiers, lasers, waveguides, X-ray imaging, bioimaging, and field emission or electroluminescent displays due to their luminescent characteristics and stability in high vacuum. $RE_2(Zr_xHf_{1-x})_2O_7$ are of great interest in recent years for their possible applications as high-temperature heating elements, oxidation catalysts, thermal barrier coatings, nuclear waste hosts, and host materials for luminescence centers. The as-prepared nanoparticles have sizes around 100 nm for $RE:Y_2O_3$ and around 30 nm for $RE_2(Zr_xHf_{1-x})_2O_7$. They are thoroughly characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microsecopy (TEM), high resolution TEM (HRTEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and UV-vis spectroscopy to delineate the structure and composition of these nanoparticles. Their room temperature luminescent properties (photoluminescence and catholuminescence) are measured as a function of the particle size and distribution. In order to process these materials for device fabrication, they are made water soluble by surface modification of these nanoparticles with DMSA (2,3-dimercaptosuccinic acid). We will discuss the effect of these nano-coatings on the optical properties of the nanoparticles.

3:00pm **EM-WeA5 Thermoelectric Properties of Concentration Graded Bulk Co-Doped TiO_2***, **N. Nguyen**,* University of Washington*, A. Yamamoto,* Advanced Institute for Science and Technology, Japan*, D. Kukuruznyak, T. Chikyow*, National Institute of Materials Science, Japan

There has been a recent increased interest in using segmented thermoelectric elements to improve the performance of the thermoelectric devices. Concentration graded of dopants in the oxides can be regarded as a segmented component composed of a single parent based material. In terms of material processing and operating temperature, concentration graded oxides is more advantageous, and may result in higher efficiency at elevated operating temperature, especially for bulk thermoelectric devices. In this work, concentration graded n-typed Co-doped TiO_2 synthesized by solid state reaction method by mixing the powder of Ti and Co oxides, followed by hot-pressed under vacuum of $3x10^{-5}$ torr and temperature of 1473 K. The distribution of the Co doping concentration in the graded samples was mapped out by using Energy Dispersive X-ray Fluorescence Spectrometer scanning technique. The 2D X-ray diffraction measurements indicate polycrystalline Co-doped TiO_2 rutile were fabricated. The Current-Voltage characteristics under the presence of the temperature gradient were generated for selected samples by applying a current source in such a way that the thermopower current was suppressed by applied current in the opposite direction. Power factors ($S^2\Sigma$) were then evaluated over a temperature range from 300 K – 800 K. Surprisingly, uniformed Co doping shows parallel declined in both conductivity and thermopower magnitude, whereas graded Co doping enhanced the power factor. This implies the enhancement of the power factor could be related to electron spin entropy effect induced by Co doping to TiO_2

4:00pm **EM-WeA8 Growth and Characterization of Vanadium Dioxide (VO_2) Thin Films Prepared by Reactive Biased Target Deposition (RBTD)***, **K.G. West**, J. Lu, W. Chen, J. Yu, Y. Pei, S.A. Wolf*, University of Virginia

Vanadium dioxide (VO_2) undergoes a well known first order metal to semiconductor structural phase transformation just above room temperature at 341K. The abruptness of the phase transformation from its high temperature tetragonal phase to its low temperature monoclinic phase is accompanied by large changes in its electrical conductivity and infrared transmission characteristics, making it an excellent candidate for sensor and switching applications. Also recently it has been observed that an electric field can induce an abrupt transition and change in electrical conductivity below the phase transition temperature, owing even greater potential for its use in practical devices. The growth of high quality VO_2 thin films can be problematic since several distinct oxide states exist. Growth conditions, such as O_2 flow rate, process pressure, and substrate temperature can highly influence the phase of the growing film. Using a novel growth technique called reactive bias target deposition (RBTD), we have prepared highly oriented VO_2 thin films on Al_2O_3 (0001) substrates at various growth temperatures ranging from 250C-550C. The influence of the growth parameters on the microstructure, and transport properties of VO_2 thin films was systematically investigated. A change in electrical conductivity of 10^3 was measured at 341K associated with the well known structural phase transition (SPT). It was observed that the SPT temperature can be tuned to higher temperatures by mixing VO_2 and other vanadium oxide phases. In addition a current/electric-field induced metal-insulator transition (MIT) was observed at room temperature with a change in electrical conductivity of 8x. The current densities required to induce the MIT in VO_2 are on order of $6x10^4$ A/cm^2. The switching time of the MIT, as measured by high frequency current pulsed measurements, was determined to be roughly 10ns. RBTD utilizes a low energy broad beam ion source that reliably produces a very high density of low energy (5-50eV) inert gas ions. A large negative potential bias is applied to the metal sputtering target. The high density of low energy inert gas ions in front of the sputtering target, seeing a very large potential difference, are accelerated to the target surface at a near normal incidence angle at high enough energies to induce sputtering. A pulsed DC bias is used to avoid target poisoning during reactive processing.

4:20pm **EM-WeA9 Elaboration, Chemical and Electrical Analyses of Intermixed and Nanolaminate HfO_2-Al_2O_3 MIM Capacitor Structures**, ***M. Bonvalot***, *M. Kahn, C, Vallee, C. Dubourdieu, O. Joubert*, CNRS, France

High quality MIM capacitors are seeing increased use in CMOS, BICMOS and bipolar chips. The economic demand for smaller devices directly leads to the request for higher MIM charge storage densities. Therefore new high ? dielectric materials, such as Al_2O_3, Ta_2O_5 and HfO_2, are being evaluated as MIM dielectrics and are or will be used in future applications. Among those materials, it is generally admitted that Al_2O_3 and HfO_2 show good potentials for this purpose. Al_2O_3 exhibits a lower k value but has a larger breakdown field than HfO_2, and thus the simultaneous use of these two materials in a MIM structure may lead to some improved electrical properties. In this work, we investigated the behaviour of nanolaminate and intermixed HfO_2-Al_2O_3 MIM capacitor structures. HfO_2 and Al_2O_3 have both been deposited by Atomic Layer Deposition (ALD) on WSi_x (x=2.3) substrates. Numerous materials stackings have been realised, such as simple HfO_2/WSi_x and Al_2O_3/WSi_x, bilayered HfO_2/ Al_2O_3/WSi_x, sandwiched Al_2O_3/ HfO_2/ Al_2O_3/WSi_x, and nanolaminate Al_2O_3/ HfO_2/ Al_2O_3/ HfO_2/ Al_2O_3/WSi_x, as well as intermixed $(HfO_2)_x$/($Al_2O_3)_{1-x}/WSi_x$ compounds. All these structures were carefully analysed by UV ellipsometry up to 8 eV, and show an overall thickness of 13 nm. ATR and variable angle XPS analyses have been performed for interface analysis. C(V) and I(V) electrical characterizations were also carried out after metallic deposition of top electrodes (Au, Al, Ni, Pt). Comparisons of these measurements are useful for identification of individual contributions to the overall electrical behaviour of the MIM structures. In particular, we studied the gain obtained in the linearity of the C(V) curves and the overall capacitance value of these numerous MIM structures. A detailed discussion will be presented on the multiple advantages of using nanolaminate and intermixed compound structures.

4:40pm **EM-WeA10 Suppression of Metal-Insulator-Metal (MIM) Capacitor Leakage Current in BaSrTiO3 (BST) Dielectrics by Ni Doping : Spectroscopic Studies Changes in Conduction Band Edge Defects States with Ni Doping**, ***H. Seo***, North Carolina State University, *Y.B. Kim*, Hanyang University, Korea, *G. Lucovsky*, North Carolina State University

A significant reduction of leakage current in MIM capacitors in Ni-doped BST dielectrics is reported. Ni-doping increases the breakdown voltage from ~10-12 V to >35 V, and reduces the leakage current by several orders of magnitude,10^2~10^3, as compared to un-doped BST. The conduction mechanism is changed from i) tunneling injection plus Poole-Frenkel transport in un-doped BST to ii) Fowler-Nordheim tunneling in the Ni-doped BST. These decreases are explained by a spectroscopic study of changes in conduction band, and band edge defect states. The large changes in breakdown voltage and leakage current between doped and un-doped BST have been correlated with changes in band edge oxygen vacancy defects detected by spectroscopic ellipsometry (SE). The ¥å$_2$spectrum from the SE measurements on Ni-doped BST is qualitatively different than that from un-doped BST. Changes in conduction band states from 3.5 to 6 eV are assigned to Ni^{2+}/Ni^{3+} transitions, and changes in band edge defect state features between 2.5 and 3 eV due to reduction of Ti^{3+}bonding at O-atom vacancies. In particular, the defect state difference is attributed to charge transfer between Ni^{2+} states, and Ti^{4+}band states, as well as Ti^{3+} pre-existing defect states of the BST host. The band edge vacancy defect is ~0.2 eV shallower in Ni-doped BST and this leads to the significant changes in transport and trapping, accounting for reductions in leakage current, and improved resistance to breakdown in the Ni-doped BST. The study demonstrates that addition of transition metal doping atoms with different valence states than Ti in BST, and/or Zr in other insulating perovskites, can have a significant effect on transport by providing a way to reduce/control leakage current and breakdown. These doping effects will be important in transition metal/rare earth atom complex oxides that have been identified for device applications, not only as high-k capacitors or gate dielectrics, but for ferro-electric devices as well.

5:00pm **EM-WeA11 Comparison Between Film Characteristics and Gas-Phase Diagnostics in Magnetron Sputtering Deposition of Superconducting YBaCuO**, ***K. Fukaya***, *K. Sasaki, J. Gao, T. Kimura, M. Watanabe, M. Inoue, A. Fujimaki*, Nagoya University, Japan, *H. Sugai*, Chubu University, Japan

$YBa_2Cu_3O_{7-d}$ (YBaCuO) thin films are promising materials for high-temperature superconducting integrated-circuit devices. Magnetron sputtering deposition is a useful method for preparing YBaCuO thin films because of the cheaper process cost than pulsed laser deposition and metal organic chemical vapor deposition. This work reports gas-phase diagnostics of magnetron sputtering deposition of YBaCuO thin films. Because of the lack in detailed plasma diagnostics, the precursors for the deposition of YBaCuO films have not been identified yet. In this work, we measured two-dimensional distributions of the densities of Y, Ba, Cu, YO, BaO, and CuO by laser-induced fluorescence imaging spectroscopy. In addition, we adopted two-photon absorption laser-induced fluorescence for measuring one-dimensional distribution of the O atom density. By comparing the results of the gas-phase diagnostics with the properties of YBaCuO films, we identified the deposition precursors for obtaining fine YBaCuO films. A YBaCuO powder target, Ar/O_2 mixture gas and a conventional rf magnetron sputtering source at 13.56 MHz were used in this experiment. The densities of Y, Ba, and Cu atoms were measured with varying the O_2 flow ratio from 0 to 100% at a total gas pressure of 400 mTorr. The Cu density decreased gradually with the O_2 flow ratio from 0 to 100%, which may be due to the decrease in the plasma density with the O_2 flow ratio, resulting in the decrease in the sputtered Cu flux. In contrast, the Ba and Y densities decreased drastically with the O_2 flow ratio, which is due to oxidation reaction in the gas phase. We observed the increases in the YO and BaO densities with the O_2 flow ratio from 0 to 10%, indicating the production of YO and BaO from Y and Ba in the gas phase, while the CuO density was below the detection limit at all the discharge conditions. On the other hand, the O atom density increased with the O_2 flow ratio from 0 to 20% and was saturated at O_2 flow ratios higher than 20%. The O atom density was estimated to be much higher than the Cu density. According to the analysis of YBaCuO films deposited on MgO substrates (670 °C) placed at a distance of 3 cm from the target, fine YBaCuO films with high crystallinity were obtained at O_2 flow ratios from 50 to 70%. Therefore, it is known by the present work that the deposition precursors for obtaining fine YBaCuO films are Cu, YO, BaO, and O.

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+TF+SS-WeA

Photovoltaics, Fuel Cells, and Alternative Energy Materials and Applications

Moderator: J.S. Lewis, RTI International

1:40pm **EN+TF+SS-WeA1 ENABLE-based Low Temperature Growth of In-rich InGaN Films**, ***T.L. Williamson***, *M.A. Hoffbauer*, Los Alamos National Laboratory, *N. Miller, R.E. Jones, K.M. Yu*, Lawrence Berkeley National Laboratory, *P. Flanigan, J. Wu*, University of California, Berkeley, *J.W. Ager, Z. Liliental-Weber, E.E. Haller, W. Walukiewicz*, Lawrence Berkeley National Laboratory

The different optimum growth temperatures for the group III-nitride compounds (e.g. GaN >900C and InN ~550C) make the growth of In-rich and fully compositionally graded InGaN films by MOCVD or MBE a considerable technological challenge. Recently, energetic neutral atomic-beam lithography & epitaxy (ENABLE) has been developed at LANL that makes possible isothermal low-temperature growth of high-quality GaN and $In_xGa_{1-x}N$ alloys over the entire composition range (0<x<1). ENABLE uses a large flux of neutral nitrogen atoms to activate surface chemical reactions, thereby mitigating the need for high substrate temperatures and allowing the growth of high quality III-nitrides at substrate temperatures far below those of other conventional techniques (<600C) at rates exceeding 2 microns/hr. We will present recent results for ENABLE-grown InN and In-rich InGaN showing spectroscopic, X-ray diffraction, Rutherford backscattering spectrometry (RBS), transmission electron microscopy, and Hall effect measurements to assess the thickness, composition, crystalline quality, and optical and electrical properties of the films. InN films show intense luminescence at the bandgap of ~0.7 eV with electron mobilities exceeding 700 cm^2/ V$^{\cdot}$sec. We will also present characterization results for compositionally graded films grown from pure GaN and grading to InN and from pure InN and grading to GaN. These results establish ENABLE as a new technique uniquely capable of growing InGaN films of widely varying composition including compositionally graded InGaN films and InN/GaN heterostructures.

2:00pm **EN+TF+SS-WeA2 Tandem-Junction Solar Cells using BeTe Buffer Layers for AlGaAs Molecular Beam Epitaxy on Silicon Substrates**, ***K.P. Clark***, *E. Maldonado, F. Amir, W.P. Kirk*, University of Texas at Arlington

Monolithically-stacked tandem-junctions allow solar cells with conversion efficiencies above the single-junction limit. An optimal bandgap combination of 1.7 eV and 1.1 eV has a theoretical efficiency above 30% for a series-connected cell. Aluminum gallium arsenide epitaxially grown on silicon is a natural implementation, but has long-standing crystal-quality challenges due to lattice mismatch, thermal expansion mismatch, and island growth of AlGaAs. We report investigations of AlGaAs molecular beam epitaxy on prelayers of the wide-bandgap II-VI compound beryllium telluride BeTe on arsenic-passivated silicon. AlGaAs is nearly lattice matched to BeTe but has a strong tendency for island formation, which is suppressed by low-temperature growth initiation. $Al_{0.15}Ga_{0.85}As$-GaAs multiple quantum-well p-i-n junction structures were processed and characterized electrically under illumination. The short-circuit photocurrent J_{SC} and open-circuit voltage V_{OC} for the Si/BeTe based junction approach within 15% and 30% respectively of those for a similar junction grown on a GaAs substrate. We report techniques for initial AlGaAs growth including solid-phase epitaxy, BeTe termination, and germanium adlayers studied using RHEED diffraction, X-ray diffraction, and transmission electron microscopy.

Supported in part by NASA.

2:20pm **EN+TF+SS-WeA3 Gaseous Deposition of Lead Sulfide Nanoparticle/Ti-Phthalocyanine Composite Films**, *I.L. Bolotin, D.J. Asunskis, A.M. Zachary,* ***A.T. Wroble****, L. Hanley*, University of Illinois at Chicago

Composite materials composed of inorganic semiconductor nanoparticles (NPs) dispersed in organic matrices may find use in photovoltaics, photodiodes, nonlinear optical devices, and other applications. This interest arises from the possibility of tuning the optoelectronic properties of the composite by varying the NP size and concentration within the organic matrix. Bulk PbS is a group IV–VI semiconductor with a narrow band gap of 0.41 eV at room temperature. Strong quantum size effects occur for <20 nm PbS NPs. Among the other potential advantages of PbS NPs is their high electron affinity, which will enhance charge transfer from an intermingled organic phase. Most of the lead salt NP photovoltaics devices produced to date have been prepared from the solution phase using colloidal techniques. However, gaseous deposition techniques possess certain advantages for the synthesis of nanocomposites: it is inherently suited to film deposition, is compatible with traditional methods of fabricating semiconductor devices, allows control of oxidation during deposition, and it can reduce the agglomeration of NPs. This work demonstrates that gaseous deposition can synthesize a composite film with <5 nm diameter PbS NPs of narrow size distribution embedded within a titanyl phthalocyanine (TiPc) organic matrix. Composite film samples were fabricated here using a cluster beam deposition source combining magnetron DC-sputtering and gas-agglomeration techniques in a fashion similar to that originally developed by Haberland and coworkers. X-ray photoelectron spectroscopy showed that PbS was successfully incorporated into the TiPc matrix during co-deposition. Transmission electron microscopy (TEM) was used measure the size, shape, distribution, and crystallinity of the NPs in these composite films. Soft-landing of PbS clusters into the TiiPc organic matrix allowed the clusters to maintain their three-dimensional structure upon deposition. In the absence of the TiPc matrix, PbS showed the aggregation into much larger, irregularly-shaped particles. PbS NPs appeared homogeneously distributed in the TiPc matrix, with particle spacings of several times the particle diameter. TEM also showed that at least some NPs deposited into TiPc were crystalline. This method also allows for deposition of composite films composed of any evaporable organic and inorganic nanoparticles that can formed by sputtering and reaction within the cluster source.

2:40pm **EN+TF+SS-WeA4 Plastic Bulk-Heterojunction Solar Cells and Near-Infrared Photodetectors**, *G. Li, Y. Yao,* University of California, Los Angeles, *L. Yu, Y. Liang, S. Xiao,* University of Chicago, ***Y. Yang***, University of California, Los Angeles **INVITED**

Polymer based solar cells and photodetectors have tremendous application in harnessing solar energy and photodetection in a cost-effective way. Here we studied the self-organization effect in polymer solar cells and first demonstrated plastic near-infrared photodetectors using low band-gap polymer. The self-organization effect in polymer solar cells based on regioregular poly(3-hexylthiophene) (RR-P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is studied in an evolutional way, with the difference being spin-coating time ts (20 to 80 sec) which controls solvent annealing time (ta) by the solvent residue. Photoluminescence (PL), ultraviolet-visible (UV-vis) absorption spectroscopy, scanning atomic force microscopy (AFM), and grazing-incidence X-ray diffraction (GIXD) were conducted on these blend films and linked to the device performance. In addition to the high performance polymer solar cells, we also demonstrated a fast response near-infrared detector using a new low band gap material. With promising results shown in this presentation, we believe the low band gap materials will open up a new perspective in near-infrared detection.

4:00pm **EN+TF+SS-WeA8 Defect Characterization of CdTe and CdMgTe Solar Cells and Their Correlation to the Device Properties**, ***R.G. Dhere****, D. Young, J. Scharf, A. Duda, B. To, R. Noufi*, National Renewable Energy Laboratory

CdTe solar cells are at the forefront of commercial thin-film solar cells because of the high laboratory efficiencies and relative ease of fabrication. The current losses for these devices are well understood, with very small room for improvement. On the other hand, open-circuit voltage (V_{oc}) of champion devices is much lower than its potential and presents the only path to improve device performance. In this paper, we present our work on the CdTe and CdMgTe devices fabricated by close-spaced sublimation and physical vapor deposition on glass/SnO_2/CdS substrates. The devices are heat-treated in chloride vapor after deposition, in a controlled ambient, in temperature range of 390°-440°C. The treatment results in recrystallization of the samples deposited at low temperature (~400° C) and selective recrystallization at the CdS/CdTe interface in samples deposited at higher temperatures. The post-deposition treatment also improves the electronic properties of the absorber due to reduced defect density and results in improved device performance. Our investigation studies the effect of bandgap variation and defect density within the space-charge region in the absorber on the device properties, particularly V_{oc}. The bandgap of the alloy is varied by changing the alloy composition of CdSTe alloy formed at the CdS/CdTe interface and CdMgTe alloy composition. We examine the bandgap range of 1.45-1.65 eV for the absorber layer. We have varied defect density in the absorber layer by adjusting the substrate temperature and degree of post-deposition chloride treatment. The structural properties of the samples are studied by atomic force microscopy. The devices have been characterized using drive-level capacitance profiling in combination with capacitance-voltage analysis, in addition to conventional photovoltaic analysis. We will present the data on the devices with a wide range of performance and investigate the correlation between device parameters and the material properties such as bandgap and defect density. This abstract is subject to government rights.

4:20pm **EN+TF+SS-WeA9 Electron Backscatter Diffraction of CdTe Thin Films - Effects of CdCl2 Treatment**, ***H.R. Moutinho****, R.G. Dhere, C.-S. Jiang, B. To, M.M. Al-Jassim*, National Renewable Energy Laboratory

Electron backscatter diffraction (EBSD) utilizes the electron beam of a scanning electron microscope (SEM) to investigate the crystallographic orientation of materials with high spatial resolution. In EBSD, some of the electrons of the SEM beam are diffracted by the crystalline planes of the sample and collected by a detector, where they form a pattern of Kikuchi lines. These patterns are characteristic of the crystal structure and orientation, and they are collected while the electron beam is being scanned, forming maps of crystallographic orientation. In contrast to X-ray diffraction, which gives the crystallographic orientation of a macroscopic volume of the bulk sample, EBSD provides the individual orientation of volumes with nanometer dimensions. To optimize the EBSD signal, the sample must be inclined by about 70° in relation to the electron beam. Consequently, in rough samples, topographic features shadow some of the diffracted electrons from reaching the detector; thus surface preparation is a common requirement. In this work, we describe the surface processing of CdTe thin films deposited by close-spaced sublimation and physical vapor deposition (PVD). Most of the films studied were too rough to produce good EBSD data. Polishing flattened the sample, but created an amorphous layer on the surface, resulting in no diffraction patterns. Ion-beam milling was not as effective in flattening the surface, but removed rough surface features, resulting in high-quality EBSD data. Etching and light ion milling after polishing also produced good results. After optimizing the sample preparation process, we studied PVD CdTe samples after $CdCl_2$ treatment using dipping or vapor processes, with different parameters. We observed a striking difference in the sample microstructure depending on the $CdCl_2$ process and parameters–with grain sizes varying from a few to several dozen micrometers. Our results showed that maintaining a steady source of $CdCl_2$ during the treatment, compared to a fixed amount, results in completely different recrystallization dynamics. We also studied the grain structure from the substrate to the surface by doing EBSD in cross sections of the samples, as well as analyzing samples after different degrees of polishing.

4:40pm **EN+TF+SS-WeA10 Effect of Selenization Temperature on the Grain Growth of Absorber Layer in Ultra Thin CIGS/CdS Solar Cells**, ***S.A. Pethe****, N.G. Dhere*, Florida Solar Energy Center

Solar cells based on $CuIn_xGa_{1-x}Se_2$(CIGS) have achieved efficiencies of 19.5% and therefore are promising candidates for economic, large-scale production. CIGS thin film solar cells having absorber thickness of 2.5 μm have shown good performance. However, CIGS being a direct bandgap material, theoretically efficient cells could be prepared with absorber thickness as low as 0.5 μm. The rationale behind decreasing the CIGS thickness is to reduce consumption of the scarce and costly resource, indium. It has been observed that the performance of the solar cells degrades as the thickness goes below 0.75 µm. 0.9 µm thick absorber layer are prepared at PV Mat Lab facility at Florida Solar Energy Center (FSEC) with device conversion efficiency of 6.26% as measured at FSEC. The reason for this degradation can be attributed to the defects in the bulk of the absorber material. We know from the Movchan&Demchishin zone model that the rate of grain growth becomes almost negligible once the grains with favored texture and orientation have consumed all the unfavorable grains. This results in columnar grain structure with parallel boundaries. Similar grain structure was observed for the CIGS absorber layers with thickness of about 2.5 µm. It was observed that the grains were finer towards the back contact and larger at the surface and as the thickness goes on reducing there is not enough material for the grains to grow and coalesce. This results in smaller grains and so larger grain boundaries. Another factor affecting the grain size is the mobility of the deposited species which can be increased by increasing the annealing temperatures during selenization. But in case of ultra thin film absorber layer the higher temperatures adversely affect the molybdenum back contact layer thus introducing higher series resistance issues. Hence, in case of ultra thin CIGS absorber layer the selenization time - temperature profile needs to be optimized to obtain a favorable columnar grain structure. The material characterization of the different absorber layers will be carried out using scanning electron microscopy and transmission electron microscopy. The absorber layers would be further fabricated on to complete the device and current-voltage characteristics would be carried out to understand the effect of different temperature-time profiles on the device parameters such as open circuit voltage, short circuit current, fill factor and finally the conversion efficiency.

5:00pm **EN+TF+SS-WeA11 Thin Film Epitaxial Growth of CuInSe$_2$ Bicrystals for Grain-Boundary Studies**, ***A.J. Hall***, *D.N. Hebert, A. Rockett*, University of Illinois at Urbana-Champaign

Photovoltaics based on CuInSe$_2$ and related materials have the highest performance of any thin film devices. The nature and role of grain-boundaries in CuInSe$_2$ devices is currently poorly understood. Previous studies on the influence of grain-boundaries in Cu(In,Ga)Se$_2$ devices have shown that they exhibit little to no detrimental effect on photovoltaic device performance. Polycrystalline CuInSe$_2$ devices currently outperform single crystal CuInSe$_2$ devices. Past studies have been focused on average electrical properties or local surface electrical measurements for observation of the influence of boundaries on film properties. Since polycrystal devices have crystal sizes on the order of 1 micron, optoelectrical measurements are difficult. In order to alleviate these difficulties, a single high-angle grain-boundary in epitaxial CuInSe$_2$ has been grown on a GaAs bicrystal substrate using a hybrid sputtering and evaporation technique. Electron backscatter diffraction and x-ray diffraction show that film growth is epitaxial across all boundaries (high-angle and twin) in the bicrystal substrates. Atomic force microscopy, profilometry, and focused ion beam cross-sectioning results indicate that surface polarity and termination have a strong influence on film thickness and morphology. Near grain boundary morphology suggests mass transport leading to boundary migration is occurring. It is proposed that high surface energy anisotropy (on the opposing $\{111\}_{A,B}$ surface facets) motivates mass transport during the growth of CuInSe$_2$ at crystal boundaries.

Exhibitor Workshops

Room: Exhibit Hall - Session EW-WeA

Exhibitor Workshops

Moderator: R. Childs, Consultant

3:20pm **EW-WeA6 New Small Dry Vacuum Pump for Scientific and Industrial Applications**, *S. Palmer*, ***K. Caldwell***, Varian, Inc.

The IDP-3 is a compact, high performance dry pump that provides affordable oil-free vacuum and easy system integration, and is suitable for a wide variety of applications. The IDP-3 employs an innovative hermetic design in which the motor and bearings are outside the vacuum space, allowing full isolation of all pumped gases. Delivering a robust pumping speed of 60 l/m and a very low base pressure of less than 250 milliTorr, the IDP-3 provides all the advantages of Varian's patented scroll pump technology in a compact, lightweight, cost-effective package.

3:40pm **EW-WeA7 Preventing The 10 Most Costly Mistakes in Vacuum Pump Operation**, ***C. Long***, FMG Enterprises

Most pump failures are not caused by the pump. They are usually caused by the tool, facilities, or poor maintenance. This short-course is a must for anyone who wants to avoid such costly mistakes. It will be taught from the perspective of a pump owner that wants to reduce overall pump operating expense. Participants will leave with a check-list, and valuable insights relative to each point. As the result of following course recommendations, participants will be able to raise the uptime available on that pump, and also be able to plan ahead of time when the pump will need to be replaced. This will greatly lower the cost of lost product for the pump owner. We will also briefly discuss: - How to choose the correct pump for the application, - What to do during the installation of the pump, - What to look for, and do while the pump is running, - When, and what PM's will need to be done to the pumps, - How to determine when a pump should be pulled for maintenance, repair or replacement, And finally why the pump owner should use FMG to maintain their pumps. What FMG can do for you and how FMG can save your company money. How FMG can partner up with your company and allow your company to concentrate on what it does best. Sample Content: 1. Improper lubrication 2. Incorrect exhaust settings 3. Unsuitable temperatures 4. Failure to properly leak-check the system 5. Oil levels and color 6. Untimely or incomplete maintenance 7. Cooling water flow-rates 8. Misaligned O-rings 9. Wrong pump or blower for the application. 10. Not using Certified pumps and technicians

Magnetic Interfaces and Nanostructures

Room: 619 - Session MI-WeA

Nanomagnetic Imaging and Spectroscopy

Moderator: D. Pappas, National Institute of Standard and Technology

1:40pm **MI-WeA1 L10 Phase FePt Magnetic Force Microscopy Probes for Magnetic Domain Images**, ***S.H. Liou***, *L. Nicholl, R. Zhang,* University of Nebraska, *L. Yuan, D. Pappas,* National Institute of Standard and Technology, *B.S. Han*, State Key Laboratory of Magnetism, China

Selecting an appropriate probe for the sample type is important when imaging magnetic domains using magnetic force microscopy (MFM). We have developed a process for fabricating probes with L10 phase FePt that can image the domain structure of both hard and soft magnetic materials. Commercially available batch fabricated probes with micromachined tips are coated with 5 nm to 30 nm of FePt. After annealing at 650 oC for 1 hour to obtain the L10 phase, the probes are magnetized in a SQUID along a direction 100 from the z-axis. This produces tips with a magnetization direction perpendicular to the sample surface. The resolution of an MFM image is related to the tip-sample distance, which is less than 20 nm for high resolution images. At these distances, the stray field of a hard magnetic sample can be large enough to alter the magnetization direction of the tip, unless the tip has a high coercivity. With our technique, we produce tips with coercivities greater than 1 T—which, as we will demonstrate in this work, is suitable for imaging the domain structure of permanent magnets. Imaging soft magnetic materials presents a different problem; namely, if the stray field of the tip is larger than the coercivity of the sample, the tip will alter the domain structure of the sample—especially at the lift heights necessary for high resolution images. Our process produces tips with a stray field low enough for imaging the domain structure of soft magnetic materials at lift heights less than 20 nm. We have tested our tips on an array of NiFe dots in the vortex state; each element in the array having a diameter of around 600 nm. Since the center of the vortex is easy to move, the stray field from the tip must be small in order to obtain images with an unperturbed vortex center. In this work, we will show images of the dots with an undisturbed vortex in the center of each dot. These results show that our probes are suitable for imaging both hard and soft magnetic materials.

2:00pm **MI-WeA2 Magnetic Structures of Frustrated Square Lattices**, ***L. Gao***, *Z. Gai, S. Retterer, J.D. Fowlkes, J. Shen*, Oak Ridge National Laboratory

Thin films of ferromagnetic magnetic materials with lithographically designed geometries are model systems for the study of artificial spin ice or frustrated systems.[1] In this work, the square lattices, which are composed of four rectangular elements, were fabricated using electron beam lithography and lift-off technique. The frustrated magnetic domain structures of the square lattices were investigated using magnetic force microscope (MFM) and scanning electron microscope with polarization analysis (SEMPA). The magnetic structure of individual permalloy element is dominated by the shape anisotropy. Single domain can be obtained by optimizing the size and the aspect ratio of the element. The lattice spacing and size of elements were changed to investigate the interactions between elements and their effects on the moment configurations. The correlations between the elements decrease with increasing spacing and decreasing size of elements. The temperature and magnetic field dependences of the moment configuration of the lattices will be presented at the meeting. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

[1] R. F. Wang, C. Nisoli, R. S. Freitas, J. Li, W. McConville, B. J. Cooley, M. S. Lund, N. Samarth, C. Leighton, V. H. Crespi, and P. Schiffer, Nature 439, 303 (2006).

2:20pm **MI-WeA3 Time Resolved X-ray Imaging of Magnetic Nanostructures Driven by Spin-transfer Torque**, ***J.P. Strachan****, Stanford Univ., *Y. Acremann,* Stanford Synchrotron Radiation Lab., *V. Chembrolu, X.W. Yu,* Stanford Univ., *A. Tulapurkar,* Stanford Synchrotron Radiation Lab., Stanford Univ., *T. Tyliszczak,* Lawrence Berkeley National Lab., *J. Katine, M. Carey,* Hitachi Global Storage Tech., *H.C. Siegmann, J. Stöhr*, Stanford Synchrotron Radiation Lab., Stanford Univ.

Spin-torque (or spin-transfer torque) is a novel phenomenon involving the transfer of angular momentum from a spin-polarized current to a ferromagnet. There is much excitement in the use of this effect for developing non-volatile, high density magnetic RAM, as well as for DC current-driven microwave oscillators. Indeed, steady-state precessional modes as well as full magnetization reversal of nanoscale magnetic elements driven by spin-torque have been observed. These observations have been via giant magneto-resistance measurements, using a reference "fixed" magnetic layer, which also serves as the spin-polarizer. Given the experimental challenges in probing thin, buried nanomagnets, the detailed magnetic configuration of the element has remained unknown. I describe a high resolution, time-resolved x-ray microscopy technique which provided the first direct images of the nanostructure during the switching process. Motion pictures with 200 ps time resolution and 35 nm spatial resolution reveal that the process is based on the transient formation of a vortex configuration. The vortex moves across the magnetic element, leaving behind a switched magnetization in its wake. A physical understanding of this unexpected mechanism is discussed, as well as the dependence on sample size and shape. It is seen that the sample dimensions are well within the single-domain regime. The highly non-uniform magnetic configuration which is transiently taken is initiated by the presence of the Oersted field, but primarily formed by the spin-torque. It is seen that other non-uniform switching mechanisms may dominate for smaller length scales.

2:40pm **MI-WeA4 Local Detection and Manipulation of Single Spins and Spin-Orbit Coupling at Surfaces**, ***K. Kern***, Max-Planck-Institut für Festkörperforschung, Germany **INVITED**

The spin state of single magnetic atoms and molecules at surfaces is not only of fundamental interest but may play an important role in future atomic-scale technologies. It can be determined via the Kondo resonance by low-temperature scanning tunneling microscopy. The Kondo effect originates from the screening of the spin of a magnetic impurity by the surrounding conduction band electrons and is characterized by a peak in the impurity's density of states near the Fermi level. As a second impurity is brought into proximity, magnetic interactions between the impurities become important and can modify the Kondo resonance considerably. Here, I demonstrate that it is possible to determine the magnetic interaction between single Co atoms adsorbed on a noble metal surface by measuring the modified Kondo spectrum. The results are compared to theoretical predictions of the magnetic interactions between single atoms. Increasing the interatomic distance of a Cobalt dimer from 2.56 to 8.1 Å we follow the oscillatory transition from ferromagnetic to antiferromagnetic coupling. Adding a third atom to the antiferromagnetically coupled dimer results in the formation of a collective correlated state. I will further demonstrate the ability to tune the coupling of individual cobalt adatoms with their surroundings by controlled attachment of molecular ligands. In the second part of the talk I will show that by scanning tunneling spectroscopy it is possible to extract the strength of the spin-orbit coupling in a two-dimensional energy band from the local density of states. The spin splitting of the surface state induces a singularity in the local density of states which can be detected as a distinct peak in the differential conductance spectrum. From the STS spectrum we can determine the Rashba energy as a measure of the strength of the spin splitting. Its detection and imaging are demonstrated for the surface alloys Bi and Pb on Ag(111), which exhibit particularly large spin-split band structures. The giant spin splitting in these systems opens up interesting perspectives in the field of spintronics.

4:00pm **MI-WeA8 Mapping Resonant Dissipative Behavior in Magnetic Nanostructures: The Role of Single Defects**, *S.V. Kalinin, S. Jesse,* Oak Ridge National Laboratory, ***R. Proksch***, Asylum Research

Dissipative dynamics in magnetic materials and nanostructures is directly related to the physics of wall pinning mechanisms and spin-lattice interactions. Understanding these mechanisms on the level of a single pinning center (e.g. dislocation, second phase inclusion, or other micro-structural element) is crucial for progress in magnetic device applications. Here, we report quantitative mapping of magnetic dissipation on a single defect center in single-crystal yttrium-iron garnet (YIG). The image formation mechanism in Magnetic Dissipation Force Microscopy is analyzed in detail, and it is shown that small frequency dispersion in the cantilever transfer function leads to qualitative errors if the Cleveland formula is used. This leads to cross-talk between the domain pattern and dissipation image. The correction algorithms based on (a) direct transfer function calibration and (b) statistical image analysis are suggested. To decouple the dissipation and force gradient signal, we have developed a novel excitation approach in SPM based on an excitation signal having a finite density in a frequency band in the Fourier domain. This band excitation method allows very rapid acquisition of the full frequency response at each point in an image and in particular enables the direct measurement of energy dissipation through the determination of the Q-factor of the cantilever-sample system. The use of standard MDFM and BE-MFM illustrated the presence of ring-type dissipation contrast associated with single defect centers, corresponding to energy loss of ~1 eV/oscillation. The distance dependence of the ring diameter suggests that the dissipation is resonant in nature and corresponds to well defined field magnitude. The crystallographic origins of the defects are analyzed. Similar contrast is observed in other nanomagnetic systems including nanocrystalline iron, and magnetic nanoparticles from magnetotactic bacteria. Research was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

4:20pm **MI-WeA9 Epitaxial Growth of Ultrathin Fe Films on Ni(111) Investigated by LEED and STM**, ***B. An***, *S. Fukuyama, K. Yokogawa*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Recently, the ultrathin Fe films on fcc substrates have attracted a great attention because of its novel magnetic properties, and thus the growth of ultrathin Fe films on Ni(111) has also been investigated by many surface techniques. However, the structures of the Fe films grown on Ni(111) have not yet been characterized in real space. In this study, we characterize the surface structures of ultrathin Fe films grown on Ni(111) at room temperature by LEED and STM. The Fe film grows first at the step edges of the Ni(111) substrate, then grows up on the large terraces of Ni(111) and the Fe films on Ni(111). The first monolayer Fe reveals two-dimensional fcc-Fe(111) on Ni(111). Some equilateral triangular lines consisting of dark spots aligned along the <1-10> direction with a spacing of 0.5 nm are observed on the monolayer Fe and interpreted by the creation of atomic vacancies in the first layer of Ni substrate due to the strain caused by the lattice misfit between the Fe monolayer and the Ni substrate. The second layer Fe reveals a striped structure consisting of parallel stripes running in the <11-2> direction with a spacing of approximately 1.7 nm. Such striped structure is attributed to the stacking fault of the second-layer Fe on the first-layer Fe. Further increasing of Fe films leads to the formation of slender islands running along the <1-10> direction. The growth processes of the ultrathin Fe films are discussed.

Nanometer-scale Science and Technology

Room: 615 - Session NS1+BI-WeA

Biological and Molecular Applications of Nanoscale Structures

Moderator: J. Randall, Zyvex Corporation

1:40pm **NS1+BI-WeA1 Multiplexed DNA and Protein Arrays Printed via Dip Pen Nanolithography**, ***N.A. Amro***, *S. Rozhok, T. Renner, J. Fragala, M. Nelson*, NanoInk, Inc.

Miniaturized nucleic acid in the form of nanoarrays will dramatically enhance the sensitivity, and spatial density of chip-based bio-assays. These nanoarrays will improve applications ranging from point-of-care diagnosis to genomic arrays used in basic research by enabling the development of

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* Falicov Student Award Finalist

next generation screening technologies that are faster, more sensitive, more reliable, and possibly more cost effective than those presently available in the life sciences market. Nucleic acid bioarrays can be printed using Dip-Pen Nanolithography® (DPN®), a new direct-write spotting technology which generates sub-micron sized features of DNA or protein on solid surfaces. This printing technique offers significant advantages over current microarray printing technologies that suffer from poor spot to spot reproducibility in terms of size, shape, and oligonucleotides density, as well as reproducibility across microarray slides. In this talk we report on recent technical advances in patterning DNA and protein patches with submicron dimensions on glass and metal coated substrates, using new commercially available DPN accessories such as multiple pen arrays and microfluidic pen loading which allows performing multiplexed DNA and protein patterning to fabricate arrays with nanoscale registration and high throughput printing. DNA and protein dot features as small as 200 nm in diameter can be routinely generated. DPN patterning of proteins and oligos, as well as screening for their biological activity, will be shown and discussed in detail.

2:00pm **NS1+BI-WeA2 Cell-Surface Interactions: The Extracellular Matrix as Mechanotransducer**, ***V. Vogel***, ETH Zürich, Switzerland **INVITED**

While cells initially respond to the surface chemistry presented on synthetic materials, they rapidly begin to assemble their own matrix. Cells can thereby sense and transduce a broad range of mechanical forces into distinct sets of biochemical signals that ultimately regulate cellular processes, including adhesion, proliferation, differentiation, and apoptosis. But how is force translated at the molecular level into biochemical signal changes that have the potential to alter cellular behavior? The molecular mechanism of fibronectin's (Fn) extensibility within extracellular matrix fibrils is controversial. Does it originate from the force-induced extension of a compactly folded quaternary structure, or from unfolding of fibronectin modules? Clarification of this issue is central to our understanding whether or not the extracellular matrix can act as a mechanotransducer that converts mechanical forces into well regulated biochemical signal changes. Different fluorescence resonance energy transfer (FRET) labeling schemes were used to differentiate between these two models and we quantified how the conformational changes of fibronectin probed by FRET relate to changes of its overall end-to-end extension. The data clearly demonstrate that cells do indeed mechanically unfold fibronectin. The functional implications of the findings are discussed as well as high resolution structural models derived from steered molecular dynamics (SMD) how force might change the functional states of this and other multidomain proteins.

2:40pm **NS1+BI-WeA4 Carbon Nanotube - Chitosan Sites for Direct Electrical Sensing of Biomolecular Events in BioMEMS**, ***S.L. Buckhout-White***, *S.K. Gupta, M.S. Fuhrer, G.W. Rubloff*, University of Maryland

Direct electrical sensing of biomolecular events is highly desirable in bioMEMS applications such as metabolic engineering platforms or biosensor systems. We are pursuing the development and integration of carbon nanotube (CNT) thin film biosensing devices in the microfluidic systems we employ for recreating metabolic pathways for drug discovery. Since these systems exploit chitosan electrodeposition as a spatiotemporally programmable reaction site for biomolecular binding and enzymatic activity, CNT biofunctionalization using chitosan would enable fabrication of the microfluidics environment with embedded CNT devices so that the devices could serve as active sites for biomolecular events and simultaneously read out those events electrically. We have developed integrated CNT devices, for use as conductance elements and/or FET's, and an easily fabricated, reusable microfluidic system using SU8 channels and a PDMS gasket for non-permanent sealing. In addition, we have electrodeposited chitosan, an amine-rich polysaccharide, onto CNT mats exposed as active sites for biomolecular binding down to 1 µm resolution. Since we have already demonstrated that proteins,[1] nucleic acids, and viruses[2] can be conjugated to localized chitosan sites in bioMEMS and retain their biomolecular functionality, we believe the integrated CNT devices are promising for sensing and controlling biomolecular assembly in multi-site bioMEMS networks that recreate metabolic pathways. This work is supported in part by the Robert W. Deutsch Foundation.

[1] Park, J.J., et al., Chitosan-mediated in situ biomolecule assembly in completely packaged microfluidic devices. Lab on a Chip, 2006. 6(10): p. 1315-1321.

[2] Yi, H.M., et al., Patterned assembly of genetically modified viral nanotemplates via nucleic acid hybridization. Nano Letters, 2005. 5(10): p. 1931-1936.

3:00pm **NS1+BI-WeA5 The Study of FET Flow Control and Separation of Proteins in Nanofluidic Channels**, ***Y.-J. Oh***, University of New Mexico, *D. Bottenus*, Washington State University, *D.N. Petsev*, University of New Mexico, *C.F. Ivory*, Washington State University, *S.R.J. Brueck, G.P. Lopez, S.M. Han*, University of New Mexico

We have studied field-effect-transistor (FET) flow control and separation of proteins in a parallel array of nanochannels (100 nm W ×500 nm D), using scanning laser confocal fluorescence microscopy (SL-CFM) and multiple internal reflection Fourier transform infrared spectroscopy (MIR-FTIRS). For fluidic FET, a DC potential is applied to the gate surrounding an isolated mid-section of the channels under longitudinal electric field along the nanochannels. The gate potential controls the surface charge on SiO_2 channel walls and therefore the ξ-potential. Depending on the polarity and magnitude, the gate potential can accelerate, decelerate, or reverse the flow of proteins. We also analyze a pH shift in the nanochannels according to the surface charge modulation and longitudinal electrical field, using Fluorescein as a pH indicator. Our MIR-FTIR analysis shows that Fluorescein dye molecules are hydrogenated and dehydrogenated in response to the gate bias and subsequent pH shift. We demonstrate that the pH shift affects the FET flow control with SL-CFM analysis. A nanochannel device containing multiple gates is used to improve the controllability of protein flow and to introduce a pH gradient along the channels for isoelectric focusing. A different potential is applied to each gate to differentially control the surface charge on the SiO_2 channel walls and to create a pH gradient along the channels. We also generate a pH gradient along the nanochannels, induced by controlled water electrolysis under longitudinal electrical field. The control and separation of proteins, which have different isoelectric points (pI), by the pH gradient along the nanochannels as a function of gate bias and longitudinal electrical field will be further discussed in this presentation.

4:00pm **NS1+BI-WeA8 Microfabricated Cantilever Arrays for Drug Screening Based on DNA-Drug Intercalation**, ***R. Desikan***, Oak Ridge Associated Universities, *H.M. Meyer III, T.G. Thundat*, Oak Ridge National Laboratory

The ability of a cantilever sensor to generate nanomechanical motion from biomolecular interactions can have wide applications in drug discovery. Microfabricated cantilever arrays offer high sensitivity multiplexed detection in real-time in liquid medium. DNA strands when selectively immobilized on one side of the cantilever surface exhibit surface stress variation during interaction with different chemicals. We have used microfabricated piezoresistive cantilever arrays to demonstrate surface stress variation due to immobilization of ssDNA, hybridization and drug interaction that could form the basis for multiplexed detection of chemicals and drugs intercalating with dsDNA. It is shown that immobilization of ssDNA results in a compressive stress while hybridization results in tensile stress. Intercalation between adjacent base pairs results in stiffening, lengthening and unwinding of the double helix, causing it to expand and lose native conformation. Intercalation of chemicals into immobilized dsDNA produces a characteristic oscillatory response pattern. We have investigated the surface stress pattern due to interaction of chemicals such as ethidium bromide and anti-tumor drugs with dsDNA immobilized on cantilever arrays. The dynamic signature pattern can provide new insight on the kinetics and nanomechanics of DNA-drug intercalation. We have used x-ray photoelectron spectroscopy to carry out elemental analysis in order to confirm the presence of the intercalating agent in the DNA. Microfabricated cantilever arrays find potential applications in drug screening, identification of various toxins, and biological sensing.

4:20pm **NS1+BI-WeA9 Nanofluidic System for Investigating DNA-Force and DNA-Protein Interactions**, ***V.R. Dukkipati***, *S.W. Pang*, University of Michigan

Nanofluidic systems are useful in the studies of single-molecule DNA-protein interactions, nanofluidics, and polymer dynamics. DNA is a flexible polymer with a large aspect ratio of 2 nm in width and length in the order of the micrometers. Due to its unique properties, it is ideally suited for investigations using nanofluidic systems for both biological and mechanical characteristics. We present an integrated nanofluidic system, which is applied to study DNA-protein interactions and DNA-force dynamics. In this system, electrodes are integrated in sealed Si nanochannels by PMMA bonding. Cr/Au electrodes are patterned on a 100 µm thick glass followed by PMMA coating and patterning to expose the electrodes. The 100 µm thick glass allows high resolution imaging of DNA at single molecule level. Si nanochannels varying from 350-500 nm in width are sealed with electrodes using PMMA bonding. A 150 µm wide, 1 µm deep microchannel is connected to each of the fluidic ports as an interface to the nanochannels. The microchannel allows the DNA molecules from the inlet port to have an easy access to the nanochannels. The DNA molecules are pumped into the nanochannel array using both hydrodynamic force and electric field. Using the hydrodynamic force, the DNA molecules near the inlet are pumped by evaporation from the outlet port, which is open to atmosphere. Using 100-300 KHz electric field generated by ac voltage applied across the electrodes integrated in the microchannel, the DNA molecules are driven from the microchannel into the nanochannel array. The linear motion generated by the electric field causes the DNA molecules to move in the nanochannels with velocity varying from 5-40 µm/s. This corresponds to a viscous drag force of 0.04-3.80 pN acting on the DNA molecules, assuming the values of viscosity of the water and the radius of the DNA molecules of 0.5 µm in nanochannels. The nanofluidic system is also used to immobilize and stretch T2-DNA molecules using the protein assisted DNA immobilization (PADI) technique. 350 nm wide and 100 nm deep channels are used to immobilize and stretch λ-DNA molecules up to 12 µm long. Further studies will be conducted on the influence of multiple sources of electric field on DNAs in nanochannels.

4:40pm **NS1+BI-WeA10 Plasma Assisted Production of Chemical Nano-Patterns: Study of the Biosensing Efficiency**, *A. Valsesia, **P. Colpo**, I. Mannelli, P. Lisboa, F. Bretagnol, G. Ceccone, F. Rossi*, European Commission - Joint Research Centre, Italy

The next challenge for the development of analytical devices for biological analysis relies on the ability to design advanced surfaces able to interact properly with the biological world. An increase of several order of magnitude of analysis capacity in biosensing devices together with lower detection limits is envisaged, due to the special interactions between the biomolecules and the nanostructured materials. The most important consequences of the nano-structuring of the bio-interacting surfaces is the immobilization of the biomolecular probes in an active state, limiting the non specific adsorption and the optimisation of their binding site accessibility for the bio-recognition of the target molecules. In our laboratory, we have developed alternative fabrication strategies for the creation of chemically nanostructured surfaces by combining Colloidal Lithography and Electron Beam Lithography with Surface Functionalization Techniques such as Plasma Enhanced Chemical Vapour Deposition (PE-CVD) of bio-functional polymers and Self Assembled Molecular Monolayers (SAM). In particular carboxylic functionalized nano-domes in a PEO-like anti-fouling matrix have been produced. We showed that these chemical nano-patterns are able to immobilize proteins selectively in the carboxylic functional nano-domains, leaving the anti-fouling matrix clear Moreover, we have compared the detection performances between uniformly functionalized surface and chemically nano-patterned surfaces when applied as platforms for antigen/antibody interactions. In particular, homogeneous PAA was compared with the PAA nano-areas in anti-fouling matrix previously described. Nano-patterned surfaces showed a considerable enhancement of the immunoreaction efficiency with respect to the non-structured surfaces, demonstrating the capability of nano-patterns to improve the binding site accessibility of the immobilized biological probes.

Nanometer-scale Science and Technology

Room: 616 - Session NS2+EM-WeA

Nanoscale Devices and Nanowires II

Moderator: D.K. Ferry, Arizona State University, F.M. Ross, IBM T. J. Watson Research Center

1:40pm **NS2+EM-WeA1 Real-time Studies of Metallic Nanodroplet Formation and Motion on Semiconductor Surfaces**, ***J.H. Wu**, W. Ye, T. Sun, H.-Y. Chen, K. Thornton, R.S. Goldman*, University of Michigan

Arrays of metallic nanodroplets are of interest for a broad range of applications including magnetic memory arrays, plasmonic waveguides, nanowire growth seeds, and negative index of refraction materials. Although nanometer-sized metallic droplets often form on compound semiconductor surfaces during epitaxial growth, thermal annealing, and/or ion irradiation, the mechanisms of their formation are not well understood. In this work, we are examining the formation and motion of metallic droplets during ion-irradiation of a variety of semiconductor surfaces. We use real-time imaging in a dual-beam focused-ion-beam system followed by quantitative analysis of the instantaneous positions, sizes, and velocities of the droplets in each movie frame. On GaAs and GaSb surfaces, randomly distributed nearly pure liquid-like Ga droplets are observed to form above a critical dose. Subsequent ion beam irradiation results in growth, motion, and coalescence of the droplets. Since droplets are not observed on Si surfaces prepared under similar conditions, the droplet formation is likely associated with the preferential sputtering of group V elements and liberation of Ga from the substrate as it is milled. Under ion beam irradiation, Ga droplet motion is observed, possibly due to Marangoni motion, which is usually driven by a surface tension gradient. Since the Ga droplets are essentially liquid spheres, the weak atomic bonds and droplet shape lead to enhanced sputtering in comparison with the surrounding substrate. The enhanced sputtering at liquid droplets leads to both thermal and surface tension gradients between the droplets and the substrate, thus providing the driving force for droplet motion. Interestingly, a higher droplet velocity is observed on GaSb than on GaAs surfaces, suggesting that droplet motion is dependent on the energetics of the Ga-substrate interface. On GaAs surfaces, most droplets move in a direction opposite to the ion beam scanning direction, presumably due to the FIB-induced thermal gradient on the surface. In addition, the droplet velocity is size-dependent, with higher velocities for larger droplets, suggesting the thermal/surface tension gradients increase with droplet size. The velocity is apparently correlated with the rate of droplet size change, suggesting that a mass transfer/exchange process occurs during droplet motion. This phenomenon is less significant for droplets that have merged with other droplets.

2:00pm **NS2+EM-WeA2 A Periodic Table of Silicon-Metal Nano-Templates for Cluster-Assembled Materials**, ***G.K. Gueorguiev**, S. Stafström, L. Hultman*, Linköping University, Sweden

The structure and bonding properties of MSi_n clusters, containing 1 to 14 Si atoms together with one transition metal atom among 24 different elements: Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ti, Zr, Hf, V, Nb, Ta, Ni, Pd, Pt, Cu, Ag, Au, were studied by first-principles calculations. Some of these clusters are known to have been synthesized. The transition metal atoms work as nucleation sites for MSi_n. We find that species with n =3, 5, 7, 10, 12 are stable and exhibit shapes independent on the metal atom envolved which establishes a systematic behavior for MSi_n. For most metals, due to p-d orbital hybridization, both MSi_{12} and MSi_{10} (the smallest endohedral species) are highly symmetric, exhibiting the shapes of a hexagonal prism (D_{6h}) and of a bicapped tetragonal antiprism (D_{4d}), respectively. For such clusters, we predict similar packing rules, but considerably different electronic properties. Nano-wires (hexagonal nano-cylinders) assembled from MSi $_{12}$are stable and with tunable electronic properties. These attributes suggest MSi_n as building blocks for cluster assembled materials. We have systematized the results on MSi_n by the organization of the transition metals in the Periodic Table.

2:20pm **NS2+EM-WeA3 Sc Silicide Epitaxial Nanowires on Si(001): A Comparison with Rare Earth Silicide Nanowires**, ***J. Nogami**, Y. Chai*, University of Toronto, Canada, *G. Ye, M.A. Crimp*, Michigan State University

Rare earth (RE) metals can form self-assembled silicide nanowires when grown epitaxially on Si(001) substrates. These nanowires form due to an anisotropy in lattice mismatch between the hexagonal form of the silicide and substrate, with extended growth occurring along the direction of low mismatch.[1,2] In this context, the growth of scandium silicides is interesting since Sc_3Si_5 has the same crystal structure as the RE silicides, but with the direction of close match along the c rather than the a axis. This raises the intriguing possibility of growing nanowires than are naturally perpendicular to RE silicide nanowires. The initial stages of Sc silicide growth on Si(001) was studied by scanning tunneling microscopy, transmission electron microscopy (TEM) and atomic force microscopy. The nanostructures can be divided into two classes: tabular rectangular islands with small aspect ratios, and highly elongated nanowires with triangular cross section. Surprisingly, there is no indication that the common growth direction of the nanowires is rotated with respect to RE nanowires. At the same time, TEM shows that the triangular nanowires have a two phase crystal structure, with a Sc rich silicide growing on top of a Si rich silicide. The differences in growth behavior with respect to the RE silicides will be explained in terms of the differences in stable silicide phases seen in the phase diagrams of these systems.

[1] Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, Y. A. Chang, and R. S. Williams, Appl. Phys. Lett. 76, 4004 (2000).

[2] J. Nogami, B. Z. Liu, M. V. Katkov, C. Ohbuchi, and N. O. Birge, Phys.Rev.B 63, 233305 (2001).

2:40pm **NS2+EM-WeA4 Time-resolved X-ray Excited Optical Luminescence Characterization of Si Nanowires***, ***R.A. Rosenberg**, G.K. Shenoy*, Argonne National Laboratory, *P.S.G. Kim, T.K. Sham*, University of Western Ontario, Canada

Due to quantum confinement effects nanostructures often exhibit unique and intriguing fluorescence behavior. X-ray excited optical luminescence (XEOL) provides the capability to chemically map the sites responsible for producing low energy (1-6 eV) fluorescence. By taking advantage of the time structure of the x-ray pulses at the Advanced Photon Source (APS, ~80 ps wide, 153 ns separation) it also possible to determine the dynamic behavior of the states involved in the luminescence. In this presentation we show how this technique can be utilized to understand the XEOL from silicon nanowires (~50 nm diameter). Analysis of the XEOL spectra revealed the presence of three peaks at 475, 540, and 640 nm whose breadth increased with increasing wavelength. To gain insight into the dynamic nature of the luminescence, time-gated spectra were obtained as the x-ray energy was varied through the Si K edge. Data were obtained using 15-140 ns and a 0-10 ns gates. For the long time gate the areas are roughly evenly distributed among each of the peaks. However, in the short time gated data the 640 nm peak is dominant. This clearly demonstrates that the relative lifetime of this state is shorter than the other two. This is in contrast to the conventional wisdom for homo-structured and single component materials, for which the lifetime usually increases with wavelength. By extracting the intensity of each peak as the x-ray energy is scanned thru the Si K edge we are able to demonstrate that the 540 nm luminescence emanates from the Si nano crystallites imbedded in the wire, the 475 nm peak originates from the oxide shell, and the 640 nm peak comes from defects located near the Si-SiO interface.

*Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

3:00pm **NS2+EM-WeA5 Enhancement of CHEI Programming Efficiency Using Extended SixZr1-xO2 Interface Formed by ZrO2 Charge Trapping Layer**, ***G. Zhang**, W.J. Yoo*, Sungkyunkwan Advanced Institute of Nano-Technology, Korea

Channel hot electron injection (CHEI) programming is widely used for NOR Flash memory operations, whose efficiency is determined by both hot electron (HE) injection level and electron capture rate in which an electron excitation and relaxation process is involved.[1] Inelastic phonon scattering is considered as the main mechanism to cause HE relaxation, where HE energy loss rate decays with larger electron/phonon temperature divergence.[2] As a result, electron capture rate of deep traps decays sharply with the increase of HE temperature (Te).[3] We consider that phonon scattering occurs actively at interfacial junction of different layers, where regularity of lattice structure is disturbed. In this work, we investigated capture rate dependent CHEI programming efficiency for different junction widths or phonon temperatures (Tp). It is found that HEs are injected into the gate stack as lucky electrons,[4] resulting in small capture rate or low programming efficiency; instead, warm electrons (WE), which are generated by thermally enhanced F-N tunneling, play a more important role in programming with higher capture rate. In this work, a practical method to effectively enhance programming speed using extended SixZr1-xO2 interfacial junction between tunnel SiO2 and ZrO2 trapping layer in SONOS type Flash memory is proposed. Cross-sectional TEM image shows that the ZrO2 is highly reactive with SiO2 to form a SixZr1-xO2 interface of graded composition over the thickness of ~2 nm. HfO2 has a similar band structure with ZrO2 but a thinner (0.5~0.7nm) interface and Si3N4 has a smaller conduction band energy offset to SiO2. We observed effectively enhanced programming efficiency at various operation temperatures for the devices using a charge trap layer of ZrO2, compared to those using Si3N4 by ~3.2 times and HfO2 by ~2.2 times. Furthermore, ZrO2 demonstrates clear advantages in low-voltage operation and large Vth window over Si3N4 and HfO2, being a very attractive material contender for next-generation NOR Flash application.

[1] B. Govoreanu, et. al., IEDM Tech. Dig., p479, 2006.

[2] W. Cai, et. al., Physical Review B, p8573, 1986.

[3] R. Passler, Solid-State Electronics, p155, 1984.

[4] S. Tam, et. al., IEEE Trans. Electron Devices.,vol.31, n.9, p1116, 1984.

4:00pm **NS2+EM-WeA8 Nano-Structured Surface Fabrication for Higher Luminescent LED by Self-Assembled Block Copolymer Lithography**, ***A. Fujimoto**, K.A. Asakawa*, Toshiba Corporation, Japan **INVITED**

Light-Emitting Diodes (LEDs) are widely used for cell phones, display panels, LCD backlights, traffic signals, and automobile rear lamp. They are expected to be used for automobile head lamps, and interior illumination. Higher luminance LEDs are required for these purposes. The total efficiency of LEDs is determined by the product of the internal quantum efficiency and the extraction efficiency. The internal quantum efficiency has been improved more than 80 %. But, the extraction efficiency remains 10 %, because of the large difference of the refractive index between substrates (n=3-3.5) and the air. Therefore, to improve the extraction efficiency is the key for higher luminance LEDs. In order to improve the extraction efficiency, we fabricated nanostructures having the antireflection and the diffraction effect onto the semiconductor surface. Nanostructures have the cone, cylinder, and the mesa part. Since nanostructures have the cone and the mesa part and the refractive index from the semiconductor to the air changes smoothly within the critical angle, the incident light within the critical angle can be extracted without a loss, and the transmittance increases about 30 % compared with that of the flat surface. Furthermore, since nanostructures have the cylinder and the cylinder has the diffraction effect, the incident light over the critical angle can be extracted as the -1st order light. Nanostructures having two functions can be expected to improve the light-extraction efficiency greatly. Such structures are usually fabricated by electron beam (EB) lithography, but are too costly for mass production. To overcome this challenge, block copolymer lithography was employed. The polystyrene (PS) - polymethyl methacrylate (PMMA) diblock copolymer was used in this study. The PMMA was removed by reactive ion etching (RIE) since the PMMA has a much faster etch rate than the PS by RIE. The gallium phosphide (GaP) substrate was dry-etched by chlorine-based inductively coupled plasma RIE using the remaining PS dots as a mask. The optical extraction efficiency of the substrates with subwavelength columnar structures improved 2.6 times compared to unprocessed flat substrates; the pillars' height was 350 nm, diameter was 130 nm, and pitch was 180 nm. We also manufactured a real LED and increased light emission volume 1.8 times compared with conventional LED at the same energy consumption.

4:40pm **NS2+EM-WeA10 Current-Voltage Characteristic of Organic Molecular Wires by Conducting Atomic Force Microscopy**, ***N.J. Lee**, S.B. Kim, I.C. Hong, S.H. Koo, Y.J. Choi, J.W. Kim, Y.S. Kim, C.J. Kang*, Myongji University, Korea

Using a atomic force microscope (AFM), with conducting cantilever the current versus voltage (I-V) characteristics of difference group substituted carotenedithiol molecules are measured. The molecules are inserted into 1-methylsulfanyl-octadecane monolayer on gold surface, and a Au nanoparticle is attached to each molecule via the protruding thiol group. To measure the current a gold coated AFM probe is used to contact with the molecule through the Au nanoparticle. A self-assembled monolayer of 1-methylsulfanyl-octadecane was analyzed by the surface plasmon resonance, ellipsometry and X-ray diffraction, which were employed to identify suitable preparation conditions of the substrate. The I-V curves of two kinds of carotenedithiol molecules substituted for different end groups appear quite different because of the different electron transport properties, bromo-phenyl substituted group put a crimp in electron transport. The phenyl-substituted carotenoid is significantly more conductive than the bromo-phenyl- substituted carotenoid. In this talk, we'll present the molecular wires possibility. The carotenoid candidate "molecular wire".

5:00pm **NS2+EM-WeA11 Fabrication, Dynamics, and Electrical Properties of Shielded Probes**, ***P.D. Rack**, B.J. Rodriguez, K. Seal, S. Jesse, A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Many biological systems respond to stimili such as electrical bias. The application of naturally occurring local biases in biosystems can be mimicked with an atomic force microscope tip. In order to minimize capillary forces and obtain high resolution images of biosystems, a liquid environment, typically with a high ionic strength, is required. A bias applied via traditional cantilevers will cause electrochemical reactions in the solution. The use of shielded probes may allow biases to be applied locally, and minimize any electrostatic force contribution to the signal being measured, whether the tip is used as an electromechanical probe or a probe of local electric force. In this case, the bias is applied locally and the signal is measured locally, both on the nanoscale. The fabrication of suitable shielded probes requires (a) good dynamic properties of the lever, (b) good insulation everywhere except for the apex, (c) high apex conductivity, and (d) apex geometry consistent with high resolution. In this presentation, we describe a process for fabricating shielded probes, and measure their dynamic and electrical properties. The commercial doped-Si tips were coated with an oxide prior to etching a small via (~ 200nm diameter) with a focused ion beam. Subsequent to the via etch, a tungsten contact was deposited in the via using electron beam induced deposition. The dynamic properties of the fabricated probes, as well as their performance in Piezoresponse force microscopy in ambient and liquid environment and I-V characteristics are discussed. The choice of other coatings or other metal plugs may allow for further improvements, and/or tunable properties. The use of shielded probes may allow precise control over the application and measurement of local fields in solution.

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Plasma Science and Technology

Room: 606 - Session PS1-WeA

Plasma-Wall Interactions

Moderator: E.V. Barnat, Sandia National Laboratories

1:40pm **PS1-WeA1 Real-Time and Wafer-to-Wafer Control Strategies to Address Seasoning of Plasma Etching Reactors[1]**, *A. Agarwal*, University of Illinois at Urbana-Champaign, ***M.J. Kushner***, Iowa State University

Seasoning of plasma etching reactors refers to the deposition of materials on the wafer and non-wafer surfaces of the chamber that change the fluxes of reactants to the wafer. This influence results from changes in reactive sticking coefficients of radicals and ions on surfaces that change the density of gas phase reactants, the removal of materials that add to the reactive fluxes to the wafer and changes in electrical properties. The negative consequences include drift, either during a process or wafer-to-wafer, in etch rates or uniformity of the process. In this paper, we discuss results from a computational investigation of the seasoning of reactors and, in particular, the use of real-time and wafer-to-wafer control strategies to eliminate process drift. These results were obtained using the Virtual Plasma Equipment Model, an implementation of sensors, actuators and control algorithms in the Hybrid Plasma Equipment Model.[2] The demonstration system is Ar/Cl_2 of Si in inductively coupled and capacitively coupled plasmas in which redeposition of etch products on walls and the wafer change reactive sticking coefficients and produce etch blocks. Sputtering of dielectrics in contact with the plasma introduce additional etch-block capable species. The diagnostics include etch rate sensors, optical emission and bias power. Actuators include power supply voltage, gas flow rate and gas mixture. We found that use of real-time-control to stabilize processes during a single etch and wafer-to-wafer control are sometimes complicated by the changing state of the wafer compared to the walls. For example, the wall conditions at the end of the prior wafer and beginning of the next wafer do not necessarily change however the new wafer does not have redeposition products. As such, actuators must be reset for the new wafer. Multiple sensors-and-actuators may be needed to account for the transition between neutral limited to ion limited processes as wall and wafer conditions change.

[1] Work supported by the Semiconductor Research Corporation and National Science Foundation.

[2] S. Rauf and M. J. Kushner, "Virtual Plasma Equipment Model: A Tool for Investigating Feedback Control in Plasma Processing Equipment", IEEE Trans. Semiconductor Manufact. 11, 486 (1998).

2:00pm **PS1-WeA2 Chamber Walls Coatings during Hard Mask Patterning of Ultra Low-k Materials: Consequences on Cleaning Strategies**, ***T. Chevolleau***, LTM, France, *M. Darnon*, LTM-CNRS, France, *T. David*, *N. Posseme*, CEA-LETI-MINATEC, France, *J. Torres*, STM, France, *O. Joubert*, LTM-CNRS, France

Changes in chamber wall conditions (e.g., chemical surface composition) are identified as one of the main causes of process drifts leading to changes in the process performance (etch rates, etch profiles, selectivity, uniformity …). The impact of a metal hard mask on the coating formed on the chamber walls during dielectric etching processes and reactor dry cleaning procedure has been investigated. We have used a technique based on x-ray photoelectron spectroscopy (XPS) to monitor the chemical composition of the layer deposited on an electrically floating sample placed on the top of a patterned wafer exposed to typical plasma processing conditions. By using this simple technique, the Al_2O_3 sample surface (or other chamber walls materials) is, similarly than the chamber walls, bombarded by low energy ions. Since the wafer is simultaneously bombarded by high energy ions, the gas phase is fed by etch products which get redeposited on the electrically floating Al_2O_3 sample and on the chamber walls surfaces. We have patterned porous SiOCH damascene structures using a TiN hard mask. After hard mask opening in a silicon etcher using Cl_2 based plasmas, we have shown that the chamber walls are coated by a thin SiOCl layer containing small concentrations of Ti. After photoresist removal in the same etcher (with an O_2 plasma), the chamber walls coating is oxidized leading to the formation of a mixed SiOx-TiOx deposit. The cleaning strategy to remove this coating from the chamber walls consists in using a two step cleaning procedure: (1) a Cl_2 based plasma (Ti removal) followed by (2) a SF_6/O_2 plasma (SiOCl species removal). During low-k etch in an oxide etcher using fluorocarbon based chemistries, the chamber walls are coated by a fluorocarbon layer containing a significant Ti concentration. We have developed a two step cleaning procedure: (1) a SF_6 plasma to remove the fluorocarbon layer and Ti based species and (2) an O_2 flash plasma (for a short time) to clean up the remaining carbon from the chamber walls.

2:20pm **PS1-WeA3 How Electron Density and Collision Rate Reflect the Properties of Chamber Wall and Substrate in IC Manufacturing**, ***M. Klick***, *L. Eichhorn*, Plasmetrex GmbH, Germany, *R. Benson*, *D. Steckert*, Micron Technologies, Inc.

Chemically active plasmas as every process plasma interact with the driven electrode and chamber wall. The wall and the electrode is heated and material as byproducts and material from the substrate condense preferably at the chamber wall. Without any additional influence, the parameters of the plasma reach an equilibrium, depending on the external parameters of the discharge as RF power. On the other hand the often used assumption that neutrals in a plasma have room temperature is quite questionable. Hence the indirect heating of the gas by the RF power was really underestimated despite this is one of the major reason of the so-called first wafer effect. There are two reason for the gas heating; the collision with fast ions in the boundary sheathes and the heating of chamber wall without proper 'thermal grounding' and a subsequent heating of the gas by the now hot surface of these chamber parts. Some authors have shown a significant increase of the gas temperature up to 1000 K in a RF plasma. The heat transmission resistances depends on the material, surface roughness, cleanliness and contact pressure. We will start at the experimental example of an increase of the surface temperature of the driven electrode at a 300 mm semiconductor production chamber with dual frequency excitation and the characterization of varying the torque of screws used for mounting. The temperature increase is characterized by the decrease of the electron collision rate. The collision rate, provided by the Self Excited Electron Resonance Spectroscopy, depends via the ohmic heating on the density of the neutrals and so finally on the gas temperature. Furthermore we will provide a qualitative discussion of the temperature effects, in particular resulting in a higher weight of stochastic heating mechanisms. The second example is the interaction of of an substrate, here a 300 mm wafer covered by mainly a polymer mask, an the plasma, in particular the electron collision rate. The interaction of plasma physical mechanisms as electron heating the plasma chemistry is analysed in the same way as indicated above.

2:40pm **PS1-WeA4 Surface Reactions of Atomic and Molecular Chlorine on Anodized Aluminum Surface in Chlorine Plasmas**, ***J. Guha****, *V.M. Donnelly*, University of Houston

Surface recombination reactions of Cl atoms on anodized aluminum have been investigated by the "spinning wall" technique in chlorine plasmas. Desorption of Cl_2 formed due to delayed (i.e. Langmuir-Hinshelwood) recombination of Cl atoms on the spinning surface was detected by mass spectrometry, and surface concentrations were measured in-situ by Auger electron spectrometry. Cl recombination probabilities were measured over a wide range of Cl atom flux by varying the plasma pressure and power. Cl_2 desorption was monitored over a time scale of 0.8 to 38 ms after the surface was exposed to the plasma (corresponding to the rotation frequencies of 35,000 and 800 rpm, respectively). The decay of Cl_2 desorption flux is highly non exponential within this time scale. Langmuir-Hinshelwood Cl recombination coefficients (γ_{Cl}) were measured by extrapolating the desorption flux to t = 0. For a typical condition of 5mTorr, 600W Cl_2 plasma the desorption flux was $2.8 \times 10^{15} cm^{-2} s^{-1}$ at t = 0. Absolute Cl atom densities close to the surface were measured by optical emission spectroscopy and Xe actinometry. γ_{Cl} values ranged from 0.01 to 0.1 and were found to increase with increasing power and decrease with increasing total pressure. From the lowest pressure, highest power condition (1.25 mTorr, 600 W) to the highest pressure, lowest power case (20 mTorr, 100 W), the percent Cl_2 dissociation varied from 28% to 6%. With plasma off, Cl_2 also adsorbs on the surface, and desorbs over the same 0.8 - 38 ms time scale. Consequently Cl_2 adsorption competes with Cl adsorption with the plasma on, particularly at high pressure and low power. Physisorbed Cl_2 appears to block adsorption sites on the surface, thereby reducing the recombination probability, as observed. From Auger analysis of the surface during exposure to a 5mTorr, 600W Cl_2 plasma, the surface stoichiometry was found to be $Al_{3.2}Si_{3.3}O_{7.6}Cl$. Auger analysis of the surface at different plasma conditions suggests that less than 10% of adsorbed Cl atoms actually participates in surface recombination.

3:00pm **PS1-WeA5 Impact of Cu Contamination on Chamber Walls on Via-Hole CD Shift in Cu Dual Damascene Etching**, ***H. Hayashi***, *K. Sato*, *K. Yamamoto*, *T. Kaminatsui*, *A. Kojima*, *I. Sakai*, *M. Hasegawa*, *T. Ohiwa*, Toshiba Corporation, Japan

With shrinkage of ULSI design rule, Cu wiring and low-k materials such as SiOC and poly arylene ether film (PAE) have been introduced to reduce RC delay in the metal interconnects. Furthermore, wafer-to-wafer repeatability of etching processes becomes a major concern. Therefore, controlling the chamber wall condition has been widely studied. In the SiOC etching process, fluorocarbon based plasma is used, which forms fluorocarbon film on the chamber walls. Typically, chamber cleaning is performed using oxygen based plasma, which removes the fluorocarbon film. Cu, which is sputtered from the Cu wiring exposed to the plasma during etching, deposits on the chamber walls and possibly remains, even after chamber cleaning. In this report, the influence of this Cu contamination on etch performance is studied. The stacked films of the PAE/SiOC hybrid dual damascene (DD) structure[1] for 45nm- node logic device were sequentially etched in the same chamber (all-in-one process). Wafers with Cu surface which becomes exposed during DD etching were etched, and it was found that the via-hole critical dimension (CD) of the second wafer of a lot decreased by 20 nm compared to the first wafer. However, SiO_2 and resist etch rates did not show any significant change. Then, plasma analyses using optical emission spectrometry with a high resolution of 0.1 nm were carried out to investigate the cause of the via-hole CD shift. It was found that the Cu emission intensity in the plasma of the second wafer was higher compared with the first wafer. This Cu emission intensity increase originated from the Cu deposited on the chamber walls during etching of the first wafer. Then, a

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* PSTD Coburn-Winters Student Award Finalist

wafer was etched after a chamber cleaning process to remove Cu was carried out, and it was found that the via-hole CD was the same as the first wafer. The Cu emission intensity became equivalent to that of the first wafer, also. The Cu emission intensity had a correlation with via-hole CD shift. Thus, Cu optical emission is sensitive to Cu contamination on the chamber walls, and the monitoring of Cu emission is an effective method of controlling the via-hole CD shift.

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[1] A. Kajita et. al., Proc. of IITC (2003) p.9.

4:00pm **PS1-WeA8 Plasma-Wall Interactions in Inductively Coupled Plasma Reactor and a Novel Method for Wall Condition Control**, ***H. Singh***, Lam Research Corporation **INVITED**

Semiconductor technology has been aggressively scaled from micron sized features to 45 nm features over the last three decades . For the upcoming 32 nm technology node, total variation from all sources for a typical gate etch process is expected to be less than 2 nm. In addition, many new materials are being introduced in recent etch stacks, adding to the productivity challenges due to increased likelihood on non-volatile etch by-products on chamber walls. Plasma-wall interactions have significant impact on the chemistry of low pressure (<100 mTorr) plasmas. Therefore, control of chamber wall condition is crucial for achieving the desired process capability. Waferless Auto Cleans (WAC) have been demonstrated as essential in controlling wafer to wafer process repeatability in volume manufacturing above 65nm node. WAC removes etch by-products deposited during the wafer etch, minimizing drifts in chamber condition. However, ensuring no buildup of etch by-products on reactor walls is not sufficient to meet the productivity requirements of sub-65 nm node in many cases. Advanced Chamber Condition Control technology (AC3$^{\text{TM}}$) is a novel method to significantly enhance the productivity of etch systems in volume production. AC3 involves deposition of a thin film on the reactor walls prior to wafer processing, thereby eliminating drift in the wall condition during production. Impact of changes in the wall conditions due to chamber wet cleans, parts aging and variability are significantly reduced, allowing CD control at the nanometer level.

4:40pm **PS1-WeA10 Recombination of Oxygen Atoms on Dynamic Stainless Steel Surfaces**, ***L. Stafford***, *J. Guha, V.M. Donnelly*, University of Houston

We investigated the desorption of O_2 molecules from electropolished stainless steel surfaces following Langmuir-Hinshelwood (L-H) (i.e. delayed) heterogeneous recombination of oxygen atoms, using the spinning-wall technique. In this experimental set-up, a cylindrical section of the wall of an inductively coupled plasma reactor is rotated and the surface is periodically exposed to the plasma, a mass spectrometer, and an Auger electron spectrometer in separate differentially pumped chambers. Measurements can be performed over a wide range of O flux by varying the absorbed power (50-600 W) and total gas pressure before plasma ignition (1.25-20 mTorr). When the substrate is spun with the plasma on, a large increase in the mass spectrometry signals and Auger chamber pressure is observed with increasing rotation frequency. This increase results from O atoms that adsorb on the stainless steel surface when it is in the plasma and then recombine over the ~1-15 ms period probed by changing the rotation frequency. L-H recombination probabilities of O atoms were determined by extrapolating the O_2 signals to t = 0 (i.e. infinite rotation frequency). For example, at an O atom flux of 10^{17} cm^{-2}s^{-1} obtained at 5 mTorr pressure and 600 W plasma source power, we have found a recombination probability of 0.035. This value is lower than those previously reported for O on stainless steel (e.g. 0.07 by Mozetic and Zalar, Appl. Surf. Sci. 158, 263 (2000), and 0.14 by Kiehlbauch and Graves, J. Vac. Sci. Technol. A 21, 660 (2003)). It is, however, similar to those previously obtained for O on anodized aluminum under comparable plasma conditions, where a Si-oxide layer was observed to form on the surface, due to the slow erosion of the quartz discharge tube. In the present study, analysis by Auger electron spectrometry during the recombination measurement also showed that the stainless steel surface became rapidly coated with a Si-oxide layer (Fe:Si:O atomic concentration ratios of ~1:2:5). This suggests that the recombination kinetics of oxygen atoms in this plasma reactor is determined by the coating on the walls, and not as much by the wall materials.

5:00pm **PS1-WeA11 The Effect of Wall Conditions on the Self-Limiting Deposition of Metal Oxides by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, *M.T. Seman, S.F. Szymanski*, ***C.A. Wolden***, Colorado School of Mines

Pulsed plasma-enhanced chemical vapor deposition (PECVD) has been engineered to deliver self-limiting growth (i.e. 1 Å/pulse) of metal oxides such as Ta_2O_5 and Al_2O_3. Pulsed PECVD may serve as a bridge between conventional ALD and PECVD, retaining monolayer control but with potentially much higher throughput. In this process the reactor walls are alternately exposed to atomic oxygen and metal precursors. The degree of adsorption in the latter step can dramatically influence both deposition rates and film quality. The impact of precursor adsorption on the plasma and gas-phase composition in these systems was measured using optical emission spectroscopy and quadrupole mass spectrometry, respectively. It is shown that the time scale for adsorption is much greater than gas-phase residence times. Adsorbed compounds significantly alter the reactor composition, particularly at the initiation of each pulse. As a consequence careful attention must be paid to reactor design and operation in order to control deposition rates and maintain quality.

Plasma Science and Technology

Room: 607 - Session PS2-WeA

Plasmas and Polymers

Moderator: M.A. Creatore, Eindhoven University of Technology, The Netherlands

1:40pm **PS2-WeA1 Activation of Polymer Surfaces by Electron Beam Generated Plasmas**, ***E.H. Lock***, *S.G. Walton, R.F. Fernsler*, Naval Research Laboratory

The activation of polymer surfaces via plasma exposure is one of the most powerful techniques to enhance the bond strength between the polymer surface and molecules, cells and thin films. Even though there are many established plasma techniques for the modification of polymer surfaces, there remain many unresolved questions regarding the most effective use of plasma processing because of the complexity of plasma-surface interactions. In order to guarantee quality and reproducibility of a given plasma process, numerous plasma effects and process parameters need to be taken into account. To ensure the maximum bond strength between a polymer and another material, the chemical and physical changes at the surface need to be well understood. Unfortunately, the conventional plasma sources are limited in their ability to address these problems and the lack of process control leads to problems with efficiency, scalability and material surface damage. Due to its unique characteristics, the electron beam generated plasma system developed at the Naval Research Laboratory allows access to operating conditions not available with traditional plasma methods. This plasma source provides individual control over the plasma parameters including plasma density, ionization region, electron temperature, ion and radical fluxes. Perhaps, the most important advantage of the system is that it minimizes the ion-induced damage to the substrate due to the inherently low plasma potentials. The objective of this work is to study the activation of polystyrene, polyethylene and polypropylene thin film surfaces exposed to plasmas produced in argon and SF6. Argon is inert and should limit surface modification to physical changes through bond breaking. SF6 provides a source of reactive radicals that can directly modify the surface. In both cases a wide range of process parameters was investigated, including pressure, gas flow rate, plasma exposure time, and substrate biasing (to increase ion energy). Ex-situ surface analysis included X-ray photoelectron spectroscopy, atomic force microscopy and various wetting tests are applied to characterize the chemical and physical properties of plasma modified polymer surface.

2:00pm **PS2-WeA2 Impact of Plasma Etching Processes on 193 nm Photoresists: Etch Resistance and Line Width Roughness**, ***E. Pargon***, *J. Thiault, M. Martin*, CNRS, France, *J. Foucher*, CEA-LETI, France, *G. Cunge, O. Joubert*, CNRS, France, *Th. Lill*, Applied Materials Inc. **INVITED**

Successful pattern transfer by lithography and plasma etching requires minimal mask erosion, degradation and roughening. However, going to 193 nm based lithography in manufacturing several years ago brought new issues such as poor etching resistance of the photoresist masks during front end and back end processes. Indeed, the transition from 248 nm to 193 nm exposure sources has introduced significant changes in the composition of the photoresist (PR), including the removal of all aromatic functional groups due to their excessive absorption at 193 nm. Due to these important chemical changes, 193 nm PR not only exhibit poor etch resistance but are also thinner limiting strongly the 193 resist budget. Moreover, it was observed that 193 nm PR present severe surface roughening after plasma etching that can lead to wiggling and striations, impacting directly the resist Line Width Roughness (LWR). The critical issue is that PR degradation during plasma etching processes is possibly transferred into the underlayers, resulting in a polysilicon gate LWR above the requirements of the ITRS (1.4nm at 3σ for the 45 nm technological node). So far there is no real understanding on how different manufacturing operations may impact the resist roughness and its transfer into complex stacks of materials. In this work patterned and blanket 193 nm PR have been exposed to typical plasma etching processes involved in gate stack etching. In this work, we will show first correlations between etch rates (measured by ellipsometry), chemical analyses of the resist surfaces after plasma exposure (FTIR, XPS) and physical modifications on blanket resist substrates (using DSC and AFM), in order to better understand the etching and roughening mechanisms of typical 193 nm resists. The evolution of the patterned resist LWR and its transfer into the underlayer during the subsequent lithography and plasma etching steps are investigated by CD-AFM. We demonstrate that the resist LWR measured before etching is a key parameter in the final polysilicon LWR. Different plasma treatments applied to the 193nm photoresist patterns prior to all the following plasma etching steps can reinforce the 193 nm resist etch resistance and smooth the resist sidewalls thus reducing the LWR of the polysilicon gate. Our results also show that resist faceting induced by the ion bombardment plays a key role in the smoothening or roughening of the resist and pattern sidewalls.

2:40pm **PS2-WeA4 Plasma Etching Performance of Thin Polymeric and Photoresist Films***, N. Vourdas, G. Kokkoris, E. Gogolides*, Institute of Microelectronics, NCSR "Demokritos", Greece

In most cases of plasma processing of polymers, plasma etch rate (ER) is treated as being a constant value throughout the plasma process. However some studies have demonstrated that ER is actually a function of film thickness,[1,2] process time[3] or both. Similar observations have been recorded for the dissolution (development) rate (DR) of polymers, revealing a DR variation vs. film thickness. In this work we present plasma ER measurements via in situ spectroscopic ellipsometry (SE) of atactic (a-), isotactic (iso-) and syndiotactic (syndio-) poly(methyl methacrylate)-(PMMA) and poly(styrene)-(PS) films on Si and SiO2 under high density O2 plasma discharges, and observe variations of ER vs. time and thickness. Based on these findings along with data obtained from the literature we try to identify the reasons for these variations and deduce the key mechanisms controlling the plasma etching performance of thin and ultra thin polymeric films. Three kinds of ER variations are recorded: (a) ER increase (~8%) within the first stages of etching (~first 10 sec), followed by a gradual increase of ~20% until ~120 nm remaining film, (b) ~25% ER decrease after ~120 nm remaining film, and finally (c) ER drastic decrease at the final stages of etching (completion of etching) until ER=0. Variations (a) and (b) occur regardless the initial thickness, while the variation (c) strongly depends on process time, correlates with the surface roughness amplitude, and indicates means to control surface roughness of polymers (maximum surface roughness in this point). For ultra thin polymer films (less than ~100 nm) ER increase (region a) is not recorded; we attribute this to thin-film effects. These variations result in a decreased average ER of ultra-thin films compared to the ER of the thicker ones. These results are of interest both when ultra-thin polymers are used e.g. EUV lithography, chemical nano-patterning etc, or when high surface roughness is needed, e.g. antireflective coatings, super-hydrophobic coating fabrication etc.

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[3] X. Hua, S. Engelmann, G.S. Oehrlein et al, JVST B 2006 24 p.1850

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3:00pm **PS2-WeA5 Fabrication of Organic Polymers with Tuned Properties and Their Correlation to Plasma-diagnostic Parameters***, G. Franz,* University of Applied Sciences, Germany*, D. Voss*, Plasma-Parylene Coating Services

Poly-parylene is one of the rare organic polymers which have passed the FDA criteria as long-term compatible for the human body. Films of the derivates C and N have been deposited applying cvd and pecvd (microwave). By a combined application of plasma diagnostics and surface analysis, is is possible to tailor the properties of the polymer poly-parylene over a wide range. In the border region, the plasma density rapidly falls with growing distance from the wall due to the strong shielding at microwave frequencies. In contrast to the usual expectation, the plasma density decreases with growing pressure for both ambients, argon and parylene. The electron temperature exhibits the expected hyperbolic behavior vs. pressure. Nevertheless, the higher deposition rate is the most significant proof of the higher density of polymer-building species as compared to cvd. As first consequence, in a pulsed plasma the ratio of the time constants of diffusion can be modeled applying the simplest approach proposed by Brown. For same power input, the plasma density in parylene is lower by more than one order of magnitude compared with argon, which is due to numerous other tracks of molecule excitation and electron loss. At the upper energy end, parylene-C definitely behaves as an electropositive gas, main loss of electrons caused by diffusion, whereas at low or medium energies, pressure-independent electron attachment is supposed to become the dominating loss mechanism leading to significantly lower plasma densities as compared to argon. Infrared spectroscopy shows the conservation of the ring structure during the plasma treatment. The contact angle exhibits a relatively flat response with respect to discharge pressure for cvd, stronger dependence for pecvd. The surfaces of the cvd-films are classically hydrophobic and lipophilic. This behavior is less pronounced in the pecvd-films. Films copolymerized with CF_4 are both hydrophobic and lipophobic in character and show very high roll-off angles (super-hydrophobicity). Subsequent plasma treatment with Ar/O_2 significantly reduces the contact angle against water (down to 30^o). The dielectric constant has found to be very low with only a slight increase to low frequencies with nearly the same value at optical frequencies. Compared with previous works, the range for influencing these surface properties has been farther opened.

4:00pm **PS2-WeA8 Study of Plasma-Surface Interactions of Styrene and Vinylpyridine Polymers in $Ar/C_4F_8/N_2$ Discharges***, **R.L. Bruce**, T. Kwon, S. Engelmann, F. Weilnboeck, M. Sumiya, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park*, B. Long, G. Willson,* University of Texas, Austin*, D.G. Nest, J.J. Vegh, D.B. Graves,* University of California, Berkeley*, A. Alizadeh*, GE Electrics Global Research Center

$Ar/C_4F_8/N_2$ gas mixtures are being used for plasma etching low-k dielectric films. It is not fully understood how addition of N_2 affects the polymer surface of an organic masking material in a fluorocarbon-rich plasma environment. Therefore, the effects of N_2 addition in fluorocarbon plasma on polymers containing nitrogen (polyvinylpyridine) and without nitrogen (polystyrene) were investigated. The polymer surface after plasma exposure was analyzed using a number of characterization tools: ellipsometry (etch resistance), atomic force microscopy (AFM) (surface roughness), and x-ray photoelectron spectroscopy (XPS) (chemical composition). Through ellipsometric analysis, we found that the etch resistance was dependent on the steady state fluorocarbon (FC) layer created during plasma etching. With AFM, we have shown that the surface roughness decreased with $\%N_2$. Using XPS, it was found that while the fluorine content in the polymer surface continually decreased with increasing $\%N_2$, the nitrogen content increased until reaching a saturation level. Furthermore, significant differences in etch resistance, surface roughness, and chemical composition were found between polystyrene and polyvinylpyridine. We investigated whether the nitrogen in the polymer enhances the effect of the nitrogen in the plasma during exposure. In addition, we examined the relationship between the reduction of FC film thickness in remote plasma conditions and the enhanced etch rate of polymers in direct plasma conditions.

4:20pm **PS2-WeA9 Advanced Plasma Treatments for Cleaning and Protection of Metal Artefacts***, **A. Milella**,* University of Bari, Italy*, F. Palumbo,* CNR-IMIP, Bari, Italy*, S. Grassini, E. Angelini,* Polytechnic of Turin, Italy*, R. d'Agostino, F. Fracassi*, University of Bari, Italy

In the framework of conservation of cultural heritage, protection of metal artefacts from corrosion and degradation phenomena which take place during burial and /or during storage and exhibition, is of outstanding importance. Restoration procedures must be non-destructive, reversible, they have to respect the integrity of the objects and to satisfy specific requirements for preserving their aesthetic appearance. In this contribution we present the development of a non-destructive and reversible procedure for cleaning and protecting precious archaeological objects, mainly Ag-based alloys, in low pressure plasma. Reference Ag alloy with micro-chemical and micro-structural features similar to ancient artefacts were used for the plasma treatments. To mimic the real artefacts, the specimens have been buried in the archaeological site of Tharros (Sardina, Italy) for 6 months. To accelerate the corrosion degradation 5% of NaCl has been added to the soil, since chlorides play a key role in the degradation of silver alloys during burial. Furthermore, to better mimic the patina present on real ancient artefacts (mainly consisting of AgCl and Ag_2S), the Ag-based alloys were also immersed in a solution of Na_2S. Cleaning of the tarnished specimens was carried out in RF hydrogen plasma. As detected by XRD and EDS analyses, the treatment effectively decreases the thickness of the patina to an extent which depends on the plasma treatment time. The hydrogen plasma removes the chlorides by forming HCl and this is accompanied by the reduction of oxidized silver (Ag^+) to metal silver (Ag^0). The conversion to Ag^0 can represent an advantage of the plasma cleaning with respect to conventional methods, generally leading to removal of silver from the artefact. Furthermore it is important to mention another benefit: existing cleaning methods are based on chemicals with environmental concerns. For protection of the Ag-based alloy from tarnishing, SiO_2-like coatings were deposited from a RF plasma fed with tetraetoxysilane/oxygen/argon mixture and the protective effectiveness was tested by electrochemical Impedance Spectroscopy (EIS) analyses. Results show that serious tarnishing of the coated samples only occurs after 72 h of immersion in 0.1 M Na_2S solution. Chemical (FTIR, XPS) and morphological (AFM, SEM) characterization of the films will be also presented.

4:40pm **PS2-WeA10 Cell Growth on Plasma Deposited Micro- and Nano Patterned Teflon-Like Coatings**, ***P. Favia***, *E. Sardella, F. Intranuovo,* University of Bari, Italy*, P. Rossini,* Plasma Solution Srl, Spin off of the University of Bari, Italy*, R. Gristina,* Institute of Inorganic Methodologies and Plasma (IMIP) CNR, Italy*, M. Nardulli*, University of Bari, Italy

Plasma processes are widely used for biomedical applications.[1] Surface chemistry and morphology of substrates to be used in cell-adhesion and growth experiments can be modified by means of plasma (RF 13.56 MHz) PE-CVD from fluorocarbon feeds. Smooth and nano/micro-structured coatings could be obtained by tuning plasma parameters. Discharges fed with hexafluoropropylene oxide (HFPO) were run in continuous mode, and teflon-like coatings with different roughness values have been obtained by changing the afterglow distance with respect to the gas inlet of the plasma reactor.[2] In our previous work,[3] a study of nano-structured surfaces obtained from C_2F_4 was related to the deposition time. FT-IR, XPS, WCA, AFM and SEM analysis were used to analyze the chemical composition and the morphology of deposited coatings that were obtained by varying the substrate position in the plasma reactor. Nano-structured and flat coatings deposited on PET substrates were coated with a very thin homogeneous plasma deposited teflon-like film from C_2F_4 (6 sccm C_2F_4, 200 mtorr, 100 W, 21 s) to obtain surfaces with different roughness but identical chemical composition, to be used in cell-growth experiments. FT-IR, XPS and AFM data show that the "teflon character" (amount of the CF_2/C1s component) of the coating increases with the afterglow distance, as well as the hydrophobic character and the roughness (R_{RMS} from 1± 0.2 nm to 350±43 nm). AFM images show different coating structures (e.g. nanopitted and cauliflower-like) as a function of the afterglow distance. Two coatings deposited at different positions, thus characterized by different morphology/roughness, have been selected for cell-growth experiments with 3T3 fibroblasts. Cell culture tests showed a different behavior when cell adhesion and growth were compared between nano-structured and flat coatings with the same surface chemistry. Acknowledgements: The MIUR-FIRB RBNE01458S project is gratefully acknowledged for the financial support.

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5:00pm **PS2-WeA11 Studies of Plasma Surface Activation for Adhesion Enhancement of Polymer Materials in Nanotransfer Printing**, ***D.Y. Lee****, G.S. Oehrlein, D.R. Hines,* University of Maryland College Park, *C.M. Stafford, C.L. Soles, D.M. DeLongchamp, E.K. Lin*, National Institute of Standards and Technology

Recently, nanoimprint lithography (NIL) and nanotransfer printing (NTP) have attracted much attention because these techniques can be used to fabricate submicron structures at a lower cost and with higher throughput than conventional photo and electron-beam lithographies. For NTP involving thermoplastic polymer materials, a low processing temperature (below the glass transition temperature (Tg) of the polymers) is attractive to minimize distortion of printed layers and to control volume shrinkage of the polymers. One key factor influencing pattern transfer is the strength of adhesion between a printed polymer layer and a thermoplastic substrate. In this study, we systematically survey the factors controlling the adhesion between two polymer surfaces treated by plasma activation. Plasma treated poly(methyl methacrylate) (PMMA) films were transfer printed onto plasma treated polyethylene terephthalate (PET) substrates using NTP at 80 and 100 °C, 500 psi for 3 min. An inductively coupled plasma (ICP) process employing either O2 or N2 was used for surface activation of the polymers. In addition, we compared direct and remote plasma with gap structure to investigate the effect of ion bombardment on interfacial adhesion. With plasma activated samples, pattern transfer using NTP was possible at temperatures below the glass transition temperature (Tg) of both polymers. The enhancement of the polymer-polymer adhesion has been attributed to terminated functional group generated by the plasma surface activation and it mainly depends on the processing temperature and chemical composition of polymer and plasma chemistry. In-situ ellipsometry was used to measure changes in the refractive index and the thickness of the surface modified layer. Atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) measurements were performed on the plasma treated polymers immediately after treatment to minimize contamination effects due to atmospheric exposure. Surface energy and water contact angle of the modified films were also measured. Adhesion was evaluated both from a wedge test and from the NTP transfer efficiency, i.e., the aerial % of PMMA film successfully transferred to the PET substrate.

Surface Science

Room: 608 - Session SS1-WeA

Reactions on Metal Surfaces

Moderator: A.J. Gellman, Carnegie Mellon University

1:40pm **SS1-WeA1 Thermally Induced Oxidation and Decomposition Products from NCO /Cu(001)**, ***E.Z. Ciftlikli****, A.V. Ermakov, J. Lallo, S. Rangan, I.G. Shuttleworth, E.Y.-M. Lee, B.J. Hinch,* Rutgers, The State University of New Jersey*, S.D. Senanayake*, Oak Ridge National Laboratory

We report on high-resolution quantitative XPS studies, and complementary NEXAFS and TPD studies of adsorbed isocyanate (NCO) species on Cu(001). Adsorbed NCO can be prepared by room temperature dissociative adsorption of isocyanic acid (HNCO).[1] XPS and NEXAFS confirm that, following hydrogen desorption, solely NCO remains. This is stable to at least 473K. However this species is prone to oxidation from any coadsorbed atomic oxygen. At temperatures as low as 373K, quantitative XPS results indicate CO_2 desorption, while the surface N concentration is conserved. NCO oxidation to adsorbed nitrogen and CO_2, continues until the atomic oxygen is depleted. This chemistry, while observed over a wide range of initial O surface coverages, is however modified in the presence of CN coadsorbates. We have also prepared NCO containing surfaces, through room temperature O_2 and C_2N_2 exposures. Under these conditions, conversion of O and adsorbed CN, to NCO, is substantial though not complete, i.e. the resulting surface hosts NCO, CN and O species. These surfaces, on annealing to 373K again demonstrate N atom production but now also, in large part, CO desorption. This apparently direct NCO decomposition, to $N_{(a)}$ and CO, is observed only in the presence of coadsorbed $O_{(a)}$ and $CN_{(a)}$. At temperatures in excess of 573K, another thermally activated process is observed that is in common to both isocyanate containing surface types; i.e. those prepared with HNCO exposure or O_2 + C_2N_2 exposures. In this latter process any coadsorbed CN appears to be only a passive bystander. We discuss possible mechanisms for these thermally activated reactions, and implications of these chemistries on other more catalytic surfaces commonly used for NO_x reduction.

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2:00pm **SS1-WeA2 Nano-Structural Information Carried by Desorbing Products; Surface-Nitrogen Removal and Angular Distributions**, ***T. Matsushima***, Hokkaido University, Japan **INVITED**

Angle-resolved (AR) product desorption analysis assigns active surface species directly emitting products. Its application is limited to products with hyper-thermal energy. This paper delivers the analysis of surface-nitrogen removal processes in both the thermal decomposition of adsorbed N2O and steady-state NO reduction on Rh(100), Rh(110) and Pd(110), in which desorbing nitrogen holds high kinetic energy. In the thermal decomposition of N2O(a) on Rh(100), N2 desorption shows two peaks at around 85 K and 110 K. At low N2O coverage, the desorption at 85 K collimates at about 66 degrees off normal toward the [001] direction, whereas at high coverage, it sharply collimates along the surface normal. In the steady-state NO+D2 reaction on Rh(100), the N2 desorption preferentially collimates at around 71 degrees off normal toward the [001] direction at 550-700 K, whereas it collimates predominantly along the surface normal at higher temperatures. At lower temperatures, the surface nitrogen removal in the NO reduction is due to NO(a)+N(a) to N2O(a) to N2(g)+O(a), whereas, at higher temperatures, the associative desorption of nitrogen adatoms is predominant. This NO reduction mechanism is also operative on Rh(110) and Pd(110) with different contributions from the two pathways. The emission angle of nascent N2 is controlled by the orientation of adsorbed N2O and the collimation angle of desorbing N2 is also affected by co-adsorbed species. In the steady-state N2O+D2 reaction on Rh(110), the N2 desorption collimates closely along the [001] direction (close to the surface parallel) below 340 K and shifts to ca. 65 degrees off normal at higher temperatures. In the reduction with CO, the N2 desorption collimates along around 65 degrees off normal toward the [001] direction above 520 K, and shifts to 45 degrees at 445 K with decreasing surface temperature. In this temperature range, adsorbed CO increases and scatters the product N2.

2:40pm **SS1-WeA4 Reactivity of Atomic Oxygen on Gold Surfaces**, ***J.L. Gong********, *R.A. Ojifinni, J.M. White, C.B. Mullins*, University of Texas at Austin

The reactivity of atomic oxygen on Au(111) has been investigated by employing molecular beam scattering and temperature programmed desorption (TPD) techniques under ultrahigh vacuum (UHV) conditions.We demonstrate that ammonia does not dissociate on the clean Au(111) surface but adsorbed O atoms, O_{ad}, facilitate $NH_{3,ad}$ decomposition. The selectivity of the catalytic oxidation of ammonia to N_2 or to NO on Au(111) is tunable by the amount of atomic oxygen precovering the surface. Both N_2 and NO are likely formed via simple recombination reactions (N_{ad} + N_{ad} and N_{ad} + O_{ad}). At low oxygen coverages ($\theta_O < 0.5$ ML) (1 ML of oxygen is defined as 1.387 x 10^{15} atoms/cm^2 and refers to a single atomic layer of close-packed gold), adsorbed ammonia is stripped to NH_x ad which decomposes to form gaseous N_2. At high O_{ad} coverages, NO is formed in a surface reaction between N_{ad} and O_{ad}, but most surface N species involved recombine to form N_2 which desorbs with a peak at ~ 460 K. Higher yields of N_2 can be obtained if the O_2/NH_3 mix is kept NH_3 rich. We also present results of low-temperature CO oxidation and the role of moisture on an atomic oxygen covered Au(111) surface. The effect of atomic oxygen precoverage on CO oxidation was examined at sample temperatures as low as 77 K. Prompt CO_2 production was observed when the CO beam impinges on the sample followed by a rapid decay of CO_2 production in all cases. At oxygen precoverages above 0.5 ML, the initial CO_2 production decreases with increasing oxygen precoverage primarily due to the decrease in CO uptake. CO oxidation at 77 K goes through a precursor mediated reaction mechanism, where CO is in a precursor or trapped state and oxygen atoms are in a chemisorbed state. The role of adsorbed water was studied by using isotopically labeled water [$H_2{}^{18}O$] to distinguish the oxygen species from that used in oxygen atom exposures [^{16}O]. Evidence is presented that shows activated water or OH groups formed from water can directly participate in oxidizing CO on an atomic oxygen covered Au(111) surface.

3:00pm **SS1-WeA5 Abstraction of ^{18}O Atoms Chemisorbed on Pd(111) by ^{16}O Atoms Incident from the Gas-Phase**, ***H.H. Kan***, *R.B. Shumbera, J.F. Weaver*, University of Florida

We investigated the reactions of gas-phase ^{16}O atoms with ^{18}O atoms initially chemisorbed on the Pd(111) surface using direct product monitoring and temperature programmed desorption. We find that $^{16}O^{18}O$ molecules desorb promptly at surface temperatures as low as 100 K during the atom-surface collisions, which suggests that ^{18}O abstraction occurs by a direct reaction with incident ^{16}O atoms. Only about 20% of the initially adsorbed ^{18}O evolves as $^{16}O^{18}O$ during the beam exposures, independent of the surface temperature from 100 K to 500 K. At all temperatures, the $^{16}O^{18}O$ desorption rate initially rises to a maximum and decays thereafter with increasing beam exposure. Above 200 K, a second maximum in the desorption rate also appears after longer exposures, with the intensity of this maximum increasing with increasing surface temperature. We find that the abstraction kinetics is primarily determined by the distribution of oxygen phases that develop on the surface during oxygen uptake from the beam. Specifically, the data suggests that the observed $^{16}O^{18}O$ desorption arises from direct reactions between gaseous ^{16}O atoms and ^{18}O atoms chemisorbed either on the bare metal or on top of a surface oxide, and that the abstraction of oxygen atoms incorporated within both surface and bulk oxides occurs with low probability. As a result, only a fraction of the ^{18}O atoms are abstracted before incorporating into oxide phases during the beam exposure. The second maximum in the $^{16}O^{18}O$ desorption rate is attributed to abstraction of ^{18}O atoms chemisorbed on top of a developing surface oxide. The increase in this rate maximum with increasing surface temperature will be discussed within the context of an exchange process between oxygen atoms within the surface oxide and oxygen atoms chemisorbed on top of the surface oxide, and a kinetic analysis of the exchange will be presented.

4:00pm **SS1-WeA8 An In Situ Investigation of Hyperactive States for CO Oxidation on Platinum Group Metal Catalysts**, ***Y. Cai***, *Z. Yan, K.K. Gath, M.S. Chen,* Texas A&M University, *D.W. Goodman*, Texas A&M Universtiy

The oxidation of carbon monoxide on platinum group metal catalysts has been studied for decades due to its technological importance in pollution control and fuel cells.[1-3] Ru catalysts were found to have dramatically different activities at ultrahigh vacuum compared with elevated pressure conditions. The formation of 1 monolayer (ML) surface oxide layer is believed to give rise to the much higher activity of Ru catalysts under high pressure conditions.[4] On the other hand, at stoichiometric reaction conditions, similar activation energies and kinetic orders were found for supported Pd, Pt, Rh and Ir catalysts at high and low pressure conditions.[3] Recent studies have shown that there are hyperactive states on Pd, Pt and Rh catalysts, with the CO_2 formation rate per metal atom site per second (turnover frequency, TOF) reaching into the thousand's, two orders of magnitude higher than the rate measured at stoichiometric reaction conditions. This hyperactive state takes place on an oxygen-rich surface at a well-defined O_2/CO ratio and specific temperature for each metal. The oxygen adsorption energies for Pt, Pd, Rh and Ru correlate directly with the O_2/CO ratio required to achieve the hyperactive catalytic state. PM-IRAS is used to investigate in situ the surface species under reaction conditions. The thickness and chemical nature of the surface oxygen layer giving rise to the hyperactive state is explored with XPS.

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4:20pm **SS1-WeA9 Imaging of Transition Metal Oxidation and Catalysis**, ***J.I. Flege***, *P. Sutter*, Brookhaven National Laboratory

Transition metals have attracted significant attention because of their high activity in oxidation catalysis. For several materials this activity is due to the formation of thin oxides under reaction conditions. The most prominent example of this type of activation is Ru(0001), which only turns into an excellent low-temperature oxidation catalyst at higher oxygen partial pressures.[1] Despite extensive efforts in characterizing this and other similar systems, a number of fundamental questions remain unanswered, e.g., regarding the initial oxidation mechanism, the nature of oxygen-rich near-surface structures, and their individual catalytic activities. Here we discuss major progress toward understanding both transition metal oxidation and the catalytic activity of the resulting oxygen-rich structures, made possible by a novel spectroscopic imaging technique: dynamic intensity-voltage low-energy electron microscopy (dIV-LEEM). In contrast to IV low-energy electron diffraction (IV-LEED), dIV-LEEM produces spectroscopic stacks of real-space images of a surface as a function of electron acceleration voltage. Hence, the technique combines the real-time nano-imaging capabilities of conventional LEEM with the structural sensitivity of IV-LEED, making it possible to obtain, for instance, local time-dependent IV-LEED characteristics at every image pixel. Combined with dynamic LEED theory, such data can be used to identify nanoscale surface phases, for real-time structural fingerprinting of complex structural transitions, and to explore cooperative effects in surface reactions. Specifically, we establish the pathway of initial oxidation of the 4d late transition metals. The initial oxidation of Ru(0001), for instance, was predicted to proceed via the formation of a thin surface oxide as a precursor to the RuO_2 bulk oxide.[2] Our dIV-LEEM movies show instead that bulk and surface oxides grow simultaneously without transforming into one another. This finding has far-reaching consequences for catalysis, which will be discussed on the basis of real-time dIV-LEEM movies during the catalytic cycle.[3] Strikingly, the coexistence of several nanoscale structures induces cooperative effects that may be visualized and quantified by dIV-LEEM analysis.

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4:40pm **SS1-WeA10 Multisite Lattice-Gas Modeling for Chemisorption and Reaction on Metal(100) Surfaces**, ***D.-J. Liu***, *J.W. Evans*, Iowa State University

A multisite lattice-gas model[1] has been developed to provide a realistic description of the chemisorption of single species (CO, O, etc) on the (100) surface of metals such as Rh, Pd, and Ir. In addition, the model describes more complicated chemisorption and reaction processes for mixed adlayers. Population of various adsorption sites must be incorporated for reliable modeling even for single species on a single surface at higher coverages. For reactions such as CO oxidation in mixed layers, distinct local reaction configurations or pathways can contribute to different peaks observed in the temperature-programmed-reaction (TPR) spectra. Thus, our general multisite lattice-gas model allows populations of different adsorption sites (e.g., bridge, top, and hollow sites) incorporating site-specific binding energy and interactions. Parameters are chosen based on comparison with experimental data and DFT results. In addition, it is necessaary to incorporate very rapid diffusion of the reacting species (with rates many order of magnitude above other rates). We utilize kinetic Monte Carlo simulations to analyze model behavior and to interpret a variety of experimental data (heat of adsorption, TPD, TPR, etc) for the above-mentioned metal surfaces.

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5:00pm **SS1-WeA11 Adsorption and Oxidation of SiH_4 on Pd(111)**, ***D. Kershner***, *J.W. Medlin*, University of Colorado at Boulder

A better understanding of metal-silicon and metal-SiO_2 interfaces would be applicable in many areas of study. Due to the buried nature of these

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* Morton S. Traum Award Finalist

interfaces in applications, they have not been well studied. To study these interfaces, a model system consisting of sub-monolayer coverages of silicon containing molecules adsorbed on single crystal metal surfaces has been investigated, using the metal as the substrate rather than the silicon/silica. In this contribution, we report on a multi-technique surface science investigation of silane adsorption and reaction on clean and O-covered Pd(111). Silane adsorption on Pd(100) and other metals has been studied previously.[1-3] These studies found that silane desorbs dissociatively, producing H adatoms and SiH_X adsorbates at cold temperatures, followed by complete dissocation of the surface SiH_X and the formation of a metal silicide phase at higher temperatures. Studies were performed using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and auger electron spectroscopy (AES). SiH_4 adsorption resulted in the formation of SiH_X species on the Pd(111) surface stable to ca. 200K. Complete dissociation occurs upon heating, however it is unclear if a silicide is formed due to the lack of splitting in the Si LVV AES peak.[4] Coadsorption of SiH_4 and O_2 leads to low temperature oxidation of surface Si atoms, forming a layer of SiO_X. This is characterized by the presence of Si-O bonds in HREELS spectra and an AES feature at 84 eV.[5] CO adsorption has also been used to probe of the effect of the SiO_X layer on Pd surface chemistry. Density functional theory studies have also been performed to investigate the structures formed during surface silicon oxidation.

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Surface Science

Room: 611 - Session SS2-WeA

Oxide Surface Structure I

Moderator: R.L. Kurtz, Louisiana State University

1:40pm **SS2-WeA1 Diffusion of Bridge-bonded Oxygen Vacancies on TiO_2(110)**, ***Z. Zhang***, Pacific Northwest National Laboratory, *Q. Ge*, Southern Illinois University, *S.-C. Li*, University of Texas at Austin, *B.D. Kay*, Pacific Northwest National Laboratory, *J.M. White*, University of Texas at Austin, *Z. Dohnálek*, Pacific Northwest National Laboratory

Since oxygen atom vacancies play a central role in the behavior of oxide materials, determining their properties is widely pursued both experimentally and theoretically. Rutile TiO_2(110) has became a model system for the studies of lattice oxygen defects - bridge-bonded oxygen vacancies (BBO_V's). Despite that, surprisingly little is known about the spatial distribution and/or mobility of these BBO_V sites. As a function of temperature between 340 and 420 K, we report here the first measurements and calculations of the intrinsic mobility of BBO_V's on a rutile TiO_2(110) surface. Under conditions where interference by adsorbates was negligible, isothermal atomically-resolved scanning tunneling microscope images that track individual vacancies in real time show that vacancies migrate along bridge-bonded oxygen (BBO) rows. The hopping rate increases exponentially with increasing temperature with experimental activation energy of 1.15 eV. Density functional theory calculations are in very good agreement giving an energy barrier for hopping of 1.03 eV. In agreement with the theory, the BBO_V distribution determined by analysis of the STM images indicates short-range repulsive interactions between vacancies on a given BBO row. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

2:00pm **SS2-WeA2 Probing the Structures of CeO_x(111) Thin Films and Ceria-Supported Metal Particles with Scanning Tunneling Microscopy**, ***J. Zhou***, *A.P. Baddorf, V. Meunier, S.V. Kalinin, S.H. Overbury, D.R. Mullins*, Oak Ridge National Laboratory

Cerium oxide and ceria-supported metal nanoparticles are important heterogeneous catalysts. They exhibit unique chemical reactivity dependent on Ce oxidation state as revealed by our previous XPS and TPD studies. To elucidate the nature of their reactivity, we investigated their structure and morphology using STM. Reducible (111) oriented thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Our data demonstrate that surface structures of ceria films are dependent on the film thickness and the degree of ceria reduction. Hexagonal superlattice structures consisting of five CeO_2 unit cells coincident with seven Ru unit cells can be produced when the films are two or three layers thick and disappear with the increase of film thickness. DFT calculations were performed to explain the origin of these superlattice structures. Fully oxidized CeO_2(111) film exhibits a fairly low density of point defects due to the formation of O vacancies. However, the number of surface defects increases as the ceria film is reduced. Metal particles (Pd and Rh) were vapor-deposited onto ceria thin films at 300 K. The growth of metal particles was investigated by STM as a function of metal coverage, post-deposition annealing temperatures, as well as Ce oxidation state. The research is sponsored by DOE BES Division of Chemical Sciences, Geosciences, and Biosciences.

2:20pm **SS2-WeA3 Structure and Stability of Cerium Oxide Surfaces in an Oxidizing Environment from First-Principles**, *M. Fronzi, A. Soon*, The University of Sydney, Australia, *B. Delley*, Paul Scherrer Institut, Switzerland, *E. Traversa*, University of Rome "Tor Vergata", Italy, ***C. Stampfl***, The University of Sydney, Australia

Because of its peculiar and desirable properties, cerium oxide, has been the object of intense interest in relation to solid oxide fuel cells (SOFC) as well as to heterogeneous catalysis, e.g., it can effectively reduce NO_x emissions as well as convert harmful carbon monoxide to carbon dioxide. Since it behaves as a good ionic transporter, and at the same time as a good catalyst, cerium oxide finds application both as an electrolyte and as an anode support in SOFCs. In anode reactions, it plays an active part in the catalysis of the fuel cell, and thus it is important to investigate the properties of the oxide surfaces exposed to an anodic fuel cell gas environment (e.g. methane, CH_4). Furthermore, for a particular subclass of fuel cells (single chamber) the anodic side is exposed to oxygen as well as the fuel. For this reasons it is of high importance to understand the behavior of cerium oxide in varying oxygen environments. Using density-functional theory as implemented in the $DMol^3$ code,[1] we investigate the structure and stability of CeO_2 surfaces under realistic conditions using the approach of ab initio atomistic thermodynamics.[2] From calculation of the surface free energy, we obtain the pressure-temperature surface phase diagram. This allows us to identify and predict stable, and potentially catalytically important, structures and stoichiometries under varying pressure and temperature conditions. We investigate many different geometries for the low index (100), (110), and (111) surfaces, including structures containing defects. For a wide range of the oxygen chemical potential we find that the thermodynamically most stable surface is CeO_2(111). For increasingly more reducing conditions, surfaces with oxygen vacancies become more stable, followed by a structure which through significant atomic relaxation, exhibits an interesting morphological transformation into a structure with a Ce_2O_3(0001)-like surface.

[1] B. Delley, J. Chem. Phys. 92, 508 (1990); ibid. 113, 7756 (2000).

[2] K. Reuter, C. Stampfl and M. Scheffler, in Handbook of Materials Modeling, Volume 1, Fundamental Models and Methods, Sidney Yip (Ed) (2005).

2:40pm **SS2-WeA4 Revealing Atomic Structures on Oxide Surfaces with the Dynamic Force Microscope**, ***M. Reichling***, Universität Osnabrück, Germany **INVITED**

Nanostructures on oxides are most important in numerous fields of science and technology. One of the most prominent ones is chemical catalysis where oxides play a major role as support, storage material and in providing catalytically active centres. Dynamic scanning force microscopy (SFM) operated in the non-contact mode is the method of choice for the atomic scale characterisation of oxide surfaces and nanostructures on surfaces. The state of the art in highest resolution dynamic SFM on oxide systems is illustrated for structures on CeO_2(111), TiO_2(110), and Al_2O_3/Ni_3Al(111). Individual atoms and atomic arrangements can be imaged and in some cases a quantitative understanding of atomic contrast formation can be obtained with the help of atomistic simulations. Defects are revealed to play a major role in surface chemical reactions studied at the atomic scale while the dynamic SFM also facilitates the manipulation of molecules on oxide surfaces.

4:00pm **SS2-WeA8 The Use of High-Field Nuclear Magnetic Resonance Spectroscopy to Study the Surface Structure of Poorly Crystalline γ-Al_2O_3 Surfaces**, *J.H. Kwak, J.Z. Hu, D.H. Kim, J. Szanyi,* ***C.H.F. Peden***, Pacific Northwest National Laboratory

γ-alumina, one of the metastable 'transition' alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ-Al_2O_3, and its formation and thermal stability have been and continue to be the subject of a considerable amount of research, including attempts to prepare model surfaces via the controlled oxidation of NiAl alloy single crystals. However, due to the low crystallinity and very fine particle size of γ-Al_2O_3, it is very difficult to apply well-established analytical techniques for determining its surface structures. Of particular importance for understanding the catalytic properties of γ-Al_2O_3, relating its surface structure to the origin of Lewis acidity has been of considerable interest and has been studied by FTIR and solid state NMR spectroscopies, and most recently by theoretical calculations. In this presentation, we report the first use of very high field (21.1T) NMR to identify and quantify surface Al species thought to be responsible for imparting Lewis acidity to the γ-Al_2O_3 surface. In particular, a peak in the NMR spectrum at ~23 ppm with relatively low intensity, can be assigned to 5-coordinated Al^{3+} ions, and can be clearly distinguished from the two other peaks representing Al^{3+} ions in tetra-, and octahedral coordination sites. Spin-lattice ^{27}Al relaxation time measurements clearly show that these penta-coordinated Al^{3+} sites are located on the surface of the γ-Al_2O_3 support. Furthermore, we report the first observation of preferential anchoring of an impregnated catalytic phase onto these penta-coordinated Al^{3+} sites by noting that BaO deposition onto γ-alumina resulted in the loss of intensity of the 23 ppm peak, and that the intensity loss observed was linearly proportional to the amount of BaO deposited. Thus, the results of this study strongly suggest that, at least for BaO, these penta-coordinated Al^{3+} ions are the nucleation sites. The implications of these results, especially with respect to the recent and extensive use of theoretical calculations for determining the γ-Al_2O_3 surface structure, will be discussed.

4:20pm **SS2-WeA9 Ab Initio Studies of Adsorption and Diffusion Processes on α-Al_2O_3 (0001) Surfaces**, ***E. Wallin**, J.M. Andersson, E.P. Münger, V. Chirita, U. Helmersson*, Linköping University, Sweden

Alumina, Al_2O_3, is one of the technologically most important ceramic materials. Due to the existence of a variety of different polymorphs, it finds use in a wide range of applications. Consequently, alumina thin film growth has been studied intensely in the past. However, the mechanisms behind the formation of different phases and microstructures are still poorly understood, especially for physically vapor deposited films. An increased atomic scale understanding of alumina surface processes would thus be an important step towards a more complete understanding and control of the deposition process. In the present work, density functional theory based methods were used to study the adsorption of Al, O, AlO, and O_2 on differently terminated α-alumina (0001) surfaces. The results show, e.g., that several metastable adsorption sites exist on the O-terminated surface, providing a possible explanation for the difficulties in growing α-alumina at lower temperatures, where the energy available for adatom diffusion to the bulk site might be insufficient. Moreover, the results show that Al adsorption in the bulk position is unstable or considerably weakened for completely hydrogenated surfaces, indicating that hydrogen, e.g. stemming from residual water in vacuum systems, might hinder crystalline α-alumina growth. Furthermore, energy barriers for different surface diffusion processes were investigated using the nudged elastic band method, showing, e.g., that the Al surface diffusion barrier is 0.7 eV on the Al-terminated (0001) surface. This is lower than what might be expected for a phase where synthesis at low temperatures is difficult (which is the case for α-alumina), supporting previous experimental studies suggesting the nucleation step of growth to be of crucial importance (see, e.g., Andersson et al., J. Vac. Sci. Technol. A 22, 117 (2004)). The computational results are discussed in the context of alumina growth and provide important insight into how different factors influence the growth and how deposition processes can be optimized in order to synthesize alumina films with desired properties.

4:40pm **SS2-WeA10 Iron Oxide Thin Films on Pd(111) and Pt(111)**, ***L.R. Merte**, J. Knudsen, H.H. Sørensen, R.T. Vang,* University of Aarhus, Denmark, *M. Mavrikakis,* University of Wisconsin-Madison, *F. Besenbacher*, University of Aarhus, Denmark

The Water Gas Shift (WGS) reaction (CO + H_2O -> CO_2 + H_2) plays an important role in the production of clean hydrogen from fossil fuels by reducing the concentration of CO in the reformed gas mixture and increasing the yield of hydrogen. The catalysts currently available necessitate a two-stage WGS process, where a high-temperature reactor is used to obtain sufficient turnover rates and a low-temperature reactor is used to push the equilibrium of the exothermic WGS reaction towards CO_2 and H_2 and thereby achieve higher overall conversion. Proposed systems for on-board hydrogen production to power, for example, vehicle-mounted fuel cells would require a WGS catalyst that is sufficiently active at low temperatures and is robust against degradation and poisoning under intermittent operating conditions. Development of such catalysts is therefore important if this technology is to be implemented. Iron-doped palladium based catalysts have been shown to be interesting candidates in this regard[1], and our goal has been to expand our current understanding of the basic processes occurring in the Fe/Pd system, among which is the formation of iron oxide under WGS conditions. In this study we have synthesized different model systems consisting of thin iron oxide films on Pd(111) and, for comparison, Pt(111) and have shown through scanning tunnelling microscopy (STM) measurements that the morphology of these films depends strongly on the preparation conditions. Furthermore, we have studied the interaction of these films with hydrogen and the structural changes occurring upon reduction. We have also used thermal desorption spectroscopy (TDS) to examine the interaction of CO with these model systems in order to identify any chemical properties unique to the Fe/Pd system that may be relevant for the WGS reaction.

[1] Zhao, S. and R. J. Gorte (2004). "The activity of Fe-Pd alloys for the water-gas shift reaction." Catalysis Letters 92(1-2): 75-80.

5:00pm **SS2-WeA11 Factors Affecting Polarization Dependent Adsorption on Ferroelectric Oxide Surfaces**, *D.B. Li, J. Garra, A. Kolpak, A. Rappe, **D.A. Bonnell***, University of Pennsylvania

Domain specific chemical reactivity has been demonstrated for ferroelectric surfaces in ambient and aqueous environments. To understand the factors that affect polarization dependent adsorption on ferroelectric surfaces, in situ studies in UHV were carried out on $BaTiO_3$ and lead zirconate titanate (PZT) surfaces. Polarization was oriented in situ with a metal coated scanning probe microscope (SPM) tip, surfaces were exposed to CO_2 at various dosages, and adsorption was monitored through its effect on local surface potential. Using SPM, we poled the ferroelectric substrates such that sub-micron meter sized out-of-plane domains terminate the surfaces. Surface potentials of these positive and negative domains were then measured by frequency modulation scanning surface potential microscopy (FM-SSPM). The influence of domain polarization on molecular adsorption was examined by comparing surface potential variation as a function of CO_2 dosages. Positive and negative domains exhibited quantitatively different variations in surface potential. The differences are discussed in terms of possible adsorption mechanisms. The effect of the magnitude of the polarization is examined by comparing results on PZT and $BaTiO_3$ with first principles calculations of surface relaxations and associated adsorption energies. The effect of defects is examined by comparing results on $BaTiO_3$ single crystals before and after UHV annealing to produce oxygen vacancies.

Thin Film

Room: 613/614 - Session TF-WeA

Oblique Angle Deposition

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

1:40pm **TF-WeA1 Fabrication of 3D Heterostructured Nanorod/Nanospring Arrays by Dynamic Shadowing Growth**, ***Y.P. He**, Y.P. Zhao*, University of Georgia

One-dimensional (1D) heterogeneous nanostructures are important building blocks for nanodevice applications. Four basic methods have been employed thus far to fabricate heterogeneous 1D nanostructures: nanolithography, direct chemical reaction, template-directed electroplating, and vapor-based methods. A practical nanofabrication technique to produce heterogeneous nanostructures with arbitrary materials must meet the following criteria: (1) The ability to fabricate heterogeneous nanostructures with arbitrarily selected materials; (2) The ability to control the dimensions and uniformity of the heterogeneous nanostructures; (3) The ability to control the alignment of the heterogeneous nanostructures; (4) The ability to control the interfacial properties of the heterogeneous nanostructures. Here, we demonstrate a simple but versatile method to fabricate three-dimensional heterogeneous nanorod structures by multilayer dynamic shadowing growth (DSG). DSG is based on geometric shadowing effect and substrate rotation in a physical vapor deposition system. By programming the azimuthal rotation of the substrate, aligned nanorod arrays with different shapes can be fabricated. By changing the source materials during the deposition, we demonstrate that complicated heterostructured nanorod arrays, such as Si/Ni multilayer nanosprings,[1] can be easily produced, and they exhibit particular magnetic anisotropic behavior. We also use the DSG technique to design catalytic nanomotors[2] with different geometries that are capable of performing different and desired motions in a fuel solution. Using the shadowing effect, a thin catalyst layer can be coated asymmetrically on the side of a nanorod backbone. Catalytic nanomotors such as rotary Si/Pt nanorods, rotary L-shaped Si/Pt and Si/Ag nanorods, and rolling Si/Ag nanosprings, have been fabricated, and their autonomous motions have been demonstrated in a diluted H_2O_2 solution. We observed that the catalytic decomposition of H_2O_2 on the surface of catalyst generated a propelling force to push the nanorod from the catalyst side with an estimated driving force on the order of 10^{-13} - 10^{-14} N. This fabrication method reveals an optimistic step toward designing integrated nanomachines.

[1] Y.-P. He, J.-X. Fu, Y. Zhang, Y.-P. Zhao, L.-J. Zhang, A.-L. Xia, and J.-W. Cai, Multilayered Si/Ni Nanosprings and Their Magnetic Properties, small 2007, 3(1), 153-160.

[2] Y.-P. He, J.-S. Wu, and Y.-P Zhao, Designing Catalytic Nanomotors by Dynamic Shadowing Growth, Nano Lett. 2007, 7(5), 1369-1375.

2:00pm **TF-WeA2 Effects of Steering and Shadowing in Epitaxial Growth*, J.G. Amar***, University of Toledo **INVITED**

While a variety of surface relaxation processes are usually assumed to determine the surface morphology in epitaxial growth, the deposition process can also play an important role. For example, in the case of unstable metal epitaxial growth, the steering of depositing atoms due to short-range (SR) and long-range (LR) attraction can significantly enhance the surface roughness and mound angle,[1] while for large angles of incidence shadowing can also play an important role. In particular, in recent experiments on grazing incidence Cu/Cu(100) growth,[2] a series of morphological transitions was observed as the angle between the beam and substrate normal was increased, from symmetric to asymmetric mounds at moderate deposition angles, to asymmetric ripples oriented perpendicular to the beam at larger deposition angles, and finally to symmetric pyramids with (111) facets at very large angles. Here we discuss the roles of steering and shadowing in determining the observed surface morphology.[3] We first present results obtained using a simplified model which includes the effects of shadowing but not SR and LR attraction. Our results indicate that many of the features observed in Cu(100) growth, including the existence of a transition from asymmetric mounds to ripples, can be explained primarily by geometrical effects. We also show that the formation of (111) facets is crucial to the development of ripples at large angles of incidence. A second transition to 'rods' with (111) facets oriented parallel to the beam is also found at high deposition angles and film thicknesses. When steering due to SR and LR attraction is included, we find two main effects. In the multilayer regime 'flux-focusing' due to attraction tends to enhance the anisotropy and reduce the critical thickness for the ripple transition. In contrast, near the transition from ripples to rods, sideways attraction tends to stabilize the formation of symmetric pyramids as is observed experimentally. The scaling of the surface roughness and anisotropy as a function of film thickness and deposition angle and the effects of growth temperature and surface relaxation processes such as edge-diffusion on the surface morphology will also be discussed.

[1] J. Yu and J. G. Amar, Phys. Rev. Lett. 89, 286103 (2002).

[2] S. van Dijken et al, Phys. Rev. B 61, 14047 (2000).

[3] Y. Shim and J.G. Amar, Phys. Rev. Lett. 98, 046103 (2007).

2:40pm **TF-WeA4 Mechanisms of Thin Film Growth under Shadowing and Re-Emission Effects*, T. Karabacak***, University of Arkansas at Little Rock **INVITED**

Over the last decades, there has been a continuing interest on the mechanisms of the dynamic growth front morphology of thin films. Several competing mechanisms such as noise, surface diffusion, and shadowing have been well known to play roles in the evolution of surface roughness. Based on these effects, various growth models have been developed within the frame work of dynamic scaling theory in order to predict the evolution of thin film morphology. However, many experimentally obtained surfaces have been realized to be much rougher or smoother than the predictions of these models. Especially in processes where the shadowing effect is important due to the existence of obliquely incident particles (such as in sputter deposition, chemical vapor deposition, and plasma etching), the morphological evolution was smoother for deposition, while it was rougher for etched surfaces compared to the expected effect of shadowing. A recently recognized "re-emission" effect that originates from the non-unity sticking probability of incident particles offers a better understanding of morphological growth process. Non-sticking re-emitted particles can lead to a rough surface during etching and a smooth surface during deposition. It is shown that competing effects of shadowing and re-emission can predict many of the experimental results reported in the literature. It is also proposed that shadowing and re-emission effects can lead to a novel "universality class" of dynamic scaling behavior of the surface roughness.

4:00pm **TF-WeA8 Ripple Growth and - Orientation during Grazing Incidence Deposition*, H. Wormeester, F.L.W. Rabbering, F.G. Stoian, R. Gastel, B. Poelsema***, University of Twente, The Netherlands

Oblique incidence deposition is widely used for the preparation of anisotropic structures in thin films with interesting magnetic or optical properties. We have studied the consequences of oblique incidence deposition for the morphology of the growth-front for a "prototypical" system Cu/Cu(001). According to previous electron diffraction measurements, deposition at grazing incidence leads to the evolution of ripples, oriented perpendicular to the plane of incidence of the atom beam. Here we present new experimental results, obtained with high resolution low energy electron diffraction and STM, for various stages in the formation of the ripples. At grazing incidence, experiments indeed show that initially the ripples are oriented perpendicular to the plane of incidence of the atom beam. At more progressed stages of growth and at very grazing incidence deposition experiments show a deviation from the ripple formation. The ripple formation has also been studied with kMC simulations, which support (or actually predicted) experimentally observed changes in ripple formation at later stages in growth. The relevant activation barriers for intra- and interlayer diffusion processes in these simulations have been tuned to describe quantitatively(!) experimentally observed morphologies in a wide range of temperatures (150-300 K) and coverages (up to 40 ML). An essential role is played by both long and short range attractive interactions between the incoming particle and the substrate. The kMC simulations show a change in ripple orientation from perpendicular to the plane of incidence to parallel to this plane around a coverage of 40 ML at a temperature of 250 K for a deposition angle of 80°. At 230K this orientation transition has been found to occur at a much earlier stage in growth. At more grazing incidence deposition only ripples parallel to the plane of incidence have been found to develop and no change in orientation has been seen for smaller deposition angles. This orientation change is related to the very strong roughening of the growth front for grazing incidence growth and the corresponding heterogeneity of incident flux.

4:20pm **TF-WeA9 Biaxial Texture of Titanium Nitride Thin Films Deposited by Off-normal Incidence Magnetron Sputtering*, D. Deniz, J.M.E. Harper***, University of New Hampshire

We studied the development of crystallographic texture in titanium nitride films deposited by off-normal incidence reactive magnetron sputtering at room temperature. For a deposition angle of 40 degrees from normal, we obtained strongly oriented biaxial textures for a range of deposition conditions using both direct current (DC) and radio frequency (RF) sputtering. Texture measurements were performed by x-ray pole figure analysis of the 111 and the 002 orientations. Typically, we find that the 111 orientation is close to the substrate normal and the 002 orientation is close to the direction of the deposition source, showing substantial in-plane alignment. For example, TiN deposited by DC sputtering at 5% $N_2/(Ar+N_2)$ flow ratio and 2.2 mTorr total pressure showed 111 planes perpendicular to the substrate and 002 planes tilted 55 degrees from the substrate normal and facing the source. However, TiN deposited by DC sputtering at 2% $N_2/(Ar+N_2)$ flow ratio and 1 mTorr total pressure showed 111 planes tilted 18 degrees from the substrate normal but away from the source and 200 planes tilted 35 degrees from the substrate normal towards the source. The strength of biaxial texture decreases as the $N_2/(Ar+N_2)$ flow ratio is increased up to 20%. These results suggest a competition between texture mechanisms related to the substrate normal and related to the deposition direction.

4:40pm **TF-WeA10 Zeno Effect and Step Edge Barrier in Organic Thin Films*, C. Teichert, G. Hlawacek***, University of Leoben, Austria*, **P. Frank, A. Winkler***, Graz University of Technology, Austria

Organic Semiconductors start to enter the market of consumer products as light emitting diodes, solar cells and thin film transistors. For the growth of reliable high quality devices a profound understanding of the processes related to formation of organic thin films is necessary. Here, we present an AFM study on the growth of para-sexiphenyl on a sputtered mica(001) surface. Para-sexiphenyl is a member of the group of small conjugated molecules with a high mobility[1] and the ability to emit blue light.[2] The morphology is characterized by the formation of mounds formed by upright standing molecules. Needle growth competes with the formation of the mounds. However, the characteristic layer distribution of the mounds can be fitted by a Poisson distribution. This shape is related to the Zeno effect known from inorganic epitaxy.[3] The mound shape for different film thicknesses has been analysed. Furthermore, statistical roughness parameters such as rms roughness σ, hurst parameter α and mound separation λ have been evaluated. Growth exponent β and dynamic exponent 1/z can be calculated and agree with the predictions made by the Zeno model. The mound separation λ and the size of the top terrace allow estimating the size of the Ehrlich Schwoebel barrier responsible for the cross-sectional shape of the mounds. Work has been supported by Austrian Science Fund (FWF) National Research Network "Interface controlled and Functionalised Organic Films" (S9707-N08).

[1] T. Birendra Singh, G. Hernandez-Sosa, H. Neugebauer, A. Andreev, H. Sitter, N.S. Sariciftci, Phys. Status Solidi B, 243, (2006) 3329.

[2] A. Kadashchuk, A. Andreev, H. Sitter, N.S. Sariciftci, Y. Skryshevski, Y. Piryatinski, I. Blonsky, D. Meissner, Adv. Funct. Mater. 14 (2004) 970.

[3] T. Michely and J. Krug; Islands, Mounds and Atoms (Springer, Berlin 2004).

Tribology

Room: 617 - Session TR1+MN-WeA

Surfaces and Interfaces in MEMS

Moderator: J.A. Harrison, United States Naval Academy

1:40pm **TR1+MN-WeA1 Glassy-like Behavior of GaAs Nanomechanical Oscillators at Millikelvin Temperatures,** ***S.B. Shim***, *S.W. Cho,* Seoul National University, Korea*, N. Kim, J. Kim,* Korea Research Institute of Standards and Science*, Y.D. Park*, Seoul National University, Korea

We report on the mechanical properties of single crystalline GaAs doubly-clamped beam resonator structures characterized by magnetomotive techniques in millikelvin temperatures. Clean nanomechanical GaAs resonators are realized from a lattice-matched GaAs/InGaP/GaAs heterostructures without plasma etching processing with typical quality (Q) factor of ~ 17,400 at 45 mK with resonance frequency of 15.816 MHz. We find dissipation (Q^{-1}) to have weak temperature dependence ($\sim T^{0.32}$) as compared to Si nanomechanical resonators of similar size ($\sim T^{0.36}$).[1] Furthermore, we find shift in the resonance frequency as function of temperature to be nontrivial with a crossover behavior (i.e. at low temperatures shift in the resonance frequency is positive with increasing temperature and at high temperature ($T > \sim 1$ K), negative). Such observations are similar to those observed in sound attenuation experiments in disordered glass systems.[2] We will also discuss other possible dissipation mechanisms as well as the effect of differing surface conditions and treatments.

[1] G. Zolfagharkhani et al., PRB 72, (2005).

[2] W.A. Phillips, Rep. Prog. Phys. 50, 1657 (1987).

2:00pm **TR1+MN-WeA2 MEMS Tribology in Extreme Environments[1],** ***J. Krim***, North Carolina State Univ.*, M. Aggleton,* Univ. of California at Irvine*, C.J. Brown,* North Carolina State Univ.*, J.C. Burton,* Univ. of California at Irvine*, D.A. Hook,* North Carolina State Univ.*, J. Wenner,* Univ. of California at Irvine*, M.T. Dugger,* Sandia National Labs*, A. Morris,* WiSpry, Inc.*, J.E. Rutledge, P. Taborek*, Univ. of California at Irvine **INVITED**

Microelectromechanical systems, MEMS, have become a remarkably successful technology since the beginnings of MEMS development 30 to 40 years ago. However the overwhelming majority of MEMS are used near room temperature and atmospheric pressure. Consequently there is little empirical data to guide the design of MEMS for use in environments such as space where low pressures and cryogenic temperatures must be tolerated. In addition, it is well known that friction and wear severely constrain MEMS design. MEMS that have sliding contact between surfaces have shorter lifetimes and lower reliability than MEMS that do not. We have measured the characteristics of two microelectromechanical systems, namely a silicon sidewall tribometer and an RF MEMS direct contact switch, at cryogenic temperatures and in ambient gas environments below atmospheric pressure, and report on the tribological issues and possible solutions for operation of MEMS in such extreme environments.

[1] This work has been supported by EXTREME FRICTION AFOSR MURI #FA9550-04-1- 0381, and partially by Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE- AC04-94AL85000.

2:40pm **TR1+MN-WeA4 Performance of RF MEMS Switch Contacts at Cryogenic Temperatures,** ***C.J. Brown***, *J. Krim*, North Carolina State University, *A.S. Morris III*, wiSpry, Inc.

A series of experiments were performed to characterize RF MEMS switch performance under variable pressure, atmospheric conditions and temperature. A vacuum system was constructed allowing for switch operation in cryogenic temperatures and pressures in the miliTorr range. Vacuum environments were chosen to limit stiction failures due to moisture; however the switches encountered bouncing problems at closure for low pressures. Helium and nitrogen were chosen as substitute atmospheres to lower stiction failure rates while circumventing switch bouncing issues. Contact resistance measurements were taken across a temperature range of 77 to 293 Kelvin using both gasses. Results showed no differences in contact resistance due to atmospheric conditions except at cryogenic temperatures. Contact resistance values were observed to be lower at cryogenic temperatures but are orders of magnitude higher than values predicted for constriction resistance in gold asperity contacts. Results obtained across the cryogenic temperature range support the conclusions of previously published work at high temperatures, which asserted changes in contact resistance were due mostly to the presence of thin films on the contacts.[1] Additionally, the data indicates these films are less mobile at cryogenic temperatures. Application of the asperity-heating model indicates contact voltages can applied which selectively disassociate films from the contact surface while not softening the gold asperity contacts. This research is funded by AFOSR MURI Grant No. FA9550-04-1-0381.

[1] B. Jensen, L. Chow, K. Huang, K. Saitou, J. Volakis and K. Kurabayashi, "Effect of nanoscale heating on electrical transport in RF MEMS switch contacts," J. Microelectromechanical Systems, vol. 14, no. 5, pp. 935-946, 2005.

3:00pm **TR1+MN-WeA5 Macro-, Micro-, and Nano-scale Lubrication using Alcohol Vapor: Implications to MEMS.,** *D.B. Asay,* Pennsylvania State University, *M.T. Dugger,* Sandia National Laboratories, ***S.H. Kim***, Pennsylvania State University

Friction, adhesion, and wear are dramatically affected by the environment in which surfaces come into contact. In the case of an alcohol vapor environment, the silicon surface reacts to form an alkoxide. Shearing these surfaces also produces higher weight oligomers. These molecules are continuously replenished in the contact region, drastically reducing wear and friction provided that the alcohol vapor pressure is near or above the vapor pressure required for monolayer coverage. At these conditions, the lubricating layer protects the silicon surfaces with little to no wear observed. Tribological properties are reported at the nanoscopic (AFM), mesoscopic (MEMS), and macroscopic (tribometer). In all cases, the vapor successfully lubricates and minimizes wear. In the case of MEMS sidewall friction, the lifetime of the device is radically increased.

4:00pm **TR1+MN-WeA8 MEMS Reliability in Harsh Environments,** ***R. Maboudian***, *C. Carraro*, University of California at Berkeley **INVITED**

Many applications require sensors and actuators that can survive harsh environments, including high temperature and high relative humidity. This presentation will examine the behavior of polycrystalline silicon based micro-electromechanical systems in a variety of harsh environments. Then, the effectiveness of self-assembled monolayers and silicon carbide for enhanced MEMS reliability under these conditions will be discussed.

4:40pm **TR1+MN-WeA10 Water Vapor Effects on the Lubrication of Silicon MEMS by Alcohol Vapor,** ***M.T. Dugger***, Sandia National Laboratories, *D.B. Asay,* Pennsylvania State University*, J.A. Ohlhausen*, Sandia National Laboratories*, S.H. Kim*, Pennsylvania State University

Adhesion, friction and wear have been the greatest limitations to development of robust MicroElectromechanical Systems (MEMS) that rely on contact between surfaces. Chemisorbed monolayers such as alkyl and amino-silanes have been successful in creating initially-free structures, but have not demonstrated adequate long duration operation in sliding contacts, and recent studies suggest that they degrade with long term static exposure to water vapor in storage. A new lubrication approach has been demonstrated on silicon surfaces, which consists of alcohol molecules in the vapor phase that form a friction and wear reducing film dynamically, preferentially at contact locations. ToF-SIMS analysis of wear tracks from pin-on-disk experiments suggest formation of high molecular weight oligomers where the stress is highest. Experiments with MEMS tribometers result in a factor of at least 10^5 increase in operation life without failure, and no wear or debris formation. Practical device operation requires lubrication in the presence of some concentration of water vapor inside sealed packages. Friction experiments in environments containing 400 ppm alcohol and 1000 ppm H_2O show that lubrication by alcohol is inhibited at these relative concentrations.

[*] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

5:00pm **TR1+MN-WeA11 Monolayer Degradation and Sidewall Tribometer Studies of Vapor Phase Lubricants for MEMS,** ***D.A. Hook***, Sandia National Laboratiories, North Carolina State University*, S.J. Timpe,* Sandia National Laboratiories, University of California Berkeley*, M.T. Dugger,* Sandia National Laboratories*, J. Krim*, North Carolina State University

Long hydrocarbon and fluorocarbon-based monolayers have been widely used in MEMS applications to prevent release related stiction as well as adhesion as devices are stored for long periods of time.[1] It has also been observed that the presence of these monolayers lowers the coefficient of friction in tribological contact. However these same contacts cause rapid degradation of these monolayers.[2] The loss of the monolayers contributes to an increase in the adhesive contact force and leads directly to device failure whether it be unpredictable operation of the device or complete cessation of movement. This study reports on degradation of (tridecafluoro-1,1,2,2-tetrahydrooctyl)tris(dimethylamino)-silane (FOTAS) monolayers on normal as well as sliding contacts in MEMS interfaces. The degradation of the monolayer in the normal loading case was probed by measuring the change in adhesive force of the contact over the course of 300,000 normal loading cycles. In the sliding experiment a decrease in oscillation amplitude was used to probe the status of the monolayer. The onset of monolayer degradation was observed in the normal contacting experiment after approximately 80,000 normal contacting cycles, while in the case of sliding degradation was observed almost instantaneously. Work funded by the AFOSR Extreme Friction MURI and Sandia National Labs MESA Project. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

[1] Srinivasan, U., Houston, M.R., Howe, R.T., Maboudian, R., "Alkyltrichlorosilane-Based Self-assembled Monolayer Films for Stiction Reduction in Silicon Micromachines", Journal of Microelectromechanical Systems 1998, 7, 252-260.

[2] DePalma, V., Tillman, N., "Friction and Wear of Self-Assembled Trichlorosilane Monolayer Films on Silicon", Langmuir 1989, 5, 868-872.

Vacuum Technology

Room: 618 - Session VT-WeA

Miniature, Portable and Space Vacuum Applications

Moderator: J.H. Hendricks, National Institute of Standards and Technology

1:40pm **VT-WeA1 Vacuum Pumping Requirements for Miniature Mass Spectrometers**, ***R. Ellefson***, Consultant

A trend in mass spectrometers (MS) for gas analysis is miniaturization to occupy less volume when attached to vacuum chambers and additionally to decrease weight and power consumption for portable and space probe instruments. This presentation identifies the pumping system requirements for different MS applications. When sample impurities like H_2, H_2O, CO, N_2, O_2 and CO_2 are being analyzed, a lower base pressure (e.g. $<10^{-8}$ Torr) is required for low background ion currents from MS outgassing resulting in a low detection limits for these species in the sample. For analyzing hydrocarbons and other species with masses greater than 44, a higher base pressure (e.g. 10^{-6} Torr) can be tolerated if the hydrocarbon background is kept low by initial cleaning and operating methods. Factors dictating the operating pressure of the MS and the resulting gas throughput are presented together with scaling rules for miniaturization. Given the pumping requirements, a high vacuum pump can be selected or adapted. A comparison is made of throughput and capture pumps for MS applications focusing on the end use of the MS as a process monitor or a field portable instrument. Examples from literature are given. Finally the pumping system for gas sampling and pressure reduction to the MS is addressed.

2:00pm **VT-WeA2 Miniature High Vacuum Pump for Mars Analytical Instruments**, ***R.J. Kline-Schoder***, *P.H. Sorensen*, Creare Incorporated **INVITED**

NASA and other organizations have pressing needs for miniaturized high vacuum systems. Recent advances in sensor technology at NASA and commercial laboratories have led to the development of highly miniaturized mass spectrometers, and miniaturized versions of other analytical instruments are under development. However, the vacuum systems required to support these sensors remain large, heavy, and power hungry. In particular, high vacuum systems of adequate performance continue to be too large for systems such as time-of-flight, quadrupole, and ion trap mass spectrometers that are intended to be man-portable or to be deployed on UAVs, balloons, or interplanetary probes. The terrestrial, man portable applications impacted by this problem include military and homeland defense systems for detecting hazardous materials as well as portable leak detectors for commercial use. For 10 years, Creare has been developing the technologies required to design and build miniature high vacuum pumps. During this time, we have designed and built two small high vacuum pumps that have the following pumping characteristics: a compression ratio for air that is greater than 10^8; a pumping speed of about 5 L/sec; and 10 W power consumption for an exhaust pressure of 10 Torr. The smallest of these pumps has a mass of 130 g, a diameter of 1.3 in., and an overall length of 2.3 in (i.e. the size of a c-cell battery). The slightly larger pump has a mass of 500 g, a diameter of 2.0 in., and an overall length of 4.6 in (i.e. the size of a soda can). The larger version is being space qualified for use on a NASA Mars mission scheduled for launch in 2009. The challenges of designing and building miniature turbomolecular/molecular drag pumps include: design of pump geometry in regions where little data exist, the need for precision machining of components, and the electromagnetic and mechanical design of very high speed, efficient, miniature electric motors. Data will be presented that show the performance, over a wide temperature range, of a brassboard prototype of the pump NASA currently plans to deploy on the Mars Science Laboratory mission.

2:40pm **VT-WeA4 Development of MEMS for Space Applications**, ***P.W. Valek***, *D.J. McComas*, Southwest Research Institute **INVITED**

Space flight missions have critical requirements such as low mass, low power, and high reliability. The technology of Micro-Electro Mechanical Systems (MEMS) naturally has many properties that address these space flight requirements. MEMS devices are built using the same techniques that have been developed by the semiconductor industry so they share the same benefits that we have come to expect from modern electronics, i.e., reduced size, low mass, low cost, etc. While there has been significant research on how MEMS technology operates in the more "normal" environments encountered for consumer electronics and biological application, for the benefits of MEMS technology to be fully realized for space applications their operation in a vacuum needs to be understood. The relative importance of different physical mechanisms shifts when going from a macro-scale world to that of the micron scale. For example, surface tension and stiction are easily dealt with on the macro scale but become significant problems on the MEMS scale. We will discuss the challenges and opportunities that are present for MEMS technology when used in space or any vacuum environment. For example, MEMS oscillators operating in vacuum have Q-values many orders of magnitude larger than when operated at atmospheric pressures.[1] We will present results from our testing of MEMS devices in a vacuum environment and discuss the implications for further space instrumentation development.

[1] McComas et al., "Space applications of microelectromechancial systems: Southwest Research Institute vacuum microprobe facility and initial vacuum test results", Rev. Sci. Inst., Vol 74, 2003.

4:00pm **VT-WeA8 The Role of Vacuum-Based Processes in Developing High Performance Chemical Microsensors**, ***S. Semancik***, *D.C. Meier, J.K. Evju, M.J. Carrier, C.B. Montgomery,* National Institute of Standards and Technology, *K. Newcomb, C.L. Keast*, M.I.T. Lincoln Laboratory **INVITED**

There is a growing demand for solid state chemical microsensors that are capable of analyzing gas phase compositions encountered in a wide range of application areas, from process control to space exploration and health care. In certain cases these small sensing devices would be used instead of more expensive and cumbersome instrumentation, and in others they would enable chemical monitoring within dispersed multipoint networks which are not amenable to instrument-based measurements. While the necessary detection characteristics vary with application, the defense/homeland security sector provides what are arguably some of the most demanding performance requirements for such microsensors: rapid detection; sensitivities to hazards such as chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) at nmol/mol (ppb) and even pmol/mol (ppt) concentrations; reliability and robustness to avoid false target readings in practical backgrounds; and, extended lifetimes. This presentation will focus on vacuum-based processing and vacuum-related phenomena that enable the fabrication and evaluation of MEMS-based, chemiresistive microsensor array devices being developed for detection of low level chemical hazards in air-based backgrounds (including interference compounds). Microarray device platforms (1000s of devices on 6 inch wafers) are fabricated at a silicon foundry through a multi-step processing schedule including nearly two dozen controlled vacuum procedures (e. g. - etching, CVD, PVD). The incorporation of nanostructured sensing materials onto the ~ 100 µm (microhotplate) array elements of our devices is achieved using a variety of methods, including thermally activated, self-lithographic CVD (at 3 Pa), and an ion etch pre-process (at ~ 10^{-5} Pa base pressure) has been shown to produce good sensing material contact to the microdevice electrodes, which is critical for attaining high sensitivity and reliable operation. In addition, vacuum phenomena come into play while evaluating the microarray sensors, since very low concentrations of target analytes (often with low vapor pressures) must be injected into air-based backgrounds and delivered to a device exposure point within our testing system. Technical aspects (enhanced analytical content for species recognition, redundant elements, etc.) that have allowed us to achieve sub-ppb CWA simulant detection with our microsensors will be discussed.

4:40pm **VT-WeA10 A Novel Electrostatic Ion Trap Mass Spectrometer**, *A.V. Ermakov*, ***B.J. Hinch***, Rutgers University

We have developed, built and tested several prototypes of a novel mass spectrometer which operates with an entirely new basic principle - i.e. using an electrostatic resonance ion trap. This mass spectrometer has an unlimited mass range, is capable of achieving higher sensitivity, and has much faster scan rates than the widely used (larger size and) more complicated quadrupole or magnetic sector mass spectrometers. In addition, the new mass spectrometer is very compact (less than 2" long), and requires very small power (in the mW range, excluding ionizer) as it uses only static potentials and a very small RF voltage (in the 100mV range). The high sensitivity of our mass spectrometer at low background pressure (below 10^{-8} torr) allows for the possible construction of an easily portable analytical instrument (handheld, if necessary.) A portable system could use only a battery powered comp act ion pump, and would not require (noisy, bulky, and energy consuming) mechanical pumps.

Biomaterial Interfaces

Room: 609 - Session BI-ThM

Biomimetic Phospholipid Interfaces

Moderator: F. Höök, Lund University, Sweden

8:00am **BI-ThM1 Surface-supported Bilayer Platforms for Fundamental Research and Biotechnological Applications*, K. Hristova*,** Johns Hopkins University **INVITED**

Approximately 20% of the open reading frames in complex organisms encode membrane-associated proteins. Despite their abundance and key roles in cell adhesion, recognition, motility, energy production, transport of nutrients and cholesterol, our knowledge of the folding and the structure of membrane proteins is limited, and lags far behind that of soluble proteins. In part, this is due to limited biophysical tools to adequately probe the physical-chemical principles underlying membrane protein function. In our laboratory we have developed a model surface-supported bilayer platform, based on a directed assembly approach that overcomes current limitations associated with traditional black lipid membranes and self-assembled membrane mimetics. The behavior of the proteins in the surface-supported bilayer, as determined by their sequence, is not altered by the assembly method. Thus, the platform is suitable for biophysical characterization of membrane proteins and can be used as a tool to probe diffusivity, secondary structure, thermodynamics of interactions, and electrical response. The long-term goal is to use the platform for biotechnological applications, including drug screens and analyte sensing.

8:40am **BI-ThM3 Supported Lipid Structures as Model Systems for Membrane Associated Interactions**, *S. Svedhem, **A. Kunze**, E. Briand, A. Wikström, B. Seantier, P. Axelsson, H. Ekstrand, M. Edvarsson, S. Petronis, M. Zaech, B. Kasemo*, Chalmers University of Technology, Sweden

Engineering of surface-supported lipid membrane model systems is currently a very active field of research. The present contribution will present a number of recent examples in this area from our group, including both different kinds of supported lipid structures; supported lipid bilayers and vesicles, tethered vesicles, and hole-spanning membranes; as well as different kinds of biomolecular interactions associated with them. The main techniques used to follow these processes are the quartz crystal microbalance with dissipation monitoring (QCM-D), surface plasmon resonance (SPR), optical reflectometry, fluorescence microscopy, and atomic force microscopy (AFM). Some new findings about the factors influencing how lipid bilayers or monolayers of intact vesicles are formed on SiO2 surfaces, e.g. with respect to cations present in the buffer, will be presented. We will also describe new results about processes on the suported lipid structures. In particular, the action of different kinds of lipases (via hydrolysis of phospholipids) on supported lipid bilayers has been monitored by different techniques, as well as the effect of lipases on tethered vesicles (including PEG-ylated vesicles of relevance for drug delivery applications). Another example that will be covered is the exchange of lipid material between charged supported lipid membranes and vesicles; potentially a method for the in situ modification of supported membranes.

9:00am **BI-ThM4 Anisotropic Diffusion in Nanopatterned Supported Lipid Bilayers*, J. Tsai*,** *E. Sun, J.C. Hone, L. Kam*, Columbia University

Membrane-associated proteins have a central role in cell-cell adhesion and communication, mediated in part by the ability of membrane proteins to diffuse along the cell surface. Many of these proteins exhibit long-range (tens of micrometers) diffusion coefficients that are orders of magnitude smaller than that expected for membrane components. Moreover, other experiments suggest that over short (submicrometer) distances, the diffusive properties of these proteins more closely resemble that of membrane lipids. To capture this anomalous diffusion in a controllable, in vitro model, glass-supported lipid bilayers were patterned with nanoscale barriers of chromium and/or titanium, creating periodic barriers that mimic the spacing of cytoskeletal elements in cells (which underlie several models of anomalous diffusion). Specifically, these barriers consisted of 50-nm wide, parallel barriers spaced at 125 and 250 nm intervals. Gaps in these barriers, measuring 30-50 nm and spaced at 500 nm intervals, were introduced to allow a limited amount of long-range diffusion across the barriers. Long-range diffusion coefficients of Texas-Red-DHPE, in a background of vesicles of Egg PC, were measured using an image-based, fluorescence recovery after photobleach approach. The long-range diffusion coefficient of lipids parallel to the barriers was similar to that on non-patterned glass for both types of metals and all geometries. In contrast, long-range diffusion perpendicular to the barriers was decreased by as much as a factor of ten, dependent on the pattern geometry. Barrier spacing, rather than gap size, was the major determinant of long-range diffusion. Barrier material had an additional influence. On surface with chromium lines, photobleach recovery agreed with a model of diffusion along a perforated surface, suggesting that this material forms perfect barriers to lipid diffusion. On surfaces patterned with titanium, diffusion across the barriers was consistently higher than predicted by the model; furthermore, lipids exhibited limited diffusion across barriers with no gaps. These results suggest a more complex interaction between the supported lipid bilayer and the substrates. The nature of this interaction is currently under investigation. In summary, we describe a controllable, nanopatterned supported lipid bilayer model that captures the complex patterns of membrane protein diffusion, which have immediate use in the study of cell-cell communication.

9:20am **BI-ThM5 Fabrication of Surface-Engineered 3D Micro-Well Arrays for High Resolution and High Throughput Analysis in a Single Cell Format*, M. Textor*,** *M. Ochsner, M. Smith, H.M. Grandin, S. Luna-Morris, V. Vogel*, ETH Zurich, Switzerland

In addition to substrate rigidity, matrix composition, and cell shape, dimensionality is now considered an important physical property of the cell microenvironment which directs cell behavior. However, available tools for the study of cell behavior in two-dimensional (2D) versus three-dimensional (3D) environments are difficult to compare, and no tools are available which provide 3D shape control of individual cells. Using microfabrication and replication techniques, we developed PDMS substrates for the culture of single cells in 3D arrays compatible with both high-resolution microscopy and high-throughput analysis. Cell adhesion was limited to within microwells by passivation of the flat upper surface through 'wet-printing' of a non-fouling polymer and backfilling of the wells with either specific adhesive proteins or lipid bilayers, the latter produced by exposing the oxidized PDMS wells to lipidic vesicles that spontaneously fused to form supported lipidic membranes. The surfaces were characterized at each fabrication stage by confocal laser scan microscopy (CLSM) in conjunction with labeled polymers and proteins, and the Quartz Crystal Microbalance (QCM-D) technique and FRAP to characterize bilayer formation on PDMS surfaces. Endothelial cells constrained within microwells were viable, although cell death was increased in very constrained microwells as has been reported for cells on flat substrates. In contrast to studies on 2D surfaces, actin stress fibers were present even within cells cultured in very constrained microwells, and in addition the cytoskeleton was 3D and not limited to the cell-substrate interface. These observations demonstrate that microwells can be used to produce microenvironments for large numbers of single cells with 3D shape control and can be added to a repertoire of tools which are ever more sought after for both fundamental biological studies as well as cell-based assays for drug development and screening. Future work is directed towards the study of (stem) cell differentiation and its dependence on surface (bio)chemistry, ligand mobility and substrate rigidity as well as the development of microwells with walls covered by cadherin-functionalized lipidic membranes simulating a microenvironment that is possibly closer to the one of cells in multicellular colonies and tissue.

9:40am **BI-ThM6 Effects of Fluidity on HIV-1 Neutralizing Antibody Binding to Membrane Surfaces*, Y. Lam*,** *W. Goo, S.M. Alam, S. Zauscher*, Duke University

Recent studies show that HIV-1 may take advantage of the phenomenon that healthy individuals do not normally produce self reactive antibodies. Broadly neutralizing monoclonal antibodies (nAbs) 4E10 and 2F5 bind to epitopes in the membrane proximal external region (MPER) on the HIV-1 transmembrane envelope glycoprotein (Env) gp41. Unlike most antibodies, however, they also react with several common membrane phospholipids. This auto-reactive characteristic may explain why they are rarely (if ever) found in HIV-1 patients. Little is known about the mechanics of these interactions between nAb and membrane. Initial surface plasmon resonance (SPR) studies suggest a two phase binding model where the nAb first encounters the membrane epitope proximal region, and then docks more securely in a second step. One theory for the mechanism behind this model suggests nAb may first bind to lipid, then diffuse on the lipid until encountering the MPER region on Env gp41. In our work, we investigate the effects of membrane fluidity in this process. Increasing temperature adversely affects this interaction, as it increases the on-rate, but more rapidly increases the off-rates. In order to eliminate rate effects, we monitor protein binding to peptide sequences embedded in mobile supported lipid bilayers and in static lipid monolayer surfaces. Quartz crystal microbalance with dissipation monitoring (QCM-D) was used to verify bilayer and monolayer formation as well as to measure nAb binding. This knowledge will provide insight into the mechanism of nAb-lipid binding, which may facilitate the production of effective HIV-1 therapies.

10:00am **BI-ThM7 Rupture, Spreading, and Healing of 2D Fluid Lipid Bilayers at Chemically and Topographically Structured Surfaces**, ***A. Parikh***, University of California, Davis **INVITED**

Interfacial organization of lipids and amphiphiles into a discrete number of molecular layers provides, arguably, one of the most pristine experimental realizations of self-organized, two-dimensional systems. it provides an experimental test-bed for the study of a rich variety of interface-dominated processes, including surface melting, low-dimensional phase transitions, surface dynamics, and phase coexistence and separation. This talk will present recent experimental evidence from our laboratories which highlight the importance of substrate structure (e.g., topography, charge, and surface energies) in influencing the dynamics of formation of interfacial single lipid bilayers and their equilibrium morphologies. This work is performed in collaboration with Babak Sanii, Michelle Smith, Alan Szmodis, Adrian Brozell, and Michael Howland. The work is supported by a grant from U.S. Department of Energy.

10:40am **BI-ThM9 Activity of Transmembrane Protein Maintained in Polymerized Lipid Membranes**, ***H. Zhang***, University of Arizona, *V. Subramaniam*, Univeristy of Arizona, *S. Burnside, G. D'Ambruoso, M. Brown, S. Saavedra*, University of Arizona

Membrane-associated proteins are of great importance in transport and signal transduction cascades and therefore are crucial pharmacological targets. With the goal of developing biosensors to screen pharmaceutical candidates, numerous research groups have reconstituted transmembrane proteins into lipid membranes, which provide a biocompatible environment. Our group has been investigating the use of synthetic lipids that can be polymerized to form a highly stable bilayer. Absorbance spectroscopy and plasmon waveguide spectroscopy (PWR) are being utilized to monitor the photoactivity of a G-protein coupled receptor (GPCR), bovine rhodopsin, in both polymerized liposomes and planar supported lipid bilayers (PLSBs), respectively. The photoactivity of rhodopsin is largely retained in some types of poly(lipid) membranes. However, the lipid structure and bilayer polymerization clearly affect the retention of protein activity. PWR is used to probe conformational changes accompanying rhodopsin photoactivation in PSLBs, whereas absorbance spectroscopy is used to directly measure formation of the rhodopsin activated state. Studies are also being performed to investigate the effect of lipid structure on the activity of other types of GPCRs, e.g. the human delta opioid receptor.

Electronic Materials and Processing

Room: 612 - Session EM-ThM

Zinc Oxide

Moderator: R.M. Wallace, University of Texas at Dallas

8:00am **EM-ThM1 Bulk and Surface Impurities and Point Defects in ZnO**, ***D.C. Look***, Wright State University **INVITED**

ZnO is a popular material at present because of potential photonic and electronic applications, such as UV LEDs and transparent transistors. As with most semiconductors, the bulk optical and electrical properties are controlled by impurities and defects acting as donors, acceptors, traps, and recombination centers. However, ZnO is somewhat unusual in that the surface also has donors and acceptors that produce electrical activity and can affect Ohmic and Schottky contact formation, among other things. Bulk donors and acceptors can be quantified by temperature-dependent Hall-effect (T-Hall) measurements, and their identities can often be determined by correlation with low-temperature photoluminescence (PL) and SIMS measurements in conjunction with doping and electron-irradiation experiments. Surface donors and acceptors, however, are much more difficult to quantify, although in this work we show that fairly reliable concentrations of surface donors (but not acceptors) can be determined by means of a low-temperature Hall-effect measurement and a room-temperature electrochemical C-V (ECV) measurement. Information on the possible identities of these surface donors can be obtained with XPS, SIMS, and other surface-sensitive techniques. We present T-Hall, PL, and ECV data on bulk, commercially available, ZnO samples grown by the vapor-phase, melt, and hydrothermal methods. Accurate concentrations of bulk donors and acceptors are obtained in all cases; the donors are tentatively assigned to various combinations of H, Al, Ga, and a Zn-interstitial complex, and the acceptors, to Li and the Zn vacancy. Fairly accurate densities of surface donors are also obtained in each case, and it is speculated that they are due to H complexes since their concentrations can be significantly increased by forming-gas anneals. To our knowledge, this is one of the first quantifications of surface donors in any semiconductor material, and the methodology should have general applicability.

8:40am **EM-ThM3 Correlation of Native Point Defects to Thermal Stability of Schottky Barrier Formation at Metal-ZnO Interfaces**, ***H.L. Mosbacker***, *C. Zgrabik, S. El Hage,* The Ohio State University, *A. Swain,* Columbus School For Girls, *M. Kramer,* The Ohio State University, *G. Cantwell, J. Zhang, J.J. Song,* Zn Technology, *D.C. Look,* Wright State University, *L. Brillson*, The Ohio State University

ZnO is an important semiconductor system for spintronic, nanoelectronic and optoelectronic devices. Important to realization of these devices is control and thermal stability of the metal-ZnO interface. We investigated this interface on bulk single crystal substrates grown by different methods from 5 different vendors. Using a remote oxygen plasma to remove ZnO surface adsorbates, subsurface defects and hydrogen, we studied Al, Au, Ir, Ni, Mo, Pd, Pt, and Ta contacts. Depth-resolved cathodoluminescence spectroscopy (DRCLS) reveals the presence of 3 defects at energies of 2.1, 2.5 and 3.0 eV. These deep level states vary in concentration with vendor, with depth from the interface, and with metal contact. Current-voltage measurements show that material containing high concentrations of defects in the subsurface strongly affects reverse currents, idealities and barrier heights acquired from current-voltage measurements. After annealing these contacts at temperatures of 350ºC, 450 ºC, 550 ºC, and 650 ºC in an argon ambient, DRCLS spectra identify defect formation that correlates to the nature of the metal-ZnO interface. Metals that form oxides show increased deep-level emissions that have been attributed to oxygen vacancies, while metals that form eutectics with Zn reveal increased luminescence from defects associated with Zn vacancies. Ta contacts annealed at 550 ºC create blocking contacts to ZnO, and DRCLS in the interface region reveal the formation of a Ta oxide. Al contacts also form blocking contacts at temperatures that depend on the native point defect densities. DRCLS of the subsurface oxide interface reveal increases in a 2.5eV transition often associated with oxygen vacancies. Au contacts that are annealed above the eutectic temperature for Au-Zn exhibit an increase of the 2.1eV defect level that correlates to Zn vacancies. Elevated temperature results demonstrate that the thermal stability of Schottky barriers also correlates to the density of native point defects. These differences in native point defect densities have a significant impact on defect formation at both elevated and room temperatures. Samples with high native defect concentrations initially can increase reactions in the subsurface, thus creating more defects associated with the metal-ZnO surface chemistry. Overall we find that metal-ZnO chemical reactions introduce interface native defects.These and native bulk defects dominate Schottky barrier properties and thermal stability.

9:00am **EM-ThM4 Separation of Surface and Bulk Conduction in ZnO using Variable Magnetic Field Hall Effect Measurements**, *C.H. Swartz, M.W. Allen,* ***S.M. Durbin***, University of Canterbury, New Zealand, *T.H. Myers*, West Virginia University

One of the major advantages of ZnO over other wide bandgap semiconductors is the availability of bulk, single crystal growth of high quality material using a variety of techniques. Of these, hydrothermally grown ZnO is somewhat unique in that it is highly resistive with carrier concentrations typically 2 - 3 orders of magnitude lower than other bulk ZnO, due to compensation from unintentionally introduced Li and Na acceptor impurities. This high resistivity makes the measurement of its electrical properties particularly susceptible to complications such as persistent photoconductivity, increased temperature sensitivity and surface conduction effects. The surface conductivity of ZnO is known to depend strongly on the ambient atmosphere and can increase significantly under vacuum conditions. After being placed in a vacuum, the expiration of atmospheric effects on the surface can take many hours and, even when equilibrium is reached, the surface conductivity remains a significant, and often dominant, contributing factor to electrical measurements. Variable magnetic field Hall effect measurements can be used to separate surface or interface conducting layers from the bulk conductivity of a given sample. In this paper, we report on the results of temperature dependent, variable magnetic field Hall effect measurements on hydrothermally grown ZnO single crystal wafers from Tokyo Denpa Co. Ltd. (Japan). Measurements were carried out over a temperature range of 80 - 300 K and magnetic field strengths up to 12 T. Multiple carrier fitting was used to remove surface conduction effects and produce temperature dependent mobility and carrier concentration data for the bulk carriers only, which was then theoretically fitted. A significantly higher bulk carrier mobility and an order of magnitude lower ionised impurity concentration was found than is apparent from standard single field Hall effect measurements. These results also indicate that the use of single field, temperature dependent Hall effect measurements to determine donor concentration and activation energies may be problematic unless surface conduction effects are first isolated.

9:20am **EM-ThM5 Nuclear Reaction Analysis Investigation of H-doped ZnO Grown by Pulsed Laser Deposition**, ***Y.J. Li***, *T.C. Kaspar, T.C. Droubay, S. Shutthanandan, S. Thevuthasan, P. Nachimuthu, S.A. Chambers*, Pacific Northwest National Laboratory

As a wide bandgap semiconductor with good light emission properties, ZnO has attracted much interest because of its potential as a multifunctional material. Recent developments in bulk crystal and epitaxial film growth, along with advances in characterization methods, have expanded our understanding of this material, and created possibilities for ZnO-based optoelectronic, spin electronic, and transparent electronic applications. However, progress has been impeded by a lack of understanding and control of dopants, impurities and defects in ZnO. Difficulties in p-type doping of ZnO result from high background donor compensation of acceptors. One of the suspected background shallow donors in ZnO is H, which has been suggested to be readily incorporated during growth.[1-2] Theoretical calculations have predicted that H can exhibit a substitutional (on the O site) multi-center bonding configuration (H_O).[3] However, there is thus far no experimental evidence for H_O in ZnO. The focus of this study is to use nuclear reaction analysis to determine the local structural environment of H in ZnO. ZnO films are being grown in ultra-high purity H_2 at 500°C by pulsed laser deposition. The $H(^{15}N,\alpha\gamma)^{12}C$ and $H(^{19}F,\alpha\gamma)^{16}O$ nuclear reactions are being used in channeling and random directions to determine the position of H in the lattice. Initial results indicate that growth of ZnO in 10 mTorr H_2 at 500°C results in a total H concentration of ~1 x 10^{20} cm^{-3}. High-resolution x-ray diffraction is being used to characterize out-of-plane and in-plane lattice parameters of the doped phase. The effects of growth conditions on crystallinity as well as H concentration and position in the lattice are being investigated, and will be described in this talk.

[1] C.G. Van de Walle, Phys. Rev. Lett. 85, 1012-1015 (2000).

[2] D.M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B.K. Meyer, S.B. Orlinskii, J. Schmidt, and P.G. Baranov, Phy. Rev. Lett. 88, 5504 (2002).

[3] A.Janotti and C.G. Van der Walle, Nature Materials 6, 44 (2007).

9:40am **EM-ThM6 Effects of Hydrogen Ambient and Film Thickness on ZnO:Al Electrical Properties**, ***J.N. Duenow***, Colorado School of Mines, *T.A. Gessert*, National Renewable Energy Laboratory, *D.M. Wood*, Colorado School of Mines, *T.J. Coutts*, National Renewable Energy Laboratory

Transparent conducting oxide (TCO) thin films are a vital part of flat-panel displays, electrochromic windows, and photovoltaic cells. ZnO-based TCOs may allow cost advantages compared to indium-containing TCOs such as indium tin oxide (ITO) or indium zinc oxide (IZO). Undoped ZnO and ZnO:Al (0.1, 0.2, 0.5, 1, and 2 wt.% Al_2O_3) films were deposited by RF magnetron sputtering. Controlled incorporation of H_2 in the Ar sputtering ambient, for films grown at substrate temperatures up to 200°C, results in mobilities exceeding 50 $cm^2V^{-1}s^{-1}$ when using targets containing 0.1 and 0.2 wt.% Al_2O_3. Because high conductivity is achieved through high mobility at lower carrier concentration, these films demonstrate decreased infrared absorption compared to films containing the commonly used 2 wt.% Al_2O_3. ZnO:Al films grown in H_2 partial pressure (ZnO:Al:H) show no detectable changes in electrical properties during temperature-dependent Hall measurements conducted up to 170°C. Reduction in ZnO:Al mobility and carrier concentration with decreasing film thickness has been reported in the past, but mechanisms for these changes remain uncertain. Our studies show that ZnO:Al:H electrical properties are suboptimal if film thickness is less than ~300 nm. In attempts to improve the electrical properties of these thinner films, depositions were performed at room temperature with and without a 60-nm undoped ZnO nucleation layer. Results show that mobility values indeed benefit from this nucleation layer for film thicknesses less than 350 nm. However, films grown without the nucleation layer reached higher mobility values at thicknesses greater than 350 nm. This abstract is subject to government rights.

10:00am **EM-ThM7 Metallic Conductivity in Transparent Al:ZnO Films**, ***O. Bamiduro***, *A.K. Pradhan*, Norfolk State University

Recently, transparent conductive oxide electrode, such as Ga or Al-doped ZnO, has attracted much attention not only as a powerful candidate material generally used for $InSnO_2$ (ITO) transparent electrodes, but also has a potential to replace ITO due to low cost, non-toxicity, and high stability in H_2 plasma atmosphere with good electrical and optical properties. Here we report on the metal-like conductivity in highly crystalline transparent (>85% in the visible region) Al:ZnO films grown on sapphire and glass substrates by the pulsed-laser deposition technique. Crystalline quality, surface morphology were studied on both types of films. Temperature dependent resistivity measurements of the films grown on sapphire and glass show metal-like conductivity with electrical resistivity, ~0.17 mOhm-cm and ~0.39 mOhm-cm, respectively, at room-temperature followed by either residual conductivity or a metal-semiconductor transition at low temperature due to the localization effect caused by the defects.

10:20am **EM-ThM8 Mixed Anion ZnOTe Thin Films by Pulsed Laser Deposition**, ***W. Wang***, *W. Bowen, J. Phillips*, The University of Michigan Ann Arbor

deposition Zinc oxide and related wide-bandgap II-VI oxide alloys have received much interest for their potential application for optoelectronic and electronic devices. The primary challenges for this material remain the achievement of p-type material for junction devices, and alloy heterostructures to span the visible and ultraviolet spectral regions. The majority of recent research on ZnO and related alloys to address these challenges has focused on the doping of ZnO by group-V elements, and the investigation of mixed cation alloys CdZnO, MgZnO, and BeZnO. Very little attention has been given to mixed anion alloys related to ZnO. ZnTe is a II-VI compound semiconductor with a 2.29eV direct band gap, and typically exhibits p-type behavior. Furthermore, ZnTe has shown the ability for controllable p-type doping by nitrogen with hole concentrations of up to 1e20 cm-3. The ability to achieve p-type characteristics and the direct bandgap of ZnTe make mixed anion alloys based on ZnO and ZnTe attractive for optoelectronic devices including visible light emitters and solar cells. In this work, we report on mixed cation ZnOTe thin films deposited by pulsed laser deposition. Thin films were deposited on sapphire and GaAs substrates using a pulsed excimer laser, ZnTe target, and varying ambients oxygen, nitrogen, and high vacuum. Deposition under high vacuum resulted in crystalline ZnTe thin films with optical bandgap energy of approximately 2.3 eV based on transmission and reflectance measurements. Deposition under nitrogen ambient shows a significant red shift in optical bandgap energy, likely due to energy states introduced by nitrogen doping. Deposition of ZnTe under oxygen ambient results in a large blue shift in optical bandgap to more than 3.1 eV, with a strong dependence on oxygen partial pressure. The structural, electronic, and optical properties of these ZnOTe thin films will be presented.

10:40am **EM-ThM9 STM, LEED and ARXPS Study of MOCVD Grown a-plane ZnO and $Mg_xZn_{1-x}O$ (0 <= x <= 0.3) Thin Films**, ***O. Dulub***, *E.H. Morales, U. Diebold*, Tulane University, *G. Saraf, Y. Lu*, Rutgers University

ZnO and $Mg_xZn_{1-x}O$ (0 <= x <= 0.3) thin films with a-plane orientation were grown on r-plane (011bar2) sapphire substrates using metal-organic chemical vapor deposition (MOCVD). The surface morphology of ZnO films with various thickness (20 - 2000 nm) was characterized by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) in ultrahigh vacuum (UHV). LEED patterns show well-ordered (1x1) surfaces. STM images reveal uniform surfaces with small, rectangular terraces during the initial growth stage (20 nm-thick film). Films with thicknesses of 100 and 450 nm have a characteristic wave-like surface morphology with needle-shaped domains running along the crystallographic c-direction. Films with a thickness of 2000 nm exhibit more flat surfaces with 20-100 nm wide domains running perpendicular to the c-axis, indicating variation in the strain effect caused by mismatch between substrate and film. On these thickest films, areas with facets of a different surface termination were observed as well. Angle-resolved x-ray photoemission spectroscopy (ARXPS) analysis of $Mg_xZn_{1-x}O$ films show that Mg atoms substitute for Zn atoms in the lattice. LEED shows that the incorporation of Mg atoms into the lattice reduces the surface roughness.

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-ThM

Surface Science Challenges for Solar Energy Conversion

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

8:00am **EN+SS+TF-ThM1 Thermal and Photoreactions of Catechol on TiO_2**, ***P. Jacobson***, Tulane University, *X.-Q. Gong, M. Connors, A. Selloni*, Princeton University, *U. Diebold*, Tulane University

The wide band gap of titanium dioxide limits its use as a photocatalytic and photovoltaic material with solar radiation as its source. One method to increase the absorption of light at visible wavelengths is by attaching metallo-organic dye complexes. These dyes frequently use catechol and phosphonic or carboxylic acids to link the dye to the titanium dioxide surface. In an attempt to better understand the adsorption of these complex dyes, we have studied the adsorption of catechol (1,2-benzenediol) on the (110) and (011) faces of rutile titanium dioxide. Catechol was preferred over 'real' dye complexes for its ease of deposition under high vacuum conditions and simple chemical makeup. Ultraviolet photoemission spectroscopy shows a gap state introduced to the TiO_2 upon catechol adsorption. Increases in the Oxygen 1s shoulder in XPS indicate dissociative adsorption of catechol and formation of surface hydroxyls. For catechol adsorption on the rutile (110) surface a 3x1 overlayer results. Similarly, adsorption on the (011) surface forms a 2x1 overlayer. Formation of surface hydroxyls upon adsorption is believed to play a role in the formation of these ordered structures. To further study the catechol - titanium dioxide complex, temperature dependent measurements using STM, XPS, and UPS were made in the presence and absence of molecular oxygen. The difference in decomposition and intermediates formed will be discussed. These techniques were also used to study UV induced photoreactions of catechol on TiO_2.

8:20am **EN+SS+TF-ThM2 N Incorporation and Electronic Structure in High-Quality Epitaxial N-doped TiO_2 Anatase Grown by Molecular Beam Epitaxy**, ***S.H. Cheung***, *P. Nachimuthu, M.H. Engelhard,* Pacific Northwest National Laboratory, *M.K. Bowman,* The University of Alabama, *S.A. Chambers*, Pacific Northwest National Laboratory

N doping in TiO_2 is of potential interest for bandgap reduction and enhanced visible light absorption for water splitting. We have previously investigated high-quality N-doped TiO_2 rutile grown homoepitaxially by molecular beam epitaxy (MBE) on TiO_2(110) and α-Al_2O_3(0001).[1] To gain broader understanding of N-doped TiO_2, we now report a detailed study of N incorporation and the associated electronic structure in high-quality TiO_2 anastase grown by MBE on $LaAlO_3$(001). A mixed beam of atomic N and O was prepared in an electron cyclotron resonance plasma source while Ti was supplied from an effusion cell. The much higher thermodynamic stability of Ti-O bonds compared to Ti-N bonds resulted in N incorporation being limited to less than 1 at. %. The high degree of structural quality was evidenced by the observation of finite thickness fringes in the vicinity of the (004) Bragg peak in high-resolution X-ray diffraction. A formal charge of -3 on substitutional N was deduced from high-resolution XPS. Photoconductivity measurement capability is being set up at the time of abstract preparation and experimental results elucidating the role of substitutional N in reducing the bandgap will be presented at the meeting.

[1] S.H. Cheung, P. Nachimuthu, A.G. Joly, M.H. Engelhard, M.K. Bowman, S.A. Chambers, Surf. Sci. 601 (2007) 1754.

8:40am **EN+SS+TF-ThM3 Lattice Site Location for N in Homoepitaxial N-doped TiO_2 (110)**, ***V. Shutthanandan***, *S.H. Cheung, S. Thevuthasan, P. Nachimuthu, S.A. Chambers*, Pacific Northwest National Laboratory

TiO_2 is one of the most heavily studied materials for photocatalytic water splitting even though the optical absorption spectrum of TiO_2 has poor overlap with the solar spectrum, and the e^-/h^+ pair recombination rate is high. Bandgap reduction is one approach to enhancing visible light absorption. N doping causes a redshift of the bandgap into the visible and visible-light-induced photochemistry has been observed in this material. We have grown $TiO_{2-x}N_x$ rutile epitaxial films on rutile TiO_2 (110) single crystal substrates using oxygen plasma assisted molecular beam epitaxy. The N concentration (x) was varied by careful control of the atomic fluxes. The N dopant site location was studied using nuclear reaction analysis (NRA) and Rutherford backscattering spectrometry (RBS) in channeling and random geometries. $^{14}N(d,\alpha)^{12}C$ and $^{16}O(d,p)^{17}O$ nuclear reactions were used to identify the locations of N and O, respectively. NRA measurements in a channeling geometry for x = 0.04 and 0.05 clearly show that N substitutes for O in this concentration range. The x = 0.04 film shows a higher degree of N substitution (~98%) than the x = 0.05 film (~75%). Angular scans obtained around <110> for the x = 0.04 film exhibit a N angular half width that is slightly narrower (~0.05°) than that of host O. This narrowing is an indication that the N atoms are slightly displaced from the idealized anion lattice sites. The angular yield scan obtained for the x = 0.05 film exhibits a slightly larger angular half width for O, indicating that O positions are perturbed by N incorporation. In contrast, NRA and RBS measurements performed on the x = 0.12 film reveal that most of the N occupies random positions within the film, and glancing incidence XRD reveals limited Ti_2N secondary phase formation. These results clearly demonstrate that the upper limit of N solid solubility in crystalline TiO_2 rutile is ~3 at. % of the anions. Higher N concentrations can be incorporated by varying the growth conditions to facilitate defect formation, but the quality of the materials drops considerably and secondary phase formation occurs.

9:00am **EN+SS+TF-ThM4 Photochemically Activated Tethering of Molecular Monolayers to Anatase and Rutile TiO_2 Surfaces**, ***H.J. Kim***, *E.C. Landis,* University of Wisconsin-Madison, *S.H. Cheung, S.A. Chambers,* Pacific Northwest National Laboratory, *T.F. Kuech, R.J. Hamers*, University of Wisconsin-Madison

Molecular interfaces to TiO_2 are an important component of dye-sensitized solar cells and other emerging systems for solar-to-electrical and solar-to-fuel conversion. Using X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy,we demonstrate that organic alkenes will link to the surfaces of titanium dioxide in both anatase and rutile forms when illuminated with ultraviolet light. This provides a versatile way to covalently link functional organic molecules directly to oxide semiconductors. Measurements have been performed on epitaxial thin films of anatase (001), bulk crystals of anatase(101), rutile (001), rutile (110), and nanocrystalline anatase. Quantitative XPS measurements have been used to investigate the kinetics of functionalization and its dependence on the structure of the bulk samples and the dependence on exposed crystal face. We will compare the functionalization of these surfaces and discuss the mechanism of the modification. Implications for tethering of photochemically active molecules to these surfaces will be discussed.

9:20am **EN+SS+TF-ThM5 Progress and Challenges in Solar Energy Conversion Using Semiconductor/Liquid Junctions**, ***N.S. Lewis***, California Institute of Technology **INVITED**

Semiconductor/liquid contacts are useful in photoelectrochemical cells as well as for probing the fundamental surface chemistry and surface physics of semiconductors. In this talk, we will discuss the thermodynamics and dynamics of charge flow across semiconductor/liquid interfaces with an emphasis on comparison of theory and experiment for charge transfer in 1-electron outer-sphere redox systems. In addition, we will discuss the principles of surface modification to control the electrical, electronic, and chemical properties of Si surfaces. Finally, we will discuss the use of photoelectrochemistry in transport, localization, and movement of charge molecules in three dimensions in solution in real time.

10:00am **EN+SS+TF-ThM7 An Organic Donor/Acceptor Lateral Superlattice at the Nanoscale: Towards an Optimum Morphology for Photovoltaic Devices**, ***R. Otero***, *D. Ecija,* Universidad Autonoma de Madrid, Spain, *G. Fernandez*, Universidad Complutense de Madrid, Spain, *J.M. Gallego,* ICMM-CSIC, Spain, *L. Sanchez, N. Martin,* Universidad Complutense de Madrid, Spain, *R. Miranda*, Universidad Autonoma de Madrid, Spain

One of the major factors limiting the efficiency of organic photovoltaic devices is the fact that, instead of free electron-hole pairs, photon absorption usually leads to the formation of tightly bound excitons (bound states of an electron-hole pair) which can diffuse only for a characteristic length of about 10 nm before radiative recombination occurs. The hitherto most successful approach to promote the dissociation of the photogenerated excitons is to use blends of phase-segregated electron-donor/electron-acceptor molecules; the so-called bulk heterojunction concept. At the interface between electron-donor and electron-acceptor areas, the difference in electron affinities drives the exciton dissociation by injecting free electrons (holes) into the electron-acceptor (electron-donor) areas. Provided that continuously connected paths between the interfaces and the electrodes exist, the free electrons and holes will be collected therein. From these considerations a number of morphological criteria can be extracted for optimum solar cell performance: first, the segregated electron-donor and acceptor domains must have a typical size of the order of the exciton diffusion length, in order to avoid wasteful radiative recombination events; second, the interface area between donor and acceptor domains, where exciton dissociation takes place, must be maximized; and, finally, donor (acceptor) domains must be continuously connected to the cathode (anode) to favour efficient charge transport. A morphology that would satisfy these three criteria could be a lateral superlattice of donor and acceptor areas with typical dimensions of some 10 nm. In this work we describe variable-temperature Scanning Tunneling Microscopy (STM) experiments that show how monolayer-thick blends of the electron donor molecule (exTTF) with the electron acceptor (PCBM) on a reconstructed Au(111) surface, segregates laterally into 'nanostripes' whose width is of the order of the exciton diffusion length; it thus corresponds closely with the morphology for optimum solar cell performance. The reason for such a peculiar nano-scale morphology can be traced back to the different interactions between the two molecular species and the herringbone reconstruction of Au(111). Our results demonstrate the potential of atomistic studies about the growth of organic semiconductors to open new directions for the design and construction of highly-efficient organic electronic devices.

10:20am **EN+SS+TF-ThM8 Solar Water Splitting for Renewable Hydrogen Production: The Role of N and Surface Modification in the Improved Stability of III-V Nitride Photoelectrodes**, *T. Schiros, J. Leisch,* ***L.-Å Näslund****, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*, T. Deutsch, J. Geisz, S. Kurtz,* National Renewable Energy Laboratory*, R. Kirby, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

III-V semiconductors are promising materials for photoelectrochemical (PEC) hydrogen production, however, material stability is a serious issue. The addition of dilute amounts of nitrogen to GaP and surface modification such as platinization result in dramatic increases in photocorrosion resistance, but the underlying mechanism is not known. We combine surface-sensitive core-level x-ray spectroscopy and microscopy with electrochemical measurements to study changes in the chemical environment and local morphology at the semiconductor-electrolyte interface during PEC hydrogen production and reveal the role of nitrogen and the platinum catalyst treatment in preserving the integrity of the surface. A detailed understanding of the interface is essential to improve control of photocorrosion and increase device stability.

10:40am **EN+SS+TF-ThM9 Surface Nanostructure and Nanochemistry of CuInSe$_2$ by Scanning Tunneling Microscopy**, *M. Mayer, L. Ruppalt, J. Lyding,* ***A. Rockett***, University of Illinois

Results of the characterization of the surface physical, chemical and energy band structure of CuInSe$_2$ (CIS) are reported based on scanning tunneling microscopy (STM) studies of epitaxial CIS thin films. Cu(In, Ga)Se$_2$ (CIGS) is the absorber layer in the highest efficiency thin-film solar cells. However, this material does not perform as well as expected, most likely due to local defects and composition fluctuations. These lead to the formation of electronic defect levels in the energy gap and band edge fluctuations, both of which can cause carrier recombination. STM images compare the structure of cleaved (110) type surfaces, which have been shown previously to be energetically unstable, with epitaxial layers of various stable surface orientations that had been cleaned by sputtering and annealing. The energetically favorable close-packed tetragonal (112) surface showed triangular facets in agreement with AFM and SEM images. The (110) face showed structural and chemical correlations with the local density of states and evidence of a Cu-deficient surface consisting of extended In-rich rows. The surface structure of the cleaved surface is consistent with suggestions that the surfaces of group III rich CIGS should be highly In-rich and should contain Cu vacancies. No significant reconstruction associated with the Se sublattice was observed. The local density of states obtained from tunneling spectroscopy exhibited large fluctuations in the energy gap and Fermi energy, providing direct evidence of the band edge fluctuations observed by photoluminescence. The gap fluctuations are correlated with the surface topography and have direct implications for the device performances.

Magnetic Interfaces and Nanostructures

Room: 619 - Session MI-ThM

Magnetic Semiconductors I

Moderator: A.T. Hanbicki, Naval Research Laboratory

8:00am **MI-ThM1 DMS Ferromagnets: Extrapolating from (III,Mn)V Materials**, ***A.H. MacDonald***, University of Texas at Austin*, T. Jungwirth,* Czech Academy of Sciences*, J. Sinova,* Texas A&M University*, J. Kucera, J. Masek*, Czech Academy of Sciences **INVITED**

The body of work on (III,Mn)V diluted magnetic semiconductors (DMSs) started during the 1990's achieved a good understanding of the origins of ferromagnetism in these materials, and of the relationship between magnetic properties and the materials science of growth and defects. From the fundamental point of view, (Ga,Mn)As and several other (III,Mn)V DMSs are now regarded as textbook examples of something which is rare, robust ferromagnets with dilute magnetic moments coupled by delocalized charge carriers. Both local moments and itinerant holes are provided by Mn, which makes the systems particularly favorable for realizing this unusual ordered state. Advances in growth and postgrowth-treatment techniques have played a central role in the field, often pushing the limits of dilute Mn-moment densities and the uniformity and purity of materials far beyond those allowed by equilibrium thermodynamics. In (III,Mn)V compounds, material quality and magnetic properties are intimately connected. I will review[1] some of this progress and use it as a spring board to discuss magnetism in other semiconductors with dilute local moments.[2]

[1] Tomas Jungwirth et al. Rev. Mod. Phys. 78, 809 (2006).

[2] Work suported by the Department of Energy under Grant No. DE-FG03-02ER45958.

8:40am **MI-ThM3 Onset of Nonlinear Transport and Two-Level Fluctuation through a Pinned Domain Wall in Patterned Lateral GaMnAs Constrictions**, ***S.W. Cho****, *H.K. Choi, J.S. Lee, T. Hwang, Y.D. Park*, Seoul National University, Korea

We report on the electrical transport measurements across clean lateral geometrical constrictions in diluted magnetic semiconductor GaMnAs. Constrictions are realized by e-beam lithography to define SiO$_x$ etch masks to pattern nanometer-sized constrictions without plasma etching processes. DC transport behavior across the nanoconstrictions changes from ohmic to non-ohmic below temperatures corresponding to epifilm T$_C$. The nonlinear IV characteristics fit well with adapted transport equation accounting for spin-flop processes across the domain wall, analogous to pn junctions.[1] Fits to theory also indicate the domain walls to be smooth and wide, inhospitable to tunneling transport, and supported by magnetoresistance behavior dominated by anisotropic magnetoresistance-like response similar to Giddings et al. observations.[2] Extending the 'spin diode' concept of Vignale and Flatté,[3] we conduct a series of dynamic measurements and observe a distinct two-level behavior dependent on bias conditions similar to certain behaviors found in bipolar junctions such as shot noise and random telegraph noise.

[1] G. Vignale and M.E. Flatté, PRL 89, 098302 (2002).

[2] A.D. Giddings et al., PRL 94, 127202 (2005).

[3] M.E. Flatté and G. Vignale, APL 78, 1273 (2001).

9:00am **MI-ThM4 Intrinsic Vacancy Chalcogenides as Dilute Magnetic Semiconductors: Theoretical Investigation of TM-Doped Ga$_2$Se$_3$**, ***I.N. Gatuna***, *F.S. Ohuchi, M.A. Olmstead*, University of Washington

The quest to functionalize semiconductors with additional magnetic properties through synthesis of dilute magnetic semiconductors (DMS) has led to a deeperunderstanding of semiconductor physics and the development of new magneticmechanisms. However, most current DMS materials (e.g., Mn-doped GaAs) are magnetic only well below room temperature, and/or have only limited compatibility with existing silicon electronics. We have investigated transition metal (TM) doping of the intrinsic vacancy semiconductor Ga2Se3 to address both scientific and technical goals. The intrinsic vacancies of this III-VI, zinc-blende-based semiconductor open possibilities for self-compensation as well as supply highly anistropic and polarizable band edge states. Ga2Se3 is also closely lattice matched to Si and may be grown heteroepitaxially on Si with high quality interfaces. Our first principles computations of X:Ga2Se3 (X = Mn, V, Cr, concentrations 5% to 16%) reveal that X atoms hybridize with neighboring Se in the p-d hybridization typical of III-V and II-VI DMS materials. This hybridization spin-polarizes states near the Fermi level in these T =0 calculations, and lowers the energy of the Se lone-pair orbitals that neighbor vacancies, reducing their prominent role in determining the properties of intrinsic Ga2Se3. There are distinct differences between substitution on a vacancy or for a Ga. Anisotropic, hole-like conductivity is predicted when X is located in a Ga site, while for X situated in a vacancy, a half-metallic state with an isotropic conductivity appears likely. Our calculations suggest that Mn offers the best choice for the dopant, perhaps because its 3d5 electronic configuration offers a large (~ 0.5 eV) separation of spin up and spin down states near the Fermi level, reducing the metallic densities of states at the Fermi level for all doping concentrations. The large energy splitting suggests that doped Ga2Se3 may be a suitable material for spintronics applications athigher temperatures than these T = 0 initial calculations.

This work was supported by NSF grant DMR 0605601, the Japan Science Promotion International Program, NIMS (Japan) - UW Joint Research Pact and NIMS (Japan) Internal Research Fund.

9:20am **MI-ThM5 Heteroepitaxial Growth and Electronic Structure of Mn:Ga$_2$Se$_3$ Thin Films on Si(100):As: Exploration of a Candidate Dilute Magnetic Semiconductor**, ***T.C. Lovejoy***, *E.N. Yitamben,* University of Washington*, T. Ohta,* Lawrence Berkeley National Laboratory*, F.S. Ohuchi, M.A. Olmstead*, University of Washington

Magnetic thin film semiconductors grown on nonmagnetic semiconductors (NMS) may provide a route to injection of spin polarized electrons into the NMS. The lack of magnetic materials with both a high Curie temperature and spin-preserving transport into electronic materials (e.g., silicon) is currently the primary obstacle to the development of useful spintronic devices. A relatively unexplored class of dilute magnetic semiconductor is transition metal doped III-VI semiconductors. Group III-VI semiconductors such as Ga$_2$Se$_3$ have intrinsic vacancies which lead to highly anisotropic growth, and which may lead to a high degree of magnetic anisotropy if the films can be made ferromagnetic through suitable doping. Scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and photoemission spectroscopy (PES) have shown the addition of small

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* Falicov Student Award Finalist

quantities of manganese, about one percent, has a pronounced effect on the growth morphology and electronic properties of Ga_2Se_3 on arsenic passivated Si(100). Co-deposition of Mn and GaSe on Si(100):As results in tall, highly anisotropic, rectangular, Mn-rich islands with edges parallel to the [011] and [0-11] substrate crystal directions. Deposition of a pure Ga_2Se_3 layer before the doped material results in a different and more laminar structure. While islands still form, these islands are much shorter and wider with seemingly random shapes subject to the constraint that every piece of the perimeter lies along the same two crystal directions. These two structures can be easily distinguished by their LEED patterns where the first case shows 1x1 spots with streak features characteristic of the undoped Ga_2Se_3 structure, whereas the second case transitions to clear 1x1 spots with no other features. The effect of small concentrations of Mn on the band structure of thin film Ga_2Se_3 is equally pronounced. The Mn doping adds a new peak in the valence band about 4.2eV below the Fermi level, an area where pure Ga_2Se_3 has a low density of states.

This work was supported by NSF grant DMR 0605601. TCL acknowledges support from NSF/NCI IGERT DGE-0504573. Some of the research was pursued at the Advanced Light Source, which is supported by the DOE under contract DE-AC02-05CH11231.

9:40am **MI-ThM6 Investigation of Cr:Ga2Se3 as a Candidate Dilute Magnetic Semiconductor for Silicon Based Applications**, ***E.N. Yitamben***, *T.C. Lovejoy, I.N. Gatuna, F.S. Ohuchi, M.A. Olmstead*, University of Washington

The intrinsic vacancy semiconductor Ga2Se3, which may be grown epitaxially on Si, poses several interesting issues for the study of dilute magnetic semiconductors. Substitution of transition metal impurities may occur on either occupied or vacant cation sites in the defected zincblende lattice. For dopants with different valence from the host cation, this may result in self-compensation of donors and acceptors, while an isoelectronic impurity can either add electrons by inserting into a vacancy, or minimally disturb the band structure by replacing a Ga. To probe the interrelationship between magnetism and free carriers in this new class of dilute magnetic semiconductors, we have performed both theoretical and experimental investigations of Cr-doped Ga2Se3 grown epitaxially on Si(001):As. Scanning tunneling microscopy shows nucleation of anisotropic islands, with the area between islands similar to pure Ga2Se3. The size and shape of the islands is dependent both on Cr concentration and on whether or not a pure Ga2Se3 buffer layer is deposited first. Despite the similar intrinsic valence between Cr and Ga, addition of a few percent Cr to Ga2Se3 results in metallic bands with minimal dispersion and leads to significant changes of the Se local environment, as measured with high resolution photoemission spectroscopy. These results may indicate Cr substituting into a vacancy rather than replacing Ga, or possibly creating local areas of CrSe, which computations show to be half-metallic. At higher concentrations, X-ray absorption and photoemission show two distinct Cr environments.

This work was supported byt NSF grant DMR 0605601. TCL acknowledges support from NSF/NCI IGERT DGE-0504573. Some of the research was pursued at the Advanced Light Source, which is supported by the DOE under contract DE-AC02-05CH11231.

10:00am **MI-ThM7 Giant Excitonic Zeeman Splittings in Transition Metal Doped CdSe Quantum Dots**, ***P.I. Archer***, *D.R. Gamelin*, University of Washington

We report the first direct observation of sp-d dopant-carrier exchange interactions in colloidal doped wurtzite CdSe nanocrystals. Doped diluted magnetic semiconductor quantum dots (DMS-QDs) were prepared by thermal decomposition of an inorganic precursor cluster in the presence of $TMCl_2$ (TM^{2+} = Mn^{2+} or Co^{2+}) in hexadecylamine and were characterized by multiple spectroscopic and analytical techniques. Using magnetic circular dichroism spectroscopy, successful doping and the existence of giant excitonic Zeeman splittings in both Mn^{2+}- and Co^{2+}-doped wurtzite CdSe quantum dots are demonstrated unambiguously.

10:20am **MI-ThM8 Size-Dependent Excited State Dynamics in Mn^{2+}-Doped CdSe Quantum Dots**, ***R. Beaulac***, *P.I. Archer, V.A. Vlaskin, D.R. Gamelin*, University of Washington

Colloidal Mn^{2+}-doped II-VI quantum dots are interesting materials for the study of magnetic and luminescent phenomena in quantum confined semiconductor nanostructures. In recent years, several reports have described luminescence, absorption and magnetism of Mn^{2+}-doped ZnS, CdS and ZnSe quantum dots. In general, the emission properties of these nano-scale materials behave much like their bulk counterparts, showing a size insensitive Mn^{2+} ligand-field emission with a long lifetime. In contrast, Mn^{2+}-doped CdSe nanoparticles are expected to behave differently from bulk because of the possibility of size-tuning the band-gap energy from below to above the Mn^{2+} emitting level. For this reason, Mn^{2+}-doped CdSe offers an interesting opportunity for fundamental studies of quantum confinement effects in doped semiconductors. Curiously, although photoluminescence spectra of self-assembled Mn^{2+} quantum dots prepared by vacuum deposition have been reported, the Mn^{2+} is either absent of only tentatively reported, even for high Mn^{2+} concentrations. Moreover, CdSe excitonic emission is observed despite the fact that the energy gap is greater than the Mn^{2+} excitation energy. We recently presented a new method for preparing colloidal doped CdSe quantum dots.[1] Importantly, these particules show a giant Zeeman splitting of their excitonic transitions, as is expected for diluted magnetic semiconductors. Here we will describe the temperature-dependent photoluminescence of these particles, which gives insight into the energy transfer dynamics in Mn^{2+}-CdSe quantum dots. A kinetic model will be described that explains the paradoxical absence of Mn^{2+} emission in Mn^{2+}-doped CdSe quantum dots reported previously.

[1] Archer, P. I.; Santangelo, S. A.; Gamelin, D. R., Nano. Lett., 7, 1037-1043 (2007).

10:40am **MI-ThM9 Structural and Magnetic Properties of Mn-implanted 3C-SiC**, ***K. Bouziane***, Sultan Qaboos University, Oman

Unlike many Dilute Magnetic Semiconductors particularly Si based ones,[1] very little attention has been paid to SiC despite its potential for high-power, high-temperature electronics and its large compatibility with the mature Si technology. With its wide bandgap, excellent transport properties and dopability, it might be a promising candidate for spintronic applications. Due to a limited solubility of Mn in the host SiC materials, we have used Mn+ implantation (energy of 80 keV and dose of 5x1015 cm^{-2}) to achieve higher Mn atomic concentration of 1.8 % in micrometric thick 3C-SiC films; aiming to enhance the Curie temperature. We have used Rutherford backscattering (RBS) and X-ray diffraction (XRD) techniques to asses the defects introduced by Mn–implantation, as well as magnetometry to investigate the magnetic properties. RBS measurements on single SiC indicate high concentration of defects at a depth of about 45 nm from the surface, with Mn randomly distributed in the host SiC material. XRD spectra show no indication of formation of secondary alloying phase. Both single and polycrystalline implanted samples were found to be ferromagnetic at room temperature with a magnetic moment per Mn atom of about 0.37μB and 0.5μB, respectively. The amorphous layer was recrystallized after annealing at 750 °C for 10 min as indicated by RBS results, yielding an enhancement of magnetic moment. First principle calculation using Full-Potential Linearized-Augmented-Plane-Wave method for different environments and vacancy configurations was performed to better understand and establish a correlation between the structure/microstructure and magnetic properties of single and polycrystalline Mn-implanted 3C-SiC.

[1] M. Bolduc et al., Phys. Rev. B 71 (2005) 033302.

Manufacturing Science and Technology

Room: 615 - Session MS-ThM

Metrology and Characterization for Manufacturing

Moderator: J. Randall, Zyvex Corporation

8:00am **MS-ThM1 Measurement of GST Thin Film Composition and Thickness**, ***M. Ye***, *C.C. Wang, G. Conti*, Applied Materials, Inc.

Recent studies demonstrated that phase change memory (PCM) can achieve fast switching speed, good reversibility and scalability, making it the most promising alternative non-volatile memory (NVM) technology for the next decade. Currently PCM is being actively studied in semiconductor industry, with $Ge_2Sb_2Te_5$ (GST) being the most widely investigated material. GST film thickness and composition are two important quantities that require close monitoring in manufacturing. We have experimented with a number of measurement techniques including x-ray reflectivity (XRR), ellipsometry, wavelength dispersive x-ray fluorescence (WDXRF), energy dispersive x-ray fluorescence (EDXRF), energy dispersive spectroscopy (EDS), Rutherford backscattering spectrometry (RBS), x-ray photoelectron spectroscopy (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and low energy x-ray emission spectroscopy (LEXES). The advantages and limitations of the various characterization and metrology techniques for GST film composition and thickness measurement are compared. XRR can measure GST film physical thickness and density independently with good precision. Our study of WDXRF shows that there is little interference between antimony and tellurium peaks, and that GST film thickness and composition can be measured simultaneously with good precision. XRR and WDXRF can often provide complementary information, which can be very helpful for troubleshooting process and hardware issues. More details will be presented in the paper. In EDXRF and EDS measurements, antimony and tellurium peaks overlap, and good peak modeling is required to deconvolute the peaks to ensure accurate measurement. RBS in general is a very good standardless analytical technique. However its use for GST application is limited since it can not resolve antimony and tellurium peaks. Particle-induced x-ray emission (PIXE) can be used together with RBS at the cost of measurement accuracy, yet PIXE still requires peak profile modeling. ICP-OES provides reasonable accurate results, but it is a destructive technique and thus not practical for process monitoring. We have also looked into XPS and LEXES for GST-related applications. The effects of sputtering process parameters such as pressure, temperature and wafer bias on GST film composition are discussed. The GST film composition variation through a sputtering target life is also monitored.

8:20am **MS-ThM2 Gate Oxide Process Control Optimization by XPS in a Semiconductor Fabrication Line***, **A. Le Gouil,** N. Cabuil, P. Dupeyrat,* STMicroelectronics, France*, B. Dickson, M. Kwan,* Revera*, D. Barge,* NXP*, O. Doclot,* STMicroelectronics, France*, J.C. Royer*, CEA/LETI-Minatec, France

The introduction of thinner films such as 15-20 Å SiON gate oxides makes in-line metrology challenges more complex. Nitrogen dose in the SiON film is strongly process deposition dependent and is one key parameter of advanced CMOS technologies. Therefore, optimized process control has to be implemented in-line to ensure process stability. Measurement techniques such as X-Ray Metrology have to move from offline characterization laboratories to fabrication lines and ultimately to in-line metrology. Among these techniques, X-ray Photoelectron Spectroscopy (XPS) is one of the best adapted metrology methods to ensure nitrogen dose monitoring of SiON gate oxides. Until recently, decoupled plasma nitridation (DPN) process monitoring has been performed on monitor wafers. However, measurements performed on monitor wafers may not fully represent actual electrical properties at the device level. Measurements on production lots allow inline detection of process excursions and provide real time feedback of process chambers' stability. Additional productivity improvements are reducing consumption of monitor wafers and their processing as well as data acquisition for correlations with device reliability parameters. The implementation in production of SiON gate monitoring on production lots implies to fully characterize the nitridation process on patterned wafers. This study is dedicated to a comparison between monitor and patterned wafers of DPN processes for 65nm node technology and below. Measurements are carried out in a next generation XPS tool with a 35µm spot size and pattern recognition capability that enable material metrology on product wafers. XPS measurements on patterned wafers are performed in specific test structures which dimensions are 50µm x 70µm using an Al Ka monochromatic X-ray source. A larger X-ray spot providing higher signal level is available for measurements on monitor wafers. First, gate oxides will be characterized for each process and tool measurement precisions will be shown. Second, nitrogen dose and thickness uniformity over the wafer will be compared and discussed. Third, different mappings protocols will be studied to identify the best compromise between throughput and an optimized mapping representative of process distribution. Finally, we will conclude with a selection of an optimized process control strategy of gate oxides.

8:40am **MS-ThM3 The Helium Ion Microscope and Applications for Semiconductor Manufacturing and Characterization***, **J. Notte**, N.P. Economou, B. Ward, R. Hill,* ALIS Corporation (Carl Zeiss SMT)**INVITED**

ALIS Corporation (a Carl Zeiss SMT company) has developed a helium ion microscope which provides high resolution images with strong contrast mechanisms. Although technically a focused ion beam (FIB) the microscope operates more like a scanning electron microscope (SEM) but with higher resolution and stronger contrast. The technology and its general capabilities are being presented in another session. This paper addresses some of the semiconductor manufacturing applications which are well suited to the helium ion microscope. Process development and process monitoring require high resolution imaging and contrast mechanisms that are sensitive to material differences. The helium ion microscope is well suited to these tasks. In particular, the secondary electron images can reveal fine details which contain topographic or material information. Grain formation is evident through well established channeling contrast mechanisms. Electrical properties can be revealed by virtue of the beam induced voltage contrast effects. Images can also be generated from the scattered helium ions, providing the ability to distinguish different materials based on their atomic number. This also has the advantage of giving a resolution which is superior to the presently used EDX analysis. Testing has been conducted to look for any effects of damage to semiconductor devices. In particular, a series of tests were conducted to examine any possible effect on the transistor turn on voltages, Vt, after various exposures to helium ions. Test results show no measurable shift. Higher dosages have been tested to look for other signs of damage. Additional manufacturing applications will be presented.

9:20am **MS-ThM5 Characterization of Electronic Materials with Atom Probe Tomography***, **T. Kelly***, Imago Scientific Instruments **INVITED**

Atom probe tomography provides three-dimensional structural and compositional analysis of materials at the atomic scale. It has been applied increasing frequently in the past few years to materials characterization challenges in the semiconductor industry. Specimen preparation advances have made it routine now to extract and analyze materials from wafers and even finished components. Major developments in LEAP technology by Imago Scientific Instruments have led to greater facility for running specimens and greater detail in quantitative analysis. Important examples of analyses of CMOS semiconductor structures and devices, thin-film multilayer structures, and even organic nanostructures will be shown.

10:00am **MS-ThM7 Structural Fingerprinting of Nanocrystals on the Basis of High Resolution Transmission Electron Microscopy and Open-Access Databases***, **P. Moeck,*** Portland State University*, P. Fraundorf*, University of Missouri at St. Louis

It is well known that many nanocrystals can not be identified from their powder X-ray diffraction pattern as it is customary for micrometer sized crystals. When nanocrystals are involved, i.e. the kinematic scattering approximation is sufficiently well satisfied for fast electrons; a new strategy for lattice-fringe fingerprinting from Fourier transforms of high-resolution phase contrast transmission electron microscopy (HRTEM) images is feasible. This strategy relies on crystal structure information that is transferred to HRTEM images in the weak-phase object approximation. Such information is contained in (i) the projected reciprocal lattice geometry, (ii) the phase angle distribution (in the imaginary part of the Fourier transform of HRTEM images), and (iii) the relative intensities at the positions of reciprocal lattice points. Systematic intensities close to zero at certain lattice points may suggest kinematical absences of diffracted beams, aiding the structural fingerprinting. Nanocrystal structure specific limitations to the application of this strategy are discussed. The first tests of this strategy have been promising and the whole procedure could be automated in the current generation of computer controlled HRTEMs. When automated, mixtures of nanocrystals could be analyzed both qualitatively and quantitatively. Since each nanocrystal would be identified individually and thousands of nanocrystals could be processed automatically, the detection limits of lattice fringe fingerprinting could readily be pushed to levels that are by far superior to those of traditional powder X-ray diffraction fingerprinting. The Crystallography Open Database (COD, http://crystallography.net) and its mainly inorganic subset (http://nanocrystallography.research.pdx.edu/CIF-searchable/cod.php) are discussed because the whole lattice-fringe fingerprinting concept is only viable if there are comprehensive databases to support the identification of unknown nanocrystals. While the COD contains the atomic coordinates, space group, lattice parameters, and other crystallographic information for more than 50,000 compounds, we provide at the research servers of Portland State University in addition interactive 3D structure visualizations and theoretical 2D lattice-fringe fingerprint plots for approximately 10,000 compounds for the mainly inorganic subset of the COD.

10:20am **MS-ThM8 The CD-AFM Technique as a Mean to Accelerate Advanced Process Development for the 45nm Node and Beyond***, **J. Foucher,*** CEA-LETI-MINATEC, France*, E. Pargon,* LTM-CNRS, France*, P. Faurie,* CEA-LETI-MINATEC, France*, M. Martin*, LTM-CNRS, France

As devices dimensions and architectures move towards the 32nm node, CD metrology needs for both production process monitoring and process development must cope with new challenges affected by unknown new materials, architectures and processes. One of the main challenges for advance node requirement is the accuracy in CD metrology which becomes mandatory not only at the R&D level but also at the manufacturing level. By simplicity and also because there was no impact on production yield, the semiconductor industry has traditionally followed a single CD value for use in statistical process control as a representation of their products on a wafer. For advanced processes, the control of profile shape and Line Width Roughness (LWR) is increasingly critical and subsequently the need in metrology accuracy for improvement of sidewall angle (SWA) and LWR is necessary. Through various examples of process development as regards advanced lithography, front-end or back-end etching, we will show that the CD-AFM technique represents a great opportunity to add accuracy in the Semiconductor manufacturing world and will allow other metrology techniques to progress in term of accuracy and subsequently will permit to decrease R&D and manufacturing cost.

10:40am **MS-ThM9 Analysis of Ion Implantation Damage in Silicon Wafers***, **R.K. Ahrenkiel***, University of Denver

Ion implantation has become the standard method for building high-density, microelectronic devices. Rapid thermal annealing (RTA) is required to activate the implanted donor and acceptor species. Also, RTA is required to heal the lattice damage created by heavy ion implants such as boron, BF2, phosphorous and arsenic. The RTA process is required to maintain the structural integrity of the semiconductor used for submicron-integrated circuits, as dopant diffusion will destroy the implantation pattern using a long-duration heat treatment. There is a trade-off between the maintenance of the implantation pattern and the elimination of radiation damage. A quick, efficient, and contactless diagnostic of the implantation damage is highly desirable in both research and production environments. The resonant-coupled photoconductive decay (RCPCD) technique uses a deeply penetrating, low-microwave-frequency probe in conjunction with pulses from a tunable laser source. The recombination lifetime of the implanted region decreases many orders of magnitude as a result of implantation. The implanted region has electrical transport characteristics that are similar to those of amorphous silicon. For example, the recombination lifetime of the implanted regions becomes sub nanosecond, and similar to that of amorphous silicon. I have found the doubled YAG laser frequency of 532 nm to be especially useful for sensitivity to implantation damage. RTA restores the crystalline structure, and the degree of restoration depends on the RTA process. The implantation damage is manifested in a sharp decrease in the recombination lifetime when using strongly absorbed light, that is primarily absorbed in the implanted region. In addition, the as-implanted layer acts as a "sink" for minority carriers that are generated in the undamaged crystalline regions. The lifetime increases with various annealing processes, and one can correlate the lifetime changes with the specific annealing protocol. I will also show data for the sheet resistance, which is correlated with the increase of lifetime in the implanted volume. In summary, I will present a method for quickly evaluating the damage elimination of various implantation-annealing processes.

Nanometer-scale Science and Technology

Room: 616 - Session NS-ThM

Nanotube Devices and Processes

Moderator: S.V. Kalinin, Oak Ridge National Laboratory, S. Evoy, University of Alberta, Canada

8:00am **NS-ThM1 Single Charge Sensing by Carbon Nanotube Single-Hole Transistor*, K. Matsumoto***, Osaka University, Japan

We have succeeded in detecting the single charge transition near the channel of single walled carbon nanotube (SWNT) single-hole transistor (SHT). Abrupt discrete switching of the source-drain current is observed in the electrical measurements of SWNT SHT. These random telegraph signals (RTS) are attributed to charge fluctuating near the SWNT SHT conduction channels. The sample has a back gate FET structure with the source-drain spacing of 73 nm. The channel is formed by thermal CVD grown single walled carbon nanotube on the SiO2 substrate. The silicon dioxide layer was deposited on the SWNT SHT to prevent the adsorption & desorption of the molecules to the carbon nanotube channel. In the drain current-gate voltage characteristics of SWNT SHT under the drain voltage of 11 mV at 7.3 K, drain current showed periodic peaks and valleys structure, with two. The large period of 3 V was attributed to Coulomb oscillation characteristic,d the small period of 0.5 V to the quantum interference property of hole. The drain current was observed only in negative gate voltage region, which indicates that the measured SWNT SHT has the p type semiconductor property. The SWNT SHT shows random telegraph signals (RTS), which were attributed to fluctuating charge traps near the SWNT SHT conduction channels. The RTS appeared two levels, upper level and lower level in drain current, the occupation probabilities of which was depended on the applied gate voltage. Using the simple model we assumed, we could estimate the distance between the trap and the channel of SWNT SHT to be L=1.03 nm. The potential energy barrier between the trap state and the Fermi level of carbon nanotube channel was also founded to be 3.2 meV. Thus, using the carbon nanotube single hole transistor, we have succeeded in detecting and analyzing the single charge transition.

8:20am **NS-ThM2 Single Molecule Sensing with Carbon Nanotubes, *B.G. Goldsmith***, *J.G. Coroneus, V.R. Khalap, A.A. Kane, G.A. Weiss, P.G. Collins*, University of California at Irvine

Due to their extremely small size, single walled carbon nanotubes (SWCNTs) provide a promising framework for building single molecule electronic devices. We have developed a procedure to controllably form single carboxyl groups on a CNT's sidewall . By limiting the chemically sensitive region of a nanostructure to a single binding site, single molecule bonding dynamics become visible. Discrete changes in the circuit conductance reveal chemical processes happening in real-time and allow SWNT sidewalls to be deterministically broken, reformed, and conjugated to target species, creating new possibilities for chemical sensing and molecular electronics.

8:40am **NS-ThM3 STM and STS Studies of SWCNT on NaCl/Ag(100), *H.-J. Shin***, *S. Clair, Y. Kim*, Riken, Japan, ***M. Kawai***, Riken and University of Tokyo, Japan

Single-walled carbon nanotubes (SWCNTs) have been considered as one of the most promising candidates for future electronic devices due to their unique electrical properties. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) have provided a lot of information about the structure and electronic properties of SWCNTs.[1,2] In most STM studies of SWCNT, it was carried out on metals or semiconductors so far. In these cases, the electronic structure of SWCNT can be perturbed by the presence of the electrons of the surface. For example, the charge transfer between metal substrate and SWCNT results in the shift of Fermi-level of SWCNT on Au(111) to the valence band.[2] In this study, we studied electronic structure of SWCNT on NaCl thin film by STM and STS. We introduced insulating layer to reduce the influence of metal surface. We deposited SWCNT on the NaCl(100) film, grown on Ag(100) single crystal by dry contact transfer technique in UHV.[3] Interestingly, the Fermi-level of SWCNT shifted to the conduction band on Ag(100), while it shifted to the valence band on NaCl film. The charge transfer due to work function difference between Ag(100) (4.3eV) and SWCNT (4.8 ~ 5.0eV) was the main reason for the Fermi-level shift of SWCNT on Ag surface. On NaCl film, it is thought that the dipole moment at the interface between NaCl and Ag brought about Fermi-level shift to the conduction band, though the work function of NaCl on Ag(100) is 3.6 ~ 4.0eV, much lower than that of Ag(100). The influence of dipole moment on the electronic structure of SWCNT will be discussed in details.

[1] J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, and C. Dekker, Nature 391, 59 (1998).

[2] M. Ouyang, J.-L. Huang, and C.M. Lieber, Annu. Rev. Phys. Chem. 53, 201 (2002).

[3] P.M. Albrecht and J.W. Lyding, Appl. Phys. Lett. 83, 5029 (2003).

9:00am **NS-ThM4 Evaluation of High k Dielectric Films for Carbon Nanotube FETs, *W. Miller***, *S.V. Krishnaswamy, J.M. Murduck, H. Zhang, J. Baumgardner, A.A. Pesetski, J.X. Przybysz, J.D. Adam*, Northrop Grumman Electronic Systems

Carbon nanotube FETs are promising candidates for future RF applications because they simultaneously offer high speed, high linearity, low power and low noise. Carbon nanotube FETs are projected to have a cut-off frequency of over 1 THz due to their small size and high carrier mobility, 1000x lower dissipated power than current GaAs devices without sacrificing linearity. Successful development of CNT electronics will enable the fielding of RF systems that are not currently possible because of prime power requirements. CNT FETs will have a large impact in RF electronics applications where linearity is critical. Based on our simulations, CNT FETs can be designed to be intrinsically linear provided one uses a gate dielectric material with dielectric constant >15. In our work we have evaluated several candidate materials such as HfO_2, ZrO_2, Ta_2O_5, TiO_2 etc. Thin films of these gate dielectric materials have been grown at various laboratories using different techniques. While sputtering is a standard technique used in the semiconductor industry, sputtering of these materials on to CNT significantly deteriorated the performance of the devices. Dielectric for gate oxide in our CNT IC process must have high dielectric constant, be compatible with CNT, have good dielectric integrity and have reasonable breakdown voltages. We will report our results on atomically smooth TiO_2 films using rf magnetron sputtering with auxiliary magnet under the substrate. In addition we will report on ALD HfO_2 and evaporated Ta_2O_5 films along with our results obtained from CNT FETs using these different gate dielectrics.

9:20am **NS-ThM5 Erbium and/or Ytterbium Doped Yttrium Oxide Nanotubes for Optical Amplifier Application, *Y. Mao***, *J.P. Chang*, University of California at Los Angeles

Yttria is one promising hosting material for rare-earth-ion-activated phosphors with applications including amplifiers, lasers, waveguides, X-ray imaging, bioimaging, and displays due to their luminescent characteristics and stability in high vacuum. In fact, in our most recent study, we have deposited Er-doped Y_2O_3 thin films by radical-enhanced atomic layer deposition (ALD)[1] and demonstrated that the Er incorporated in Y_2O_3 can reach a concentration as high as 10^{21} cm^{-3} with outstanding room temperature photoluminescence (PL) at 1.54 µm in thin Er-doped (6-14 at. %) Y_2O_3 films deposited at 350°C.[2] Meanwhile, nanomaterials exhibit physical properties, in particular, increased luminescence efficiency, which are not observed with their bulk counterparts. Hence, in this talk, we present our recent work on the synthesis of nanotubes of rare-earth (RE, Er and Yb) doped Y_2O_3, by a solution synthetic method. The processing temperature, pH, time, addition rate of NaOH, the concentration of precursors, and the annealing temperature dictated the nucleation/growth of RE doped $Y(OH)_3$ nanotubes. These tubes were converted to RE doped yttria by high temperature annealing and the resulting nanotubes had varying RE dopant concentrations (0-100%) with sizes ranging from 40-500 nm in diameter and 2-10 µm in length. X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microsecopy (HRTEM), selected area electron diffraction (SAED), and extended x-ray absorption fine structure (EXAFS) were combined to delineate the structure and composition of these nanotubes. The erbium coordination number and local bonding environment are assessed by synchrotron based EXAFS analysis, and are shown to dictate the measured photoluminescence intensity.[3] Their room luminescent properties (PL and catholuminescence, CL) are outstanding and even superior than the thin films synthesized by ALD. Finally, we will discuss their electronic properties and the application of these doped yttria nanostructures as small and compact planar optical amplifier.

[1] T.T. Van and J.P. Chang, Appl Phys Lett, 87, 011907 (2005).

[2] T.T. Van, J. Hoang, R. Ostroumov, K. L. Wang, J. R. Bargar, J. Lu, H.-O. Blom, and J.P. Chang, J Appl Phys, 100, 073512 (2006).

[3] T.T. Van, J. R. Bargar, and J.P. Chang, J Appl Phys, 100, 023115 (2006).

9:40am **NS-ThM6 Ultrahigh-Vacuum Scanning Tunneling Microscopy Study Into the Adsorption of N-methyl-pyrrolidone Molecules on Carbon Nanotubes**, ***Z.T. Wang****, P.M. Ryan, N.P.P. Niraj, J.J. Boland*, Trinity College Dublin, Ireland

The most common processing technique for carbon nanotubes involves dispersing them in a liquid media. However, due to their high molecular weight, nanotubes suspend and are not soluble in all known solvents. Usually, surfactants are used to overcome this obstacle.[1] Recently people found that pristine single wall carbon nanotubes can be spontaneously dispersed and even exfoliated in an N-methyl-pyrrolidone (NMP) solvent, forming a carbon nanotube solution.[2] The negative free energy of mixing NMP with nanotubes leads to the strongly adsorption of a huge number of NMP molecules on the nanotubes in NMP solution and even dried-powder. In our experiments, carbon nanotubes processed by the NMP solvent are deposited on clean Si(001) substrates using a dry deposition method[3] and investigated using an ultrahigh-vacuum (UHV) scanning tunneling microscope (STM). We find that NMP molecules diffuse from the nanotubes and become irreversibly chemically adsorbed on Si(001) surfaces due to the strong interaction of nitrogen with Si dangling bonds, indicating NMP molecules remain bound to nanotubes even under UHV conditions. However a few remaining molecules reversibly bound to the nanotubes are observed using STM and are seen to emerge from tube bundles. The molecules can migrate on the bundles during imaging and finally become bound to the Si(001) substrate. After all NMP molecules are removed, there is no defect left on the nanotubes.

[1] G. S. Duesberg et al, Chemical Communications, 435 (Feb, 1998)

[2] S. D. Bergin et al, unpublished.

[3] P.M. Albrecht and J. W. Lyding, App. Phys. Lett. 83, 5029 (2003).

10:00am **NS-ThM7 Growth Promotion and Etching of Carbon Nanotubes by CO_2 in Chemical Vapor Deposition using CH_4 Gas**, ***Y. Suda****, T. Saito, A. Okita, J. Takayama,* Hokkaido University, Japan, *J. Nakamura,* Tsukuba University, Japan, *Y. Sakai, H. Sugawara*, Hokkaido University, Japan

Oxidant has been used for growth promotion of carbon nanotubes (CNTs) in CVD since the work by Hata, et al.[1] We report the effect of CO_2 addition to CH_4 gas on CNT growth. The CVD chamber is evacuated down to 10^{-6} Torr by a turbo-molecular pump followed by a rotary pump. We used $Mo_{(0.025)}/Fe_{(0.05)}/MgO_{(0.925)}$ or $Mo_{(0.025)}/Ni_{(0.05)}/MgO_{(0.925)}$ as a catalyst, H_2 gas as a reductant and CH_4 gas as a feedstock.[2] CO_2 gas was introduced during the CNT growth at a temperature of 800°C and its concentration in CH_4 was varied from 0.0037% (37 ppm) to 50%. The other experimental parameters are as follows: H_2 gas pressure = 100 Torr and flow rate = 100 sccm for reduction; CO_2/CH_4 gas pressure = 100 Torr and flow rate = 76 sccm for growth. The CNT yield and the G/D ratio in the Raman spectra of CNTs grown in 10%-CO_2/CH_4 were slightly higher (~86%) than that grown in CH_4 only (~71%). However, CNTs were hardly grown when the CO_2 concentration was more than 20%. Decreasing the CO_2 concentration down to 37 ppm, it was found that single-walled CNTs (SWCNTs) with a yield of ~10% were grown and that the yield for 60 min was 1.5 times higher than that for 10 min. This suggests that the SWCNT growth in a CO_2/CH_4 gas mixture continued for 60 min. The G/D ratio obtained from 37 ppm-CO_2/CH_4 was almost the same as that grown from CH_4 only. The radial breathing mode (RBM) obtained by a 632.8 nm excitation shows that the SWCNT diameter ranges from 0.9 to 1.3 nm and that a few metallic SWCNTs were eliminated but most of semiconducting SWCNTs remained.

[1] K. Hata, et al, Science, 306 (2004) 1362-1364

[2] L.-P. Zhou, et al, J. Phys. Chem. B, 109 (2005) 4439-4447.

10:40am **NS-ThM9 Effect of Nitrogen Dopant on the Structure and Electrocatalytic Activity of Arrayed Multi-Walled Carbon Nanotubes**, ***Y.-G. Lin****,* National Chiao Tung University, Taiwan, *Y.-K. Hsu,* Academia Sinica, Taiwan, *J.-L. Yang, S.-Y. Chen,* National Chiao Tung University, Taiwan, *K.-H. Chen,* Academia Sinica, Taiwan, *L.-C. Chen*, National Taiwan University

With the recent advancements in nanoscience and nanotechnology, carbon nanotubes (CNTs) have drawn a great deal of attention as novel catalyst supports due to their unique structure, high surface area, stability, and excellent mechanical and electrical properties, all of which could offer improvements for fuel cell applications. We have developed a method to synthesize well-aligned nitrogen-containing carbon nanotube (CNx NT) by microwave-enhanced chemical vapour deposition with a source gas of CH4, N2, and H2. Here we report our recent results on employing different flow rate of nitrogen to control the structure and electrochemical activity of CNx NTs. The effect of nitrogen on the structure and electrochemistry has been examined by Raman spectroscopy, scanning electron microscopy (SEM), X-ray photonelectron spectroscopy (XPS), and cyclic voltammetry (CV) using the redox probe of Fe(CN)63-/Fe(CN)64-. From the structural investigation, as the flow rate of N2 gas is higher than 120 sccm, the average diameter of the nanotubes goes beyond 100 nm. The intensity ratio of the D band to G band of Raman spectrum increased with increasing N2 flow rate from 0 to 40 sccm, and then rapidly decreased with further increase in the flow rate of N2. Similarly, XPS results showed the highest nitrogen concentration occurred at 40 sccm and the intensity of pyridine-type N bonding which causes the interlinked node morphology inside the CNx NTs increased with increasing N2 gas flow rate. Hence, the nitrogen-incorporation promotes the disorder in graphitic structure in the initial stage; however, further increase in the N2 flow rate won't enrich the nitrogen concentration in CNx NTs, but raise the growth temperature leading to enhanced graphitization. In addition, CNx NT electrode with N2 flow rate of 40 sccm was found to significantly improve the electron transfer kinetics of Fe(CN)63-/4- redox couple, approaching almost reversible electron transfer kinetics. The reason could be ascribed that the nitrogen treatment at 40 sccm creates disordered and chemically active sites which play a key role to facilitate electron transfer.

Plasma Science and Technology

Room: 606 - Session PS1-ThM

Plasma-Surface Interactions II

Moderator: C.A. Wolden, Colorado School of Mines

8:00am **PS1-ThM1 Plasma Modification of Surface Traps in Mesoporous TiO_2**, ***D.J.V. Pulsipher****, E.R. Fisher*, Colorado State University

Plasma surface modification can be effective in permanently modifying inorganic nanosurfaces. Particularly, mesoporous films formed from TiO_2 nanoparticles are interesting candidates for modification due to their important surface states needed for photovoltaic and photocatalytic applications. Plasma processing offers the opportunity of selectively modifying surface states to facilitate their investigation. Electron trap states in TiO_2-based devices, which are predominately located on TiO_2 particle surfaces,[1] can be detrimental in photovoltaic devices or beneficial in photocatalytic devices; consequently, controlling the quantity of these surface states by learning what causes and affects them will lead to more efficient devices. Here, low temperature inductively coupled plasmas are used to modify the surfaces of mesoporous TiO_2 films. Precursor gases such as O_2, H_2O, and H_2 have been used. Film surface states were primarily monitored by X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). The binding energy of a second O1s peak in the XPS spectra increases for increasing O_2 plasma powers in the range of 75-225 Watts, and the modified films have at least a 6% increase in surface altering oxygen sites which persisted for more than 6 months. PL results suggest[2] a decreased density of surface traps in oxygenated films.

[1] N. Kopidakis, N. R. Neale, K. Zhu, J. van de Lagemaat,A. J. Frank, J Appl. Phys. Lett. 87, 202106.1 (2005).

[2] D. Zhang, J. A. Downing, F. J. Knorr, J. L. McHale, J. Phys. Chem. B 110, 21890 (2006).

8:20am **PS1-ThM2 A Robust Passivation-Enhanced Cryogenic Process used for Silicon Deep Etching**

L.E. Pichon*, E.H. Oubensaid, C. Duluard, R. Dussart, P. Lefaucheux,* GREMI/CNRS, Université d'Orléans, France*, M. Boufnichel,* STMicroelectronics Tours, France*, P. Ranson,* GREMI/CNRS, Université d'Orléans, France*, L.J. Overzet*, University of Texas at Dallas

The need to scale down integrated circuits can be achieved by reducing transistor dimensions and also by 3D-integration. The latter takes advantage of high aspect ratio features and uses the silicon wafer volume as well as its surface. As a consequence, deep silicon etching is of crucial importance for 3D-integration. At GREMI laboratory, the cryogenic process is investigated for etching high aspect ratio structures in silicon. Generally, an inductively coupled SF_6/O_2 plasma is used to simultaneously etch silicon and deposit a passivation layer on the sidewalls at low temperature. When the wafer is warmed up to ambient temperature, the passivation film desorbs. Thus, the sidewalls are clean and have a low roughness.[1] The standard cryogenic process allows high etch rates but the passivation layer is not robust. This reduces the use of the cryogenic process in industry. To overcome this problem, passivation mechanisms have been investigated. A previous work has shown that SiF_4 plays a significant role in passivation layer formation.[2] Hence, it is possible to deposit a SiO_xF_y passivation film in SiF_4/O_2 plasma when the silicon substrate is cooled down to cryogenic temperatures. Moreover, a study has shown that the robustness of the passivation film is enhanced when it is grown using a SiF_4/O_2 plasma rather than SF_6/O_2 plasma[2]. We will show the use SiF_4/O_2 plasmas to reinforce the passivation layer during a standard cryogenic process. In brief, the SF_6/O_2 anisotropic etching plasma is regularly stopped and the silicon substrate is exposed to a SiF_4/O_2 plasma to strengthen the SiO_xF_y passivation film. This passivation-enhanced cryogenic process allows to significantly reduce the undercut (e.g. by a factor of 6 for a 10 μmm wide trench). Besides, the undercut can be completely eliminated for submicron trenches with an aspect ratio of 15 while the etch rate dropped only by a factor 1.3. We will present the passivation-enhanced cryogenic process and its performances.

[1] R. Dussart et al, J. Micromech. Microeng., 14 (2004) 190-196

[2] X. Mellhaoui et al, J. Appl. Phys., 98 (2005) 104901 .

8:40am **PS1-ThM3 3-D Profile Simulation of Silicon Etching: The Effects of Redeposition on Surface Roughening**

H. Kawai*, W. Guo, Y.P. Yin, H.H. Sawin*, Massachusetts Institute of Technology

Line edge roughness (LER) on the sidewalls of gate electrodes in metal oxide semiconductor transistors is one of the most challenging issues in the microfabrication process today. Since the roughness does not scale with the feature size, the problem becomes more significant as critical dimensions get smaller for the future technology nodes. To understand LER, we have developed a 3-dimensional feature scale profile simulator to model and simulate the surface and sidewall roughening during the etching process of polysilicon in chlorine, hydrogen bromide and argon plasmas. We simulated the etching process using a dynamic Monte Carlo model, where the simulation domain is discretized into an array of cubic cells. The local surface conformation is fitted with a polynomial, which is used to compute the surface normal, scattering angle, and flux on the 3-D surface. Our results show that the roughening in physical sputtering process is a strong function of ion incidence angle and redeposition of sputtered materials. At normal ion incidence, the surface remains smooth, but at very grazing ion incidence, the surface is roughened along the ion beam direction. At grazing angle, the roughness is enhanced by the redeposition of sputtered materials. The simulator is also capable of modeling the transfer of roughness from the photoresist layer to the underlying layer during the gate etching processes.

9:00am **PS1-ThM4 In Situ Measurement of the Ion Incidence Angle Dependence of the Ion-Enhanced Etching Yield in Plasma Reactors**

R.J. Belen*, S. Gomez,* University of California Santa Barbara*, M. Kiehlbauch,* Lam Research Corporation*, E.S. Aydil*, University of Minnesota

In sputtering and ion-assisted etching processes, the material removal rate is quantified through the use of the sputtering yield, which depends on the energy and the incidence angle of the ions bombarding the surface. The sputtering or ion-assisted etching yield is defined as the number of surface atoms removed per ion impinging on the surface. The most widely used expression for the sputtering yield assumes that it is a product of separable functions of the ion energy and incidence angle and is proportional to the square root of the ion energy and $f(\varphi)$, a function that attempts to capture the dependence of the yield on the ion incidence angle, φ, measured with respect to the surface normal. We demonstrate a technique to measure the dependence of the etching yield on the ion incidence angle by examining cross-sectional scanning electron micrographs (SEM) of features etched under realistic plasma conditions in an arbitrary plasma reactor. The idea for the technique described herein is based on the observation that ions bombarding the surface of a semi-circular shaped feature impinge on various points along the feature at different angles that span the range from normal incidence, , φ, = 0°, to grazing incidence, , φ, = 90°. Thus, the technique is based on measuring the etch rate as a function of position along the walls of features that initially have nearly semi-circular cross sections. These initial feature shapes can be easily obtained by wet or isotropic plasma etching of holes patterned through a mask. The etch rate as a function of distance along the feature profile provides the etching yield as a function of the ion incidence angle. The etch rates are measured by comparing digitized SEM cross-sections of the features before and after plasma etching in gas mixtures of interest. We have applied this technique to measure the ion incidence angle dependence of the Si etching yield in HBr, Cl_2, SF_6 and NF_3 plasmas and binary mixtures of SF_6 and NF_3 with O_2. Advantages and limitations of this method will be discussed.

9:20am **PS1-ThM5 Modeling of Angular Dependence in Plasma Etching Used for Profile Simulation**

W. Guo*, Y.P. Yin, H.H. Sawin*, Massachusetts Institute of Technology

We have completely modeled the angular etching behavior for poly-silicon etching in chlorine chemistry as well as oxide in fluorocarbon chemistry at various operating conditions, including different neutral-to-ion flux ratios, ion energies and ion incidence angles. With this angular model incorporated into the 3-dimensional profile simulation, we can quantitatively predict the line-edge roughness on the sample sidewall. We developed the angular model within the framework of the translating mixed-layer kinetics model described previously. Unlike other kinetics models, we estimated the concentrations of chemical complexes based on the surface composition and assumptions of random atomic mixing and bonding within the top surface layer. Angular curves of various fundamental reactions including physical sputtering, ion-induced etching and dangling bond creation are analyzed using simulation tools such as TRIM. Based on those individual angular curves we predicted the apparent angular dependences at different neutral-to-ion flux ratios and ion energies for poly-silicon etching in chlorine plasmas as well as oxide etching in fluorocarbon chemistry. The simulated etching yields showed quantitative agreement with experimental data. At low neutral-to-ion flux ratio, the etching yield peaks around 60 degree off-normal angle then drops off, similar to physical sputtering. At high neutral-to-ion flux ratio, the etching yield monotonically decreases with ion incidence angle, which is indicative of ion-induced etching. Surface fractions remain stable as a function of ion incidence angle for both poly-silicon and oxide etching, consistent with experimental observation.

9:40am **PS1-ThM6 Geometrical Effects on Etching Profile Evolution**

H. Fukumoto*, K. Eriguchi, K. Ono*, Kyoto University, Japan

Two-dimensional etching profile evolution in two different geometries, an axisymmetric hole and an infinitely long trench, has been calculated to clear the effects of geometrically different structures on etching profile evolution. In the simulation, SiO_2 etching by CF_4 plasmas is assumed because of widely employed processes for the fabrication of contact and via holes, which have various and unique geometrical shapes. The model takes into account the transport of particles in microstructures, together with surface reactions therein through sputtering, ion-assisted etching, chemical etching, and deposition. The model includes ions and neutrals (CF_x^+, CF_x, F; x=1~3) coming from the plasma, under different conditions of particle temperature, density, and ion energy. The simulation domain is enclosed by the sheath-surface interfaces and the feature surfaces of SiO_2 with an inert etching mask. The neutral particles from the plasma onto substrate surfaces are assumed to travel in microstructures with diffusive reflections on feature surfaces, while the ions accelerated through the sheath on the substrate travel with specular reflections on feature surfaces. The cell removal method is employed to represent the feature profile evolution, where the SiO_2 is represented by two-dimensional discrete cells. Numerical results indicate that the etching profiles of hole and trench have the similar tendency under different plasma conditions. However, the two etching profiles have some differences each other; the profile evolution is narrower and slower in the hole than in the trench, where the incident neutral fluxes are more reduced in the hole. Moreover, the profile of the trench has lateral etches such as undercut and bowing on sidewalls. The lateral etches decrease with increasing the ratio of neutral fluorocarbon fluxes, where the neutral fluorocarbons contribute to deposition. The velocity distribution of neutral particles also contribute to the difference of the etching profile evolution in the two structures; in effect, the velocity distributions are the more anisotropic in the hole, because more neutral particles interact with mask sidewalls in the hole, so that more anisotropic particles are conducted onto bottom surfaces after passing the mask features. Thus, it follows that geometrical structures contribute significantly to the behavior of neutral particles therein, and characterize the resulting etched profiles.

10:00am **PS1-ThM7 Growth Precursor Measurements and Study of Plasma Chemistry by Means of Mass Spectrometry**, ***J. Benedikt**, A. Consoli,* Ruhr-University Bochum, Germany*, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands*, A. von Keudell*, Ruhr-University Bochum, Germany **INVITED**

The knowledge of absolute fluxes of reactive species such as radicals or energetic ions to the surface is crucial in understanding the growth or etching of thin films. These species have due to their high reactivity very low densities and their detection is therefore a challenging task. Mass spectrometry (MS) is an ultra sensitive technique and it will be demonstrated in this talk that it is an optimal choice for identification of growth precursors and for the study of plasma chemistry in general. MS measures the plasma composition directly at the surface, it is not limited by (non)existence of accessible optical transitions, as is for example laser spectroscopy, and when properly designed and carefully calibrated, it provides absolute densities of measured species. Two examples of application of MS will be presented. First, the composition of remote argon/acetylene expanding thermal plasma at the position of the substrate has been analyzed by means of molecular beam threshold ionization MS. More than twenty species have been detected including radicals with densities as low as 10^{10} cm^{-3}. Resonantly stabilized radicals, with C_3 being the most important one, have been identified as growth precursors of hard hydrogenated amorphous carbon films and the plasma chemistry pathway leading to their formation has been understood. In the second example, a temporal evolution of neutral species densities during initial stage of dust particle formation in a low pressure acetylene discharge has been measured. Mass spectra with time resolution of 100 ms have been obtained using a step-scan approach and they have been decomposed and quantitatively and qualitatively analyzed using Bayes statistics and calibration measurements. Based on a comparison of our results with in literature available positive and negative ion mass spectra measurements and plasma chemistry modeling of comparable plasma, the electron attachment to larger C_nH_2 species is proposed as an initial step in dust particle formation. Additionally, the analyses indicates the involvement of vinylidene, isomer of acetylene, or vinylidene anion in formation of first aromatic ring and it shows that surface reactions are a significant source of aromatic compounds.

10:40am **PS1-ThM9 Ground and Metastable Atom Densities in Rare-Gas Diluted O_2 and N_2 Plasmas and Silicon Oxynitride Growth**, ***T. Kitajima**, T. Nakano,* National Defense Academy of Japan*, T. Makabe*, Keio University, Japan

The application of rare gas diluted O_2 plasmas for oxide growth have gained interests due to the improved growth rate and film property. Metastable O atoms produced by rare gas metastables may contribute to the enhanced diffusion or reaction of the oxygen atoms at the interface of the film and the substrate. We have shown the increase of the metastable $O(^1D)$ atoms produced in the rare gas diluted O_2 plasma by VUV absorption spectroscopy.[1] The kinetics of the increased $O(^1D)$ atoms and the film growth can be explained by the deduced atom flux using diffusion model. In the study, we extend the scheme to the nitridation of silicon and finally to the oxynitride growth. The ground state $N(^4\ S)$ density in the rare gas diluted N_2 CCP is measured by the VUV absorption spectroscopy using 120 nm emission from the discharge light source ($N(^4\ P) \rightarrow N(^4\ S)$). $N(^4\ S)$ density is 8×10^{10} cm^{-3} for 0.5 Torr and 30 W in pure N_2 CCP and stays 5×10^{10} cm^{-3} even for 1 % of N_2 fraction in Ar diluted N_2 plasma. The trend is also found for the case of He diluted N_2 plasma and should be due to the reduced energy loss of electrons by vibrational excitation. The grown nitrides are examined by the depth profiles of XPS and the growth rate corresponds to the trend of $N(^4\ S)$ density. Detailed results and the case of oxynitrides are shown in the presentation.

[1] T.Kitajima, T.Nakano, and T.Makabe, Appl. Phys. Lett. 88, 091501 (2006).

Plasma Science and Technology

Room: 607 - Session PS2-ThM

Plasma Diagnostics I

Moderator: V.M. Donnelly, University of Houston

8:00am **PS2-ThM1 Ion Flux Measurements in an $Ar/NH_3/SiH_4$ - Remote Plasma using a Pulse Shaped Double-Side Capacitive Probe**, ***M.C. Petcu**, A.C. Bronneberg, M.A. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

In this work the investigation of an Ar - fed remote expanding thermal plasma (ETP) where NH_3/SiH_4 mixtures are injected downstream, is reported. Our interest is mainly focused on ion flux and ion densities measurements at different gas phase compositions. The ion and electron densities measurements using various methods and different plasma conditions have been previously reported in literature. For example, double and single cylindrical Langmuir probes have been successfully used to measure the ion density in non - depositing Ar/NH_3 ETP. A limitation of Langmuir probe measurements is to determine the ion densities in depositing plasmas, e.g. $Ar/NH_3/SiH_4$ mixtures, due to the formation of a resistive layer on the probe. An alternative approach is to use a single-side electrostatic probe, as already proposed in literature. This technique is compatible with the presence of insulating layers, showing the potential for absolute ion flux determination. The method is based on the discharging of an RF-biased capacitance in series with the probe. An alternative method, based on the use of pulse shaped double-side capacitive probe to measure ion flux in Ar/NH_3 and $Ar/NH_3/SiH_4$ plasma mixtures is here proposed. Our approach allows an accurate ion flux determination from the linear discharging of the capacitor connected in series with the collecting surface. Such approach could be easily implemented in a sensor for ion flux control in various discharges, e.g, in the case of a biased substrate to induce ion bombardment during film growth. When Ar/NH_3 mixtures are investigated, a decrease of the ion flux from 10^{18} to 10^{16} $cm^{-2}s^{-1}$ as a function of the NH_3 flow rate is measured and attributed to the consumption of Ar ions due to the charge exchange reaction between Ar ions and NH_3 molecules, followed by the dissociative recombination with low energy electrons. These results are also confirmed by Langmuir probe measurements. Furthermore, the addition of SiH_4 is showing an interesting behavior, i.e., a local increasing of the ion flux presently attributed to the formation of lighter ions, in conditions of high Ar ion depletion due to the high molecular gas flow rates. These measurements, together with mass spectrometry analysis, will be presented and commented in terms of plasma chemistry channels developed in an $Ar/NH_3/SiH_4$ plasma.

8:20am **PS2-ThM2 In Situ Plasma Analysis and Sheath Modeling of Silicon Deep Trench Etching in Capacitively Coupled Dual Frequency HBr/NF3 Plasmas**, ***M. Reinicke***, Dresden University of Technology, Germany, *S. Wege, S. Barth, A. Steinbach,* Qimonda Dresden, Germany, *G. Wenig, A. Kersch,* Qimonda Munich, Germany*, J.W. Bartha*, Dresden University of Technology, Germany

Facing critical dimensions below 50nm requires significantly improved knowledge about complex process mechanisms for DRAM technology development. To extend the knowledge of physical and chemical interactions during high aspect ratio (HAR) silicon etching using HBr/NF3/O2 plasmas, in situ plasma analysis has been performed at the latest generation of multi frequency capacitively coupled MERIE plasma reactors. Focus of this presentation is a detailed investigation of ion angular and energy distribution functions (IAEDFs) since these distributions are considered to be most essential for characterization of plasma-induced silicon deep trench etching using reactive plasma chemistries. Ion distribution functions (IDFs) were measured for basic Ar, HBr, NF3, as well as complex HBr/NF3/O2 plasma chemistries at the ground electrode of the plasma reactor using an in situ Hiden Analytical EQP500 combined energy and mass analyzer. Measured IDFs are compared to calculations using the Hybrid Plasma Sheath Model (HPSM) simulator. Difficulties in measuring IDFs are minimized by simulation of ion trajectories and a careful determination of the relevant transmission functions specific for the plasma monitor used. The hybrid-fluid simulator was additionally modified by implementation of differential cross sections resulting from ab-initio calculations for relevant ion-atom collisions. Finally, combination of measurement and simulation for investigation of the complex nature of multi frequency high voltage rf plasma boundary sheaths is shown to yield valuable information on the IAEDF for ions impacting the substrate and hence influencing etch process results.

8:40am **PS2-ThM3 Noninvasive Monitoring of Ion Current and Ion Energy during Plasma Processing**, ***M.A. Sobolewski***, National Institute of Standards and Technology **INVITED**

The bombardment of substrate surfaces by energetic ions plays an important role in plasma etching and other plasma processing applications. To obtain optimal results, ion current and ion kinetic energy must be carefully controlled. Unfortunately, directly measuring ion current or energy in situ, at a wafer surface during plasma processing, is difficult or impossible. To solve this problem, a technique for indirectly monitoring ion current and energy has been developed. It relies on measurements of the waveforms of rf current and voltage applied to the wafer electrode, which are interpreted by fundamental physical models of the plasma and its sheaths. The technique is noninvasive, i.e., there is no need to insert any probe into the plasma reactor, and it is suitable for use during actual processing in industrial equipment. This talk will describe the technique, the models it uses, and validation tests performed in an rf-biased, inductively coupled plasma reactor. It will also present results from experiments that demonstate the use of the technique to monitor ion current and ion energy during fluorocarbon etch processes and argon sputtering processes, including processes that were perturbed by reactor drift and equipment "faults." I will also discuss the present limitations of the technique and potential extensions of the technique to make it applicable to other plasma processes and other types of plasma reactors.

9:20am **PS2-ThM5 Application of an RF Biased Langmuir Probe to Etch Reactor Chamber Matching, Fault Detection and Process Control**, ***D.L. Keil**, J.-P. Booth, N. Benjamin, C. Thorgrimsson,* Lam Research Corporation, *M. Brooks,* San Jose State University / Lam Research Co., *G. Curley,* Ecole Polytechnique / Lam Research Co., *L. Albarede, D. Cooperberg*, Lam Research Corporation

As feature size shrinks below 45 nm the demand for precision plasma etch process monitoring has increased. The final etched profile is determined by physical processes occurring at the wafer-plasma interface which are typically driven by neutral flux, ion flux and ion energy. However, typically only the RF delivery, gas flow, and chamber temperature are monitored. These measurements are too far removed from the actual physical processes of interest to be of value in tool matching, fault detection and advanced process control. This work examines the usefulness of an RF -biased planar Langmuir probe approach.[1] This method delivers precise real-time (10 Hz) measurements of the ion flux and tail weighted electron temperature and is insensitive to contamination and deposition on the probe. Data was taken during wafer processing, and indicates the utility of this approach for tool matching, process diagnosis, tool fault detection and advanced process control.

[1] J.P. Booth, N. St. J. Braithwaite, A. Goodyear, and P. Barroy, Rev. Sci. Inst., Vol. 71, No 7, July 2000, pgs. 2722-2727.

9:40am **PS2-ThM6 A New Diagnostic Method of Very High-Frequency Plasmas Produced in Insulated Vessels**, ***H. Shindo**, K. Kusaba*, Tokai University, Japan

A new method to measure electron energy by an emissive probe has been proposed. The method is based on measurement of the functional relationship of the floating potential and the heating voltage of emissive probe. From the measured data of the floating potential change as a function of the heating voltage, the curve of the probe collection current-voltage can be analytically obtained. The present method has several important advantages of the following: (1) it is even applicable to radio-frequency plasma in which the potentials are usually fluctuating, (2) also applicable to plasmas which are produced in non-conductive containers. One of key issues in the method is to achieve a perfect floating condition for radio-frequency. To ensure this condition, the probe circuit was optically connected into the measurement circuit. In the experiment, the emissive probe 30 micrometer diameter tungsten was heated by 40 kHz pulse voltage, and the floating potential at the heating voltage off period and the floating potential difference between the heating off and on period were measured by digital oscilloscope in argon plasma. The measurements were made in plasmas, produced by a variety of frequencies of 2 MHz to 60 MHz, and these plasmas are both the capacitively coupled and inductively coupled. It was shown that the plasma electron energy probability function could be obtained without any RF compensating circuit even in capacitively coupled plasmas. In particular at the frequency of 60 MHz, since the method is very sensitive near the plasma potential, the clear indication for the depletion of the low energy electron could be obtained. This low energy electron depletion is due to high plasma potential. Therefore, in the inductively coupled plasma at the frequencies below 27 MHz this low energy electron depletion was obtained near the induction antenna, but at the further positions from the antenna the energy distribution became Maxwellian. This change in the electron energy distribution found in ICP was very systematic with the frequency, the gas pressures and the distances from the antenna. Thus the present method is quite innovative in that it is applicable to the potential fluctuating RF plasma and measurements are all done in a floating condition of probe.

10:00am **PS2-ThM7 On-wafer Real Time Monitoring of Charge-Build-up Voltages during Plasma Etching in Production Equipment**, ***J. Hashimoto**, Y. Yatagai, T. Tatsumi, S. Kawada, M. Konishi, I. Kurachi,* Miyagi Oki Electric Co.,Ltd., Japan, *Y. Ishikawa, S. Samukawa*, Tohoku University, Japan

For requirements of high performance and large scale integration to semiconductor devices, transistor size has been shrunk down to nano-scale regime. Recently, 32nm gate length has been already developed and even 22nm gate length is under studying. As a result, gate insulator thickness of MOSFETs must be thin as less than 1nm in 22nm technology. Consequently, gate oxide breakdown caused by the plasma damage is a significant concern. In addition, extraordinary shape of via hole and etching stop caused by the electron shading effect must be solved to realize high aspect ratio via holes.These issues are attributed to charge-up during plasma etching processes. It is absolutely necessary for solution of them to monitor charge-up phenomena precisely. There are two typical methods to monitor them so far. One is measurement of electrical charge on the blank wafer after processing. The other is charge monitoring by using NVM(Nonvolatile memory). However, both methods dose not function for monitoring them in real time or on the actual patterned wafer. Consequently, the charge-up phenomena during device fabrication plasma etching can not be understood in detail.We succeed to monitor real time charge-up phenomena on the actual patterned wafer by using On-Wafer Monitoring Sensor newly proposed by Dr. Samukawa. In this study, an etcher for production was employed. From data of charge-up quantity under various etching conditions such as gas chemistry, RF power and pressure with various types of On-Wafer Monitoring Sensors, the charge-up phenomena can be revealed and will be reported in the presentation.

10:20am **PS2-ThM8 In-Situ Wafer-Based Plasma Sensor Analysis in Inductively Coupled Plasmas**, ***M.J. Titus**, D.B. Graves*, University of California, Berkeley

In-situ, wafer-based plasma sensors are currently being explored to attack plasma process control and process development challenges. One such commercially available sensor tool is the PlasmaTemp$^{\text{TM}}$ sensor wafer, developed by KLA-Tencor. PlasmaTemp$^{\text{TM}}$ includes an on-board electronics module, coupled with wireless communication, which allows data storage of 30 temperature sensors embedded onto the wafer at different radial positions. In the present work, we focus on molecular gas (e.g. O_2) inductively coupled plasmas (ICPs). Wafer heating mechanisms in molecular gas plasmas can involve effects in addition to those identified in atomic gas plasmas (i.e. ion bombardment and ion-electron recombination). These mechanisms include thermal conduction from the neutral gas, when bulk temperatures are in excess of ~1000K, and atom recombination on the wafer surface. We report a combination of plasma diagnostics and modeling, sensor wafer modeling, and experimental measurements for a variety of conditions in an Ar/O_2 inductively coupled plasma for wafer temperature measurements as well as for other plasma characteristics such as plasma density, ion flux and optical emission intensity.

10:40am **PS2-ThM9 Plasma Process Development and Control with Real-Time Critical Process Parameter Detection at the Wafer Surface**, ***M.R. Tesauro**, R. Koepe, T. Remus,* Qimonda Dresden GmbH & Co. OHG, Germany, *G.A. Roche, P. MacDonald*, KLA-Tencor

Improved semiconductor manufacturing equipment / process diagnostics and control are ever more critical as the push toward ever smaller microelectronics device geometries continues. This is especially true for the fabrication process of controlled destruction: plasma etch. Improved plasma etch process diagnostics can be advantageous for initial development of stable processes to enable fast and profitable manufacturing ramp-up as well as assuring well-matched process results from the multiple plasma processing chambers required for volume manufacturing. Traditionally the focus of diagnostics and control has been on monitoring process chamber inputs (e.g. RF Power, pressure, gas flows, etc.) and outputs (e.g. product critical dimensions, etch rates, particle tests, etc.). Sensors which monitor the average plasma environment (e.g. plasma emission monitoring, advanced RF sensors, etc.) have further improved equipment and process control. Improved technologies now make possible process variable measurement directly at the wafer surface by incorporating sensors into an autonomous data collection sensor wafer. We present the results of such a wireless sensor wafer containing an array of temperature sensors to address issues of process stability and chamber matching. We will show how the unique properties of the thermal â?ofingerprintâ? of the actual plasma process measured near the wafer surface can be used to detect and correct differences between chambers and control for shifts following critical hardware replacement. In addition an example of the potential for process instability detection by thermal fingerprint on the wafer during development instead of during product ramp-up will be presented, showing the advantages and increasing necessity for time-resolved critical process parameter detection at the wafer surface.

Surface Science

Room: 608 - Session SS1-ThM

Oxide Surface Structure II

Moderator: F.P. Netzer, Karl-Franzens University Graz, Austria

8:00am **SS1-ThM1 Observation of a (√3 x √3)R30° Reconstruction on ZnO (000-1)**, ***S.T. King****, S.S. Parihar, K. Pradhan, H.T. Johnson-Steigelman,* University of Wisconsin - Milwaukee*, Z. Zhang, P. Zschack,* Argonne National Laboratory*,* ***P.F. Lyman***, University of Wisconsin - Milwaukee

High energy polar-terminated metal oxide surfaces stabilize by a fascinating set of energy-lowering mechanisms.[1] While MgO(111) and NiO(111) stabilize via a sequence of surface reconstructions, most studies have shown that the (0001) (Zn-polar) and (000-1) (O-polar) faces of ZnO remain unreconstructed. Surface stabilization has been attributed to incomplete charge transfer between the Zn- and O-polar surfaces resulting in metallic surface states.[2] However, a recent He-atom scattering study of H-free ZnO (000-1) observed a (1x3) reconstruction, which de-reconstructs upon H exposure.[3] We extend the knowledge of ZnO surface reconstructions by investigating a (√3x√3)R30° reconstruction on ZnO (000-1) by low energy electron diffraction, x-ray photoelectron spectroscopy, and surface x-ray diffraction. While this reconstruction has been observed on the (0001) face,[4] to our knowledge this is the first reported observation on the O-polar surface. The implications of this reconstruction on understanding ZnO surface stabilization mechanisms will be discussed.

[1] C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)

[2] A. Wander et al., Phys. Rev. Lett. 86, 3811 (2001)

[3] M. Kunat et al., Phys. Rev. B 66, 081402(R) (2002)

[4] Y. Margoninski and R. E. Kirby, J. Phys. C 8, 1516 (1975)

8:20am **SS1-ThM2 $Cu_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ Rocksalt Oxide Surfaces: Novel Environment for Cu^{2+}, Zn^{2+} and Its Effect on the NiO Electronic Structure***, K.J. Gaskell,* ***M.A. Langell***, University of Nebraska

The effect on surface composition, electronic structure and bonding has been investigated for rocksalt $Cu_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ solid solutions, which form at the nickel-rich end of the phase diagram up to approximately x = 0.3. Octahedral coordination presents an unusual environment in solid state oxides for the "guest" Cu^{2+} and Zn^{2+} cations, and their bonding properties can be shown to be significantly different in the rocksalt environment. For example, ab initio calculations of the $Zn_xNi_{1-x}O$ valence band structure indicate that zinc interacts with the lattice oxygen primarily through the Zn 4s orbitals and is less covalent than in wurtzite ZnO. Photoemission results also provide insight into the bonding, and the Ni 2p photoemission changes substantially with increased guest ion concentration due to attenuation in non-local screening effects. The charge-transfer nature of the NiO electronic structure, however, remains largely intact. Auger parameter analysis confirms that the guest ions are octahedrally coordinated, and Auger and x-ray photoelectron spectroscopies show comparable surface and bulk concentrations until phase separation occurs.

8:40am **SS1-ThM3 Surface Study of In_2O_3 and Sn-doped In_2O_3 Thin Films with (100) and (111) Orientations**, ***E.H. Morales,*** Tulane University*, M. Batzill,* University of South Florida*, U. Diebold*, Tulane University

In_2O_3 and Sn-doped In_2O_3 (Indium-Tin Oxide, ITO) exhibit optical transparency combined with low electrical resistivity, and find application in flat panel displays and solar cells. Relatively little is known about their atomic-scale surface properties, mainly because of challenges in preparing single crystal samples. We have grown epitaxial In_2O_3 and ITO films on Yttrium Stabilized Zirconia. The (100) surface has polar character, and the (111) orientation is non-polar. The films were prepared using oxygen-plasma assisted electron beam epitaxy in ultra high vacuum (UHV) conditions. The growth was monitored with Reflection High Energy Electron Diffraction (RHEED). Samples were characterized with X-ray Photoemission Spectroscopy (XPS) and Angle Resolved XPS (ARXPS) using Al-Ka radiation and Low Energy Electron Diffraction (LEED) in-situ, as well as synchrotron-based Ultra-Violet Photoemission Spectroscopy (UPS) . The films were stoichiometric, except for ITO(100), where ARXPS indicates Sn segregation. In_2O_3 (100) shows faceting in LEED, while ITO(100) stays flat with a 1x1 surface termination. Thus, it appears that Sn-segregation to the surface stabilizes the polar In_2O_3 (100). In_2O_3 (111) exhibits a (√3x√3)R30° reconstruction in LEED. Up to 9 at% Sn in ITO (111) does not seem to alter this reconstruction. Resonant photoemission measurements indicate a Sn-derived band gap state with resonance at 30 eV photon energy on the ITO (100) film; this gap state is far less pronounced on ITO (111). Interestingly, the valence band maximum is located at 2.5 and 2.7 eV below the (surface) Fermi level for ITO (100) and (111), respectively. This is ca. 1 eV higher than expected for a heavily n-type doped material with a direct optical band gap of 3.7 eV. Reasons for this apparent discrepancy will be discussed.

9:00am **SS1-ThM4 Structure of the Polar Oxide Surface MgO(111) (√3 x √3)R30°**, ***S.E. Chamberlin****, H.C. Poon, D.K. Saldin, C.J. Hirschmugl*, University of Wisconsin - Milwaukee

Structures of polar oxide surfaces have been of great interest with several models proposed to compensate the "polar surface instability problem," including 1.) adsorption of foreign species, e.g. a hydroxylated surface, 2.) surface faceting, and 3.) metallization.[1] MgO(111), the polar surface of a prototypical rocksalt structure, has been shown to maintain a 1x1 structure when annealed to low temperatures and reconstruct when heated to higher temperatures,[2] and thus represents an ideal system for detailed structural analysis. Detailed surface structure for the 1x1 and progress towards a structure for the (√3 x √3)R30° reconstruction will be presented. The data have recently been obtained with a novel, low-current delay-line-detector LEED (DLD-LEED) system to minimize electron damage. An hydroxylated 1x1 surface was found to be in good agreement with photoelectron diffraction and electronic structure calculations,[3] but LEED-IV and Direct Methods results for the MgO(111) (√3 x √3)R30° will be shown where the structure does not agree with previously published models.[2,4]

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[4] A. Subramanian, L.D. Marks, O. Warschkow, D.E. Ellis, Phys. Rev. Lett. 92, 200411 (2004)

9:20am **SS1-ThM5 Monocrystalline TiO_2 Nanoparticles Growth on Au(111) Surface by RLAD Method**, ***D.V. Potapenko,*** Columbia University*, J. Hrbek,* Brookhaven National Laboratory*, R.M. Osgood*, Columbia University

Titanium oxide is a promising photocatalytic material and has been the subject of much research throughout the last two decades. Nanostructuring is one approach for tailoring the properties of a catalyst. Recently, two methods of preparation of titania nanoparticles on Au(111) surfaces were reported (Z. Song at al. 2005 and E. Farfan-Arribas et al. 2005); yet no light-induced chemistry was observed on such nanoparticles to date. In order to prepare photoactive nanoparticles, we have conducted an extensive STM study of the growth of TiO_2 on a Au(111) surface by Reactive Layer Assisted Deposition (RLAD). The method consists of physical vapor deposition of Ti on a predeposited layer of oxygen-containing reactant followed by annealing to a higher temperature that removes the excess of the reactant. In the experiments with water as a reactive layer, we investigated the dependence of morphology of the produced arrays of titania nanoparticles on the thickness of the water multilayers. At water coverages above 50 ML we found evidence for role of an intermediate liquid water layer formed as the temperature is increased. The dynamics of water evaporation, rather than the underlying Au surface reconstruction, determined the particle distribution on the surface in this case. This relatively thick water layer also has caused us to observe evidence of the titanium hydride formation. At temperatures above 300 K the hydride decomposed leaving the titanium buried under a gold layer. The typical size of initially formed titania nanoparticles was 1 nm. At more elevated temperatures, nanoparticles coalesced so that by a temperature of 900 K about 80 % of the titania material was converted into single-crystal, flat islands with edges parallel to Au [1-10] directions, with their heights being a multiple of 0.55 nm. The atomic structure of the islands will be discussed. We have also attempted to use NH_4NO_3 as a reactive layer and the corresponding results will be presented.

9:40am **SS1-ThM6 Reactive Ballistic Deposition of Porous TiO_2 Films**, ***D.W. Flaherty,*** University of Texas at Austin*, Z. Dohnálek,* Pacific Northwest National Laboratory*, T.E. Engstrom,* University of Texas at Austin*, A. Dohnálková, B.W. Arey, D.E. McCready, N. Ponnusamy,* Pacific Northwest National Laboratory*, C.B. Mullins,* University of Texas at Austin*, B.D. Kay*, Pacific Northwest National Laboratory

Nanoporous, high-surface area films of TiO_2 are synthesized by reactive ballistic deposition of titanium metal in an oxygen ambient.[1] Auger electron spectroscopy (AES) is used to investigate the stoichiometric dependence of the films on growth conditions (surface temperature and partial pressure of oxygen). Scanning and transmission electron microscopies show that the films consist of arrays of separated filaments. The surface area and the distribution of binding site energies of the films are measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption (TPD) of N_2. TiO_2 films deposited at 50 K at 70° from substrate normal display the greatest specific surface area of 100 m^2/g. In addition, the films retain greater than 70% of their original surface area after annealing to 600 K. The combination of high surface area and thermal stability suggests that these films could serve as supports for applications in heterogeneous catalysis. The research described in this presentation was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

[1] David W. Flaherty, Zdenek Dohnálek, Alice Dohnálková, Bruce W. Arey, David E. McCready, Nachimuthu Ponnusamy, C. Buddie Mullins, and Bruce D. Kay, J. Phys. Chem. C 111 (2007) 4765-4773.

10:00am **SS1-ThM7 Complexities and Surprises in the Epitaxial Growth of Pure and Doped TiO_2,** ***S.A. Chambers***, Pacific Northwest National Laboratory **INVITED**

TiO_2 is a transition metal oxide of considerable interest in several areas of surface, interface and thin-film science. Recent cation doping film growth studies show that certain transition metal dopants with unpaired d electrons, in concert with structural defects, impart a new form of high-temperature ferromagnetism in which dopant spins are aligned by electrons associated with the defects.[1-3] Anion (principally N) doping film growth studies show that substitutional N gives rise to a substantial red shift in the bandgap, paving the way for enhanced visible solar light absorption and the associated photophysical and photochemical energy conversion processes. However, N, which should be an acceptor in TiO_2, is actually fully compensated by conduction band electrons from interstitial Ti(III), which in turn results from Ti indiffusion during growth.[4,5] These insights were gained by our ability to grow and painstakingly characterize very well-defined, high-quality epitaxial films of pure and doped TiO_2. In the process of growing these materials with an unprecedented level of control, we have learned a great deal about the nucleation and growth of the different polymorphs of TiO_2.[6] The roles of atomic fluxes, growth temperature, dopants, overall growth rate and substrate structural properties have been elucidated one by one, and these results constitute a rich source of insight into the way transition metal oxide films nucleate and grow. In this talk, I will give an overview of our work on pure and doped rutile and anatase homoepitaxy and heteroepitaxy. This work has been supported by the US DOE, Office of Science, Division of Materials Science and Engineering, and Division of Chemical Sciences.

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[3] T. C. Kaspar et al. Phys. Rev. B 73, 155327 (2006).

[4] S. H. Cheung et al., Surf. Sci. 601, 1754 (2007).

[5] S. A. Chambers et al., Chem. Phys., to appear (2007).

[6] R. Shao et al., Surf. Sci. 601, 1582 (2007).

10:40am **SS1-ThM9 In-Situ Polarization and Structure of 4 and 10 Layer Epitaxial $BaTiO_3$ Films,** ***A.P. Baddorf,*** Oak Ridge National Laboratory, *J. Shin, V.B. Nascimento,* University of Tennessee, *S.V. Kalinin,* Oak Ridge National Laboratory, *E.W. Plummer*, University of Tennessee

Ultrathin films of ferroelectric materials lose their ferroelectric properties due to the depolarizing field opposing the polarization. It is important to understand the limits and conditions limiting nanoscale ferroelectrics, which are being considered for a number of sensors, memories, and transistor devices. For $BaTiO_3$, ferroelectricity has previously been observed experimentally down to 12 layers and predicted by first-principles calculations in 6 layer films. Film environment and interfaces play a critical role in ferroelectric properties. We have grown BaTiO3 ultra-thin films $SrRuO_3/SrTiO_3$ using laser-MBE in high oxygen pressures (10 mTorr). The large 2.3% lattice mismatch in this system requires careful choice of growth conditions. For ultrathin films, RHEED oscillations and patterns during growth show that layer-by-layer growth of flat, highly strained films is possible. We report in-situ, ultrahigh vacuum characterization of epitaxial films using low energy electron diffraction (LEED I-V) and scanning tunneling spectroscopy (STS). Films produce sharp (1x1) LEED patterns, indicating a well-ordered tetragonal phase structure. Comparison of observed diffraction intensities for 4 and 10 layer films at 130 and 300 K with calculated intensities reveals a vertical displacement of the central Ti, corresponding to a polarization consistent with compressive strain. Structures and polarization change dramatically after exposure to small quantities of water. STS shows discontinuous jumps at +/- 2.5 V that may indicate polarization switching. Research was sponsored by the Division of Materials Sciences and Engineering and the Center for Nanophase Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

Surface Science

Room: 611 - Session SS2-ThM

Surface Structure of Compound Semiconductors

Moderator: Y.J. Chabal, Rutgers University

8:00am **SS2-ThM1 Structural and Surface-Morphological Analysis of InN Layers Grown by HPCVD,** ***G. Durkaya,*** *M. Alevli, R. Atalay,* Georgia State University, *W. Fenwick, I. Ferguson,* Georgia Institute of Technology, *N. Dietz*, Georgia State University

InN, a promising group III-nitride material for development of advanced optoelectronic structures, has still many not understood growth specific physical properties. InN layers investigated in the contribution were grown by high-pressure chemical vapor deposition (HPCVD) method, a technique that has been developed to counter the vast different partial pressures in this material system. In this study, we utilize and correlate Raman, XRD and AFM data to analyze the structural and electrical properties of the InN layers. The line shape analysis of the InN E2(high) Raman line is correlated to the crystalline quality of the layers and compared with the XRD pattern and AFM surface morphology studies for various growth conditions. The Raman line shapes for the A1(LO) phonon mode in these layers are analyzed and fitted to theoretical simulations in order to provide an estimate on the free electron concentration. The estimates are linked to results obtained by IR reflectance spectroscopy.

8:20am **SS2-ThM2 Desorption of Hydrogen from the Indium Nitride Surface Studied by HREELS**, *R.P. Bhatta,* ***B.D. Thoms****, M. Alevli, N. Dietz*, Georgia State University

Thermal desorption of hydrogen from the N-polar InN surface has been studied by acquiring vibrational spectra using high resolution electron energy loss spectroscopy (HREELS). The reductions in intensity of the N-H stretching and bending vibrations in HREEL spectra upon annealing indicated loss of surface hydrogen and was attributed to recombinative desorption. Annealing to 375 °C for 15 min resulted in a small amount of hydrogen desorption while heating to 425 °C for the same amount of time resulted in complete removal of surface hydrogen. A shorter anneal time of 30 s raised the temperatures for both the onset and completion of desorption by about 50 °C. Since temperatures are typically 500 °C or greater for many of the common growth techniques, this result indicates that desorption of surface hydrogen is occurring during growth and may be an important mechanism for the production of reactive sites during the growth of InN. In addition to the desorption of hydrogen, an increase in the carrier concentration of the film was also observed upon annealing to 475 °C or higher as shown by a shift of the conduction band plasmon excitation to higher energy .

8:40am **SS2-ThM3 Preparation and Characterization of β-Si_3N_4 Surfaces,** ***V.M. Bermudez***, Naval Research Laboratory **INVITED**

β-Si_3N_4 is an important electronic material with numerous device applications. Yet, in contrast to other such materials, relatively little is known about its fundamental surface properties. This talk will discuss recent theoretical and experimental work relating to the preparation and properties of β-Si_3N_4 surfaces. The growth and characterization (via IR spectroscopy and XPS) of thin films will be examined, together with methods for preparing an atomically-clean and stoichiometric surface in UHV. Ab-initio calculations of the physical and electronic structure of the (0001) surface, which provide insight into the interpretation of electron-spectroscopic data, will be described. In particular the nature of the relaxation and the electronic states at the surface will be discussed. Data from Auger, photoemission (UPS and XPS) and electron energy-loss spectroscopies will be examined in relation to the theoretical results, and preliminary chemisorption data will be presented. Strong surface-charging effects are observed in UPS and XPS which take the form of rigid shifts of the spectra by 1 eV or more with adsorption and with x-ray or VUV irradiation. These will be examined in the context of electron and hole trap states in the band gap. Brief mention will also be made of IR internal-reflection studies of wet-chemical processing of β-Si_3N_4 films.

9:20am **SS2-ThM5 Linear Smoothing Coefficient in Epitaxial Growth of GaAs on Rough Substrates,** ***M.B. Whitwick,*** *T. Tiedje, T. Li*, University of British Columbia, Canada

By a combination of theoretical and experimental work, using GaAs as a model system, we show that time evolution of surface morphology during epitaxial growth can be used to obtain rather detailed information on step densities and adatom dynamics. From in-situ light scattering we find that homoepitaxial growth on randomly rough GaAs (100) substrates causes the surface to smooth towards a characteristic surface roughness determined by kinetic roughening. A recent theoretical model for the surface morphology as a function of growth time,[1] based on a Burton-Cabrera-Frank picture of crystal growth[2] in which adatoms incorporate at step edges, suggests that the smoothing of GaAs can be described by a conservative Kardar-Parisi-Zhang type equation in which the dominant linear term in the growth equation is due to a negative Ehrlich-Schwoebel potential barrier for adatom migration at step edges. The surface smoothing rate is found experimentally to depend on the deposition rate and temperature during growth. In the model the coefficient of the linear term in the growth equation is inversely proportional to the step density (~F/S), where F is the flux of deposited adatoms and S is the step length density. Although the full growth equation is nonlinear, for low amplitude roughness the linear term dominates. We have used this fact to determine the linear smoothing coefficient as a function of substrate temperature (400-610 C) and growth rate (0.01-10 ML/s) by in-situ UV (244 nm) diffuse light scattering along the [011] and [01-1] directions. The coefficient of the linear smoothing term was found to have a power law dependence on flux with exponent of 0.7 and an exponential temperature dependence on temperature with activation energy 0.50 eV. The surface step density was measured ex-situ by AFM. The step density was found to be ~0.10±0.05 1/nm with a tendency towards higher density at high growth rates. This step density is in good agreement with the step density inferred from theoretical expression for the linear smoothing coefficient. The coefficient of the nonlinear smoothing term is also found to be in good agreement with theory.

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[2] W.K. Burton, N. Carrera, F. Frank. Phil. Trans. Roy. Soc. 243(866):299-358. (1951).

9:40am **SS2-ThM6 Spectroscopic Study of Acid and Base-Activated Thioacetamide Passivation of GaSb and InAs Surfaces**, ***R. Stine***, U.S. Naval Research Laboratory, *D.Y. Petrovykh*, U.S. Naval Research Laboratory and University of Maryland, *E.H. Aifer, L.J. Whitman*, U.S. Naval Research Laboratory

A wide range of III-V semiconductor heterostructure devices are under development for applications in electronics, optoelectronics, and sensing. However, the performance of III-V devices following processing is often detrimentally affected by the formation of mid-bandgap electronic states and the subsequent pinning of the surface Fermi level. Chemical passivation of the device surfaces can stabilize their properties by inhibiting the regrowth of native oxides that can otherwise contribute to Fermi level pinning. Traditionally, this passivation has been accomplished by the formation of surface sulfide groups through wet chemical treatment with an inorganic sulfur-containing compound, such as ammonium sulfide or sodium sulfide. More recently, though, the use of thioacetamide (TAM), an organic sulfur containing compound, has been shown to have a number of advantages over traditional inorganic methods,[1-3] including milder reaction conditions and a higher degree of control over the reaction. Although studies have shown the effect of TAM passivation on the electronic properties of devices, little information has been available on the actual chemical reactions that take place at the surfaces. Here, we present detailed X-ray photoelectron spectroscopy (XPS) studies of these surface reactions on gallium antimonide and indium arsenide-important materials for infrared optoelectronics. A comparison of TAM passivation performed under acidic versus basic conditions shows that acidic-TAM treatment produces a thicker sulfide layer that is better suited to the prevention of re-oxidation than that formed under basic-TAM treatment, regardless of exposure time or TAM concentration. We have determined the relative amounts of III-sulfides versus V-sulfides and tracked the rate of re-oxidation for each component independently over time.

[1] Petrovykh, et al., Appl. Phys. Lett. 86, 242105 (2005)

[2] Petrovykh, et al., Surf. Interface Anal. 37, 989 (2005)

[3] Aifer, et al., Proc. SPIE 6542, in press.

10:00am **SS2-ThM7 STM Imaging and DFT Modeling of the Group III-rich Reconstruction of InAs(100)-c(8×2)/(4×2)**, ***D.L. Winn***, *J. Shen, J.B. Clemens, A.C. Kummel*, University of California, San Diego

The atomic group V reconstruction of the III-V (001) surfaces have been extensively studied since these surfaces are favorable for MBE growth. The group III rich surfaces are of III-V semiconductor can be readily prepared by heating the group V rich reconstructions. The group III rich surfaces may be favorable for ALD oxides growth since they exhibit a low reactivity to O_2 because the usually lack group V dimers. InAs(001) is well documented to have a (4×2) reconstruction, however, the details of the reconstruction are still under debate. Atomically resolved filled and empty state scanning tunneling microscopy (STM) images of the InAs(001)-c(8×2)/(4×2) surface reveal that the reconstruction is made up of single atom rows that run in the [110] direction which are separated by ~17 Å. In addition, atomically resolved STM images show that the row structure is most likely comprised of undimerized atoms. Cl2 was deposited onto the surface (which has been shown to preferentially react with III atoms on III-V semiconductors) to confirm that the rows were in fact comprised of In atoms. The experimental results suggest that the most probable structure for InAs(001)-c(8×2)/(4×2) is the undimerized or dimerized β3(4×2) reconstruction. The reconstruction consistent of a top layer of bicoordinated or tricoordinated In atoms at the center of the rows and tricoordinated As atoms in the second layer at the edges of the rows. Density functional theory (DFT) STM simulations were used to confirm the experimental findings. DFT reveals that the dimerized and undimerized structures are nearly degenerate consistent with STM images show the In dimerization may be temperature dependent. Both the undimerized and dimerized β3(4×2) structures lack As dimers and have a low reactivity to O2 consistent with a surface which is suitable for ALD gate oxide deposition.

10:20am **SS2-ThM8 Scanning Tunneling Microscopy Study of Interfacial Bonding Structure and Annealing Effect of In_2O/InAs(001)-c(8x2)/(4x2)**, ***J. Shen***, *D.L. Winn, A.C. Kummel*, University of California, San Diego

The key to fabricating a III-V MOSFET is forming an electrically passive oxide-semiconductor interface. In an effort to identify an unpinned oxide/semiconductor interface on InAs, a detailed study of In_2O adsorbed to InAs(001)-c(8x2)/(4x2) was performed. Scanning tunneling microscopy (STM) and density functional theory (DFT) were used to ascertaining how In_2O adsorbates bond to the clean InAs(001)-c(8x2)/(4x2) surface. The InAs(001)-c(8x2)/(4x2) surface consists of a top row of In atoms which are bonded to tricoordinated As atoms containing partially filled dangling bonds. STM results showed that the initial In_2O molecules only occupy specific sites at the edge of the rows. These In_2O atoms most likely form new In-As bonds to the surface. This is a favorable bonding structure for oxide/semiconductor interfaces since it avoids As-O bond formation which is likely to create states in the band gap. In addition, the formation of In-As bonds restores the tricoordinated As atoms to a more bulk-like bonding environment. A height analysis was performed to determine growth mechanism. At low coverage (20% monolayer), the In_2O adsorbates formed islands that are elongated in the [110] direction. Prior to all the first layer sites being occupied with In_2O molecules, second layer growth was observed on the islands. Each layer of oxide has a distinct height, however, the second and subsequent layers appear to be amorphous. In addition, the effect of annealing In_2O/InAs(001)-c(8x2)/(4x2) was studied. The annealed samples were more ordered and uniform. The oxide molecules on the annealed samples filled in the troughs and formed ordered islands with rows in [i10] direction. Comparisons of oxide height distributions before and after annealing, show the oxide height is reduced from 1.5 Å to 1 Å. This is consistent with the In-In bond formation between two nearest neighbor In_2O atoms in the [i10] direction. Most importantly, for both room temperature deposition and annealing, the clean surfaces lattice is left unperturbed, the In_2O adsorbates never cause the abstraction of any surface atoms on the InAs(001)-c(8x2)/(4x2) surface and the In_2O molecules only occupied specific sites. The formation of an ordered oxide-interface without disruption of the InAs(100)-c(8x2)/(4x2) lattice is favorable for creating an unpinned oxide-semiconductor interface.

10:40am **SS2-ThM9 Bonding Hybridization in the Group III-rich Reconstructions of InGaAs(100)-(4×2)**, ***T. Song***, *D.L. Winn, J. Shen, A.C. Kummel*, University of California, San Diego

The group-V (As or Sb) rich reconstructions of III-V semiconductors have been extensively investigated since these surfaces are favorable for MBE growth. However, the group-III (Ga or In) rich reconstructions can readily be prepared by heating the group-V rich reconstructions, and the group-III rich reconstructions may be favorable for ALD gate oxide deposition due to their low reactivity to oxygen. Although the group-III rich surfaces have several potential applications, many III-V semiconductors, including InGaAs, have unidentified group-III rich reconstructions. Four different group-III rich 4x2 reconstructions of In0.5Ga0.5As(001)-(4×2) were modeled using DFT: ζ (4×2), β2(4×2), β3(4×2), and the undimerized β3(4×2) structures. Multiple polymorphs (Ga and In positions) were investigated. The undimerized β3(4×2) reconstruction most closely matches the experimental room temperature STM images of In0.53Ga0.47As/InP(001)-c(8×2)/(4×2). This reconstruction consists of a top row of undimerized In/Ga atoms which are bonded to tri-coordinated As atoms. In the undimerized β3(4×2) structure, the row In/Ga atoms are sp hybridized. Conversely, in the dimerized β3(4×2) reconstruction, the top row In/Ga atoms are sp2 hybridized. DFT calculations showed that the undimerized β3(4×2) reconstructions are more stable in energy. The density of states (DOS) of the β3(4×2) reconstructions showed that the undimerized β3(4×2) structure had a band gap while the dimerized β3(4×2) structure was metallic. The correlation between hybridization and electronic structure is due to the influence of hybridation and bonding structure on the filling of the dangling bonds.

Thin Film

Room: 613/614 - Session TF-ThM

Thin Films for Electronic Applications

Moderator: P.D. Rack, The University of Tennessee

8:00am **TF-ThM1 Superconductivity in Very Clean and Doped MgB$_2$ Thin Films**, ***Q. Li***, *A.V. Pogrebnyakov, J.M. Redwing, X.X. Xi*, Pennsylvania State University **INVITED**

MgB$_2$, with a T$_c$ of 40 K, is arguably the first superconductor to show clear multiband superconductivity and two energy gaps. It has the highest T$_c$ among BCS superconductors, which makes it very attractive for many applications. The interplay between the interband and intraband scattering has resulted in many unusual properties. In this talk, I will review our results on MgB$_2$ thin films made by hybrid physical-chemical vapor deposition (HPCVD). Very clean epitaxial MgB$_2$ thin films on (0001) SiC and sapphire substrates have been obtained with a slight increase of T$_c$ from the bulk value due to the epitaxial strain. From the normal state magnetoresistance measurement, we have shown a complex dependence on the orientation of the applied magnetic field, with a maximum magnetoresistance (MR~136%) observed at the field H parallel to c plane at low temperature. However, the angular dependence changes dramatically as the temperature increases, and at high temperatures, the magnetoresistance maximum changes to the H perpendicular to c direction. We attribute the results to the multiple bands with different Fermi surface topology and different electron-phonon coupling in MgB$_2$. By introducing carbon carrying gas during HPCVD deposition, C-doping in the films was achieved. The upper critical field was found to increase with C doping. The upper critical field can be increased to above 60 T in H parallel to ab direction and 40 T in H perpendicular to ab direction. C-doped polycrystalline films coated on SiC filbers also show H$_{c2}$ above 55 T, which make it possible as a coated conductor for high field applications.

[1] Work supported by NSF and conducted in collaboration with B. T. Liu, Y. F. Hu, J. Chen, V. Ferrando, P. Orgiani, Q. R. Feng, H. Gao, L. Shan, H. H. Wen, A. Gurevich, D.C. Larbalestier, J. B. Betts, C. H. Mielke.

8:40am **TF-ThM3 Optical Radiation Selective Devices Based on III Nitrides**, ***D. Starikov***, *J.C. Boney, P. Misra, N. Medelci, R. Pillai*, University of Houston

Wide direct band gap of the III nitride materials allows for several advanced optoelectronic applications in a very wide spectral range from 200 nm to 1.77 µm. Both light emission sources and photodetectors with advanced properties can be achieved through tailoring layered III nitride structures with various layer order, chemical composition, conductivity and thickness. In addition, substrate selection plays an important role in the fabrication of these devices as well as in achieving desired device properties. Along with the efficiency of light emission or detection, in most cases it is important to provide selectivity of the optical radiation generated or sensed by the optical device. Such selectivity can be achieved by using spectral and polarization properties of optical radiation. In this paper we present results on the growth, processing, and modeling of multi-band photodiode structures, broad-spectrum avalanche LEDs, and polarization-sensitive photodetectors based on III nitrides grown by Radio Frequency Molecular beam epitaxy on silicon, sapphire, and lithium-aluminum oxide (LiAlO$_2$) substrates. Dual-band visible- and solar-blind UV/IR photodetectors as well as broad spectrum UV-enhanced avalanche LED structures have been demonstrated. The peak responsivities of the dual band photodetectors are 0.0038 and 0.055 A/W at the wavelengths of 349 nm and 1000 nm, respectively. The broad spectrum emission from the avalanche LEDs extended from 300 to 650 nm with a maximum at ~425 nm. Results on optimization of the dual-band photodiodes as well as on testing of polarization-sensitive GaN and InGaN photodetectors grown on non-polar LiAlO$_2$ substrates, which are currently in progress, will be presented in the final paper. Various advanced applications of the optical radiation sensitive devices based on III nitrides will be discussed.

9:00am **TF-ThM4 EXAFS Study of Local Bonding Structures of Ge$_2$Sb$_2$Te$_4$, Ge$_2$Sb$_2$Te$_5$, and Ge$_2$Sb$_2$Te$_7$ with Bond Constraint Analysis**, ***D.A. Baker***, *G. Lucovsky, M.A. Paesler*, North Carolina State University, *P.C. Taylor*, Colorado School of Mines

Studies of amorphous (a-) semiconductors have been driven by technological advances as well as fundamental theories. Observation of electrical switching,[1] for example, fueled early interest in a-chalcogenides. More recently a-chalcogenide switching has been applied successfully to programmable memory devices[2] as well as DVD technology where the quest for the discovery of better-suited materials continues. Thus, switching grants researchers today with an active arena of technological as well as fundamental study. Bond constraint theory (BCT) and rigidity theory provide a powerful framework for understanding the structure and properties of a-materials. Application of these theories to switching in a-chalcogenides holds the promise of finding the best composition suited for switching applications. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy[3] is an ideally suited technique to investigate the switching properties of these materials. Films of amorphous Ge$_2$Sb$_2$Te$_4$, Ge$_2$Sb$_2$Te$_5$, and Ge$_2$Sb$_2$Te$_7$ exhibit differing bonding structures and bond statistics, which result in different electronic and optical properties. Results of new EXAFS experiments on these three critical compositions in the Ge-Sb-Te system are presented in light of BCT and rigidity theory.

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9:20am **TF-ThM5 CVD of Ru from C$_6$H$_8$Ru(CO)$_3$**, ***T.S. Lazarz***, *Y. Yang, N. Kumar, W. Noh, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

Ruthenium is being investigated for multiple uses in microelectronics, including DRAM capacitors,[1] metal gates in p-MOSFETs,[2] and in the copper dual damascene process.[3] Previous studies have generally prepared Ru films by evaporation or by CVD from ruthenocene or its ring-substituted analogues. Other ruthenium compounds such as β-diketonates, arenes, dienes and carbonyls have also been investigated as CVD precursors. In all cases, however, the growth rates been unsatisfactory (< 2 nm/min), the films have been contaminated by heteroatoms due to ligand incorporation, or there have been nucleation problems on covalent substrates.[4] We have used the single-source liquid precursor tricarbonyl(1,3-cyclohexadiene)ruthenium(0), C$_6$H$_8$Ru(CO)$_3$, to deposit metallic ruthenium films by CVD at substrate temperatures ranging between 150 and 600 °C on several types of substrates, including covalent. Ligand removal is expected to be relatively facile from this Ru(0) compound due to the ruthenium atom being in oxidation state zero on the precursor molecule. The Ru growth rates are rapid, with a maximum of 19 nm/min. The oxygen content is below AES detection limits (< 1 at. %), and the carbon content is estimated to be low. In-situ spectroscopic ellipsometry indicates negligibly short delays before film nucleation on Si, SiO$_2$, or sapphire substrates. The resistivities are comparable to the bulk resistivity, ranging between 11 and 21 µΩ-cm. The texture of the films depends on deposition temperature. At lower temperatures, films are strongly textured mostly in the (0002) direction, whereas at higher temperatures the films are less textured. Since C$_6$H$_8$Ru(CO)$_3$ gives high growth rates, low resistivities, and nucleates readily on all surfaces tested, C$_6$H$_8$Ru(CO)$_3$ is an excellent precursor for depositing thin ruthenium films.

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9:40am **TF-ThM6 The Properties of Ultra Thin Ru-P Amorphous Films Deposited with Ru$_3$(CO)$_{12}$ and P(CH$_3$)$_3$ for Cu Metallization**, ***J. Shin***, *H. Kim, L.B. Henderson, G.S. Hwang, J.G. Ekerdt*, University of Texas at Austin

For advanced VLSI devices, Cu metallization has replaced Al due to its low resistivity and high intrinsic electromigration resistance. It is well known that Cu requires liner materials that function as a diffusion barrier, a seed layer for electroplating, and an adhesion promoting layer. Ru has been considered as a promising liner material for Cu metallization, however it has been reported that Ru itself is not an effective Cu diffusion barrier due to its microstructure, which is polycrystalline and features a columnar structure. Therefore, controlling the microstructure of Ru films is crucial in obtaining the required liner properties. Here we report ultra thin Ru alloy films having amorphized microstructure by incorporating P into the films. The metal (Ru) - metalloid (P) amorphous films were grown at 300°C by co-dosing triruthenium dodecarbonyl (Ru$_3$(CO)$_{12}$) and trimethylphosphine (P(CH$_3$)$_3$) into a cold wall chemical vapor deposition system having base pressure of 5x10^{-8} Torr. X-ray photoelectron spectroscopy (XPS) was employed to analyze the film composition and chemical states of the elements in the films, and grazing angle X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used for microstructure analysis. Amorphous films were formed when more than ~ 15 at% of P was incorporated, and the amorphous microstructure remained stable after 3 hrs of annealing at 400°C. Electrical resistivity was measured with a four point probe, and a 15 nm thick amorphous Ru-P film showed a resistivity of ~ 200 Ωcm. Strong adhesion between Ru-P and Cu films was observed in annealing experiments, which revealed adhesion strength in the order of Ru-P alloy > Ta > TaN. More conformal films were grown on trench features by introducing $P(CH_3)_3$ as a result of the improved film step coverage due to the inhibited reaction and lowered sticking coefficient of $Ru_3(CO)_{12}$ by the adsorption of the $P(CH_3)_3$ molecules on the Ru surface. The barrier capability of the Ru-P films against Cu diffusion evaluated by bias temperature stress (BTS) technique will be discussed. First principles density functional theory calculations and ab-initio molecular dynamic simulation results will also be presented to elucidate the interaction between Ru and P, short range order of amorphous structure, and the causes for P stabilizing the Ru based metal - metalloid amorphous films.

10:00am **TF-ThM7 Surface Morphology of Epitaxial Cu Layers: The Effect of Roughness on Electron Scattering**, ***J.M. Purswani***, *D. Gall*, Rensselaer Polytechnic Institute

Single crystal Cu layers, 12 to 600 nm thick, were grown on MgO(001) by ultra-high vacuum magnetron sputtering. X-ray diffraction θ-2θ, ω-rocking curve, and pole figure scans show that layers grown at temperatures $T_s \leq$ 100 °C exhibit a cube-on-cube epitaxy, while $T_s \geq$ 200 °C results in polycrystalline copper layers. The surfaces of the single crystal layers exhibit regular mound structures, as observed by in-situ scanning tunneling microscopy. The mounds grow in width with increasing layer thickness t, from 21 nm for t = 24 nm to 33 nm with t = 119 nm. In-situ vacuum annealing at 200 and 300 °C leads to a successive smoothening of the surfaces for all thickness values. For example, for t = 24 nm, the RMS roughness is 1.3 nm for the as-deposited layer and decreases to 0.7 nm after the post-deposition anneal. The measured resistivity increases for decreasing layer thickness, from 1.70 μΩ-cm for t = 604 nm to 2.91μΩ-cm for t = 24 nm. This increase is consistent with the Fuchs-Sondheimer model, indicating completely diffuse surface scattering. The diffuse surface scattering is attributed to atomic level roughness, as quantified by the average width of atomically smooth surface terraces, which increases from 0.5 nm for the as-deposited layer to 1.5 nm for the film annealed at 300 °C. Therefore, even the smoothest layers exhibit terraces that are only 8 atoms wide, which is insufficient to result in specular electron surface scattering.

10:20am **TF-ThM8 Investigation of Ru-Ta-N Ultrathin Films as Diffusion Barrier for Cu Metallization**, ***C.-W. Chen***, *J.-S. Chen*, National Cheng Kung University, Taiwan

In this study, the diffusion barrier properties of ruthenium-based thin films which contain different atomic percentage of tantalum and nitrogen are investigated in Cu/barrier/SiO_2/Si system. The Ru-Ta-N films were deposited by co-sputtering from Ru and Ta targets in Ar+N_2 atmosphere. Pure Ru and Ru-N films sputtered in Ar and Ar+N_2 ambient, respectively, were studied as the comparison. The thickness of Ru, Ru-N and Ru-Ta-N samples is all set at 10 nm. The thermal stability of the Cu/barrier/SiO_2/Si multilayers is assessed by annealing the samples in vacuum at 400~700 °C for 30 min. No significant change of sheet resistance is detected for the Cu/Ru-Ta-N/SiO_2/Si system after annealing up to 700°C. However, the sheet resistance of the sample with pure Ru barrier increases abruptly after annealing at 400°C, and the sheet resistance of the sample with Ru-N barrier increases abruptly after annealing at 500°C. The performance of Ru-Ta-N barriers are also confirmed by Auger electron spectroscopy and Rutherford backscattering spectrometry in which Cu shows no obvious diffusion into underlayers after annealing at 500°C. As compared to pure Ru and Ru-N, the Ru-Ta-N films exhibit better electrical properties and capability for preventing Cu diffusion regardless of the different Ta contents. Correlation between the film resistivity and the microstructral characteristics of sputtered Ru, Ru-N and Ru-Ta-N films in the Cu/barrier/SiO_2/Si multilayer systems upon annealing are discussed.

10:40am **TF-ThM9 A Study on the Amorphous Ta-Zr Films as Diffusion Barrier in Cu Metallization**, ***C. Li***, Nanyang Technological University, Singapore, *J. Hsieh*, Ming-Chi University of Technology, Taiwan

Binary alloys with amorphous structure have been used as diffusion barrier in many electronic components for their better resistance to the movement of thermally and electrically conductive atoms. Some other advantages for using such amorphous films including their high crystallization temperature and good electrical conductivity are also important for the function of electronic components. For instance, films such as Cu100-xTax, Zr40Cu60, Ta50Co50, Ta100-xNix (x=35,50) and Co55W45, all exhibit low resistivity (<200 μ?-cm) and high crystallization temperature (Tx ~800oC, except Ta-Co and Cu-Zr) in literature. However, when they are employed as diffusion barriers for Al, Cu or Au metallization, some of the films (Cu100-xTax, Ta100-xNix (x=35,50) and Co55W45) demonstrate a failure at temperatures much lower than their crystallization point. This may due to the low reaction temperature of these metal with Si substrate which is only around 200-300oC. Based upon these earlier studies, one improvement can be made on the existing amorphous films is to replace the noble or near noble metals (Cu, Ni etc.) with some refractory metals such as Ta, W, Ti or Zr because their reaction temperatures with Si are usually higher than 500oC. Examples of such films as Ta-W and Ti-W can be found in the literature. In this study, a modeling and experimental works on the amorphous binary alloys will be presented for its barrier performance on the metal diffusions. For experiments, a layer of Cu/Ta50Zr50/SiO2/Si stack is made by the deposition of Ta and Zr on thermally oxidized Si substrate by co-sputtering in the Ar plasma. Experimental results indicate that the amorphous barrier can indeed suppress the penetration of Cu atoms into Si substrate upon annealing at temperature higher than 500oC. Further investigations on the thermal stability reveal that the top Cu layer may enhance the formation of metal silicides such as TaSi2 and ZrSi2 inside the barrier. These silicides can increase the activation energy of Cu diffusion and therefore enhance the barrier's performance. In addition, a failure mechanism of the diffusion barrier is proposed based on both thermal stability and residual tensile stresses. A qualitative model for this proposal shall be analyzed by numerical simulations also.

Tribology

Room: 617 - Session TR2+BI+NS+MN-ThM

Biolubrication, Sensing and Adhesion

Moderator: R.W. Carpick, University of Pennsylvania

8:00am **TR2+BI+NS+MN-ThM1 Resonant Nanomechanical Sensors for Protein Detection**, ***P.S. Waggoner***, *H.G. Craighead*, Cornell University

Micro- and nanoelectromechanical systems (MEMS and NEMS) are of interest in sensing applications due to their high sensitivity, label-free operation, and potential for mutilplexed detection on a single chip. Resonant MEMS and NEMS devices have demonstrated detection of masses on the order of femtograms or less, transducing changes in mass into changes in resonant frequency. Appropriate functionalization of the sensor surface allows specific, label free detection for analytes of choice. In this work we have detected prostate specific antigen (PSA), a biomarker used in the early detection of prostate cancer, as a model system using immunospecific functional layers present on the resonator surfaces. We have also studied the surface chemistry in order to minimize non-specific binding during sensor functionalization and use. In addition, sandwich assay techniques have been investigated for use in secondary mass tagging in order to enhance sensor response for dilute analytes while still preserving specificity.

8:20am **TR2+BI+NS+MN-ThM2 Correlation between XPS Data and Liquid Phase Self-Assembly of Alkanethiols**, ***H.M. Meyer III***, *T.G. Thundat, R. Desikan*, Oak Ridge National Laboratory, *R.G. White*, Thermo Fisher Scientific, UK

The relative ease in which self-assembled monolayers (SAM) can be applied have made them part of the standard tool set used for functionalizing and patterning surfaces at the nanoscale. Recently, alkanethiol-based SAMs have been used for immobilizing selective chemical receptors on the gold-coated side of a microcantilever. In this configuration, adsorption on the funtionalized side of the microcantilever generates nanomechanical motion (i.e. bending) which can be accurately sensed and used for detecting a variety of chemical and biological molecules. Achieving reliable selectivity and sensitivity depends primarily on the reproducible formation of the functional layer on one side of the microcantilever. We have recently investigated the effect of chain length on the packing density of the alkanethiols and, in turn, how this affects the sensitivity of the sensor. We present XPS characterization of microfabricated cantilevers functionalized with alkanethiol-based SAMs. The results are correlated with similar cantilevers that have been monitored during adsorption/immobilization of the same alkanethiols in the liquid phase. Previous liquid phase results indicated an unusual change in packing density of the thiol molecules as the chain length was increased and were difficult to correlate with preliminary XPS data, indicating major difference between how these films form in liquid phase vs. post-formation analysis in-vacuuo. These new results attempt to illuminate those differences. Research sponsored in part by grant NSF Award ID 0330410 in collaboration with Drs. V.P. Dravid, G. Shekhawat, and A. Majumdar and in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

8:40am **TR2+BI+NS+MN-ThM3 Surface-Chemical Aspects of Implant Biotribology and Biomimetic Lubrication***, **N.D. Spencer***, ETH Zurich, Switzerland **INVITED**

Following implantation of a hip prosthesis, the synovial membrane reforms and generates a liquid, pseudo synovial fluid (PSF), which is comparable in composition to synovial fluid itself. This complex solution of proteins, glycoproteins, polysaccharides and lipids is then responsible for the lubrication of the implanted joint. Surprisingly, the interactions of PSF components with the surfaces of joint materials, such as UHMWPE, CoCrMo, or alumina, remain remarkably unexplored. Not only is their relative propensity for adsorption unknown, but, once adsorbed, their efficacy for lubrication remains to be determined. We have investigated these issues by means of tribometry (on both macro and nano scales), combined with fluorescence microscopy, and determined, for example, that while albumin, the major component of PSF and the model protein used for implant testing, is strongly adsorbed on the surface of implants, it can be displaced during sliding by Î±-glycoprotein, a species present at much lower concentrations, but a much more effective lubricant. The fluorescence approach has also enabled us to detect transfer of polyethylene under conditions where it was not previously thought to occur. Natural lubricated surfaces tend to be soft and covered with species such as polysaccharides that have the ability to retain large amounts of water. We have attempted to imitate and understand this mechanism of lubrication by means of tethering various highly hydrated polymer chains in a brush-like structure onto both hard and soft surfaces and measuring their tribological properties. Interestingly, on soft surfaces, the effect of chain tethering seems to be to effectively eliminate boundary lubrication entirely. Fluid-film-like behavior is thought to persist to very low sliding speeds, by virtue of water retention in a thin layer between the brush-covered surfaces.

9:20am **TR2+BI+NS+MN-ThM5 In-situ Measurement of Boundary-Lubrication on Articular Cartilage Surfaces***, J.M. Coles,* Duke University*, G.D. Jay,* Brown University*, F. Guilak, **S. Zauscher***, Duke University

The diarthrodial (synovial) joints of the body enable locomotion and activity while withstanding millions of cycles of loading at several times body weight. Recent macroscopic tribological experiments and biochemical analyses suggest that heavily glycosylated proteoglycans encoded by the gene proteoglycan 4 (Prg4), which are expressed by synoviocytes in synovial fluid as lubricin and by superficial zone chondrocytes of articular cartilage as surface zone protein (SZP), provide boundary lubrication in cartilage in the absence of interstitial fluid pressurization. Improved understanding of the role of Prg4 on the cartilage surface could thus provide important insight into the development of new therapies for joint diseases such as OA. The development of powerful new methods for the genetic manipulation of mice has led to the creation of modified murine strains in which specific gene inactivation (PRG4-/-) results in age-related joint degeneration that recapitulates the symptoms of OA. Here we show that atomic force microscopy with a colloidal probe is uniquely suited to study boundary lubrication of murine cartilage in-situ and in absence of other lubrication mechanisms. Here we report on friction measurements on the superficial surface layer of articular cartilage from the femoral head of Prg4 knockout and wildtype mice under boundary lubrication conditions. Furthermore, we report on the measured RMS roughness and Young's modulus to quantify morphological and mechanical changes of the cartilage superficial zone induced by the absence of Prg4. Our measurements suggest that the absence of Prg4 leads to increased friction, as well as degradation of the mechanical and topographical properties of cartilage. We propose that, while lubricin plays a role as a boundary lubricant, its role in chondroprotection is equally, if not more, vital.

9:40am **TR2+BI+NS+MN-ThM6 Humidity Dependent Ordering of Water and its Effect on Adhesion and Friction between Silica Surfaces***, **B.I. Kim**, J. Bonander*, Boise State University

Adhesion and friction related to water are major problems limiting both the fabrication and long-term use of micro-machines. Adhesion and friction between two silica surfaces were measured as a function of separation distance using interfacial force microscope (IFM) for different relative humidity (RH) between 3% - 78%. The IFM provides force-distance curves without having the "snap-to-contact" problems associated with atomic force microscopy using voltage-controlled force feedback. The measured friction force-distance curves show that the friction force is oscillatory as the separation changes below thickness of water droplet. The oscillatory period is close to the mean diameter of a water molecule. The number of oscillation increased as the relative humidity increases up to RH 60% while it decreased with humidity above RH 60%. The origin of the oscillatory feature in the "interfacial" water may come from the "solid-liquid transition" between solid (ordering) and liquid (disordering). Strong correlation between the number of oscillation and the strength of the adhesion and friction indicates that the humidity dependent adhesion and friction may be attributed to the ordered structure of water molecules between two silica surfaces.

10:00am **TR2+BI+NS+MN-ThM7 Nanomechanical Properties of Arachidic Acid Langmuir Blodgett Films***, **G. Oncins***, University of Barcelona, Spain*, J. Torrent-Burgues,* Universitat Politecnica de Catalunya, Spain*, F. Sanz*, Universitat de Barcelona and Center of Nanobioengineering of Catalonia (IBEC), Spain

Scanning Probe Microscopies development has given biophysics the possibility to deal with the interactions arisen in biological membranes from a nanomentric point of view, revealing that van der Waals, hydrogen bonding and electrostatic interactions play a crucial role in the membrane cohesion. Unfortunately, although interesting experimental conclusions have been reported in the past, these systems are complex and difficult to study.[1] In order to isolate the effect of the different cohesive interactions, Langmuir-Blodgett (LB) fatty acid monolayers provide excellent model systems because of the controlled area per molecule, linear hydrocarbon chain geometry, amphiphilic nature, high mechanical stability and the possibility to test solid and liquid phases at room temperature. The nanomechanical properties of arachidic acid LB films extracted at surface pressures of 1, 15 and 35 mN/m and deposited on mica are investigated by Atomic Force Microscopy, Force Spectroscopy and Friction Force Microscopy. It is experimentally demonstrated that the molecular ordering depends on the extraction pressure, while discrete molecular tilting angles of 50°, 34° and 22° are detected and identified as conformations that maximize van der Waals interactions between alkyl chains. The vertical force (F_v) needed to puncture the monolayer strongly depends on the molecular tilting angle, ranging from 13.07±3.24 nN at 1 mN/m to 22.94±5.49 nN at 35 mN/m. The friction force (F_f) measurements performed from low Fv until monolayer disruption reveal three friction regimes corresponding with a low F_f elastic monolayer deformation at low F_v, followed by a sharp increase in F_f due to a sudden plastic deformation of the monolayer. The last regime corresponds with the monolayer rupture and the contact between tip and substrate. Interestingly, as the extraction pressure increases, the friction coefficient of the monolayer reduces while the F_v needed to trigger the monolayer plastic deformation increases, facts that are discussed in terms of sample compactness and monolayer rupture mechanism.[2]

[1] Garcia-Manyes, S.; Oncins, G.; Sanz, F. Biophys. J. 2005, 89, 1812.

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10:20am **TR2+BI+NS+MN-ThM8 Optimal Roughness for Minimal Adhesion***, D.L. Liu,* Worcester Polytechnic Institute*, J. Martin,* Analog Devices Inc.*, **N.A. Burnham***, Worcester Polytechnic Institute

Differing views on the effect of surface roughness on adhesion have appeared in the literature recently. Molecular dynamics has been used to simulate the contact of two surfaces and found that atomic-scale roughness can have a large influence on adhesion, causing the breakdown of continuum mechanics models.[1] An experimental study showed that roughness can determine the adhesion in nanometer contacts and indicated that continuum mechanics still works down to nanometer length scales.[2] In this work, we use a single-asperity model to describe a smooth tip in contact with a rough surface and predict that there is an optimal size of asperity that will yield a minimum of adhesion. Experimentally, adhesive forces on silicon wafers with varying roughness from 0.2 nm to 39 nm were measured using AFM (atomic force microscope) cantilevers with varying tip radii ranging from 75 nm to 9.08 um. It is found that for all tip radii, the adhesion falls significantly for roughness greater than 1-2 nm and drops at higher roughness for larger tips. Minimum adhesion was observed as predicted in the 1-10 nm range and the optimal roughness for minimal adhesion increases as the tip radius increases, which is also consistent with our predictions. The work presented here should help minimize adhesion in future MEMS devices and progress the understanding of adhesion between the atomic- and macro-scale.

[1] B. Luan and M.O. Robbins, Nature 435, 929-932 (2005).

[2] E.J.Thoreson, J. Martin, N.A. Burnham, J. Colloid Interface Sci. 298, 94-101 (2006).

10:40am **TR2+BI+NS+MN-ThM9 A Tribological Study of Bound plus Mobile Lubricants for MEMS Application from the Nano- to the Macro-scale Regime***, **B.P. Miller**, M. Brukman,* North Carolina State University*, C.C. Baker,* Naval Research Laboratory*, R.J. Nemanich,* North Carolina State University*, K.J. Wahl,* Naval Research Laboratory*, J. Krim*, North Carolina State University

One possible solution to the in-use stiction problem in Micro-Electro-Mechanical systems (MEMS) is the introduction of a bound plus mobile lubricant combination.[1] For this system, one monolayer of the bound lubricant (perfluorodecyltrichlorosilane, PFTS) bonds to the surface of the device. The mobile lubricant (tricresyl phosphate, TCP) can replenish the layer after rubbing contacts wear it away, thus keeping the device free of contamination. Friction behavior of this lubricant combination was examined over three different regimes using a macroscopic tribometer, an AFM, and a quartz crystal microbalance (QCM). A comparative study of bound only versus bound plus mobile lubricants showed a decrease of the coefficient of friction with the addition of the mobile lubricant to the bound layer. Dynamic properties of the mobile film were characterized with the QCM. This work is funded by AFOSR Extreme Friction MURI Grant #FA9550-04-1-0381.

[1]W. Neeyakorn, M. Varma, C. Jaye, J. E. Burnette, S.M. Lee, R. J. Nemanich, C. Grant, J. Krim, Dynamics of Vapor-Phase Organophosphates on Silicon and OTS, Tribology Letters, in press.

Vacuum Technology

Room: 618 - Session VT-ThM

Pumping, Pressure Measurement and Calibration

Moderator: J. Luby, BOC Edwards

8:00am **VT-ThM1 Review of Seven Years Field Application Experience of an EPX Single Mechanism for High Vacuum Pumping**, ***A.D. Chew***, *C. Shaw*, BOC Edwards, UK **INVITED**

A single dry pump mechanism capable of reaching high vacuum and itself exhausting to atmospheric pressure has been a "vacuum-technology panacea". The development and deployment of a single-shaft, high-speed EPX pump isince has gone some considerable way to achieving this goal. This paper will describe the stages in the development history and expanding applications the pumps has been applied to. This will be further illustrated by specific applications examples, reliability and economic experiences.

8:40am **VT-ThM3 How to Efficiently Combine Ion Pumps and Getter-Palladium Thin Films**, ***C. Paolini***, *M. Mura*, *F. Ravelli*, Varian S.p.A., Italy

Non-evaporable getters (NEG) have been extensively studied in the last years for their sorption properties towards many gases. In particular, an innovative alloy produced in the form of thin films by magnetron sputtering was developed and characterized at the European Center of Nuclear Research (CERN). It is composed of Ti-Zr-V and protected by an overlayer of palladium (Pd), according to a technology for which we got the license. The use of NEG-Pd thin films in combination with ion getter pumps allows to obtain a simple and easy to handle pumping device for UHV and XHV applications. In order to show how it is possible to apply this coating technology to the internal surface of different types of ion pumps, several tests were carried out on pumps of various shape, size (in terms of nominal pumping speed) and type (diode, noble diode and triode). A special care was taken during the thermal cycle of bakeout and activation of the pumps, in order to preserve the internal film from the contamination due to the sputtering of the cathodes and/or from the interdiffusion of its components. Some important remarks about the most appropriate conditions of pressure and temperature will be discussed. The performances of the NEG-Pd coated ion pumps were evaluated in terms of ultimate pressure, nitrogen and hydrogen pumping speed. The contribution of the thin film is particularly relevant for the pumping of this last gas, due to its high sticking factor for palladium and to the great sorption capacity of the underlying getter. Finally, the possibility of further improvement of the performances by substituting the palladium with other Pd-based alloys will also be evaluated.

9:20am **VT-ThM5 Vacuum Improvements and Characterizations for the Jefferson Lab Polarized Electron Source**, ***M.L. Stutzman***, *P.A. Adderley*, *J. Grames*, *M. Poelker*, Thomas Jefferson National Accelerator Facility

Improving vacuum is a necessary step toward improving photocathode lifetime in DC high voltage polarized electron sources, which is an important goal for both the CEBAF nuclear physics accelerator at Jefferson Lab and future facilities. A new load-locked photogun vacuum system has been constructed using many vacuum improvements, including vacuum firing and NEG coating the gun high voltage chamber. The vacuum characteristics of the new photogun are described in the context of traditional vacuum measurements but perhaps more importantly, a vacuum assessment is made by comparing new and old photogun performance.

9:40am **VT-ThM6 Theory and Design of a Pirani-style Thermal Conductivity Vacuum Gauge with Unique Geometries and Control Circuitry**, ***P.C. Arnold***, Brooks Automation, Inc.

Characteristics of Pirani-style gauges and their causes for inaccuracy due to errors in temperature compensation will be presented. The principles of sensor thermal end losses as they contribute to pressure indication errors as well as errors due to changes in ambient temperature and non-uniformities in mounting structures will be discussed with special attention to reducing those uncertainties. The design, called Conductron (R) technology, is found to have usable pressure indication up to an atmosphere without utilization of gas convection enhancement geometry which causes orientation dependency. A geometry and method of operating the gauge, departing from the conventional Wheatstone bridge, that avoids common pitfalls of conventional Pirani gauge operation will be described. Certain operational measurements will be shown to avoid the more difficult determinations of (a) power lost to gas conductance and (b) measurement of sensor environment temperature, often used in both transducing these data to an indicated pressure and also providing temperature compensation. Also shown will be a unique method for arriving at the indicated pressure from those operational measurements. A pressure range from the low mTorr to atmosphere is encompassed by this design.

10:00am **VT-ThM7 Capillary Flow Meter for Calibrating Spinning Rotor Gauges**, ***R.F. Berg***, National Institute of Standards and Technology

Below 1 Pa, the NIST Pressure & Vacuum Group generates known pressures by flowing gas through an orifice with a calculable impedance. The gas flow is a leak from a small volume held at a higher pressure. Slowly inserting a piston into the volume holds the volume's pressure constant, and the known insertion rate and cross section of the piston, plus the pressure and temperature of the volume, yield the gas flow rate. This talk will describe the performance of new gas flow source based on a capillary flow impedance. Knowing the input pressure, output pressure, and temperature of the capillary yields the gas flow rate through the capillary. The capillary flow meter uses large pressures (30 - 300 kPa) that can be accurately measured, it requires no moving parts aside from valves, and it provides a steady flow for days instead of minutes. The new flow meter comprises a coil of quartz capillary with an inner diameter of 0.1 mm and a commercial pressure gauge package. Its maximum flow rate of 0.2 micromol/s (about 0.2 standard cubic centimeter per minute) covers the range that is useful for calibrating spinning rotor gauges. The flow meter relies on a hydrodynamic model that was developed for NIST transfer standards for larger gas flows with a relative uncertainty better than 0.1 %. A preliminary comparison at 0.1 micromol/s showed agreement between the piston flow meter and the capillary flow meter to within 0.2 %. Comparisons at other flow rates and extension of the hydrodynamic model to handle exit pressures below 30 kPa will be discussed.

10:20am **VT-ThM8 A Non-Destructive Partial Pressure X-Ray Analysis Method for Kr and Xe Gas Filled Encapsulated Devices**, ***P.F. Somssich***, *K.J. Zuk*, Osram Sylvania

A method to non-destructively measure the gas fill pressure of glass-encapsulated gas devices, e.g. lighting products will be described. The technique, first developed at GTE Laboratories in Waltham, MA, has recently been further expanded to include a wider range of devices (0.02cc and above) and pressures (15 Torr to 10 Atm.), all of which contain a xenon or krypton fill gas. When analysis results of an EDXRF instrument are combined with that of an absolute pressure-volume analyzer, calibration curves were generated allowing for subsequent non-destructive fill pressure determinations with an accuracy of approx. +/- 10%. The EDXRF analysis generates additional useful qualitative information which will also be presented, e.g. detecting the presence of iodine and other salts. Possible applications for 100% quality testing of products using a variant of the test, sub-second analysis, will be discussed.

Biomaterial Interfaces

Room: 609 - Session BI+AS+NS-ThA

Surface Analysis and Related Methods for Biological Materials

Moderator: S.L. McArthur, University of Sheffield, UK

2:00pm **BI+AS+NS-ThA1 Creating and Probing Model Biological Membranes**, ***S.G. Boxer***, Stanford University **INVITED**

During the past few years, our lab has developed a wide range of methods for patterning lipid bilayers on solid supports.[1] These 2D fluids are interesting both as a model for biological membranes and as a physical system with unusual properties. Methods have been developed for controlling the composition of patterned membrane corrals by variations on microcontact printing and microfluidics. Charged components can be moved around within these fluid surfaces by a form of 2D electrophoresis. The planar geometry of supported bilayer systems is ideal for high resolution imaging methods. The lateral (x-y) composition of membranes can be analyzed by high spatial resolution secondary ion mass spectrometry (SIMS) using the NanoSIMS 50 (Cameca) at the Livermore National Laboratory. Results will be described for simple membrane compositions[2] and phase separated domains[3] suggesting the potential of this method for the analysis of membrane organization in complex membranes. Extensions of this approach to more complex systems including membrane-associated proteins will be described. If time permits, a complimentary optical imaging method offering sub-nm resolution in the z-direction (perpendicular to the membrane surface) will be described in the context of imaging conformational changes in membrane proteins.

[1] J. T. Groves and S. G. Boxer, Accounts of Chemical Research, 35, 149-157 (2002).

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2:40pm **BI+AS+NS-ThA3 Activation Thermodynamics for Phospholipid Flip-Flop in Planar Supported Lipid Bilayers Measured by Sum-Frequency Vibrational Spectroscopy**, ***T.C. Anglin***, *H. Li, J.C. Conboy*, University of Utah

Basic transition state theory is used to describe the activation thermodynamics for phospholipid flip-flop in planar supported lipid bilayers prepared by the Langmuir-Blodgett / Langmuir Schaeffer method. Kinetics of flip-flop are determined as a function of varying temperature and lateral surface pressure for model bilayers of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) using sum-frequency vibrational spectroscopy (SFVS). The temperature and pressure dependence of the kinetics of DSPC flip-fop provide a complete description of the activation thermodynamics for flip-flop in the gel state, including free energy of activation, area of activation, and entropy of activation. This is the first description of phospholipid flip-flop according to basic transition state theory with explicit treatment of the free-energy dependence of the process and determination of the entropic contribution to the transition state.

3:00pm **BI+AS+NS-ThA4 Observation of Electrical Characteristics at Cells Membrane using by Electrostatic Force Microscopy**, ***Y.J. Kim***, Myongji University, Korea, *H.D. Kim*, Seoul National University, Korea, *Y.S. Kim*, Myongji University, Korea, *K.H. Lee*, Seoul National University, Korea, *C.J. Kang*, Myongji University, Korea

Recent advances in atomic force microscopy (AFM) made it possible to investigate the biological materials in a single molecule level. Moreover, the AFM has been used to measure the fine structure of individual live cell even under physiological liquid. The images of cells measured show finer structure of cell boundary compared with those of SEM after fixation. Since electrostatic force microscopy (EFM) using conducting cantilever to AFM allows us to observe the electrical properties of the surface, it is also used to study the various properties of the cell membrane. Reportedly, it is known that protein expression depends on the cell kinds and shows the non uniform distributions, which causes the electrical potential difference on the cell surface in the local area. Thus mapping the electrical potential of a cell using EFM and comparing it with that of reference group, we are able to extract the information to differentiate the cells. In this work, we have identified the breast cancer cells (MCF7) and normal breast epithelial cells (MCF10A) derived from the same origin by fractal dimension analysis using AFM and the electrical properties of the cell membrane measured from the EFM will be also discussed. The results show that AFM imaging with EFM measurement might be feasible methods for analyzing surface structures of living cells with high resolution, and it could provide new insights into cell surface structure.

3:40pm **BI+AS+NS-ThA6 Two and Three Dimensional Analysis of C. Albicans Biofilms with Cluster SIMS**, ***B.J. Tyler***, *S. Rangarajan*, University of Utah, *J. Moeller, H.F. Arlinghaus*, University of Muenster, Germany

The high tolerance of microbial biofilms to important antimicrobial agents creates an import problem for treatment of infections associated with implanted medical devices. Several important hypotheses for this drug resistance involve mass transport limitation within the biofilms. We have been using 2_D and 3_D ToF-SIMS analysis to investigate transport of drugs and nutrients through C. albicans biofilms. Analysis has been performed using a novel ToF-SIMS system which incorporates a cryo-sectioning chamber and precise temperature control during analysis. This instrument has allowed us to map the distribution of key nutrients and drugs with in the biofilm as well as to identify viable vs. nonviable cells. Through these studies, we have determined that the multiple cellular layers and extracellular polymers are not the most important mass transport barrier. Common drugs are able to permeate to the bottom of the biofilm within 5 minutes but are still unable to penetrate the cell wall of persister cells found at the base of the biofilm. Current work is focusing on cell wall and membrane changes within a subpopulation of the biofilm cells which apparently limits transport of antimicrobials into the cells. Multivariate statistical techniques have been crucial for the analysis of these samples and discussion of the relevant statistical methods employed will be presented.

4:00pm **BI+AS+NS-ThA7 XPS, ToF-SIMS and NEXAFS Investigation of Peptide Adsorption onto SAMs**, ***J.S. Apte***, *L.J. Gamble, D.G. Castner*, University of Washington

The interactions between proteins and surfaces are critical to the success or failure of implants in the body. When adsorbed onto a synthetic surface, proteins often denature which can trigger the foreign-body response. It is therefore essential to develop methods to examine these interfacial phenomena. This work uses X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and near-edge X-ray absorption spectroscopy (NEXAFS) to characterize the structure of α-helix and β-sheet peptides adsorbed onto self-assembled monolayers (SAMs). The α-helix peptide is a 14-mer made up of lysine (K) and leucine (L) residues with a hydrophobic periodicity of 3.5. The β-sheet peptide is a 15-mer also made up of L and K residues with a hydrophobic periodicity of 2. A β-sheet peptide with the same structure but with valine (V) substituted for L was also studied since V has a higher tendency than L to form β-sheet structures. All peptides have the hydrophobic side-chains on one side of the peptide and the hydrophilic on the other. The SAMs studied were thiols on gold containing the ω-groups $-CH_3$, -OH, -COOH, $-NH_3^+$ and $-CF_3$. XPS nitrogen atomic percent was used to measure adsorption isotherms for the peptides. The α-helix peptide forms a monolayer (8.2% N) on the COOH-terminated SAM at an adsorption concentration 50 times lower than on the CH_3-terminated SAM (0.01 mg/mL compared to 0.5). The surface coverage on the CH_3 SAMs appeared to be patchier compared to the COOH SAMs, since they had standard deviations of 2-3% N. Atomic force microscopy images of the adsorbed peptides were generated to examine this patchiness. Also, the adsorption process depended on buffer salt concentration. Little peptide adsorption was detectable on the methyl SAMs when adsorbed from a 0.1x buffer. ToF-SIMS was used to investigate the ratio of K to L characteristic mass fragments at 84 and 86 m/z, respectively. The 84/86 (K/L) ratio on CH_3 SAMs (1.2) was the same, within experimental error, as the ratio on COOH SAMs (1.1). Polarization dependent NEXAFS experiments at the nitrogen K-edge indicated the β-sheet was lying down on the SAM surfaces. The α-helical peptide exhibited significantly less polarization dependence than the β-sheet peptide, probably due to the different structure of the backbone amide groups in the α-helical peptide.

4:20pm **BI+AS+NS-ThA8 Isolation and Detachment of Small Cell Populations from a Thermoresponsive Polymer**, ***H.E. Canavan***, *K. Gallagher-Gonzales, J.A. Reed*, University of New Mexico

Poly(N-isopropyl acrylamide) (pNIPAM) has proven to be an efficient and non-destructive means of detaching intact sheets of mammalian cells. In addition, cell sheets detached from pNIPAM maintain their association with the extracellular matrix (ECM) during and following detachment from a coated surface, enabling their use in tissue engineering. To date, the majority of those studying cellular interactions with pNIPAM have focused on harvesting large domains of cells for such tissue engineering applications. However, there are many other applications for which the non-destructive release of smaller populations, or even isolated cells, is desirable. For example, isolated cells are required to ascertain the extent of transmembrane protein receptor upregulation when assaying the efficacy of cancer therapeutics on cell populations via flow cytometry (FC). In this work, arrays of thermoresponsive domains were fabricated to isolate defined populations of cells using a variety of techniques. The surface chemistry, thermoresponse, and topography of the films generated were verified via X-ray photoelectron spectroscopy (XPS), contact angle measurements, and atomic force microscopy (AFM), respectively, and compared to controls. The cell releasing properties of the films were characterized by incubating baby hamster kidney (BHK) and bovine aortic endothelial cells (BAECs). The behavior of the cells from isolated cells and small cell populations were characterized and compared to large cell population controls.

4:40pm **BI+AS+NS-ThA9 Surface Characterization of Ordered Nanopatterns made from Self-Assembly of Mixed Nanoparticles,** *S. Pillai, G. Singh,* The University of Aarhus, Denmark, *C. Blomfield, A. Roberts,* Kratos Analytical Ltd, UK, *R.L. Meyer,* ***P. Kingshott***, The University of Aarhus, Denmark

Controlled patterning of surfaces with different chemistries and structures at nanoscale length scales is highly desirable for understanding the fundamental mechanisms of protein and cell interactions with biomaterials. The use of nanoparticles (NPs) to pattern surfaces by colloidal lithography or templating using one type of NP is well known for applications such as biosensors,[1] biomaterials[2] and tissue engineering.[3] We demonstrate that by using mixed nanoparticles unique highly-ordered patterns can be obtained by simple self-assembly from buffer onto hydrophobic surfaces from both concentrated and dilute two-component NP suspensions.[4] The new method uses suspensions of poly(styrene) (PS) NPs of different size (d = 500 to 60nm) with different NP ratios and volume fractions. The ordering is independent of the NP surface chemistry (sulfated, carboxylated, or aminated PS) or zeta potential and occurs over a broad pH range (4-10). The method is demonstrated for two types of hydrophobic surfaces, a commercial adhesive carbon tape and octadecyltrichlorosilane (OTS)-modified glass where patterns of hexagonally packed large particles are inter-dispersed with smaller particles. However, very poor ordering is achieved using gold, mica and HOPG (highly oriented pyrolytic graphite) as substrates. The morphologies of the nanoparticle assemblies are characterised extensively by SEM and AFM. In addition, XPS and ToF-SIMS are used to characterise the surface chemistry of the NP surfaces, which also provides knowledge of the mechanisms of NP assembly by showing that the ordering is most likely associated with charge screening by buffer salts resulting in an entropically driven assembly process. These preliminary results indicate that use of two component NP assemblies opens up the possibilities of decorating surfaces with well-defined chemical nanopatterns capable of selective attachment of different proteins and/or protein resistant molecules.

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Electronic Materials and Processing

Room: 612 - Session EM-ThA

High-K/High Mobility Substrates and Power Electronics

Moderator: C. Eddy, Naval Research Laboratory

2:00pm **EM-ThA1 Growth and Characterization of III/V Compound Semiconductors on Silicon**, *S.F. Cheng, R.L. Woo,* ***L. Gao****, R.F. Hicks*, University of California, Los Angeles

III-V materials are promising materials for high speed, low power devices in next-generation integrated circuits. However, a roadblock to implementing these materials in integrated circuit applications is the heteroepitaxial growth of III-V on silicon. Here, we have developed a process flow for the selective-area metalorganic vapor-phase epitaxy (MOVPE) of GaAs on Si (100) substrates. Arsenic passivation was demonstrated in the reactor environment at a temperature of 650 °C. The subsequent deposition of GaAs was carried out in a two-step process, with nucleation at 250-550 °C and second-step growth at 630 °C. High-resolution x-ray diffraction of films nucleated at 350°C or below exhibited polycrystalline grains, whereas films nucleated at 400 °C and above were single crystal. A clear c(4×4) LEED pattern of GaAs deposited on a blanket Si substrate is demonstrated for the first time. Growth on patterned Si indicates improved crystallinity as determined by XRD and plane-view TEM. The photoluminescence of SA-MOVPE GaAs on Si is shown to be nearly identical to homoepitaxial GaAs. The potential of these materials for the fabrication of high-speed devices will be discussed at the meeting.

2:20pm **EM-ThA2 STM Imaging of Selective Bonding of Hf, O, and HfO_2 on InAs(001)-(4x2)/c(8x2)**, ***J.B. Clemens****, A.C. Kummel*, University of California, San Diego

Hafnium oxide (HfO_2) has been successfully used as a high-κ gate oxide on Si(100) and is being investigated as a high-κ gate oxide for high mobility III-V semiconductors. To form an electronically passive interface on a III-V semiconductor is challenging because the bonding to the group III and group V atoms must be distinct to leave both atoms in their bulk oxidation states with an unchanged electronic structure. The bonding of Hf, O, and HfO_2 on the InAs(001)-(4x2)/c(8x2) surface was probed with scanning tunneling microscopy (STM) to determine the exact bonding positions at low coverage. The InAs(001)-(4x2) surface is advantageous for these studies since it has a row and trough structure with In atoms at the center of the rows and As atoms at the edges of the rows which are easy to image in STM. Furthermore, the InAs(001)-(4x2) surface contains no As-As dimers so surface atoms are rarely displaced during oxide and oxygen dosing. Although the sticking probability for O_2 on this surface is very low (~0.015%), it is found that O_2 bonds preferentially to the first layer undercoordinated In rows. This is consistent with O-metal bond formation being thermodynamically more favorable than As-O bond formation. Furthermore, the As atoms on the edge of the row have only half-filled dangling bonds so they are poor electron donors and less likely to react with oxygen than As dimer atoms found on other III-V reconstructions. Conversely, STM shows that Hf bonds initially to the second-layer tricoordinated As atoms along the edges of the In rows of the InAs(001)-(4x2) surface. This is consistent with the Hf atoms donating electrons to the unfilled dangling bonds of the second layer tricoordinated As atoms. In order to investigate the bonding geometry of HfO_2 on the InAs(001)-(4x2) surface, Hf and O_2 are co-deposited. Current work will show the result of annealing these surfaces in order to create ordered submonolayer coverages of HfO_2.

2:40pm **EM-ThA3 Materials and Process Needs for Power Electronic Integration**, ***K.D.T. Ngo****, G.Q. Lu,* Virginia Tech, *P. Chow*, Rensselaer Polytechnic Institute **INVITED**

A typical switched-mode converter contains semiconductor, conductive, magnetic, dielectric, and thermal-management elements. The wide variations in materials and processes employed to make these components, the large dimensions, and the requirements for low losses have limited the chance for integration. *** The integration strategy pursued divides the power electronic converter into three building blocks: Active, Passive, and Filter Integrated Power Electronics Modules (AIPEM, PIPEM, and FIPEM). Electro-magneto-thermal structures are described for realization of the functionalities expected from the structures. Materials and processes have been identified to verify the operation of the integrated structures. While the entire converter cannot be integrated using current technologies, the equipment and process steps to fabricate the three types of IPEMs are similar. *** The AIPEM structure (e.g., an "embedded-power" module) contains the semiconductor devices, the associated ancillary functions (e.g., gate drives, sensing, and protection), and thermal management elements (e.g., heat spreader, heat sink, and micro-channel coolers). Interacting with the AIPEM to shape the conversion gain is the PIPEM (e.g., an integrated inductor/capacitor/transformer network) containing passive components designed to propagate energy at the switching frequency. The FIPEM (e.g., an integrated lossy transmission line for EMI filtering), on the other hand, contains passive components designed to attenuate at the switching frequency, or the frequencies beyond the useful power bandwidth. *** Semiconductor materials employed include silicon, silicon carbide, and gallium nitride. Nano-material technology has been developed for bonding and interconnects, and multiferroic nano-composites for passive integration. Other common metals, polymers, and ceramics are also used. *** Exemplified processes include "Metal Post Interconnected Parallel Plate Structure," "Flip Chip on Flex," "Dimple-Array Interconnect," and "Embedded Power." Sputtering, plating, etching, spin-coating, screen-printing, tape casting, sintering, and solder reflowing are typical process steps. New materials and processes are needed for high yield and reliable operations under wide ranges of temperature, fields, vibration, pressure, and other environmental conditions.

3:40pm **EM-ThA6 DFT Molecular Dynamics Simulation of Ge-O-Al Selective Bond Formation at the a-Al2O3/Ge(001) Interface**, *E.A. Chagarov,* ***A.C. Kummel***, University of California, San Diego

Density-Functional Theory simulations of interface formation between amorphous Al2O3 oxide and Ge(001)-(2x4) surface were performed to model the chemical bonding at the oxide-semiconductor interface. A realistic DFT sample of amorphous Al2O3 was developed using "melt and cool" hybrid Classical-DFT Molecular Dynamics (MD) approach. Initially, 24 samples of 100 atoms were prepared by classical MD runs by melting initially crystalline sample. The spatial distribution of the atoms in each sample was quantified using Radial Distribution Functions (RDF), coordination distribution, and average coordination number. The sample with an atomic spatial distribution closest to the experimental geometry was DFT annealed to obtain a more realistic fully relaxed DFT geometry. The DFT annealed a-Al2O3 sample was placed on a 8 layer Ge(001)-(2x4) slab and partially relaxed for 200 steps with the fixed Ge atoms allowing the a-Al2O3 to adjust to Ge surface topography and to form oxide-Ge bonds. Subsequently, the top 5 layers of Ge were unfrozen, and the whole a-Al2O3-Ge system was annealed, cooled and relaxed to form a-Al2O3-Ge interface. DFT simulations of a-Al2O3-Ge interface revealed that during annealing, Al atoms migrate out of interface, while O atoms migrate into the interface. The bonding of a-Al2O3 to Ge occurs mainly through O atoms forming a low density Al-O-Ge bonds to the Ge dangling bonds on the surface. It was found that several O atoms diffused into Ge bulk forming interstitials. Electronic structure analysis of the interface demonstrated that Density of States (DOS) of the interface region was approximately a superposition of a-Al2O3 and Ge(001)-(2x4) DOS curves without significant new features. The oxygen-rich a-Al2O3/Ge interface is consistent with Al forming stronger bonds to O than to Ge and with experimental results. The small changes in electronic structure for a-Al2O3/Ge interface formation are consistent with the oxide reducing the number of Ge dangling bonds and only forming a low density of weakly ionic Al-O-Ge bonds.

4:00pm **EM-ThA7 Band Alignments of Y2O3 on Different Group IV Substrates**, *S.Y. Chiam,* Imperial College London, UK, *W.K. Chim,* National University of Singapore, *A.C. Huan,* Institute of Materials Research and Engineering, Singapore, ***J. Zhang,*** Imperial College London, UK, *S.J. Wang, J.S. Pan,* Institute of Materials Research and Engineering, Singapore, *S.G. Turner*, Imperial College London, UK

Band alignment is an important property for oxides-semiconductor lineup especially for MOS devices. Band offsets for many oxides-semiconductor has and can be predicted by charge neutrality level (CNL) model (gap states model). This model however is based on an essentially "bulk" phenomenon of gap states dipoles. There have been, however, differences in the measured valence band offsets (VBO) and conduction band offsets (CBO) of oxides (especially rare-earth oxides) and the predicted offsets from the CNL model. In this work, we present the experimental data for rf-sputtered Y2O3 on Si, Ge, strain-Si, strain-SiGe and relaxed SiGe. The virtual substrates were grown by GSMBE. Some of these substrates expect differences (based on various sources, investigating changes in conduction and valence band) in the valence and conduction band of less then 0.1eV. However, the VBO and CBO between the oxide and these substrates amounts often to >0.5eV. In addition, we have pre-sputtered a thin mono-layer of Y metal before deposition of the Y2O3 (in-situ). This reduces the valence band offset for the films on all the substrates. This can be explained by changes in either interface structure and/or chemical nature at the interface (dipoles). Our work shows the importance of the nature at the interface in determining the offsets between an oxide and semiconductor.

4:20pm **EM-ThA8 High-k/III-V Integration: from GaN to InSb**, ***P.D. Ye***, Purdue University **INVITED**

The principal obstacle to III-V compound semiconductors rivaling or exceeding the properties of Si electronics has been the lack of high-quality, thermodynamically stable insulators on GaAs (or on III-V materials in general). For more than four decades, the research community has searched for suitable III-V compound semiconductor gate dielectrics or passivation layers. The literature testifies to the extent of this effort with representative, currently active approaches including sulfur passivation, silicon interface control layers (Si ICLs), in situ molecular beam epitaxy (MBE) growth of Ga2O3(Gd2O3), ex situ atomic layer deposition (ALD) growth of Al2O3 and HfO2, jet vapor deposition (JVD) of Si3N4, ALD, PVD or MBE of HfO2 + Si or Ge ICL, Al2O3 plasma nitridation or AlN passivation. The research on ALD approach is of particular interest, since the Si industry is getting familiar with ALD Hf-based dielectrics and this approach has the potential to become a manufacturable technology. In this talk, the authors will review some of our previous work on integration of ALD high-k dielectric Al2O3 on GaAs, InGaAs and GaN, and demonstration of high performed depletion-mode III-V MOSFETs. But for very large scale integrated (VLSI) circuits or high-speed digital applications, enhancement-mode (E-mode) III-V MOSFETs within the Si CMOS platform are the real devices of interest. We will discuss on the detailed CV measurements (high frequency-low frequency CV, Quasi-static CV, split-CV, and photo-CV) on high temperature annealed ALD Al2O3 and HfO2 dielectrics on GaAs and InGaAs. InGaAs includes In0.2Ga0.8As/GaAs, In0.53Ga0.47As/InP and other In-rich InGaAs materials. We will focus on some new results on inversion-type E-mode NMOSFET fabricated on p-type In0.53Ga0.47As, and InP surfaces using ALD Al2O3 and HfO2 dielectrics. The maximum inversion current of ~ 400 mA/mm and Gm of ~ 130 mA/mm and the middle gap interface trap density Dit of low 10x11/cm2-eV to 2x1012/cm2-eV is achieved at these material systems. We will also briefly report on some new CV results on high-k/InSb surface. The work is in close collaborations with G.D. Wilk, Y. Xuan, H.C. Lin, Y.Q. Wu, T. Shen, T. Yang, Z. Cheng, A. Lochtefeld, J. Woodall, M. Lundstrom, M.A. Alam, R.M. Wallace, J.C.M. Hwang, A. Liu, W. Wang, M. Santos. We also would like to thank B. Yang, M. Hong, R. Kwo, H. Gossmann, K.K. Ng, J. Bude and others who contributed significantly at the initial stage of this research.

5:00pm **EM-ThA10 Study of High-κ Dielectrics on InGaAs for CMOS Applications**, ***F.S. Aguirre-Tostado****, C. Hinkle, K.J. Choi, M. Milojevic, S.J. McDonnell, J. Kim, M.J. Kim, E. Vogel, R.M. Wallace*, University of Texas at Dallas

Scaling and performance of integrated circuits has been pushed to the limit where the substitution of Si itself by higher mobility channel materials. Bulk electron mobilities for GaAs and InGaAs are well above those obtained for Si. At room temperature, the electron mobility of InGaAs exceeds the 10,000 cm^2/V-s making this material a good candidate for high-performance logic applications. In this paper we will describe chemical, structural and electrical properties of high-κ dielectrics on InGaAs channels. The chemistry and structural properties of $LaAlO_3$, $HfAlO_3$ and HfO_2 on InGaAs will be presented using in-situ XPS and LEISS analysis as well as HRTEM and XRD analysis. The thermal stability for relevant thermal budgets associated with dopant activation in a surface channel MOSFET InGaAs based device is examined in view of the electrical characteristics of MOS capacitors. This work is supported by the MARCO MSD Focus Center.

Magnetic Interfaces and Nanostructures

Room: 619 - Session MI-ThA

Magnetic Semiconductors II

Moderator: J. Shen, Oak Ridge National Laboratory

2:00pm **MI-ThA1 Ferromagnetism and Dopant Ordering in Semiconducting, Epitaxial Ti-doped α-Fe_2O_3 Hematite**, ***T.C. Droubay****,* Pacific Northwest National Laboratory, *A. Celik-Aktas,* University of Wisconsin-Milwaukee, *K.M. Rosso,* Pacific Northwest National Laboratory, *S.M. Heald,* Argonne National Laboratory, *S.H. Cheung, C.M. Wang,* Pacific Northwest National Laboratory, *M. Gadjardziska-Josifovska,* University of Wisconsin-Milwaukee, *S.A. Chambers*, Pacific Northwest National Laboratory

The classical visualization of a ferromagnetic semiconductor is the random substitution of a fraction of the original atoms within the semiconductor lattice with magnetic atoms, most commonly transition metal ions. An alternate approach which has not garnered much attention until recently is the ordered substitution of non-magnetic metal ions into an otherwise antiferromagnetic semiconductor lattice. Ti-doped α-Fe_2O_3 has been suggested as such a material if Ti(IV) substitutes preferentially in one magnetic sublattice, effectively creating a ferrimagnetic semiconductor. To examine the ordering more fully, we have used oxygen plasma-assisted MBE to grow Ti-doped hematite on α-Al_2O_3(001) for various dopant levels between the endpoints Fe_2O_3 and $FeTiO_3$. Excellent heteroepitaxy was achieved by first growing a Cr_2O_3 buffer layer to grade the lattice mismatch. Fe was predominantly found to be in the +3 charge state by Fe K-shell XANES and Fe 2p photoemission, except at concentrations nearing x = 0.15. Ti was found to be exclusively in the +4 charge state and to uniformly substitute for Fe(III) in the hematite lattice by Ti K-shell XANES and EXAFS, accompanied by a significant site distortion. The resultant epitaxial films for low dopant concentration are magnetic at room temperature albeit with a fraction (~0.5 μ_B/Ti atom) of the 4 μ_B/Ti saturation magnetization expected if a magnetic ordered phase had nucleated exclusively. DFT predicts that the magnetically ordered and magnetically random structures are nearly iso-energetic which explains the weak normalized moment. We have investigated the atomic structure of the low-doped epitaxial ferromagnetic films using high-resolution TEM and electron diffraction analysis. HRTEM and electron diffraction confirm the lack of long-range chemical ordering of Ti along the [001] direction. HRTEM images show weak but discernable lines in $(Ti_xFe_{1-x})_2O_3$ along the growth direction with an average in-plane periodicity of ~0.94nm. Electron diffraction patterns corroborate this ordering by displaying additional diffraction spots perpendicular to the growth direction. These satellite spots are suggestive of Ti dopant ordering in the basal plane. A proposed atomic model of the dopant ordering including DFT calculations will be discussed in relation to the observed experimental electronic and magnetic properties.

2:20pm **MI-ThA2 Carrier-Dopant Exchange Interactions in Colloidal Mn^{2+}:ZnO Quantum Dots**

S.T. Ochsenbein, *K.M. Whitaker, W.K. Liu, D.R. Gamelin*, University of Washington

Magnetically doped semiconductor nanocrystals present an interesting motif for possible spintronics applications. In such so-called diluted magnetic semiconductors (DMSs) the interaction between charge carriers and the dopant ions is the key factor defining their spintronics functionality. Ferromagnetism in some DMSs is attributed to carrier-mediated interaction between the dopant ions for example,[1] and thus depends strongly on carrier-dopant interactions. The effect of quantum confinement in DMS nanostructures on carrier-dopant interactions has been the subject of theoretical considerations,[2] but experimental investigations are scarce. We present experimental results addressing electron-Mn^{2+} interactions in colloidal Mn^{2+}:ZnO nanocrystals. Photochemical injection of conduction band electrons[3] allows the interaction between these quantum confined electrons and the Mn^{2+} ions to be studied by electron paramagnetic resonance (EPR) spectroscopy and magnetic measurements. The microscopic origins of the resulting perturbed magnetic properties will be described.

[1] Dietl, T.; Ohno, H.; Matsukura, F., Phys. Rev. B 2001, 63, 195205.

[2] Bhattacharjee, A. K., Phys. Rev. B. 1998, 58, 15660.

[2] Liu, W. K.; Whitaker, K. M.; Kittilstved, K. R.; Gamelin, D. R., J. Am. Chem. Soc. 2006, 128, 3910. .

2:40pm **MI-ThA3 Growth and Properties of Epitaxial Co- and Mn-doped ZnO Films**

T.C. Kaspar, *T.C. Droubay, Y.J. Li, M.H. Engelhard, P. Nachimuthu, V. Shutthanandan, Z. Zhu,* Pacific Northwest National Laboratory*, S.M. Heald, D.J. Keavney,* Argonne National Laboratory*, C.A. Johnson, D.R. Gamelin,* University of Washington*, S.A. Chambers*, Pacific Northwest National Laboratory

Doping ZnO with transition metal ions may be a promising route to realize dilute magnetic semiconductors which are ferromagnetic above room temperature. Although several groups have reported room temperature ferromagnetism in both Co:ZnO and Mn:ZnO, significant controversy persists as to whether the observed ferromagnetism is intrinsic to doped ZnO or is due to extrinsic factors such as secondary phase formation. Of particular concern is the formation of ferromagnetic Co metal clusters in Co:ZnO, and potentially ferromagnetic Zn-Mn oxides in Mn:ZnO. The difficulty lies in the small quantity of secondary phase required to explain the observed weak ferromagnetism, often comprising less than 5% of the dopants (which themselves are generally only 10% or less of the total cations in the material). Conventional materials characterization techniques, such as x-ray diffraction (XRD) and transmission electron microscopy (TEM), can be insensitive to the small volume fraction of secondary phase involved, making detection difficult. Spectroscopic techniques, particularly x-ray absorption (XAS), can provide much more information on the charge state and local environment of the dopant. However, the detection limit at the K-edge is about 5% of the dopants for metal formation; oxide secondary phases can be more difficult to detect. A related issue concerns the determination of the location and role of p-type dopants in ZnO, since ferromagnetic ordering is only expected in Mn:ZnO when the material is p-type. Here we present a detailed study of Co:ZnO and Mn:ZnO thin films deposited by pulsed laser deposition. The ZnO quality and majority dopant behavior were probed by conventional characterization techniques such as XRD, TEM, and XAS, which indicated dopant substitution for Zn in ZnO. The possibility of a small fraction of secondary phase formation was investigated with several techniques including x-ray linear dichroism, Raman spectroscopy, and x-ray photoelectron spectroscopy (XPS) sputter depth profiling. In Co:ZnO, localized Co metal formation at the film surface under reducing conditions was not detectable by K-edge XAS but was clearly observed by XPS sputter depth profiling. The presence and location of the potential p-type dopants N and Li were investigated by secondary ion mass spectrometry and nuclear reaction analysis. The implications of secondary phase formation on ferromagnetism in Co:ZnO and Mn:ZnO will be discussed.

3:00pm **MI-ThA4 Manipulating Ferromagnetism in Co^{2+}:ZnO by Controlling Interstitial Zinc Concentrations**

C.A. Johnson, *D.R. Gamelin*, University of Washington

Demonstration of reproducible intrinsic high-temperature ferromagnetism in diluted magnetic semiconductors (DMSs) is an important step toward their use in devices. Recently it has become apparent that understanding the defects in Co^{2+}:ZnO is paramount to understanding the microscopic origins of its ferromagnetism. We will describe that Co^{2+}:ZnO films can be made ferromagnetic by annealing under Zn vapor to create the Zn_i lattice defect.[1] Oxidation of the Zn-treated Co^{2+}:ZnO films at elevated temperatures results in a controlled quenching of the ferromagnetism as the Zn_i migrates out of the lattice and is oxidized.[2] These changes can be followed kinetically using both magnetic measurements and magnetic circular dichroism spectroscopy. These results demonstrate that ferromagnetism of Co^{2+}:ZnO thin films can be controlled by controlling Zn_i concentrations and provide new insights into the microscopic origins of this interesting magnetism.

[1] Schwartz, D.A. and D.R. Gamelin, Adv Mat, 2004. 16 2115-2118.

[2] Kittilstved, K.R., Schwartz, D.A., Tuan, A.C., Heald, S.M., Chambers, S.A., Gamelin, D.R., Phys Rev Let, 2006. 97 0372203.

3:40pm **MI-ThA6 Optimal Dopant Control of High-Tc Diluted Magnetic Semiconductors via Subsurfactant Epitaxy or n-p co-doping***

Z. Zhang, Oak Ridge National Laboratory and University of Tennessee **INVITED**

Recent developments of diluted magnetic semiconductors (DMS) seem to suggest that one must rely on nano-phase separations inside the DMS films of III-V and column-IV semiconductors in order to achieve high magnetic ordering temperatures (Tc>300K). Here we present two conceptually new and intriguing approaches to enhance substitutional doping of Mn in Ge and Si, based on first-principles calculations. One is via subsurfactant epitaxy, the other is via n-p co-doping. In the former case, the resultant materials exhibit homogeneous distributions of substitutional Mn dopants with Tc>300K, as observed experimentally. In the latter case, we find that co-doping faciliates the efficiency of Mn substitutional occupation, and observe dramatically enhanced anisotropy in the ferromagnetic coupling between the dopants. These results will be compared in connection with the recent developments of the field emphasizing the importance of nano-columns within the DMS.

*Work done in collaboration with Wenguang Zhu, Hanno Weitering, Changgan Zeng, Enge Wang, Tim Kaxiras, Mina Yoon, Klaus van Benthem, and Matthew Chrisholm. Supported by US. NSF (Grant No. DMR-0606485), the NSF of China, and by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with ORNL, managed and operated by UT-Battelle, LLC.

4:20pm **MI-ThA8 Formation Mechanism of Self-assembled Nanocolumns in (Ge,Mn) Epitaxial Films***

W. Zhu, University of Tennessee*, **M. Yoon***, University of Tennessee and ORNL*, **Z. Zhang***, ORNL and University of Tennessee

The spatial distribution of magnetic dopants in diluted magnetic semiconductors is critical in determining the magnetic property of the materials. Traditionally, the magnetic dopants were viewed to be homogeneously distributed in the host semiconductors. Recently, self-assembled Mn-rich nanocolumns were observed experimentally in (Ge,Mn) epitaxial films, which exhibit remarkable magnetic properties.[1] Here, we propose a microscopic formation mechanism for the nanocolumns, involving the interplay between the electrostatic attractions of oppositely charged Mn ions and effective long-range repulsions due to elastic effect. Based on first-principles calculations and kinetic Monte Carlo simulations, we show that the proposed mechanism can successfully explain the formation of the self-assembled Mn-rich nanocolumns in the (Ge,Mn) epitaxial systems. We also discuss the potential applicability of the proposed model to other related systems.

[*] Work supported by US. NSF (Grant No. DMR-0606485), and by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with ORNL, managed and operated by UT-Battelle, LLC.

[1] M. Jamet et al., Nat. Mater. 5, 653 (2006); A. P. Li et al., Phys. Rev. B 75, 201201(R) (2007).

4:40pm **MI-ThA9 Ferromagnetism in Mn Doped Ge Thin Films**

J. Yu, *J. Lu, K.G. West, L. He, R. Hull, S.A. Wolf*, University of Virginia

Ferromagnetism in Group IV semiconductors produced by transition metal doping is of great interest due to their potential applications in spintronics. In this study, we use ion implantation to introduce Mn ions into Ge. 0.5~4 at. % Mn ion was implanted into 200 nm Ge thin films. Both single implantation and dual implantation were used to prepare samples. The dual ion implantation was performed at 75 °C to improve the uniformity of Mn distribution and avoid formation of a ferromagnetic Mn5Ge3 phase which forms at higher implant temperatures. The implantation damage to Ge was healed by rapid thermal annealing at temperatures ranging from 300 to 800 °C in forming gas. Moment vs. Temperature showed that the ferromagnetic transition temperature was ~ 60 K for 4% samples annealed at 300 °C for 1.5 minutes. The saturation moment at 5K is 0.12 Bohr magnetons per Mn. Transport measurements using the Van der Pauw method were performed to study the correlation between the magnetization and resistivity of Mn:Ge. Significant magnetoresistance and anomalous Hall effect were observed on samples annealed at 300 °C for 1 and 1.5 minutes. The normal and anomalous Hall coefficients are both calculated and confirmed with transport measurement. Cross-section TEM study is underway to determine the phase composition and the distribution of Mn ions in this dual implanted sample annealed at 300°C.

5:00pm **MI-ThA10 Atomic and Electronic Structure of Manganese Alloys on Ge(100) Surface**, ***H. Kim***, *G.E. Jeong, K.H. Chung, S.-J. Kahng*, Korea University

Ferromagnetic metals on semiconducting surfaces are promising for spintronics application. The surface structures of Mn5Ge3(111) alloy on Ge(100) surfaces were studied with scanning tunneling microscope. The plateau structures of Mn5Ge3 were prepared by solid phase epitaxy. Clear hexagonal atomic structures were observed on top of the plateau structures. In support of diffraction experiments and previous theoretical predictions, we were able to confirm that the plateau structures are Mn5Ge3 alloys with the top surfaces along (111) directions. Several atomic patterns, with strong bias-energy dependence, were observed in topography images. As the patterns are compared with theoretical predictions, it is believed that the atomic structures of second layers were observed at certain energy levels. Three types of defect structures were observed in STM images, whose atomic structures will be discussed.

Manufacturing Science and Technology

Room: 615 - Session MS-ThA

MEMS Manufacturing

Moderator: R. Ghodssi, University of Maryland

2:20pm **MS-ThA2 Double-Exposure Gray-Scale Technology for Improved Vertical Resolution of 3D Photoresist Structures**, ***L.A. Mosher***, University of Maryland, *B.C. Morgan*, U.S. Army Research Laboratory, *R. Ghodssi*, University of Maryland

We report the development of a new double-exposure gray-scale photolithography technique to batch fabricate three-dimensional structures in photoresist with improved vertical resolution. Deep reactive ion etching is used to transfer the patterned photoresist into silicon, enabling a complete three-dimensional microfabrication platform with many applications for MEMS devices, such as lenses and microengines. Gray-scale photolithography utilizes a photomask to spatially control the ultraviolet light intensity incident on a photoresist layer. This control is achieved by diffraction through sub-resolution pixels on the mask using projection photolithography. Projection optics keep only the zeroth order intensity, preventing the higher-order diffractions from reaching the wafer. The local pixel size is correlated to the transmitted intensity and therefore determines the height in photoresist after development. Vertical resolution, determined by the number of available pixels, is limited by the mask vendor. Current mask fabrication techniques allow for tens of pixel sizes, which is insufficient for some MEMS applications. We introduce a double-exposure gray-scale technique, utilizing two gray-scale exposures prior to a single development. In this technique, two pixel sizes are used with two partial exposures, resulting in a third unique photoresist height after development. By using all pixel combinations, we achieved an exponential increase in the number of available levels. Our initial test design utilized only eight pixel sizes, but realized 64 unique height levels in photoresist after development. We created an empirical model to correlate the pixel combination and exposure times with the photoresist height, which facilitates the design of pixel layouts for nearly arbitrary geometries. This model was used to optimize the exposure times to minimize the average and maximum vertical step height. We fabricated a seventeen-pixel test structure based on this model and observed a significant improvement over single-exposure. A decrease in the average vertical step height from 0.19 µm to 0.03 µm was achieved as well as a decrease in the maximum vertical step height from 0.63 µm to 0.24 µm. Detailed modeling parameters and experimental results from double-exposure gray-scale structures will be presented.

2:40pm **MS-ThA3 MEMS Manufacturing in a High Volume CMOS Wafer Fabrication Facility**, ***G.D. Winterton***, Texas Instruments Inc. **INVITED**

The original concept of the digital micromirror device (DMD) is a far cry from the current embodiment of today's devices. Design, process, and packaging innovations of the past decade have enabled Texas Instruments Digital Light Processing (DLP) devices capable of transitioning from on to off over 5000 times a second with native contrast ratios in excess of 4000:1. TI's philosophy is to manufacture the DLP MEMS device in an existing high volume CMOS wafer fab. This philosophy constrains the MEMS processes to be compatible with existing CMOS processes. Sharing the facility with standard CMOS allows TI to benefit from the economies of scale which exist in a high volume CMOS fab. The MEMS group has a dedicated team of development, integration, and process engineers embedded within the larger fab engineering organization. This facilitates synergy between the engineering teams and leverages the experiences of the larger organization. MEMS manufacturing has additional requirements not found on standard CMOS. Most MEMS are 3D devices requiring very tight control of film thicknesses to control the spacing between MEMS elements. Film stresses are of much greater concern in MEMS processing which has required additional control methodologies to be put in place to facilitate much tighter control than standard CMOS. TI DLP products utilize sacrificial photoresist layers to create the spacings between the MEMS elements. Standard lithographic tools and techniques are used to create the patterns and traditional plasma etching are used to define these features. The metal deposition process cannot use traditional sputter etch techniques due to the presence of photoresist on which the metal is being deposited onto. The metal must also be deposited at low temperatures to avoid resist reticulation. Photoresist stripping and cleaning techniques had to be developed which could integrate into the fab without affecting the sacrificial resist layers or inducing unwanted topography. Special care is paid to surface conditions to avoid stiction effects since metal-to-metal elements cone in direct contact during device operation. The final step prior to packaging is the plasma removal of the sacrificial resist layers to release the MEMS elements. Significant engineering effort has been dedicated to packaging since particles are a major source of defects. Control of the internal package environment is an area of special concern to control stiction during the lifetime of the product.

3:40pm **MS-ThA6 Manufacturing Challenges and Method of Fabrication of On-Chip Capacitive Digital Isolators**, ***P. Mahalingam***, *D. Guiling, S. Lee, R. Figueroa, W. Tian, Y. Patton, I. Khan*, Texas Instruments

Digital isolators permit high-speed data transmission in industrial and process control applications which involve hazardous voltage environments. Texas Instruments introduced on-chip capacitive isolation technology for digital isolated couplers which enables products to provide isolation voltage up to 7000Vrms and ~12000V surge capability. An innovative, robust method of manufacturing low noise, 10kV peak on-chip capacitive digital isolator integrated in a BiCMOS process flow is presented this paper. Silicon based on-chip capacitive isolators used here are fabricated in a high performance precision analog 5V, 0.3um digital CMOS process with extremely low noise performance, and uses a lightly doped bulk, p-type substrate. Electrical measurements of on-chip capacitors reported here follow UL 1577, IEC 60747-5-2, and CSA standards. These include two tests (a) ramped voltage test from 4kVrms to 10kVrms to force device breakdown, which would quantify highest allowable overvoltage (VIOTM) , and (b) pulsed constant voltage test where 50 short pulses of 8kV and higher (to force breakdown) at 1us intervals are applied to device under test (DUT) for both polarities of the device, bottom-injection and top-injection. In this work, on-chip capacitors used for high voltage isolation is built using a dielectric stack which is a combination of pre-metal oxide, and/or the various dielectrics from metal-1 to top-metal depending on whether the bottom electrode is moat or metal-1. The choice of dielectric employed in these capacitors is based on the results of a I-V measurement study which examined electrical breakdown voltage of various dielectric materials such as silicon nitride, silicon oxynitride, oxides such as HDP, TEOS at various film stresses. Silicon nitride and oxynitride have the best isolation properties and offer unique advantages in meeting the isolation capacitor requirements. The challenges of integrating silicon nitride and oxynitride films as part of a dielectric stack in CMOS metallization scheme, the influence of the order in which these films are deposited in the dielectric stack on isolation capacitor's BVrms capability, pulse voltage performance, and device reliability are discussed. A model is developed to optimize dielectric film stresses in order to ensure isolation capacitor manufacturability by allowing wafer warpage to be maintained lower than the regime in which stepper chucking errors occur during downstream lithography processes.

4:00pm **MS-ThA7 A Novel Crystallized Silicon Thin Film Transistor Based Piezoresistive Cantilever Label Free Biosensor**, ***C. Zhan***, *P. Schuele, J. Conley, J. Hartzell*, Sharp Laboratories of America, INC.

This paper reports a novel integrated biosensor based on the piezoresistive effect of laser crystallized silicon (c-Si) thin film. The sensor is comprised of a c-Si resistor integrated on a PECVD SiO2 cantilever using low temperature surface micromachining techniques. Once the cantilever is deflected mechanically, the electrical response of the integrated thin film resistor changes accordingly. The fabrication and measurement results of crystallized silicon thin film resistor on a cantilever are presented. Our unique laser crystallized a-Si film enables a high quality thin film piezoresistor be accommodated on a small and thin cantilever using MEMS surface micromachining techniques. The integrated piezoresistive cantilever transducer can be selectively functionalized and implemented in large arrays for biosensing applications. The device consists of a c-Si thin film resistor embedded in a PECVD SiO2 cantilever. The air gap between the cantilever and the substrate is defined by a PECVD a-Si sacrificial film, which was removed during release etch step. When the cantilever is deflected by an external force, pressure or surface stress, a uniaxial strain is induced along the longitudinal direction of the cantilever. The strain stretches or compresses the thin film resistor and therefore changes the resistance. The fabrication process is a standard TFT process flow compatible surface micromachining process. Only two extra masks, one for sacrificial mesa patterning and another for cantilever outline patterning, are introduced to the standard TFT flow to realize the c-Si TFT based piezoresistive cantilever biosensor. A 1.5 um thick a-Si is PECVD deposited as the sacrificial film and a TMAH based release etchant is used to release the MEMS cantilever. The PECVD SiO2 films of the standard TFT process are used to form the body of the cantilever. One design of the cantilever is 140um long, 50um wide and 0.5um thick. The c-Si TFT active thin film is used to form the piezoresistor. The thickness of the active c-Si piezoresistor is 100nm. Initial tests on our fabricated MEMS piezoresistive biosensors confirm the piezoresistive effect. External mechanical actuation tests were performed using a micropositioner for calibration. The minimum detectable cantilever deflection is 3nm at 3dB signal to noise ratio. Currently, the sensitivity of the fabricated cantilever biosensor is 3.07uv/nm. The biosensing tests are on the way and results will be updated.

4:20pm **MS-ThA8 Divergence in N/MEMS and Semiconductor Manufacturing*,* *J.D. Evans***, Defense Advanced Research Projects Agency (DARPA) **INVITED**

Nano and Micro Electro-mechanical System (N/MEMS) technology seeks to build small devices (nano/milli scale features) using processing equipment similar to that utilized in the semiconductor industry. Because of similarities in scale and equipment, the performance and potential growth of N/MEMS, as an industry, has been often compared to the growth of the semiconductor industry. However, similarity of length scale and fabrication equipment is not sufficient to ensure similar market performance. In fact, the MEMS and semiconductor industry face dramatically different technical and market dynamics that cause one to question whether this comparison can allow one to draw any meaningful conclusions. In this talk, the author will focus on four fundamental differences between N/MEMS and semiconductor industries: (1) difference in scalability (with implications for a "Moores' Law for MEMS"), (2) difference in process diversity, (3) difference in manufacturing volume, and (4) differences in required fabrication precision (N/MEMS requires higher fabrication precision than semiconductors). These differences suggest that N/MEMS industry faces a fundamentally different set of technical and market constraints than faced by semiconductor industry, and lead one to expect a fundamentally different market evolution. While they do not diminish the fundamental importance of N/MEMS technology, the differences do suggest a need for N/MEMS specific expertise in evaluating and exploiting N/MEMS opportunities, and may suggest a need for a new set of fabrication technologies specifically designed for the N/MEMS markets. DARPA Distribution Statement "A": Approved for Public Release, Distribution Unlimited.

Nanometer-scale Science and Technology

Room: 616 - Session NS-ThA

Nanoscale Sensors

Moderator: N.A. Burnham, Worcester Polytechnic Institute, V. Vogel, ETH Zürich, Switzerland

2:00pm **NS-ThA1 Nanomechanics in Life Science*,* *M. Hegner***, CRANN, University of Dublin, Ireland **INVITED**

Future diagnostics will depend on fast, specific assays to allow personalized medical diagnostics. Increasing efforts in our group have therefore been put into the development of instrumental measurement- and functionalization schemes for cantilever-based sensors for the label-free detection of physical- and chemical phenomena of biological interactions. Cantilevers arrays offer an elegant approach where physiological ligand-receptor binding interactions occurring on the sensor generate nanomechanical signals like bending or a change in mass that is optically detected in-situ. This allows a comprehensive characterization of biological interactions: The measured mass gives information about the binding event whereas the measured surface stress (structural changes) gives insights in the effects of the ligand on the biological systems. We report on new styles of combined measurements in the field of proteomics, genomics and present fast dynamic assessments of micro-organism growth on cantilever arrays.

2:40pm **NS-ThA3 Nanomechanical Resonance of Clamped Silicon Nanowires Measured by Optical Interferometry*,* *M. Belov,*** University of Alberta, Canada, *N.J. Quitoriano, S. Sharma, T.I. Kamins,* Hewlett-Packard Laboratories*, S. Evoy*, University of Alberta, Canada

Highly-sensitive transducers for the detection and assaying of molecular systems based on nanomechanical beams have been proposed. Mechanical objects with lateral dimensions reaching the sub-100 nm range, with high resonant frequencies and quality factors, are now routinely fabricated using surface micromachining. The surface machining procedures employed in NEMS fabrication are inherently slow, offer limited yield and usually employ plasma-assisted etching techniques that may introduce surface damage and significantly change the mechanical properties of the resonating element. The direct growth of cantilevered nanowires by chemical vapor deposition methods (CVD) offers, alternatively, a potent way for the efficient production of high-quality NEMS resonators, with sub-50nm diameters, circular profiles and small clamping losses. We report the synthesis and characterization of vibrating silicon nanowires grown by CVD. These highly-oriented and clamped silicon structures were laterally grown from the sides of etched silicon posts using a metal-catalyzed chemical vapor deposition process. The diameters and lengths of the structures ranged from 40 to 400 nanometers and from 2 to 20 micrometers, respectively. The substrates were mounted onto a piezoceramic disc, installed in a vacuum chamber and actuated at varying frequencies. The laser beam focused onto the vibrating structure was reflected back and the detected signal, proportional to the deflection of the beam relatively to the substrate, was processed by a spectrum analyzer. The data were acquired at temperatures ranging from 77°K up to 293°K, and at pressures ranging from atmospheric down to the low 10^{-6} Torr. Typical resonant frequencies ranged from 1 to 20 MHz, in agreement with the Euler-Bernoulli analysis of vibrating structures. The resonant frequency of the nanowires typically showed a 0.25% increase as the nanowires were cooled from T = 293°K to T = 77°K as a result of changing Younǵs modulus. We also measured qualities of the resonators over the same temperature range. We discuss the energy dissipation processes that dominate the performance of these devices at various temperatures and pressures. This work was partially supported by Alberta Innovation and Science and by Hewlett-Packard Laboratories.

3:00pm **NS-ThA4 Electronic and Structural Properties of Ti and Pd Decorated Carbon Nanotubes*,*** *A. Felten, J. Ghijsen,* Namur University, Belgium, *W. Drube,* HASYLAB, Germany, *R.L. Johnson,* University of Hamburg, Germany, *D. Liand, G. Van Tendeloo,* University of Antwerp, Belgium, *M. Hecq,* Mons University, Belgium, *C. Bittencourt,* Materianova, Belgium, ***J.J. Pireaux***, Namur University, Belgium

The study of the electronic interaction between metal atoms and carbon nanotubes is essential in order to improve performances of devices such as nano-transistors or gas sensors, for example to achieve low-resistance electrical contacts. Palladium and titanium decorated multiwall carbon nanotubes appear to be good candidates for such applications. In this work, both high resolution transmission electron microscopy (HRTEM) and photoemission spectroscopy have been used. Different amounts of Ti and Pd were evaporated onto both pristine and oxygen plasma functionalized carbon nanotubes. HRTEM images show the evolution of the morphology of the metal overlayer onto the nanotube surface. Evaporation of Ti on pristine nanotubes leads to a continuous coverage even for a very low amount of evaporated metal. In contrast, Pd deposition is characterized by the formation of small clusters. Oxygen plasma treatment is seen to improve the Pd cluster dispersion and size distribution. Analysis of the core and valence bands in photoemission spectroscopy reveals also strong differences between the two metals. The appearance of a new peak at lower binding energy on the C 1s level for Ti decorated nanotube is associated to the formation of Ti-C bonds (high coverage), with evidence of a charge transfer from titanium atoms to the carbon nanotube at low coverage For Pd on the contrary, the absence of new features in both Pd 3d and C 1s spectra are suggesting the absence of a mixed Pd-C phase.

This work is financially supported by the Nano2Hybrids (EC-STREP-033311) and PAI 6/1 projects, and by DESY and the EC under contract RII3-CT 2004-506008 (IASFS).

3:40pm **NS-ThA6 Albert Nerken Award Lecture - On Surface Analysis and Nanotechnology: A Personal Odyssey*,* *R.J. Colton*****, Naval Research Laboratory **INVITED**

This Albert Nerken Award address recounts some science and technology highlights of my career in areas of surface analysis and nanoscience—a personal odyssey on SIMS, SERS, STM, AFM, nanomechanics, molecular dynamics, and single molecule biosensing. This presentation will recount the early observation of cationized molecular ions, magic numbers in large inorganic ion clusters, and UHV-SERS (of pyridine on silver of course). Early STM and AFM work addressed the then mysterious graphite imaging

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* Albert Nerken Award Winner

mechanism and the usefulness (once realized) of tip-surface force interactions. Examples of just how useful these force measurements can be led to new technology for surface and molecular mechanics with the help of molecular dynamics simulation. But can you really make a single molecule biosensor? We'll see. My presentation will close with a brief overview of NRL nanoscience programs on nanomaterials, nanoelectronics and nanosensors/devices.

4:20pm **NS-ThA8 Combined Scanning Tunnelling Microscopy & Stress Measurements to Elucidate the Origins of Surface Forces**, ***D.E. Meehan***, *N.T. Kinahan*, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland, *T. Narushima*, National Institutes of Natural Sciences, Japan, *J.J. Boland*, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland

The concept of surface stress has been discussed extensively in terms of its role in controlling single crystal reconstruction and the growth morphology of thin films. In contrast, much less is known about the role of surface stress in surface chemical reactions, where differences in atomic size, electronegativity, and the incorporation of surface vacancies are likely to be of great importance, particularly in the case of nanoscale systems where surface effects are expected to dominate. In order to address the role of stress in surface chemical reactivity, we have developed a novel measurement system capable of investigating the underlying origins of surface stress in the context of atomic surface structure.[1] This system combines for the first time two distinct measurement capabilities: (i) measurement of surface stress based on the displacement of a large (50x10x0.28mm) silicon cantilever sample; and (ii) atomic resolution observation of the surface structure of the same cantilever sample. The former measurement incorporates a capacitive detection method capable of detecting energy changes with meV/atom resolution, while the latter measurement incorporates a scanning tunnelling microscope (STM) capable of observing structural changes occurring on the surface of the cantilever sample. Although non-trivial, the development of this combined measurement system was accomplished through careful electrical and mechanical design, accompanied by the incorporation of a novel sample heating method permitting localized heating of the cantilever sample. The system is also equipped with a device capable of applying external mechanical stress to the cantilever sample, thus enabling investigation of the effects of artificially induced stress on surface-based chemical reactions. The combined application of these two measurement capabilities yields detailed information regarding the atomic-scale structure, dynamics and interactions of the surface under investigation, which will ultimately be used to elucidate the origins of surface forces, and contribute to a deeper understanding of atomic-scale phenomena. Here, we present an introduction to the measurement system, a discussion on the challenges encountered during the development process, followed by a demonstration of the capabilities of the system itself.

[1] T. Narushima, N. T. Kinahan, J. J. Boland, Rev. Sci. Instrum. 78, 053903 (2007).

4:40pm **NS-ThA9 A Hydrogen-Sensitive Polymer Nanostructure with Reversible Conductance**, ***A.R. Laracuente***, *M. Yang, W.K. Lee, L. Senapati, P.E. Sheehan, S.C. Erwin, L.J. Whitman*, Naval Research Laboratory

There is considerable interest in the use of polymer nanostructures for flexible electronics and sensors. We have previously written poly(3-dodecylthiophene-2,5-diyl) (PDDT) nanostructures between gold electrodes using thermal Dip-Pen Nanolithography (tDPN). tDPN uses a heatable atomic force microscopy cantilever to directly deposit "inks" that are solid at room temperature. When a PDDT-coated tip is heated close to or above the PDDT glass transition temperature, PDDT flows from the tip to the substrate surface with molecular-scale order.[1] We have discovered a novel property of such PDDT nanostructures: their conductivity can be increased by more than five orders of magnitude (from $<10^{-4}$ S cm^{-1} to 10 S cm^{-1}) by exposure to energetic electrons (5 keV). In contrast, spin-coated polymer thin films deposited on similar gold electrodes do not show any electron-induced conductivity. Interestingly, the electron-induced conductivity of the PDDT device reverts to a semi-insulating state by exposure to H_2, with a measurable change in conductance occurring following exposures as low as 6×10^{-4} Torr·s. Repeated shifting between the high and low conductivity states is possible. Significantly, exposure to oxygen, argon, or ambient air does not affect the conductance, suggesting that PDDT nanostructure devices deposited by tDPN have potential as H_2 sensors. We propose a mechanism for the conductance modulation based on H desorption and re-sorption from the side-chains of the polymer. This mechanism is supported by a two terminal response theory based on Green's-function-based Landauer-Büttiker multichannel formalism.

[1] Yang et al., J. Amer. Chem. Soc. 128, 6774 (2006).

5:00pm **NS-ThA10 CO_2 Sensing and CO and H_2O Interactions on Mats of Gold Nanoparticle Decorated GaN Nanowires**, ***C. Berven***, *S. Chava, A. Heieren, R. Abdelrahaman, D. McIlroy*, University of Idaho, *M.G. Norton*, Washington State University

We report on the use of macroscopic mats of gold-nanoparticle-decorated GaN nanowires for the detection of CO_2 and the possible generation of CO_2 along with H_2 by interactions of CO and H_2O on the surfaces of the gold nanoparticles. The sensor consisted of a mat of GaN nanowires grown on a sapphire substrate (d ~ 1 cm) using a vapor-liquid-solid growth technique.[1] The mat was ~ 20 µm thick and the nanowire diameters and lengths were ~ 200 nm and ~ 5 µm, respectively. The nanowires were decorated with gold nanoparticles using a chemical vapor deposition process resulting in a continuous layer.[2] The gold was reduced by selective wet etching to create a sparse coverage of nanoparticles. Current-voltage (I-V) measurements were performed when exposed to vacuum, CO, CO_2 and water vapor. All measurements were performed at 300 K and in the dark at pressures of 50 Torr to 1 atm with a maximum vacuum of 5 mTorr. When exposed to just water vapor or CO the currents were only attenuated slightly from the vacuum state. When exposed to CO_2, the current was attenuated to a much larger degree. We have previously published data and a model to explain the sensitivity of similar device to methane[3] which was due to the nanowires acting like Chem-FETs and where the selectivity was attributed to the morphology of the nanoparticles. When the device was exposed to CO followed by H_2O, we saw significant reduction in the current, similar to that of just CO_2 implying that what is being sensed is CO_2 that was the by-product of the reaction of CO + H_2O occurring on the gold nanoparticles. This is not unreasonable since nanoparticle gold is known to be quite reactive.[4] As a consequence of CO_2 being detected after the mixing of CO and H_2O on the nanoparticles, we speculate that H_2 is also being generated giving a possible new mechanism for H_2 generation for fuel cells.

[1] V. Dobrokhotov, C. Berven et al., J. Appl. Phys. 99, 104302 (2006)

[2] A. D. LaLonde, et al., J. Mater. Res. 20, 549 (2005)

[3] V. V. Dobrokhotov, C. Berven et al., Nanotechnology 17, 4135-4142 (2006)

[4] M. Haruta, Applied Catalysis A: General 222, 427 (2001) .

Plasma Science and Technology

Room: 606 - Session PS1-ThA

Plasma Diagnostics II

Moderator: C.B. Labelle, Advanced Micro Devices, Inc.

2:00pm **PS1-ThA1 Development of Atomic Radical Monitoring Probe for Spatial Distribution Measurements and its Application to Reactive Plasma Processes**, ***S. Takashima***, Nagoya University, Japan, *S. Takahashi, K. Yamakawa, S. Den*, Katagiri Engineering Co., Ltd., Japan, *H. Kano*, NU-EcoEngineering Co., Ltd., Japan, *M. Hori*, Nagoya University, Japan

Atomic radicals such as hydrogen(H), nitrogen(N), oxygen(O), and carbon(C) play important roles in the reactive plasma processes. In order to realize nano-scale etching processes and fabricate high functional nano-structure materials using the plasma processes, it is indispensable to clarify the mechanism of the etching or the deposition processes and control the process plasmas at the particle level. Moreover, it is necessary to develop the plasma processes based on not external parameters such as power, pressure, and gas mixture but the internal parameters such as radical densities, their energies, and so on. In our previous studies, we have developed the compact measurement system of the atomic radicals such as H, N, O, and C in the reactive process plasmas. The technique of the system is a vacuum ultraviolet absorption spectroscopy (VUVAS) using an atmospheric pressure microdishcarge hollow cathode lamp (MHCL). The MHCL was 9mm in diameter. So, the system for measuring the atomic radical densities can be easily handled. Using the system, we have carried out the measurements of the densities in various process plasmas and clarified the behaviors of the radicals. However, the two opposite ports are necessary to measure the densities using the system. Moreover, it is difficult to measure the spatial distribution of the atomic radical densities in reactive process plasmas. In this study, we have developed the monitoring probe for the atomic radical density measurements. The probe consisted of the MHCL, the optical part, the probe part, and the VUV monochromator. The size of the probe installed to the plasma was 2.7 mm in diameter. The necessary port for the measurements was only one. Moreover, we can measure the spatial distribution of atomic radical densities by moving the probe along the chamber radius. Using the probe, we carried out the spatial distribution of the H radical densities in the remote H_2 plasmas. The densities drastically decreased from 1.2×10^{12} cm^{-3} to 4.4×10^{11} cm^{-3} near the chamber wall at the pressure of 1.33 Pa, the RF power of 300 W. It was considered that the drastic decrease of the H atom density near the wall was due to the surface loss of the H radical on the chamber wall made of the stainless steel. The atomic radical monitoring probe was the ubiquitous measuring tool because using the probe, anyone can measure the atomic radical densities in any material process plasmas at any time.

2:20pm **PS1-ThA2 Measurement of Absolute Density of Argon Metastables by using Laser Adsorption Spectroscopy**, ***T. Ohba***, *T. Makabe*, KEIO University, Japan

Absolute density of Ar metastables(1s$_{3,5}$) was measured in a two-frequency capacitively coupled plasma (2f-CCP) in pure Ar by using Laser Adsorption Spectroscopy (LAS) in order to investigate the spatial profile. The axial density distribution of metastables is experimentally characterized as a function of pressure (25 mTorr - 100 mTorr) and bias amplitude (100 V - 400 V). Axial density profile of Ar metastables shows a broad peak in front of the electrode driven at 100 MHz, and gradually decreases toward the opposite electrode biased at 500 kHz. With decreasing pressure, the density approaches to more defusive profile as expected. The typical density of Ar(1s$_5$) is 10^{11} cm^{-3}, and the density ratio between Ar(1s$_5$) and Ar(1s$_3$) changes from 10 to 9.3, when we increase the pressure. Under the present external plasma condition, the bias amplitude has less influence on the axial magnitude and distribution of the metastables. It implies the complete functional separation between the driving and bias power in the 2f-CCP in the present system. The spatiotemporal transport of low energy electrons will be discussed through the fundamental collision process of Ar(1s$_5$) by using optical emission and absorption spectroscopy.

2:40pm **PS1-ThA3 Gas Phase Studies of CH3OH Plasmas Using Optical Emission Spectroscopy**, ***K.J. Trevino***, *E.R. Fisher*, Colorado State University

Plasmas are traditionally used for deposition, etching, and surface modification of various types of materials, most notably in the semiconductor industry. Plasma systems have recently been utilized in a non-traditional application, water remediation. Three steps are involved in this process; determining which organic molecules can be detected, developing effective detection systems, and establishing the efficacy of abatement. Recent studies of dense medium plasma systems have developed oxidation mechanisms for organic molecules, converted organic contaminants to less toxic species, and examined aromatic compound breakdown with GC/MS. Here, we have investigated the use of an inductively coupled plasma (ICP) system with optical emission spectroscopy (OES) for the purpose of non-intrusive detection as well as abatement of organic molecules in contaminated water. Our data demonstrate that not only is detection of organic molecule breakdown possible for a variety of species, but abatement is also possible. Currently we are able to detect <100 ppm contamination and are exploring this technique for the desired detection limits in the ppb range. OES data for the detection and abatement of CH3OH and larger organic molecules such as urea and methyl tert-butyl ether in aqueous solutions will be presented.

3:00pm **PS1-ThA4 Measurement of the Gas Temperature Distribution in UHF-ECR Dielectric Etching System**, ***H. Kobayashi***, *K. Yokogawa, K. Maeda, M. Izawa*, Hitachi, Ltd., Japan

Plasma etching is widely used for the fabrication of semiconductor devices. In this process, particle contamination continue to be an issue. Recently, for the purpose of controlling the particle transport, use of the thermophoretic force, that move the particles toward lower gas temperature region, has been investigated. We measured the particle behavior in plasmas by using UHF-ECR etching apparatus having a laser particle monitor. The laser particle monitor consist of 532nm-YAG laser, lenses to form the laser sheet light passing above the wafer, and CCD camera to detect the laser light scatted by particles. We injected particles into plasmas by gas puffing and we found that particles gathered above the wafer center, when plasma density was decreased at the wafer center. Though, particles moved away from the region above the wafer, when plasma density was increased at the wafer center. We simulated particle transport by considering gas viscous force and thermophoretic force. And, it was predicted that there existed gas temperature gradient of 1000 K/m. In this study, the gas temperature distribution across the wafer was investigated. The gas temperature can be assumed to be equal to the rotational temperature of the nitrogen molecules. Thus, we measured the emission spectra of the second positive system of nitrogen molecules. The rotational temperature was determined by comparison of the measured spectral profiles and theoretical spectral profiles calculated by assuming rotational temperatures. The emission from the plasmas was measured through the top plate. Nitrogen and CHF$_3$ gases were used for plasma discharge by considering the SiOC damascene etching. When plasma density was increased at the wafer center, the gas temperature at the wafer center and the wafer edge were 450 K and 460 K, respectively. On the contrary, when plasma density was decreased at the wafer center, the gas temperatures at the wafer center and the wafer edge were 410 K and 510 K, respectively. Consequently, we confirmed that the gas temperature distribution across the wafer can be controlled by changing plasma distribution and the gas temperature gradient of 1000 K/m can be made.

3:40pm **PS1-ThA6 Research at CPMI Towards Making EUVL a Success**, ***D.N. Ruzic***, *S.N. Srivastava, K.C. Thompson, H. Shin, J.R. Sporre, E.R. Ritz*, University of Illinois at Urbana-Champaign

Center for Plasma Material Interactions (CPMI) at the University of Illinois is currently expanding efforts to solve critical problems for timely implementation of extreme ultraviolet lithography. The research at CPMI is focused on variety of different problems being currently faced in this technology. A commercial extreme ultraviolet light source (XTS 13-35) is investigated to characterize the debris ejecta. A fully calibrated ion diagnostic device (spherical sector ion energy analyzer) is developed, which is used for measuring the ion debris fluxes and their energies in absolute units. Ion debris is measured both from Xe as well as Sn EUV sources. Several mitigation schemes are investigated and tested for their effectiveness in the XTS 13-35 source. Recent work towards debris mitigation includes gas curtain, pulsed foil trap, plasma based mitigation, mixed fuel experiments. In the case of mixed fuel experiments, by adding 5% of H$_2$ in the main fuel (Xe), the ion energies and fluxes could be reduced by half of the original value. Using pulsed foil trap mitigation, 4 keV Xe$^+$ ion flux could be reduced about 4 times whereas Xe^{2+} ion flux were dramatically reduced by a factor of about 90. Mirror samples are exposed to the EUV source and erosion due to harsh plasma debris is measured for variety of different EUV compatible materials (C, MLM, Si, Mo, Pd, Mo-Au, Au). For example, the measured erosion on EUV exposed multilayer mirror (MLM) sample is about 13 nm ± 2 nm. Comparison with theory predicts the major damage from high energy ions itself, but also indicates the role of neutral particles. To advance the debris diagnostic tool, the detector is further modified to account for neutral debris measurement. Ion and neutral debris measuring capabilities allowed us to perform life time testing. We have also studied the problems with Sn EUV sources and currently developing methods to clean Sn effectively from the mirror surface without actually harming the surface underneath. Reactive ion etching is found to be a viable solution and variety of different samples are tested and processed through the cleaning techniques. Encouraging results in this area has motivated us to do a full blown test in the EUV source and install an integrated cleaning system, which could run in a manufacturing environment.

4:00pm **PS1-ThA7 Inductively Coupled Plasma Radio Frequency Electrical Characteristic Measurement for Deposition of CNTs.**, ***W.-C. Chen***, Academia Sinica, Taiwan, *C. Mahony*, University of Ulster, UK, *K.-H. Chen*, Academia Sinica, Taiwan, *L.-C. Chen*, National Taiwan University

Here we investigate radio frequency (RF) inductively coupled plasma (ICP) as an in-line sensor for characterizing vertical aligned carbon nanotubes (CNTs) deposition plasma via correlation of the real/imaginary RF current/voltage. The plasma dual directional coupler (PDDC) was used to measure the forward and reflected voltage before the ICP matching network in Ar plasma. Then we introduce a homemade external circuit to give impedance Z, which includes the parasitic inductances of capacitors, parasitic capacitance of inductors and cable resistances. Component values in the circuit model can be determined by analysis of VHF (very high frequency) bridge and spectrum analyzer data. With arising reaction pressure in Ar plasma, the corresponding current & voltage will be change. The maximun current in Ar plasma can be observed at the pressure of 60 mtorr and power of 200 Watt. Indicating much higher electrons density and effective collision frequency in this plasma condition. Measured values of Z with rising RF input power of plasma shows the reactance X to vary from negative to positive values. These correspond with observed E to H transition in this ICP. We will discuss RF harmonics during CNTs deposition condition in Ar & CH4 and relate them to process repeatability and reliability.

4:20pm **PS1-ThA8 Process Control through Diagnostics and Understanding: Multi-frequency Discharges and Atmospheric Pressure Plasmas**, ***T. Gans***, Queen's University Belfast, UK **INVITED**

Despite its technological importance, power coupling and ionisation mechanisms in radio-frequency (rf) discharges are not yet fully understood. Of particular interest are multi-frequency discharges and recently developed non-equilibrium rf discharges at ambient pressure. Insight into the complex dynamics requires close combination of advanced diagnostics and specifically adapted simulations. Phase resolved optical emission spectroscopy (PROES) in combination with particle-in-cell (PIC) simulations reveal details on the dynamics within the rf cycle. Multi-frequency discharges can provide additional process control for technological applications. The electron dynamics exhibits a complex spatio-temporal structure. Excitation and ionisation, and, therefore, plasma sustainment is dominated through directed energetic electrons created through the dynamics of the plasma boundary sheath. These electrons are predominantly produced during contraction of the low frequency sheath. This can be understood in the following picture. During the phase of low-frequency sheath expansion power dissipation is highest which determines plasma heating. This power is, however, deposited into a large number of electrons in the vicinity of maximum sheath expansion. The dissipated power during the collapse of the low-frequency sheath is deposited into a much smaller number of electrons, since the electron density close to the electrode surface is significantly lower. The power dissipation per electron can, therefore, be higher during the sheath collapse, which then creates energetic directed electrons. Recently developed rf discharges at ambient pressure bear enormous potential for future technological applications providing high reaction rates without the need of expensive vacuum systems. Fundamental discharge mechanisms are, however, only rudimentarily understood. The atmospheric pressure plasma jet (APPJ) is a homogeneous non-equilibrium discharge. A specially designed rf μ-APPJ provides excellent optical diagnostic access to the discharge volume and the interface to the effluent region. This allows investigations of the discharge dynamics and energy transport mechanisms from the discharge to the effluent. PROES measurements in the discharge volume show similar excitation and ionisation mechanisms as in capacitively coupled rf discharges at low pressure. An interesting phenomenon is the interaction between the two plasma boundary sheaths.

Plasma Science and Technology

Room: 607 - Session PS2+BI-ThA

Plasmas in Bioscience

Moderator: P. Favia, University of Bari, Italy

2:00pm **PS2+BI-ThA1 Time-of-Flight Secondary Ion Mass Spectrometry Analysis of Fibrinogen Adsorbed to Low-Fouling Tetraglyme Surfaces**, ***L. Mayorga***, *R. Michel, D.G. Castner, T.A. Horbett*, University of Washington

Antibody binding and ToF-SIMS were used to probe the conformation of fibrinogen (Fg) adsorbed to low and high fouling surfaces, including tetraglyme and FEP. Fg on implants plays a key role in the foreign body response (FBR) by mediating the adhesion of monocytes via the Mac-1 integrin.[1] PEO-like tetraglyme coatings generated via radio frequency glow discharge plasma display ultra-low Fg adsorption (Γ_{Fg} < 10 ng/cm^2) from low concentration blood plasma solutions and low monocyte adhesion.[2] However, subcutaneously implanted tetraglyme still exhibits FBR encapsulation. With 3 mg/ml Fg in buffer (with tracer amounts of ^{125}I-Fg added), Γ_{Fg} increased to 60 ng/cm^2 on tetraglyme and 800 ng/cm^2 on FEP. Nonetheless, the actual amount of Γ_{Fg} on glyme surfaces under any of the conditions tested is not enough to fully account for the observed monocyte adhesion in vitro. The Fg on glymes was relatively low, but adhesion was relatively high, suggesting that Fg might be in a more potent state on the glymes. To understand the role of Fg conformation in mediating monocyte adhesion, we used a monoclonal antibody to measure the degree of monocyte binding site (γ 377-395) exposure on adsorbed Fg. Epitope exposure per ng of adsorbed Fg was highest on low-fouling tetraglyme samples pre-adsorbed with low concentration Fg. In addition, ToF-SIMS was used as in previous studies[3] to characterize the conformation of Fg adsorbed to the tetraglymes. By pairing these two different approaches to study the conformation of adsorbed Fg, we will be able to relate surface analysis results with cell and protein binding data, which will allow us to better understand protein-cell interactions in the FBR.

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2:20pm **PS2+BI-ThA2 Interaction of Peptide Ions with Self-Assembled Monolayer Surfaces**, ***J. Laskin***, *O. Hadjar, P. Wang, Z. Yang*, Pacific Northwest National Laboratory

Interaction of ions with surfaces is an area of active research in surface science relevant to a broad range of other scientific disciplines such as materials science, mass spectrometry, imaging and spectroscopy. Our research is focused on fundamental understanding of interaction of hyperthermal (1-100 eV) peptide, protein and polymer ions with organic surfaces under ultrahigh vacuum conditions. Two major processes are dominant for this range of collision energies: reactive and non-reactive scattering of ions and ion loss on the surface as a result of neutralization or soft-landing (SL) of projectile ions. Scattering and deposition of large ions following collisions with SAM surfaces was studied using a unique Fourier transform ion cyclotron resonance mass spectrometer developed in our laboratory. Ion activation by collisions with surfaces is rather poorly characterized from a fundamentals perspective. We explored the effect of the physical and chemical properties of SAM surfaces on the energy transfer in collisions. Our studies demonstrated that energy distribution functions are well-represented by Maxwell-Boltzmann distributions indicating fast thermalization of ions by collisions. A notable discovery was a sharp transition between slow unimolecular decay of large ions at low collision energies and near-instantaneous decomposition (shattering) in higher energy surface collisions. Shattering of ions on surfaces opens up a variety of fragmentation pathways for large complex ions that are not accessible to conventional ion activation techniques. We have conducted first systematic study of several factors that affect SL of peptide ions on SAM surfaces. Deposition of peptide ions of different composition and charge state on SAM surfaces was followed by in situ and ex situ SIMS analysis. Peptide ions are attractive model systems that provide important insights on the behavior of soft landed proteins. We were able to measure for the first time the binding energy between peptide ions and hydrophobic SAM surfaces. We also demonstrated very strong binding of peptide ions to hydrophilic surfaces and covalent linking of peptides to reactive SAMs. Fundamental principles derived from such studies of interaction of protonated peptides with hydrophobic or hydrophilic surfaces are relevant to the understanding of the transport of biomolecules through membranes in living organisms and provides a clear pathway for highly-selective preparation of biological surfaces.

2:40pm **PS2+BI-ThA3 A New Approach to Nano-Fabrication of Functional Structures : Wet Nanotechnology and Bio Nano Process**, ***I. Yamashita***, Matsuhita Electric Industrial Co. Ltd. Japan **INVITED**

We proposed a new method for the fabrication of functional nano-structures in an aqueous solution, which could be used in semiconductor processes or electron devices and can be called a wet nanotechnology (WNT). The WNT employs aqueous solutions as the environments for nano-blocks, which are thermally agitated, to self-organize into the functional nano-structures. The final structures could be designed in the initial nano-block structures and functional nanostructures can be produced economically. This is the same with the way how the lives are carrying out in the nature. So far, we invented several processes using the WNT and proteins, which collectively we named Bio Nano Process (BNP).[1] So far, the BNP produced several key components of the electron devices. Firstly, a floating nanodots gate memory (FNGM) was produced employing a cage-shaped protein, apoferritin (collaborative project with Dr. Fuyuki at NAIST). Nanoparticles (NP) were biomineralized in the apoferritin cavity, which produced homogenous NPs such as CdSe, ZnSe, CdS, Co3O4, InOx, Fe2O3 and so on. A 2D ordered array of the apoferritins with NP was made on the Si wafer by self-assembly and heat-treated The obtained 2D ordered array of NPs was applied for the FNGM.[3] Secondly, we used 7nm Fe2O3 NPs, which were produced and placed on Si wafer by the BNP, as the nanometric etching mask to fabricate Si single crystal nanocolumn (a collaborative project with Dr. Samukawa at Tohoku Univ). The neutral beam etching successfully produced single crystal Si columns with 7nm diameter and high aspect ratio4. We further extended the BNP application and produced a large bio-template for single electron transistor (SET).[5] A ball and spike type protein supramolecules which has a central cage-shaped protein and protruding spikes was produced by the self-assembly of genetically made chimera proteins. These experimental results demonstrated that the BNP can fabricate the inorganic nanostructure using protein supramolecules. The WNT and BNP are opening up a biological path to nano-electron devices.

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3:40pm **PS2+BI-ThA6 Improvement of the Adhesion of PECVD-deposited DLC Films on Metals**, ***J.-C. Schauer***, *J. Winter*, Ruhr-Universität Bochum, Germany

The coating of a material with a wear and corrosion resistant coating is required in many realms. Concerning biomedical applications for example a coating of implants made of shape memory alloys such as NiTi is needed to protect the implant against wear and corrosion and the surrounding tissue against the release of metal ions. One candidate for such a coating is a thin film of diamond like carbon (DLC, hard configuration of a-C:H), since it is very hard, wear resistant, has a low friction coefficient, is chemically inert and biocompatible. But up to the present the coating of most metals with a

DLC film has shown many difficulties. The bad adhesion between substrate and DLC is due to the poor chemical binding between most metals and carbon and/or due to high internal stresses occurring in DLC films. One promising technique to overcome the problem of poor adhesion of the coating to the substrate is the deposition of a very thin interface layer on the substrate before the coating is deposited on top. By a correct material choice such an interface can replace weak coating-to-substrate bonds with strong coating-to-interface layer bonds and interface layer-to-substrate bonds. Another effect of the interface layer can be the reduction of internal stresses in the interface region. By the use of at least two layers on top of each other the probability of pinholes or defects going from the surface to the substrate is decreased. This is especially important if toxic substrates are to be coated. Therefore, we use a thin amorphous hydrogenated silicon (a-Si:H) film as an intermediate layer between metal and DLC film to enable the coating of metals with DLC films. Due to the formation of strong silicide bonds the adhesion of DLC films on metal is increased significantly. The thin films under investigation are deposited in a capacitively coupled discharge with acetylene and silane as precursor gases for the DLC and a-Si:H films, respectively. The a-Si:H films have a thickness of only several 10 nm, whereas the DLC films can have a thickness of 100 nm or more. It will be shown that an intermediate layer of a-Si:H significantly increases the adhesion of DLC on metals and how the film properties of a-Si:H and DLC influence the strength of adhesion. The influence of different parameters like applied power, substrate temperature, hydrogen content in the films, and others on the adhesion of the films also under durability tests will be presented.

4:00pm **PS2+BI-ThA7 Polymeric Surfaces Chemical Modification by Low-Pressure Plasma Processes for Application to DNA Array Technology**, *P. Rivolo*, Politecnico di Torino, Italy, ***S. Lo Bartolo***, LaTEMAR, Ctr of Excellence funded by MIUR; Biodiversity SpA, Italy, *D. Perrone*, Lab. Materiali e Microsistemi, Italy; Politecnico di Torino, Italy, *S. Fiorilli*, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy, *I. Vallini*, LaTEMAR, Ctr of Excellence funded by MIUR; Biodiversity SpA, Italy, *C. Ricciardi*, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy, *M. Quaglio*, Lab. Materiali e Microsistemi, Italy; Politecnico di Torino, Italy, *G. Mantero*, Biodiversity SpA, Italy, ***C.F. Pirri***, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy

The low cost of production, the easy handling and the large variety of polymeric materials favour them as attractive candidates to replace classic glass slides in micro-array biomolecular diagnostics. However, the lack of reactive functional groups, at polymeric surfaces, makes difficult their use as substrates for immobilization of molecules such as DNA fragments, in either cDNA or oligodeoxyribonucleotide (ODN) format, for a variety of applications to DNA micro-array technology including microscale sequencing, mRNA expression monitoring and single nucleotide polymorphism analysis. In this contribution, modification of surface chemical properties of cyclo olefin copolymer (COC), polystyrene (PS), polyethylene (PE) and polycarbonate (PC) is reported. The surface of polymeric substrates, properly molded by hot embossing, was modified introducing monotype functional groups[1] and using them for subsequent covalent grafting of linker molecules, active for amino-oligonucleotide probes immobilization.[2] A first step consisting of non-equilibrium low-pressure air and water RF plasma was used to activate the polymer surface, forming oxidized species such as -C-O-, -C=O, -C-OH, -CHO, -COOH. Successively, a liquid-phase reduction by a $NaBH_4$ solution was carried out to increase the yield of –OH groups in order to enhance the amount of covalently grafted 3-aminoproylsilane (3-APTES), a reaction carried out by vapour-phase process.[3] The last step was performed by a liquid phase reaction between glutaraldehyde and amino-groups of grafted 3-APTES. After this, polymer surface shows -CHO species suitable for the reaction with the amino-modified probes. Characterization of the functionalised polymeric surfaces was performed by contact angle measurements and reflection-absorption infrared spectroscopy (RAIRS)[4]. Modification efficiency of different polymers substrates was evaluated by well-modified Arrayed Primer EXtension (APEX) protocol with colorimetric and fluorimetric detection methods.

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4:20pm **PS2+BI-ThA8 Patterning of Plasma Polymers for Bioarrays**, ***G. Mishra***, *S.L. McArthur*, University of Sheffield, UK

Modern day technological advancements have allowed us to overcome critical challenges posed in proteomic research. As a direct result of developments in miniaturisation and automation, the current market has seen ever growing numbers and varieties of high density arraying slides being used for proteome research and application. Needless to say that these developments have been matched with state of art instrumentation and data analysis packages to achieve true automated multiplex analysis. Yet, issues like non-specific adsorption of biomolecules to solid substrate and control over the orientation during immobilization need addressing. Key to these issues could be the precise control over surface modification and patterning. Plasma polymerisation presents a versatile approach to surface modification of these devices. The range of monomers available for plasma polymerisation makes this manufacturing approach even more suitable for use in systems where multiple coatings with specific properties are required for a single device. The ability to spatially define reactive regions to reduce non-specific background adsorption is integral to this project. In this study we use a range of patterning techniques including photolithography and physical masks and compare the resultant pattern resolution and chemical functionality using XPS, ToF-SIMS and AFM. Plasma polymerisation when used in conjugation with photolithography has allowed us to simultaneously obtain high spatial and chemical resolution. Multivariate analysis of ToF-SIMS spectral and image data has allowed us to critically study and address issues associated with the chemical specificity and spatial resolution of the multilayer patterning approach. Our results suggest that complex multilayer plasma coatings can be produced without compromising the chemical properties of the deposited polymer layers.

4:40pm **PS2+BI-ThA9 BSA Adsorption onto Oxygen Plasma PTFE Modified Surfaces**, *B. Broze*, ***N. Vandencasteele***, Universite Libre de Bruxelles, Belgium, *P. Viville*, Materia Nova, Belgium, *R. Lazzaroni*, *M. Hecq*, Université Mons Hainaut - Materia Nova, Belgium, *D.G. Castner*, University of Washington, *F. Reniers*, Universite Libre de Bruxelles, Belgium

The adsorption of bovine serum albumine on surfaces is usually a first good test for potential biological applications. In this study, PTFE surfaces were exposed to a remote RF oxygen plasma. The plasma was characterized using optical emission spectrometry, whereas the PTFE surface was characterized using monochromatized XPS, dynamic contact angle and atomic force microscopy. The modified surfaces are then exposed to BSA. The presence of protein was then evidenced by the presence of the N1s peak in the XPS spectrum, by AFM images, and by the change in the contact angle. We show that at low plasma power (or DC-bias) and short treatment times, the contact angle decreases, leading to slightly more hydrophilic surfaces. Small amounts of oxygen (up to 5%) are detected on the surface. BSA adsorbs on these surfaces. An increase in the plasma power leads to an increase of the sample roughness and to an increase of the hydrophobicity. On superhydrophobic (angles above 160°) surfaces, BSA does not absorb any more. No oxygen is present in the XPS spectrum. A correlation was established between the change of the contact angle, the amount of adsorbed protein and the roughness. It is shown that the decrease of the contact angle, and the hysterisis between the advancing and receding angles are good probes for protein adsorption.

5:00pm **PS2+BI-ThA10 Composition and Structure Study of the AP Plasma Deposited Hydrophobic Thin Film**, ***C. Chen***, *W. Hsieh*, *C. Liu*, *W. Hsu*, *C. Lin*, Industrial Technology Research Institute, Taiwan

In this study hydrophobic thin films were prepared by plasma enhanced chemical vapor deposition at atmospheric pressure by means of two layer compositions on the surface of glass. The bottoms were using Ar and hexamethyldisilazane (HMDSN) as the carrier and monomer gases respectively to deposit silicon oxide and offer microstructure. The deposited glasses were further coating a hydrophobic layer using fluoroalkylsilane (FAS) as the chemical precursor. Meanwhile, to evaluate the effects of fluorine contained of the water repellency of substrate, CF4 was introducing into the plasma zone during plasma depositions. The chemical structure of the thin film was characterized using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopies (FTIR) measurement. Morphologies and topography of the coatings were examined by scanning micro spectroscopy (SEM) and atomic force microscopy (AFM). FTIR measurement indicated that a SiO2 layer can successful deposit on the glass and the porosity of the thin films was direct proportion with thin film thickness. The SEM results indicated that the thickness of the thin films increasing almost linearly with coating times and the thickness was about 143nm after three times of deposition. AFM results reveal nano-clusters were well distributed on the surface after two layers deposition but introducing CF4 during deposition will slightly reduced the roughness because of decompose reaction between CF4 plasma and the Si atom in the thin films. The deconvolution of the C1s core-level spectra and atomic ratio from XPS measurement indicate FAS can be react and deposited on the top layer. The contact angles of the double layers was 134.0 degree which are great than traditional fluoro-polymer such as polytetrafluoroethylene (PTFE). Otherwise, bypass introducing CF4 during plasma polymerization the contact angle will increased to 143.3 degree indicate the AP plasma can be used to deposit super hydrophobic thin film on the glass surface.

Surface Science

Room: 608 - Session SS1-ThA

Environmental Surfaces

Moderator: J.T. Dickinson, Washington State University

2:00pm **SS1-ThA1 Influence of Surface Oxides on the Colloidal Stability, Mobility and Sorption Properties of Carbon Nanotubes in Aquatic Environments***, **H. Fairbrother**, B. Smith, H.-H. Cho, F.K. Bangash, M. Shin, W.P. Ball*, Johns Hopkins University **INVITED**

Carbon nanotubes (CNTs) are a unique and versatile class of nanomaterials with enormous commercial potential. This has been responsible for a rapid increase in their production rates and, as a result, larger quantities of CNTs will inevitably find their way into the environment. The ecological and toxicological impacts of these nanomaterials are, however, still poorly understood. Many purification and functionalization strategies incorporate oxygen-containing functional groups into the surface of CNTs, and similar modifications can occur after CNTs are released into the environment through exposure to oxidizing agents. To address this issue surface analytical techniques have been developed to quantify both the concentration of oxygen and distribution of surface oxides produced on CNTs by different oxidative treatments. In this presentation the effect of oxidation and the introduction of surface oxides on the colloidal stability and sorption properties of CNTs in aquatic environments will also be discussed. A suite of CNTs with different levels of oxygen content were prepared by refluxing pristine CNTs in HNO_3 solutions of various concentrations; X-ray photoelectron spectroscopy (XPS) showed that the surface oxide concentration increased from 3% for the pristine nanomaterials to 12.5% for CNTs treated in ~16M HNO_3. The corresponding variation in oxide distribution has been probed using chemical derivatization in conjunction with XPS. UV-vis spectroscopy shows that well-defined relationships exist between the level of CNT surface oxidation and their colloidal stability; specifically, more highly oxidized CNTs remain stable over a wider range of aquatic conditions. The sorption properties of CNTs also display systematic variations as the level of surface oxidation increases: adsorption of ^{14}C labeled-naphthalene, a hydrophobic organic chemical, decreased linearly while divalent heavy metal contaminants like Zn^{2+} showed an increasing affinity towards more highly oxidized CNTs. Relationships that exist between specific types of surface oxides, particularly carboxylic acid groups, and CNT behavior in aquatic environments will also be discussed. In general, our studies highlight the fact that even comparatively small changes in surface oxygen concentration are responsible for pronounced changes in CNT properties.

2:40pm **SS1-ThA3 Reactions of Sulfur Dioxide on Calcium Carbonate and Iron Oxide Single Crystal and Particles Surfaces under Ambient Conditions***, J. Baltrusaitis, **V.H. Grassian***, University of Iowa

Reactions of sulfur dioxide under ambient conditions on environmentally important interfaces - calcium carbonate and iron oxide - single crystal and particle surfaces - have been investigated. A custom-designed X-ray Photoelectron Spectroscopy (XPS) ultra-high vacuum chamber is coupled to an environmental reaction chamber so that the effects of adsorbed water and molecular oxygen on the reaction chemistry can be followed. Atomic force microscopy provides additional spatial details about the reaction chemistry. It is determined that both the extent of reaction, the chemical speciation, which includes adsorbed sulfite and adsorbed sulfate, and reaction mechanisms are controlled by the environmental conditions. In addition, the two interfaces behave quite differently. Adsorbed water plays a key role in reactions of sulfur dioxide on calcium carbonate but not on iron oxide whereas molecular oxygen enhances the extent of reaction of sulfur dioxide on iron oxide but not calcium carbonate. Mechanisms to explain the reaction chemistry of sulfur dioxide on these two important environmental interfaces under different conditions are proposed. Atmospheric and environmental implications of these reactions are also discussed.

3:00pm **SS1-ThA4 pH Dependent X-ray Photoemission Studies of Hexylamine at the Aqueous-Vapor Interface***, **M.A. Brown***, University of California, Irvine*, B. Winter*, Max-Born-Institut fur Nichtlineare Optik und Kurzzeitspektroskopie, Germany*, M. Faubel*, Max-Planck-Institut fur Dynamik und Selbstorganisation, Germany*, J.C. Hemminger*, University of California, Irvine

The understanding of molecular arrangements and interactions at the aqueous-vapor interface is important in many chemical and biological systems where the pH dependent chemistry may vary greatly from that of the bulk. We examine the surfactant properties of hexylamine (C6H13NH2) and the protonated hexylamine ion (C6H13NH3+) at the aqueous-vapor interface. The state of this acid/base equilibrium couple should shed light on the local pH of the aqueous interface, as well as the relative aqueous solvation of the two species. Chemical shifts are observed in the N (1s) and C (1s) photoemission spectra due to protonation of the amine, allowing us to clearly identify and quantify the two species. The experiments use a 15 µm liquid micro-jet free vacuum surface at a micro-focus x-ray beamline of the BESSY synchrotron radiation facility. The bulk pH of solution is varied by addition of HCl in order to vary the degree of hexylamine protonation. Varying the energy of the ejected photoelectrons by carrying out experiments as a function of x-ray wavelength allows us to generate a depth profile of the aqueous-vapor interface. The core level O (1s), N (1s) and C (1s) photoemission spectra were collected as a function of photoelectron kinetic energy, creating a molecular level picture of the entire interfacial region. Results show that the concentration of hexylamine (C6H13NH2) is greatly enhanced at the interface relative to the protonated hexylamine ion (C6H13NH3+). Peak broadening, and relative peak intensities vary with bulk pH, and are attributed to changes in molecular packing.

3:40pm **SS1-ThA6 Heterogeneous Uptake of Ozone on Solid Potassium Iodide***, M.A. Brown, J.T. Newberg, M.J. Krisch*, University of California, Irvine*, B.S. Mun*, Advanced Light Source, LBNL*, P. Ashby*, Molecular Foundry, LBNL*, **J.C. Hemminger***, University of California, Irvine

Ozone, a powerful oxidant trace gas found throughout both the troposphere and stratosphere is believed to oxidize alkali halides in the form of sea-salt aerosols and is considered to be a significant candidate for the formation of reactive gas phase molecular halogens. Recent studies suggest that although iodide is a minor component of sea-salt spray its concentration at the interface of aqueous solutions and at the interface of dried solid crystalline sea-salt particles is greatly enhanced relative to the bulk concentration. X-ray photoelectron studies described here show, under conditions in which a low defect density KI surface is completely devoid of adsorbed water molecules the surface oxidation by ozone results in a thin molecular layer of KIO3 that is self-passivating. We report for the first time the reaction probability (?) at room temperature for the reaction KI(s) + O3(g) ? KIO3(s) of ? = 1.4 (±0.7) x 10-4. Results of the low defect density system are compared with the results of a high defect density polycrystalline KI surface. In-situ SPFM imaging provides molecular insight into the site specificity of the chemical reaction on the surface of KI (100).

4:00pm **SS1-ThA7 Surface Science Investigations of Photoprocesses in Model Interstellar Ices***, J.D. Thrower*, Heriot-Watt Univ., UK*, D.J. Burke*, Univ. College London, UK*, M.P. Collings*, Heriot-Watt Univ., UK*, A. Dawes, P.J. Holtom*, The Open Univ., UK*, F. Jamme*, Univ. of Nottingham, UK*, P. Kendall*, The Open Univ., UK*, W.A. Brown*, Univ. College London, UK*, I.P. Clark*, Central Laser Facility, CCLRC, UK*, H.J. Fraser*, Strathclyde Univ., UK*, **M.R.S. McCoustra***, Heriot-Watt Univ., UK*, N.J. Mason*, The Open Univ., UK*, A.W. Parker*, Central Laser Facility, CCLRC, UK

In the last decade or so, the astronomy and astrophysics communities have come to realise that physical and chemical processes occurring at the surfaces of interstellar dust grains play a key role in the chemical evolution of the Universe. Grain surfaces promote the formation of molecular hydrogen and simple hydride species such as water, ammonia and methane. As such, at the temperatures found in the most chemically rich regions of the interstellar medium (ISM), typically 20 K or less, they reactively accrete icy mantles containing these species. Condensation of molecules from the gaseous ISM occurs in parallel, producing water-rich icy mantles that are readily observed in the infrared in many lines of sight towards star-forming regions. These mantles play a crucial role as reservoirs for small molecular coolants during the earliest phases of star formation, promoting the formation of small, long-lived stars such as our own Sun. They also act as chemical nanofactories driven by energy from photons and cosmic rays to produce increasingly complex chemical species from simple ice mixtures, hence seeding the Universe with a complex chemical soup. While numerous studies exist in the literature seeking to understand the chemical evolution of water-rich icy mixtures during irradiation by light and charged particles, the majority of these high vacuum studies have failed to address the fundamental question of the disposition of the incident energy. How much of the photon or charged particle's energy goes into driving physical processes (morphological change, desorption, etc.) as opposed to driving chemical processes? Here we will report on recent surface science investigations aimed at addressing this most fundamental of questions in laboratory astrochemistry.

4:20pm **SS1-ThA8 Monolayer Etch Pits Produced by Pulsed 248-nm Irradiation of Cleaved Alkali Halide Surfaces in 10^{-5} Pa Water Vapor**[1], ***S.C. Langford****, K. Kimura, J.T. Dickinson*, Washington State University

On single crystal NaCl, 248-nm laser radiation can roughen steps and produce monolayer islands and etch pits at fluences well below the macroscopic damage threshold.[2] These effects are dramatically altered by the presence of 10^{-5} Pa water vapor. In this work, we extend these observations to single crystal KCl and KBr. Atomic force microscopy (AFM) images of NaCl, KCl, and KBr cleavage surfaces exposed to pulsed 248-nm laser radiation in ultrahigh vacuum show monolayer islands; the island density increases with increasing laser fluence. We attribute island formation to the aggregation of alkali halide monomers desorbed from steps onto terrace sites as a consequence of UV exposure; this desorption accounts for the observed step roughening. In the presence of water vapor at pressures of 10^{-5} to 10^{-3} Pa, fifty 248-nm pulses at 100 mJ/cm^2 produce monolayer etch pits on KCl and KBr. Higher fluences are required for NaCl. Quadrupole mass spectrometry on the products emitted during laser irradiation show much more intense alkali and halogen emissions in the presence of water vapor, consistent with the observed etching. Although the mechanism for enhanced etching in the presence of water vapor is not clear, the erosion of alkali halides during electron irradiation at room temperature is hindered by the accumulation of alkali metal.[3] Water vapor may hinder alkali aggregation, perhaps by dissociative adsorption at halogen vacancies. We show that water vapor at similar partial pressures has comparable effects on alkali halide surfaces exposed to 2 keV electrons.

[1] This work was supported by the U.S. Department of Energy-under Grant DE-FG02-04ER-15618.

[2] K.H. Nwe, S.C. Langford, and J.T. Dickinson, J. Appl. Phys. 97, 043502 (2005).

[3] B.M. Szymonski, J. Ruthowski, A. Poradzisz, Z. Postawa, and B. Jørgensen, in Desorption Induced by Electronic Transitions—DIET II (Springer, Berlin, 1985), p. 160-168.

4:40pm **SS1-ThA9 The Adsorption and Desorption of H_2O, H_2S and SO_2 on Amorphous Carbon Films**, ***E. Broitman***, *W. Michalak, J.B. Miller, A.J. Gellman,* Carnegie Mellon University, *M.A. Alvin*, U.S. Department of Energy

There is a renewed interest in the development of efficient catalyst-sorbents for the capture and conversion of sulfur containing compounds that poison the catalysts and separation membranes, often used in modern processes for hydrogen generation. It is well known that sulfur-containing molecules interact with activated carbon surfaces by both physisorption and chemisorption, where surface chemistry and pore structure appear to contribute to the strength of the interaction. However, because it is difficult to control and characterize their surface properties, the fundamental nature of the adsorption onto activated carbons is still not well understood. In this work, we obtain precise control of surface properties by modeling activated carbons with amorphous carbon (a-C) films deposited under ultra high vacuum conditions. Carbon films with controlled and defined microstructure (sp^2/sp^3 ratio), surface chemistry (dangling bonds, oxidation state), and morphology (roughness, porosity) were deposited by DC magnetron sputtering. Temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) were used to study H_2O, H_2S and SO_2 surface chemistry on these films. For comparison, experiments were also carried out on a highly oriented pyrolytic graphite (HOPG) surface. H_2O, H_2S and SO_2 physisorb on HOPG and on a-C films by a cluster growth mechanism. At lower coverages, the molecules adsorbed in the first two-dimensional layer and on the edges of the three dimensional (3D) islands have a weaker interaction (lower binding energy) than molecules within 3D islands. Water desorbs from a-C with one peak, while H_2S and SO_2 desorb with two features, corresponding desorption from the monolayer and the multilayer. The three adsorbates interact with the a-C surface with different strengths: at low coverage, energies of desorption, E_{des}, from a-C films were 11.3, 8.2 and 10.2 kcal/mol for H_2O, H_2S and SO_2, respectively. XPS analysis after TPD experiments on HOPG and a-C films revealed no reactions between the carbon surfaces and the adsorbates. On the other hand, H_2S adsorption on oxidized films, a-CO_x, revealed the presence of residual elemental sulfur, thereby indicating that the oxygen of the films had reacted with the adsorbate.

5:00pm **SS1-ThA10 Atomic Scale Features on Air Exposed Mica Surfaces Revealed By UHV Dynamic SFM**, ***F. Ostendorf***, *C. Schmitz, S. Hirth, M. Reichling*, University of Osnabrueck, Germany

Mineral surfaces play a key role in many reactions regarding mineral dissolution, precipitation and crystal growth. The most prominent of this type of surfaces in nano biology and material science is Muscovite mica. Air cleaved mica surfaces have been investigated by dynamic force microscopy operated in the non-contact mode (NC-AFM) under ultra-high vacuum (UHV) conditions with atomic resolution. In contrast to the common assumption that a simple degas under UHV conditions leads to a true atomically flat and clean surface, we demonstrate that the sample surface always exhibits a high density of small defects and clusters. In addition to these defective features we find flat and layered, hexagonally shaped islands exhibiting two different types of atomic scale patterns on different length scales: namely a rectangular pattern and a Moiré superstructure. In general one can consider that potassium ions of a mica surface - when cleaved in air - react with water and carbon dioxide. This composes potassium carbonate. By detailed measurements with atomic precision we clearly identify the unit cells of both patterns. The rectangular pattern is associated with the potassium carbonate unit cell. For growing potassium carbonate crystallites on mica surfaces the slight lattice mismatch needs to be compensated. This compensation is reflected by the observed Moiré superstructure. Finally we yield strong evidences that crystallites of potassium carbonate emerge due to the reaction with water and carbon dioxide and grow by Ostwald ripening on mica surfaces.

Surface Science

Room: 611 - Session SS2+EM+TF-ThA

Organics and Carbon Films on Silicon

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS2+EM+TF-ThA1 Reactivity of n-type/p-type H:Si(111) for Photoadsorption of CH_3Br**, ***T. Yamada***, RIKEN, Japan, *H. Ozawa,* The University of Tokyo, Japan, *H.S. Kato,* RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

Ultraviolet photo-assisted adsorption of CH_3Br gas was examined on hydrogen terminated Si(111)-(1x1) surfaces of n-type (P-doped, resistivity 7-10 Ωcm) and p-type (B-doped, 10-40 Ωcm) substrates. After treatment of Si substrates at $1x10^{-5}$ Pa of CH_3Br pressure with simultaneous irradiation by high-pressure Hg lamp (100W) for 10 min - 3 hours at room temperature, high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) were applied to detect the adsorbate. On n-type H:Si(111), hydrocarbon adsorbates were observed, and on p-type H:Si(111), Si-Br stretching signal (450 cm^{-1}) was exclusively detected. To survay the mechanism of reaction, we divided this adsorption process into UV irradiation in ultrahigh vacuum (UHV) and following CH_3Br introduction without UV. Although a small amount of hydrocarbon contaminant was deposited on both n-type and p-type substrates during UHV UV irradiation, the post-adsorption of CH_3Br resulted in increase of only hydrocarbons on n-type, and only Br on p-type. This result indicates that the irradiation of UV on H:Si(111) promoted photo-assisted desorption of H and leaves hydrogen vacancies, namely, dangling bonds. The difference of adsorption product between the n-type and p-type should be associated with the electronic structure of substrate modified with dopant atoms. We performed molecular-orbital calculations of various H-terminated Si(111) model clusters (sized from 32 Si atoms to 400 Si atoms) with H vacancies on the surface and a few Si atoms replaced with P or B atoms, on the basis of density functional theory (DFT). It was demonstrated that the orbital protruding over the dangling bond was the highest filled electronic orbital on P-doped cluster, whereas on B-doped, it was the lowest unoccupied orbital. This result did not change if we change the number of dangling bonds or dopant atoms. Although this approximation is too rough because of orders-of-magnitude higher dopant level than the real substrates, the result matches the classical formalism of semiconductor band bending near the surface. We further performed DFT calculations on the dangling bond coordinated with a CH_3Br molecule. The dangling bond on n-type/p-type substrate attracts theCH_3 group/Br atom, respectively. It was recognized that the effects of dopant are crucial for the adsorption selectivity of surface dangling bonds towards organic molecules.

2:20pm **SS2+EM+TF-ThA2 Effects of Dative Bond Formation on Si(114) Reaction Pathways**, ***D.E. Barlow***, Nova Research, Inc., *S.C. Erwin, A.R. Laracuente, L.J. Whitman, J.N. Russell, Jr.*, Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface with a single domain-like surface reconstruction composed of parallel rows of dimers, rebonded atoms, and tetramers.[1] We have used transmission FTIR, STM, and DFT to compare the reactions of ethylene and acrylonitrile at the Si(114)-(2x1) tetramer sites. These sites have a diene-like structure, allowing us to investigate the potential Diels-Alder reactivity of an unusual Si surface structure.[2] In particular, we have investigated the effects of conjugated, electron-withdrawing substituents on the dieneophile. For organic reactions, such substituents typically increase the reaction rate, often by several orders of magnitude. Ethylene reacts as the dieneophile in a Diels-Alder reaction at the tetramer site with a reaction probability of ~10^{-2}. Surprisingly, however, we find that acrylonitrile does not undergo the Diels-Alder reaction at the tetramer sites. Rather, exposure of the clean Si(114) surface to acrylonitrile leads to three distinguishable ketenimine (-C=C=N-) structures in the FTIR spectra. Polarized transmission FTIR results indicate the presence of ordered ketenimine arrays, with strong registry to the Si(114) surface and site-dependent orientation. We have distinguished the acrylonitrile adsorption structures at the tetramer sites from those at the dimer and rebonded atom sites by analyzing site-dependent heterofunctionalized Si(114) surfaces on which we have first passivated a large portion of rebonded atom and dimer sites with ethylene, allowing the acrylonitrile to preferentially react with the remaining tetramer sites. From the polarized FTIR spectra, we conclude that the -C=C=N- structures are aligned parallel to <110> at the rebonded atom and dimer sites, but perpendicular to <110> at the tetramer sites. The differing ethylene and acrylonitrile reactivities on Si(114) further emphasize the variable reaction pathways possible for dative bonding on reconstructed Si surfaces.

[1] S. C. Erwin, A. A. Baski, and L. J. Whitman, Phys. Rev. Lett. 77, 687 (1996).

[2] D. E. Barlow, et al., J. Phys. Chem. B 110, 6841 (2006).

2:40pm **SS2+EM+TF-ThA3 Surface Chemistry of Silicon: Making the Connection to Molecules**, ***J.M. Buriak***, *D. Wang, Y. Qiao, J. Chai*, University of Alberta, Canada **INVITED**

The chemistry of semiconducting surfaces is a field of intense interest, not only for the prospect of exciting cutting edge applications, but also from a fundamental perspective.[1] Control over the surface reactivity of silicon and other semiconducting materials is critical for interfacing new molecular devices on chips and other nanotechnological applications, and to perhaps replace oxide overlayers as feature sizes on transistors become smaller than 50 nm. In this talk, we will attempt to provide a preliminary reactivity 'road map' towards understanding the organometallic surface chemistry of silicon that, interestingly, can vary greatly from that of silicon-based molecules. For example, by using the silicon surface as an electrode, electrochemistry can drive reactions that have no obvious parallels with molecular chemistry. As a result, molecules as diverse as alkynes and tetraalkylammonium salts can serve as organic sources to prepare organic monolayers directly on silicon, bound through Si-C bonds.[2] We will also discuss our latest results concerning the patterning of silicon surface reactivity on the nanoscale (features sizes<30 nm); both conjugated organic monolayers and monodisperse metallic nanocrystallites can be interfaced directly to the surface of silicon for a variety of applications.

[1] Buriak, J. M. "Organometallic Chemistry on Silicon and Germanium Surfaces", Chemical Reviews, 2002, 102, 1271-1308.

[2] Wang, D.; Buriak, J. M. "Trapping Silicon Surface-Based Radicals", Langmuir, 2006, 22 6214-6221.

3:40pm **SS2+EM+TF-ThA6 Liquid Methanol Reaction with H-terminated Silicon Surfaces**, *D.J. Michalak,* University of California, Berkeley, *S. Rivillon Amy,* Air Products and Chemicals, Inc., *A. Esteve,* LAAS, France, ***Y.J. Chabal***, Rutgers University

The reaction of hydrogen-terminated Si(111) and oxide terminated silicon surface with neat anhydrous liquid methanol (CH_3OH) has been studied with high resolution Fourier transform infrared spectroscopy (FTIR) to determine several factors regarding the surface chemistry. First, a high temperature reaction of atomically smooth H-Si(111) surfaces in neat anhydrous CH_3OH liquid produces methoxylated surfaces that are virtually free of subsurface oxidation. At long reaction times (t > 3h), the surface saturates with Si-OCH_3 sites covering ~30% of a monolayer, with a residual ~70% comprised of Si-H sites. The virtually-oxide free surface facilitates two important conclusions. First, surface reaction mechanisms involving the insertion of oxygen atoms in the subsurface Si-Si back bonds can be ruled out. Because subsurface oxidation often presents deleterious surface electrical trap states, the absence of significant oxidation also holds important implications for the use of alcohol-terminated precursors in the functionalization of surface chemistry for use in electronics devices. Second, the vibration modes of the clean surface are very sharp and allow a more careful analysis of surfaces that contain subsurface oxidation. Specifically, it has been observed previously that, despite the presence of subsurface oxidation on some methoxyl-terminated surfaces, no evidence for subsurface oxygen atoms has been observed directly below Si-H sites. This is surprising from the standpoint that the surface still retains nearly 60-70% unoxidized Si-H sites. It was proposed that the oxidiation may reside underneath Si-OCH_3 sites. In this work, comparison of partially oxidized surfaces with the virtually oxide-free surfaces demonstrates that the presence of blue shifted Si-OCH_3 vibrational modes is correlated with the presence of subsurface oxidation. This assignment is corroborated by studies performed on oxide-terminated surfaces that present similar, but blue shifted modes to those observed on the oxide-free H-Si(111) surface. Thus, this work demonstrates that while virtually oxide-free surface can be made, there is a large selectivity towards the formation of oxide underneath atop Si-OCH_3 sites relative to the Si-H sites, which retain almost exclusively unoxidized backbonds. Finally, mechanisms for the formation of oxide are presented with regard to these new results.

4:00pm **SS2+EM+TF-ThA7 Dissociative Electron Attachment Induced Growth of Thin Graphite Films or Graphene on Si(111)-7×7**, ***D. Oh***, *H. Abernathy, N. Sharma, P.N. First, M. Liu, T.M. Orlando*, Georgia Institute of Technology

There is currently keen interest in developing good strategies for the growth of a few layers of graphite or graphene on substrates such as Si. We are exploring the use of low-energy electron induced dissociation of adsorbed benzene, naphthalene and phenylacetylene in the production of graphite/graphene films with good lateral heterogeneity. In this study, benzene, naphthalene or phenylacetylene is chemisorbed onto reconstructed Si(111)-7×7 surfaces. These adsorbates are fragmented via low-energy electron bombardment at energies which are dominated by dissociative electron attachment resonances. In general, the incident electron beam can be captured by low-lying π^* states of the chemical precursors and can lead to controlled dissociation and the formation of reactive radicals and negative ions. These fragments can then react to form a network structure of predominantly sp^2 hybridization. The deposited carbon overlayer is examined with Auger electron spectroscopy, Raman spectroscopy and scanning tunneling microscopy. The quality of the deposit and the viability of this non-thermal growth strategy will be discussed.

4:20pm **SS2+EM+TF-ThA8 Adsorption Irregularities of 1,3 Cyclohexadiene and Naphthalene on Silicon(100) Investigated by STM, DFT and an Extended Frontier Orbital Analysis**, ***P.M. Ryan,*** CRANN, Trinity College Dublin, Ireland, *L.C. Teague,* National Institute of Standards and Technology, *J.J. Boland*, CRANN, Trinity College Dublin, Ireland

We consider the reactions of 1,3-cyclohexadiene (1,3-CHD)[1,2] and Naphthalene on Si(100) and examine possible origins for the surface adsorption selectivity evident from STM measurements. The major adsorption products for both molecules are identified by STM. DFT calculations are carried out in order to examine the energetics of the major products and their associated structural analogs. The calculations reveal that the theoretical product distributions based on thermodynamics alone, for both systems, differ significantly from the experimental ones. We explain, using an extended frontier orbital analysis, that secondary orbital interactions which can discriminate between certain concerted reactions and are unavailable at the Γ point due to symmetry considerations become feasible at other κ points in the surface Brillouin zone. We propose that these interactions play a role in the kinetics of the adsorption process and may account for the observed reaction selectivity.

[1] Teague, L.C. and J.J. Boland, STM Study of Multiple Bonding Configurations and Mechanism of 1,3-Cyclohexadiene Attachment on Si(100). Journal of Physical Chemistry B, 2003. 107(16): p. 3820-3823.

[2] Teague, L.C., D. Chen, and J.J. Boland, DFT Investigation of Product Distribution Following Reaction of 1,3-Cyclohexadiene on the Si(100)Surface. Journal of Physical Chemistry B, 2004. 108(23): p. 7827-7830.

4:40pm **SS2+EM+TF-ThA9 CNTs on a Si(100) Surface: Dry Deposition, STM/STS, and Contacts**, ***B. Naydenov***, Trinity College Dublin, Ireland, *J.J. Boland*, Trinity College Dublin and CRANN, Ireland

We present a cryogenic STM study of carbon nanotubes (CNTs) deposited on Si(100) surfaces. Imaging and spectroscopic results by means of LT-STM will be demonstrated and analyzed. Using STM-manipulations, contacts (different metals) with the CNTs are formed and characterized. Aspects of the CNTs purity, preparation, and interaction with the substrate will be discussed.

Thin Film

Room: 602/603 - Session TF1-ThA

Photovoltaics, Fuel Cells, and Alternative Energy Materials and Applications

Moderator: M. Drees, Luna Innovations Incorporated

2:00pm **TF1-ThA1 High Throughput Fabrication and Screening of Thin Film Electrocatalysts for Fuel Cell Applications**, *J.M. Gregoire, **M. Kostylev**, J. Jin, R.B. van Dover, F.J. DiSalvo, H.D. Abruna*, Cornell University

We describe methodologies for the generation and screening of combinatorial libraries of electrocatalyst materials for fuel cell applications. Composition spread thin films are codeposited via DC magnetron sputtering. The films are then screened for catalytic activity using a fluorescence indicator. The high-throughput nature of both the fabrication and screening processes, coupled with the versatility of the deposition system, allow for the rapid testing of a broad range of potential fuel cell electrocatalyst materials. Details of the techniques, fluorescence test results and characterization data for some catalytically active films will be presented.

2:20pm **TF1-ThA2 Atomic Layer Deposition of Alternative Energy Materials**, *X. Jiang, J.S. King, **S.F. Bent***, Stanford University

Atomic layer deposition (ALD) is a method for depositing thin films of semiconducting, insulating and metallic materials using an alternating series of self-limiting reactions between gas phase precursors and the substrate. Over the past several years, ALD has grown steeply in popularity as a choice for the semiconductor industry. However, ALD's real potential for impact may lie in even more novel applications, including those in alternative energy. This presentation will describe our recent studies using ALD for the deposition of thin films for both fuel cell and solar cell applications. For solid oxide fuel cells (SOFCs), we have explored ALD for the fabrication of an ultra-thin Pt film for use as the electrocatalyst, and a Pt mesh structure for a current collector, as a means of improving catalyst performance at lower temperatures. Pt ALD was carried out using (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) and O_2 as precursors and N_2 as a carrier and purging gas. Ex situ analysis of the as-deposited Pt films shows that the platinum film is of excellent uniformity, with no measurable impurities and low electrical resistivity. In addition to the blanket deposition of platinum, we have used the technique of area selective ALD, by combining the methods of ALD and microcontact printing, for fabrication of spatially patterned Pt, to be used as a current collector grid for SOFCs. Working SOFC fuel cells were fabricated with ALD-deposited Pt, and their performance was characterized by a potentiostat-impedance system. The results show that comparable initial performance can be achieved with ALD deposited Pt anodes compared to the RF sputtered Pt anodes with only one-eighth the platinum loading required in the ALD film. For the photovoltaic application, we will describe a vertical nanostructured geometry in which the carrier diffusion length is decoupled from solar radiation absorption, enabling high efficiency cells to be fabricated inexpensively out of low quality materials. We will describe how ALD and other deposition methods can be used to deposit thin films of photovoltaic materials to make nanocomposite solar cells.

2:40pm **TF1-ThA3 Investigation of Bulk and Grain Boundary Diffusion of Oxygen in Yttrium Stabilized Zirconia Via Nuclear Reaction Analysis***, ***M. Finsterbusch,*** Montana State University and Technische Universitaet Ilmenau, Germany, *H. Chen, W. Priyantha,* Montana State University, *V. Shutthanandan,* Pacific Northwest National Laboratory, *R.J. Smith,* Montana State University, *J.A. Schaefer*, Technische Universitaet Ilmenau, Germany

Yttria stabilized zirconia (YSZ) is one of the most common solid ionic conductors considered for the electrolyte in solid oxide fuel cells operating at temperatures near $800^{o}C$. The addition of yttria into zirconia not only stabilizes the cubic fluorite phase of zirconia over a wide temperature range, but also introduces oxygen vacancies due to the smaller valency of Y^{3+} vs. Zr^{4+}. High oxygen ionic conductivity associated with vacancy hopping is seen in YSZ for yttria doping levels around 10%. Numerous studies have been carried out to understand oxygen transport and surface exchange kinetics in single crystal YSZ.[1-3]However, for polycrystalline YSZ the description of diffusion processes is more complex due to the presence of interfaces and grain boundaries that act as preferential sites for variation in composition and chemical state of the atomic species with respect to the bulk. In this study ^{18}O tracer depth profiles were obtained using $^{18}O(p,\alpha)^{15}N$ nuclear reaction analysis for both YSZ single crystals and sintered polycrystalline pellets. Samples were cleaned and pre annealed in a tube furnace for 8 hours at $800^{o}C$ in air. Afterwards they were exposed for various times at a pressure of 10 Torr of 99% pure ^{18}O at various temperatures up to $900^{o}C$. By contrasting the differences of ^{18}O transport for the two structures, the influence of grain boundaries on oxygen transport and exchange kinetics were extracted.

*HiTEC is funded by DOE as a subcontract from Battelle Memorial Institute and Pacific Northwest National Laboratory under Award No.DE-AC06-76RL01830.

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[2] N.I. Joos, P.A.W. van der Heide, J.R. Liu, R. Christoffersen, W.K. Chu, C.A. Mims; Mat. res. Soc. Symp. Proc. Vol. 548, Page 605-610

[3] P.S. Manning, J.D. Sirman, R.A. De Souza, J.A. Kilner; Solid State Ionic 100 (1997) 1-10.

3:00pm **TF1-ThA4 Thermal Stability and Oxidation Resistance of Protective Coating on Stainless Steel Interconnect for Solid Oxide Fuel Cells**, ***H. Chen****, J.A. Lucas, W. Priyantha, R.J. Smith, P.E. Gannon, M. Deibert,* Montana State University, *V.I. Gorokhovsky,* Arcomac Surface Engineering, *V. Shutthanandan, P. Nachimuthu*, Pacific Northwest National laboratory

Chromia forming ferritic stainless steels are being considered for application as interconnects for planar solid oxide fuel cells (SOFC) because of their low cost and flexibility. Many SOFC designs will operate at temperatures exceeding 700°C. At these temperatures, ferritic steels lack environmental stability in the SOFC environment, and as a result may degrade the performance of the SOFC. In this study, an effective, dense and well adherent TiCrAlYO coating was deposited on 430SS using filtered arc deposition technique. XRD indicates that nanocrystalline spinel is the dominant crystal structure in the coating. Rutherford backscattering with He and non-Rutherford scattering with proton were used to characterize the composition and the thermal stability of the coatings. The chromium volatility of the coated steel plates at 800°C was measured using ion beam analysis. Significant reductions in oxidation rates as well as reduced Cr volatility were observed for the coated alloys.

3:40pm **TF1-ThA6 Optimizing the Structure and Composition of Heterostructured Ceria / Zirconia Multilayers through Oxygen Plasma Assisted Molecular Beam Epitaxy**, *S.V.N.T. Kuchibhatla, P. Nachimuthu, C.M. Wang, V. Shutthanandan, M.H. Engelhard, L.V. Saraf, **S. Thevuthasan***, Pacific Northwest National Laboratory, *S. Seal*, University of Central Florida

Mesoscopic fast ion conduction in nanometer-scale planar heterostructures is gaining attention from researchers in the field of solid-state ionic conducting devices. One such device and the most popular among alternative energy sources is solid oxide fuel cell (SOFC). In SOFCs oxygen ions should be effectively conducted from cathode to anode through an electrolyte. Hence, it is quite essential to develop electrolyte materials that offer low and intermediate temperature ionic conductivity. Currently, yttria stabilized zirconia (YSZ) is the most widely used electrolyte, but the need for temperatures in the range of 800oC-1000oC imposes various restrictions in expanding the SOFC technology. Samaria doped ceria has been extensively studied as an alternative to YSZ at intermediate temperatures. Structural configuration of these thin films plays a major role in oxygen ionic conduction and we have initiated several studies to understand the influence of structure and chemistry of these thin films on oxygen ionic conductivity. We have synthesized high quality single- and poly- crystal films of Sm doped ceria(SDC) and Sc stabilized zirconia (ScSZ) using oxygen plasma assisted molecular beam epitaxy and characterized those using several surface and bulk sensitive techniques. The effect of growth temperature on the domain structure and the ionic conductivity are features of interest in the research associated with single- and poly- crystal SDC films. It appears that the strain, chemistry and structure at the interface play a role on ionic conduction in the SDC and ScSZ multi-layer films. The enhancement in oxygen ionic conductivity through some of these films at low temperatures are encouraging.

4:00pm **TF1-ThA7 Controlling the Doping Concentration and Thermoelectric Applications of NaxV2O5 Thin Films**, ***S. Iwanaga****, M. Marciniak, R.B. Darling, F.S. Ohuchi*, University of Washington

A high thermoelectric coefficient has been reported for $Na_xV_2O_5$ thin films. $Na_xV_2O_5$ structure consists of V_2O_5 layers, where Na atoms are retained between the layers, leading to various phases depending on the Na concentration. From the view point of processing this class of material for thermoelectric device applications, the precise control of the Na concentration and stabilization of the desired phase are the key issues. Recently, we presented a possibility of a solution route to make $Na_xV_2O_5$ thin films. Here, we report that through this new processing route, we can control the crystal phase of $Na_xV_2O_5$ thin films, specifically between β- and γ- phases, through annealing conditions and the choice of the substrates. β-phase is preferred for thermoelectric applications due to high Seebeck coefficient and a relatively good electrical conductivity. We found that on quartz substrate, high temperature annealing (600 C) leads to predominantly β- phase. By using soda-lime glass, which contains high Na_2O, as a substrate, the Na concentration in $Na_xV_2O_5$ films increases with increasing annealing time: coexistence of β- and γ- phases (10 minutes annealing) develops into γ- phases dominated film upon annealing for >30 minutes. Our results suggest that the Na concentration can be kinetically controlled in this material system. The possibility of $Na_xV_2O_5$- based thermoelectric device is proposed.

4:20pm **TF1-ThA8 From Uncontrolled and Controlled Size and Shape Intercalated Nanostructures to Bulk Materials for Thermoelectric Device Applications: Old and New Materials - New Techniques**, ***N. Sorloaica-Hickman***, University of Central Florida

The properties of all materials are highly dependent on structure, composition, size and shape. As we seek to explore and utilize novel phenomenon at the nano, 2-dimensional and 3-dimensional scale, a basic understanding of structure/composition/size/shape property relations alone are not enough unless this understanding is made in the context of a specific device and in relation to the practical, economic considerations. This investigation requires a highly integrated approach to all aspects of development of these integrated devices, including theoretical prediction, synthesis, processing and characterization in concert with device design, optimization and implementation. Theoretical and experimental results predicted that the nano-scale materials have better thermoelectric properties that bulk materials.[1] Previous theoretical work on the effect of the grain boundaries in polycrystalline materials indicated that the scattering of the phonons in smaller grains could be very beneficial for the efficiency of the thermoelectric materials.[2] This presentation will highlight some new directions in size and shape controlled nanostructure (grains) and bulk thermoelectric materials research based on our theoretical and experimental investigations. Specific configurations where size and shape of the nanostructures that will constitue the bulk materials are controlled during fabrication will be discussed. Preliminary calculations of the electronic and thermal properties as a function of the composition, size and shape of the intercalated nanostructure will be also presented. We will also describe the synthesis techniques of the nanostructures and the method to incorporate these structures into bulk materials during fabrication. However, the challenge remains to achieve higher performance results in integrated systems in order to more rapidly incorporate them into standard thermoelectric devices.

[1] M. S. Dresselhaus, J. P. Heremans, in Thermoelectrics Handbook: Macro to Nano (Ed: D. M. Rowe), Taylor and Francis, CRC, Boca Raton, FL 2006, Ch. 39, p. 39-1-39-24.

[2] J. W. Sharp et al , Boundary Scattering and the Thermoelectric Figure of Merit, Phys. Stat. Sol. (a) 187, No. 2, 507-516 (2001).

4:40pm **TF1-ThA9 Fabrication of Multilayered Thin Film Cooling Devices**, ***Z. Xiao***, Alabama A&M University

Multilayered thin film cooling devices were designed and fabricated for the application of highly efficient solid-state micro cooling. Multilayered Bi_2Te_3/Sb_2Te_3 (p-type) and $Bi_2Te_3/Sb_2Te_xSe_{3-x}$ (n-type) superlattice thin films were used as the material systems for fabrication of the cooling devices. The multilayered films were grown by e-beam evaporation and had a periodic structure consisting of alternating Bi_2Te_3/Sb_2Te_3 layers or $Bi_2Te_3/Sb_2Te_xSe_{3-x}$ layers, with 5-10 nm thickness each. The cooling device consists of pairs of n-type and p-type legs, which are connected electrically in series and thermally in parallel. Under the applied voltage, both electrons in n-type legs and holes in p-type legs move from the cooling end, carrying heat, therefore, heat is pumped away from the cooling end to the hot end, where the heat is finally ejected away. Large number of pairs of n-type and p-type legs with size ranging from 7 µm by 14 µm to 30 µm by 40 µm is integrated in a single device using microfabrication techniques. Photomasks were designed for the fabrication of the cooling devices, and clean room-based microfabrication techniques were used to fabricate the devices. The developed cooling device is a good candidate for the application of high-efficiency solid-state micro cooling. The electrical and thermal parameters of the material systems such as the electrical conductivity, thermal conductivity, and Seebeck coefficient will be characterized and the cooling efficiency will be measured. The results will be reported in the conference.

Acknowledgements: The author thanks CERDEC for financial support for the research.

5:00pm **TF1-ThA10 Optical Characterezation of InN layers grown by High-Pressure CVD**, ***M. Alevli***, *G. Durkaya*, Georgia State University, *R. Kirste*, Technische Universität Berlin, Germany, *A. Weesekara, A.G.U. Perera*, Georgia State University, *A. Hoffmann*, Technische Universität Berlin, Germany, *N. Dietz*, Georgia State University

A growing number of potential applications such as high-efficient heterojunction solar cells,thermoelectric devices and terahertz detector will become possible as Indium Nitride (InN) and In-rich group III-nitride(N) materials become more mature and can be integrated with other-rich group III-N alloys. Understanding and controlling the physical properties of the InN is of essential importance next to its integration as a component of $(Ga_{1-x}In_x)N$ alloy system, which is crucial for fabrication of wavelength tailored high-efficient LEDs and displays. The present limitations in this area are in the growth of high quality InN and In-rich group III-N at processing conditions that are compatible with GaAlN aloys.The difficulties arise from the low dissociation temperature of In-rich groupIII-N, requiring extraordinarily high nitrogen overpressure to stabilize the material up to optimum growth temperatures. Our research explores the growth of InN and In-rich group III-N by high-pressure chemical vapor deposition (HPCVD), an approach that allows controlling and stabilizing the vast different partial pressures of the constituents. The results show that the chosen HPCVD pathway leads to high-quality single crystalline InN, demonstrating that HPCVD is a viable tool for the growth of In-rich III-N alloys. The structural analysis of InN deposited on GaN-Sapphire substrate by XRD show single phase InN(0002) peaks with full width half maximum below 400 arcsec. The optical transmission analysis shows that an apparent band gap is around 1.4 eV with absorption centers at 0.8 eV and 0.4 eV. The strength of the low energetic absorption centers are closely related to the precursor ratios and the utilized growth temperatures. Infrared reflectance spectroscopy is used to estimate the high frequency dielectric constant, the free carrier concentrations and carrier mobilities in these layers. The free carrier concentration is found to be in the upper 10^{19} cm^{-3} with the corresponding mobilities around 600 $cm^{+2}V^{-1}s^{-1}$.A further reduction of residual extrinsic impurities in the precursor and carrier gas is presently explored to further reduce the free carrier concentration in the layers.The modeling of the IR-reflectance spectra indicate the present of two distinct InN layers: one with electron concentrations below $5x10^{17}cm^{-3}$,which is followed by second layer in the upper $10^{19}cm^{-3}$ closer to the surface.

Thin Film

Room: 613/614 - Session TF2-ThA

Computational Aspects of Thin Films

Moderator: B.C. Holloway, The College of William and Mary

2:00pm **TF2-ThA1 Computational Study of the Interfacial Structure of Aluminum/α-Alumina**, ***B.D. Devine***, University of Florida, *A. McGaughey*, Carnegie-Mellon University, *S.R. Phillpot, S.B. Sinnott*, University of Florida

Several experimentally observed orientations for the interface between FCC aluminum grown on the (0001) face of α-alumina were studied through molecular dynamics using a modified variable charge potential. This many-body, empirical potential allows for the realistic modeling of both the metallic and ceramic phases in large-scale, atomistic simulations. The effects of temperature, surface terminations and coherency on the interfacial structure and energy were investigated. The efficiency of the molecular dynamics simulation allows for study of periodic systems oriented with minimal strain along the preferred relationship of $<1010>_{Al2O3} \parallel <110>_{Al}$ as well as secondary orientations along $[2112]_{Al2O3} \parallel [011]_{Al}$ and $[2112]_{Al2O3} \parallel [231]_{Al}$. The results are compared to experimental data and to the results of density functional theory calculations. This work is supported by the National Science Foundation (DMR-0426870).

2:20pm **TF2-ThA2 Analytical Simulation of Conformal and Super-Conformal CVD on High Aspect Ratio Vias and Trenches**, *Y. Yang*, ***J.R. Abelson***, University of Illinois at Urbana-Champaign

The need to coat or fill recessed features such as trenches or vias is frequently encountered in micro- and nano-fabrication processes. Chemical vapor deposition is commonly used because of the combination of good conformality and high growth rate. With the continuous scaling down of feature sizes and the increase of aspect (depth/width) ratios, it has become a major challenge to maintain the growth conformality and filling efficiency. We developed a numerical model that is capable of simulating the film thickness profiles produced by CVD in trenches and vias with aspect ratios ≥ 10:1. In this model, the precursor transport is described by Knudson diffusion, and the precursor concentration and reaction rate distributions are solved numerically from the continuity equation. The evolution of the deposition profile during a filling process can also be predicted. We employ this model to understand the critical issues associated with CVD on high aspect ratio features. We show that the precursor reaction probability is the key factor that governs the deposition conformality. The model predicts the precursor reaction probability that is required to conformally coat or to completely fill trenches with aspect ratios ranging from 5:1 to 100:1. These simulations are in close agreement with the experimental profiles we have obtained for HfB_2 and CrB_2 films grown using single-source borohydride precursors. Traditionally the precursor reaction probability is controlled primarily by the growth temperature. We show that if a Langmuir surface reaction mechanisms is operative then the precursor pressure is a far more effective parameter to reduce the reaction probability. We have developed a new approach to obtain super-conformal coating (bottom-up filling) of high aspect ratio features, and we have demonstrated proof-of-concept with CrB_2 and HfB_2 films. In this method, a suppressor species is introduced into the growth system to reduce the surface reaction rate of the precursor. We simulate the deposited film profile as a function of the suppressor pressure, precursor pressure, trench aspect ratio, and the relative reaction rates of the suppressor and precursor species. We will discuss methods to optimize the filling process by varying the suppressor pressure in time during film growth.

2:40pm **TF2-ThA3 Computational Investigation of Surface Polymerization by Ion Assisted Deposition**, *W.-D. Hsu,* University of Florida, *S. Tepavcevic, L. Hanley,* University of Illinois at Chicago, ***S.B. Sinnott***, University of Florida **INVITED**

Density functional theory-MD (DFT-MD) simulations are used to study surface polymerization by ion-assisted deposition (SPIAD) of thiophene on alpha-terthiophene oligomers on a silicon surface to determine the dominant mechanisms responsible for the SPIAD process. Polythiophene is a conductive polymer that has attracted much interest in recent years because its properties are desirable for applications that include light emitting diodes, field effect transistors, and photovoltaics. Optimization of the performance of polythiophene in these devices requires the development of processing methods that can simultaneously control its chemistry and morphology on the nanometer scale. One such method is SPIAD, where conducting polymer thin films are grown on substrates by the simultaneous deposition of hyperthermal polyatomic ions and thermal neutrals in vacuum. Both neutral and positively charged systems are considered in the DFT-MD simulations in order to assess the effect of charge on the results, which were compared to experimental data. The incident energies range from 100 to 500 eV. The simulations indicate that the differences in the collision outcomes between the neutral and positively charged events are small in most cases, but the atoms in the +1 charged system experienced slightly larger forces and velocity variations than the atoms in the neutral system. Several key bond dissociation and polymerization mechanisms are predicted in the simulations that are also observed experimentally. The most important prediction is that incident thiophene ions break apart on collision with the 3T film. Both the experiments and simulations indicate that incident thiophene ions chemically modify the structure of the oligomer film by covalently bonding to the 3T oligomers. The insight gained from this integrated experimental and computational work can be used to optimize the SPIAD process for polythiophene and other conducting polymer systems. This work is supported by the National Science Foundation (CHE-0200838).

3:40pm **TF2-ThA6 Modelling, Growth and Characterisation of Stress-Balanced Thin Films on Stress-Free Virtual Substrates**, ***S.G. Turner,*** Imperial College London, UK, *L. Yu,* Chinese Academy of Sciences, China, *K. Chua, M.R. Levy,* Imperial College London, UK, *X. Li,* University of Oxford, UK, *J. Zhang*, Imperial College London, UK

The Si/SiGe material system on a Si platform gives opportunities to develop Si-based optoelectronic devices, allowing monolithic integration.[1] The 4% mismatch requires strain to be properly managed in structures that exceed the critical thickness for relaxation. Growing a stress-balanced structure on a virtual substrate (VS) allows such control. This work characterises the composition, tilt and strain state of the VS, and that of thin layers. Growth was carried out under ULPCVD & GSMBE modes in a modified VG Semicon system. We grew a fully-relaxed SiGe VS on Si(001), compositionally graded from pure Si. We show that a composition overshoot in the graded layer is needed to achieve the required in-plane lattice parameter, and determine its value. We examined x-ray reciprocal space maps (RSM) about the 004 and 224 reflections, obtaining average tilt of the VS with respect to the substrate and tilt distribution. Results from misoriented substrates show that the VS tilts to reduce the difference between low-index planes and the physical surface by >5%, explained by the preferential introduction of misfits with certain Burgers vectors. A fully-relaxed VS provides a good template for stress-balance between thin metastable layers by considering average force in the structure.[2] Predictions from linear elasticity (LE) theory (assuming linear interpolation of alloy elastic constants) were tested by depositing a DBR on a fully-relaxed VS.[3] The DBR consisted of 25 repeats of a Si/SiGe (32%) bilayer of ~190nm thickness, grown at 590°C and 520°C respectively. RSMs (giving lattice parameters) revealed the bilayer was coherent to the VS, supporting the validity of the linear extrapolation. This was compared to density functional theory calculations of the elastic constants. Reflectivity was 75% at 1.4 microns, and x-ray analysis showed fringes typical of well-ordered interfaces, suggesting a good stress-balance was realised. The composition overshoot part of the VS remains under compressive strain and coherent to the subsequent grown layers. We propose to compensate this using tensile Si, obtaining a true stress-free structure. We demonstrated this for varying VS compositions. We thus show that the precise strain state of thin films can be accurately manipulated.

[1] Kuo et al., Nature Vol. 437 p1334

[2] Ekins-Daukes et al., Crystal Growth & Design Vol. 2 p287.

[3] Kawaguchi et al., APL Vol. 79 p476.

4:00pm **TF2-ThA7 Intra- and Interlayer Mass Transport Rates during Layer-By-Layer Homoepitaxial Pt(111) Growth from Hyperthermal Beams (5-50 eV)**, ***V. Chirita,*** *D. Adamovic, E.P. Münger, L. Hultman,* Linköping University, Sweden, *J.E. Greene*, University of Illinois, Urbana-Champaign

We employ multi-billion time step embedded-atom method molecular dynamics simulations to study homoepitaxial growth of Pt(111) using low-energy (0.2 - 50 eV) hyperthermal Pt fluxes. We deposit 5 monolayers at 1000K and with deposition rates approaching experimental conditions. The results reveal a transition from a three-dimensional (3D) multilayer growth mode to layer-by-layer growth at ~ 20 eV which is maintained for energies of up to 50 eV. In order to determine the mechanisms responsible for the observed change in the growth mode, we resolve, with picosecond resolution, both irradiation-induced and thermally activated processes. This allows us to determine, with unprecedented accuracy, the energy dependence of the net intra- and interlayer migration rates during the deposition process. Results show, that for all energies, irradiation events are completed within 10 ps following energetic impacts and that these processes dictate the growth mode. As expected, thermal migration is not affected by the deposition energy. For Pt deposition energies above 20 eV, the net interlayer migration induced by irradiation is towards the surface. This type of mass transport occurs via exchange mechanisms between surface and sub-surface atoms. On the growing layers, we observe primarily the descent of adatoms at step-edges and the recombination of adatoms with surface vacancies, i.e. mainly thermally activated processes. However, thermally activated net downward migration is an order of magnitude less than irradiation-induced upward migration. Intralayer migration is shown to depend strongly on adatom surface coverage. Results show that adatoms are the primary source of in-layer mass transport, which is observed to peak at a coverage of ~ 0.05 ML. Sputtering is observed to occur for energies higher than 25 eV. However, the yield is too small, less than 1% at 50 eV, to have a significant effect on island nucleation and coalescence kinetics.

4:20pm **TF2-ThA8 Synthesis and Theoretical Modeling of Fullerene-like Phospho-Carbide Compounds**, ***A. Furlan,*** *G.K. Gueorguiev, H. Högberg, S. Stafström, L. Hultman*, Linköping University, Sweden

First-principles DFT calculations predict that Fullerene-like (FL) CPx compounds can have resilient mechanical behavior similar to FL-CNx, but for a lower V element concentration. P is a higher period element compared to N. This means a higher freedom with respect to chemical bonding which is likely to affect the structure of the CPx compounds compared to FL-CNx. The results of theoretical simulation of synthetic growth of FL-CPx structures show that the substitution of N with P makes the formation of tetragon defects energetically favorable and that P-P bonds are plausible. This implies stronger curvature and interlocking of graphene planes. Concurrent inter- and cross-linking of the bent graphene planes induced by the P atom leads to cage- and onion-like structures which promise improved mechanical properties of the FL solids. In this paper we also present results from magnetron sputtering deposition of CPx thin films. The films were deposited by DC magnetron sputtering in Ar atmosphere from a compound graphite-P target containing between 5 and 15 at.% of P. Higher proportions of P in the target should be avoided since P-rich species in the deposition flux might result in P-segregation during film growth. The substrates were Si and NaCl wafers kept at a bias voltage in the range of -20 V to -50 V, and substrate temperature ranging from 150 ^{o}C to 780 ^{o}C. As-deposited coatings were analyzed using XPS, nanoindentation, SEM, and TEM. The preliminary results show that incorporation of P into the film is promoted at lower substrate temperatures and higher bias voltages. Nanoindentation experiments show that resistance to indentation and hardness of the CPx increases for decreasing substrate temperature and increasing bias voltage.

4:40pm **TF2-ThA9 High-Throughput Determination of Sputtered Film Composition: The Importance of Resputtering**, *J.M. Gregoire, M.B. Lobovsky, M.F. Heinz, F.J. DiSalvo,* ***R.B. van Dover***, Cornell University

The use of traditional characterization techniques to determine elemental compositions in composition spread thin films is time-intensive. Combinatorial, high-throughput studies of thin film materials demand high-throughput determination film composition. We discuss the possibility of calculating codeposited film compositions from deposition profiles obtained during single-source sputtering. In the context of DC magnetron sputtering, we find that while this technique is appropriate for the Pd,Pt,Ti system, it yields atomic ratios in a Pt,Pb composition spread thin film that vary significantly from values measured with wavelength dispersive x-ray spectroscopy. A model for resputtering during codeposition is presented to account for these discrepancies, and the model is used to calculate resputter rates during Pt,Pb codeposition. We also employ our model to estimate the resputtering susceptibility of commonly sputtered elements.

5:00pm **TF2-ThA10 General Theory of Optical Reflection from a Thin Film on a Solid and its Application to Heteroepitaxy**, *Y.Y. Fei, X.D. Zhu, **X. Wang***, University of California at Davis*, H.B. Lu, G.Z. Yang*, Chinese Academy of Sciences

Light reflection from an optically smooth yet atomically rough film on a smooth solid substrate formed by deposition or erosion is a convenient source of information on morphology and chemical make-up of the film. We show that changes in optical reflectivity for s-polarized (TE mode) and p-polarized (TM mode) components, defined as $(r_p - r_{p0})/r_{p0} - (r_s - r_{s0})/r_{s0} = \Delta_p - \Delta_s$, induced by such a film, is generally related to structural and chemical properties of such a film through a mean-field theory. Here r_{p0} and r_{s0} are the reflectivity of a bare substrate, and r_p and r_s are the reflectivity when the film is added onto the substrate. According to the theory, $\Delta_p - \Delta_s$ consists of a term that is proportional to the thickness of the rough portion of the film, a term that is proportional to the density of unit cells embedded in terraces, and a term that is proportional to the density of unit cells situated at step edges. The proportionality constants are functions of the overall thickness and chemical make-up of the film. We apply the theory to analysis of a wide range of growth and adsorption experiments studied with the oblique-incidence reflectivity difference (OI-RD) technique.

Tribology

Room: 617 - Session TR3+NS-ThA

Nanotribology and Nanomechanics

Moderator: P.R. Norton, University of Western Ontario, Canada

2:00pm **TR3+NS-ThA1 Quantitative Direct-Observation Nanomechanical Testing in the Transmission Electron Microscope**, ***O.L. Warren**, Z. Shan, S.A.S. Asif,* Hysitron, Inc.*, E.A. Stach,* Purdue University*, A.M. Minor*, Lawrence Berkeley National Laboratory **INVITED**

The increasingly strong interest in measuring and understanding the sometimes extraordinary mechanical properties of nanomaterials and individual nanostructures has encouraged us to develop the first depth-sensing indenter compatible with quantitative nanomechanical testing in the transmission electron microscope (TEM). This ambitious undertaking has encountered a number of significant technological hurdles to overcome; nevertheless, we have achieved a versatile in-situ TEM instrument that compares favorably to leading conventional nanoindenters in terms of control modes and performance specifications. Scientifically, we have exploited the unique capabilities of this novel instrument to perform direct-observation nanoindentation into thin films and monolithic materials using sharp indenters, direct-observation nanocompression onto hollow and solid nanospheres as well as onto crystalline and amorphous nanopillars using miniature flat punches fashioned with a focused ion beam (FIB), and direct-observation bending of nanowires using the aforementioned flat punches. This presentation will share the powerful nature of time correlating the often discrete features of force-displacement curves to the accompanying morphological and microstructural changes that are directly observed in the corresponding TEM movies. Our research results range from some validating current mechanistic thinking to others that are counterintuitive and therefore a challenge to conventional wisdom.

2:40pm **TR3+NS-ThA3 Tribology in Full View**, ***L.D. Marks**, A. Merkle*, Northwestern University **INVITED**

Experiments in tribology have long suffered from the inability to directly observe what takes place at a sliding contact - the classic buried interface problem. As a consequence, although many friction phenomena at the nanoscale have identified, there can be interpretation issues resulting from indirect or ex-situ characterization of the contact surfaces or because the experimental measurements are volume averaged, rather than giving direct insight into what is taking place at a single asperity-asperity contact. We have been recently exploiting a unique instrument that allows us to simultaneously slide a tip across a surface and look at the sample using transmission electron microscopy. Using this technique, we can directly image the nanoscale processes taking place at scales from 0.2 nm to microns, as well as obtain local chemical information from techniques such as electron energy loss spectroscopy. Using this instrument we have recently observed "liquid-like" deformation where the material is solid, but behaves as if it was a liquid due to very rapid surface diffusion, similar to the classic case of liquid-like growth of gold and silver particles; the formation of a graphitic transfer layer during sliding of tungsten on graphite as well as in-situ observation of graphitization of diamond-like carbon during sliding observed by electron energy loss spectroscopy. Further results include observation of wear debris during sliding of tungsten on graphite whose size is consistent with a dislocation standoff model and a recently published dislocation model for friction at the nanoscale. These and additional results will be described.

3:40pm **TR3+NS-ThA6 Atomic-scale Friction on Ultra Thin Films**, ***T. Filleter**, W. Paul, R. Bennewitz*, McGill University, Canada

Friction force microscopy (FFM) provides a powerful method to study the microscopic origins of friction. FFM has previously demonstrated that a single sharp asperity scanned over an atomically flat crystalline surface can exhibit a periodic stick-slip movement following the periodicity of the underlying lattice.[1] This has been observed for a range of different crystalline surfaces, including alkali halides and metal single crystals.[2,3] In this work we have extended the FFM technique to study atomic-scale friction on a model solid lubricant system. The system was chosen to satisfy two criteria; be composed of materials with well known bulk atomic frictional properties, and to be topographically well defined with atomic resolution. The model system, which satisfies both criteria, are ultra thin films of KBr grown on a single crystal Cu(100) substrate. Ultra thin films have been grown under ultra high vacuum conditions with a thickness of up to five monolayers of KBr on an atomically flat Cu(100) substrate. The films have first been characterized using high resolution noncontact atomic force microscopy (NC-AFM). The first and second monolayers are found to grow in a carpet-like mode overtop of the existing Cu monatomic steps. Subsequent layers grow as rectangular islands with a minimum of corner and kink sites. Atomically resolved NC-AFM topography images of the films reveal a regular superstructure in the growth which is consistent with the KBr/Cu lattice mismatch. FFM measurements show that, as expected, the KBr films do act as a solid lubricant exhibiting lower friction than the bare Cu(100) surface. It is also observed that layers with a thickness of two and greater monolayers supports stable atomic stick-slip friction. The atomic frictional properties on films as thin as two monolayers (0.66 nm) are found to be consistent with that of bulk KBr. Lateral force maps of films exhibiting a topographic superstructure do not reveal a superstructure in the lateral force. The bare Cu(100) substrate has also been found to support stable stick-slip friction which has previously not been achieved.

[1] Bennewitz, R., Materials Today, May 2005, p.42

[2] Socoliuc, A., et. al, Phys. Rev. Lett. 92, 13 (2004) 134301/1-4

[3] Bennewitz, R., et. al, Phys. Rev. B 60, 16 (1999) R11301-4.

4:00pm **TR3+NS-ThA7 A Scanning Tunneling Microscope and Quartz Crystal Microbalance Study of Heating and Wear at a Sliding Interface**, ***B.D. Dawson**, S.M. Lee, J. Krim*, North Carolina State University

In order to probe the rise in temperature of a sliding interface, a Scanning Tunneling Microscope and Quartz Crystal Microbalance has been combined to produce a rubbing action of a tungsten tip on a copper and indium electrode, respectively. The amplitude of oscillation[1] and wear of the electrodes is observed directly with the STM. Negative frequency shifts, which are indicative of a liquid-solid interface,[2] were observed for tungsten on indium rubbing. The chamber was heated and negative frequencies were observed at reduced sliding speeds, implying surface melting at the indium interface. This work was funded by The National Science Foundation and the AFOSR Extreme Friction MURI.

[1] B. Borovsky, B. L. Mason, and J. Krim, J. Appl. Phys. 88, 4017 (2000).

[2] C. M. Flanigan, M Desai, and K. R. Shull, Langmuir. 16, 9825 (2000).

4:20pm **TR3+NS-ThA8 Radial Breathing Mode Frequencies of Single-Walled Carbon Nanotubes Determined by Nanoindentation with an AFM**, ***J. Fraxedas**,* ICMAB-CIN2-CSIC, Spain*, G. Rius, F. Pérez-Murano,* IMB-CNM-CSIC, Spain*, A. Verdaguer*, ICN-CIN2, Spain

We have experimentally determined the radial breathing mode frequency of individual single-walled carbon nanotubes with a diameter of 1.3 nm by nanoindentation measurements using an Atomic Force Microscope with commercial microfabricated silicon cantilevers with ultrasharp tips, evidencing the sensitivity of such instruments to frequencies in the THz range, well above the resonance frequencies of the cantilevers (ca. 130 kHz).[1]

[1] Europhys. Lett. 78 (2007) 16001.

4:40pm **TR3+NS-ThA9 The Importance of Nanoscale Meniscus Formation During High-Speed Sliding Contacts**, ***C.M. Mate**, R.N. Payne, Q. Dai,* Hitachi San Jose Research Center*, K. Ono*, Hitachi Central Research Laboratory, Japan

To help determine the nanoscale origins of friction at high-speed sliding contacts, we have developed a High Shear Rate Apparatus using technology from the disk drive industry. This technique enables us to study friction, adhesion, and wear at ultra-high sliding speeds (1 to 100 m/s) for a small pad contacting a rotating disk with an atomically smooth surface and covered with a nanometer thick lubricant film.[1] We find that the sliding characteristics are dominated by the non-equilibrium meniscus of lubricant that forms between the pad and disk surfaces and by the vibrational dynamics of the sliding interfaces. In particular, the high sliding speed results in the friction, adhesion, and bounce dynamics being asymmetric with respect to sliding direction for a pad tilted at a slight angle with respect to the rotating disk surface. These differences are attributed to the mechanical action of the lubricant layer against the converging and diverging wedges of the pad, leading to an asymmetric meniscus to form around the contact pad at high speeds. Under suitable conditions, we also find a self-excited vibration of the slider pad, a few nanometers in amplitude, which is induced by friction hysteresis coupled with adhesion hysteresis.

[1] C. M. Mate, R.N. Payne, Q. Dai, and K. Ono, "Nanoscale Origins of Dynamic Friction in an Asymmetric Contact Geometry", Phys. Rev. Lett. 97 (2006) 216104.

5:00pm **TR3+NS-ThA10 Effects of Interfacial Structure on Atomic-Scale Friction Examined using MD***, J.A. Harrison*, *M.T. Knippenberg, J.D. Schall, G. Gao, P.T. Mikulski*, United States Naval Academy

The development of micron-sized devices, such as microelectromechanical devices, for terrestrial and space applications has prompted the need for protection of the surfaces of these devices. Self-assembled monolayers (SAMs), both alkanethiols and alkylsilanes, are possible candidate for the passivation and lubrication of these devices. The fundamental problem associated with controlling friction is a lack of understanding of the underlying atomic-scale processes that govern both friction and wear. We have conducted extensive molecular dynamics (MD) simulations using our AIREBO potential aimed at understanding the atomic-scale mechanisms of friction in SAMs. We have examined the way in which the contact forces present at the interface influence friction and made direction connections between interfacial structure and friction. We have examined the effects of changing the interface structure in several ways. Some of these include changing the structure of the SAM (e.g., end-group, chemical identity, hybridization, connectivity of chains) and altering the roughness of the interface. In this talk, we will discuss our most recent findings that have examined the way in which the structure of both the SAM and the tip influence friction. ** Work supported by The Office of Naval Research and The Air Force Office of Scientific Research as part of the Extreme Friction MURI.

Vacuum Technology

Room: 618 - Session VT1-ThA

Adsorption/Desorption Phenomena on Vacuum Materials

Moderator: N. Peacock, MKS Instruments, Inc.

2:00pm **VT1-ThA1 Surface Morphology and Surface Composition of Vacuum Fired Stainless Steel****, M. Leisch***, Graz University of Technology, Austria **INVITED**

Stainless steel is one of the most used construction materials in vacuum technology. Especially in XHV applications a high temperature treatment (vacuum firing) is commonly used to reduce outgassing of this material. There is a considerable body of work on outgassing of hydrogen from stainless steel. The results are basically described by two models: the diffusion limited model and the recombination limited model. Since recombination is strongly related to surface morphology and composition, surface characterization has been performed by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The surface near composition has been measured by atom probe depth profiling analysis. After vacuum firing a significant change in surface morphology can be observed in AFM and STM. The high temperature treatment leads to a complete reconstruction of the surface. The recrystallization process leads to an increase of the overall surface roughness with deep grooves up to 1000 nm in depth at the grain boundaries. On top of the crystallites wide flat terraces over 100 nm in width bounded by bunched atomic steps and facets can be observed. The high resolution STM micrographs additionally show stacking faults and local defects on these terraces assigned to (111) planes. The atom probe depth profiling analysis on vacuum fired samples results in a noticeable surface enrichment of nickel and certain depletion of chromium in the first atomic layer. In the second atomic layer chromium enrichment was measured. From the knowledge of surface structure and surface composition a recombination limited outgassing is very unlikely. Comparison with experimental studies on hydrogen desorption by thermal desorption spectroscopy strongly support the explanation by the diffusion limited model. It can be assumed that subsurface defects form traps with different energetic levels. The increase in diffusion energy after emptying the higher subsurface levels may also explain the observed outgassing behaviour of stainless steel.

*Work supported by province of Styria, Austria Zukunftsfonds project P119.

2:40pm **VT1-ThA3 Monte Carlo Simulation of Temperature Programmed Desorption Including Binding Energies and Frequency Factors Derived by DFT Calculations*, P. Thissen*,** *O. Ozcan,* Max-Planck Institut for Iron Research, Germany, *D. Diesing,* Institut of Physical Chemistry Essen, Germany, *G. Grundmeier*, Institut of Macromoleculare Chemistry Paderborn, Germany

Temperature-programmed desorption (TPD) techniques are important methods for the determination of kinetic and thermodynamic parameters of desorption processes or decomposition reactions. A sample is heated with a temperature program ß(t) = dT/dt (with the temperature T usually being a linear function of the time t) and the partial pressures of atoms and molecules evolving from the sample are measured, e.g. by mass spectrometry. When experiments are performed using well-defined surfaces of single-crystalline samples in a continuously pumped ultra-high vacuum (UHV) chamber then this experimental technique is often also referred to as thermal desorption spectroscopy (TDS). A Monte Carlo model has been developed for describing the temperature-programmed desorption of adsorbates from single crystal surfaces. The developed Monte Carlo Program requires the input of frequency factors and unity bond order binding energies BE (for the top position) for every bond under examination. For the first time the required values are now calculated using a DFT code. The virtue of both methods (Monte Carlo and DFT) is combined in the present work. Our new model takes into account the effects of surface diffusion, the influence of surface-adsorbate (S-A) and adsorbate-adsorbate (A-A) interactions and the coverage dependence of the activation energy for desorption derived by precise calculations on an atomically defined level. The inclusion of localized (S-A) and (A-A) interactions has a pronounced effect on the shape of the predicted TPD spectrum. Only a single peak is observed in the absence of (S-A) and (A-A) interactions, whereas multiple peaks are found when these interactions are included. The inclusion of (S-A) and (A-A) interactions is also shown to produce a nonlinear decline in the activation energy for desorption as a function of increasing adsorbate coverage.

3:00pm **VT1-ThA4 Temperature Programmed Desorption Measurements of the Binding Energy of Water to Stainless Steel Surfaces*, J.H. Hendricks*,** *P.J. Abbott,* National Institute of Standards and Technology, *P. Mohan,* NPL India, *J.P. Looney*, Brookhaven National Laboratory

The presence of water vapor is the limiting factor in achieving ultra-high vacuum (UHV) in an unbaked stainless steel system. While the "water problem" has been of scientific and technical interest for many decades, fundamental measurements of water interactions with stainless steel systems are not well characterized, including the binding energy and sticking coefficient of water on stainless steel. In addition, outgassing rate measurements of water from stainless steel surfaces are typically hampered by the problem of re-adsorption, leading to inaccurate measurement results. The NIST Pressure and Vacuum group has undertaken a study of the binding energy of water to stainless steel surfaces. A temperature programmed thermal desorption apparatus was constructed for this purpose and will be described in detail. The apparatus uses computer control to linearly heat a stainless steel filament at a rate of 3 °C/s while a quadrupole mass spectrometer detects the thermally desorbed species. The system is designed with a high pumping speed to minimize the problem of re-adsorption/desorption, and has reproducibly shown a water thermal desorption peak at 139 °C. A model for thermal desorption, first employed by Redhead in 1962[1] was used to determine the activation energy, or binding energy of water to stainless steel. This technique has reproducibly yielded a water binding energy between 25.6 and 26.0 kcal/mole. These results may justify lower baking temperatures than are traditionally used for achieving UHV. Future work will focus on the apparent interplay of water desorption and hydrogen desorption observed during UHV system bake-outs.

[1] Redhead, P.A., Vacuum, 12, 203 (1962).

Vacuum Technology

Room: 618a - Session VT2-ThA

Large Vacuum Systems

Moderator: N. Peacock, MKS Instruments, Inc.

3:40pm **VT2-ThA6 Recent Advances to Enhance Space Simulation**, ***F.G. Collins***, The University of Tennessee Space Institute **INVITED**

Accurate ground-based simulation of low earth orbit (LEO) conditions experienced by a satellite has proven to be a challenge. The continuous progress that has been made toward this goal will be reviewed. A satellite in LEO has a speed relative to the atmosphere of approximately 8 km/s. The neutral atmospheric molecules exchange momentum upon collision with the surfaces of the satellite, leading to drag, lift, and moments, but ground facilities still have trouble simulating pure beams of this speed for the relevant atmospheric gases in their ground state. A facility that is making progress toward this goal will be described. The most important atmospheric molecule, atomic oxygen, collides with ram-direction satellite surfaces with a relative energy of 5 eV. Energetic atomic oxygen atoms plus solar UV radiation produce synergistic effects that result in many chemical reactions on or in the vicinity of the outer satellite surfaces. These can lead to structural or operational damage and the spacecraft glow phenomena. It is desirable to generate large beams of atomic oxygen in the ground state, with the atoms possessing energy of 5 eV. Several techniques for attempting this will be reviewed. Solar radiation has a wide spectrum. The UV spectrum is a composite of many emission lines and continuum, which must be simulated using special lamp systems. Satellite surfaces are exposed to high energy protons, electrons, and other particles. These are simulated in combined effects space simulation chambers for materials degradation studies. Thruster plumes, surface outgassing, and liquid dumps lead to surface contamination. Contamination can reduce the effectiveness of thermal control paints, the output of solar cells, and the effectiveness of optical lenses. Some electric thrusters exit directly to the vacuum of space, which must be simulated if the thruster plume is to be accurately simulated. Specially designed cryogenic pumps designed to simulate the conditions that these electric thrusters will experience in orbit will be described. All of the facilities to be reviewed require special diagnostic instrumentation, much of a specialized type. Some of this instrumentation will be described and the limitations of older techniques will be noted. Satellites in LEO also are immersed in a plasma but the effects of plasma charging, which has been well reviewed elsewhere, will not be covered. Links to inventories of space simulation chambers will be given.

4:20pm **VT2-ThA8 Performance of a Unique Cryogenic Pumping System for Spacecraft-Thruster Interaction Studies**, *C.G. Ngalande*, University of Southern California, ***A.D. Ketsdever***, Air Force Research Laboratory, Edwards AFB, *S.F. Gimelshein*, University of Southern California

With the advent of advanced propulsion systems, the interactions of spacecraft thruster plumes and spacecraft materials is receiving renewed attention. Chamber IV of the Collaborative High Altitude Flow Facility (CHAFF-IV) was designed to obtain high fidelity spacecraft-thruster interaction data. CHAFF-IV uses a total chamber pumping concept by lining the entire interior of the chamber with an array of cryogenically cooled surfaces. The main pumping surface consists of a unique radial fin array which allows for the pumping of both neutral and ion effluents. A Monte Carlo numerical simulation has been performed to investigate the pumping efficiency of the radial fin array. In general, it has been found that longer fin widths and smaller fin thicknesses result in higher pumping efficiency. For a particular geometry, there is an optimum fin-separation distance at which the radial fin array pumping efficiency is maximum. A comparison of the pumping efficiency of the radial fin array with a flat pumping surface has shown that particles with high sticking coefficient such as neutrals will be pumped better with flat panel whereas particles with low sticking coefficients such as ions will be efficiently pumped with the radial fin array. CHAFF-IV is expected to pump, not only plume, but also sputtered material. Since ions are highly energetic, they will cause sputtering of both the array material and the pumped molecules. If not properly accounted for, these two populations can substantially increase the overall magnitude of pressure in the chamber making highly accurate tests impossible[1]. The Monte Carlo simulation has also been used to investigate CHAFF-IV's ability to pump these sputtered particles. A set of experiments has been performed to investigate the pumping efficiency of the radial fin array as manufactured. These experiments compared the radial fin results to a more traditional flat plate pumping surface with a neutral plume. These results indicate that there are flow regimes in which the radial fins are more efficient at pumping neutral molecules than a flat surface.

4:40pm **VT2-ThA9 Outstanding Problems in Vacuum Gas Dynamics from an Industrial Point of View**, ***M. Wüest***, INFICON Ltd, Balzers, Liechtenstein

Many industrial vacuum processes in the semiconductor, coating, tribology, lighting or food packaging industry occur in the transitional flow regime in the pressure range between 10^{-3} - 1 mbar. Industry wants high throughput in its vacuum processes, which requires fast pumping and venting. To achieve an optimum equipment design, the conductance of the vacuum flow path needs to be calculated. This is not an easy endeavour, as many assumptions in the derivation of the analytical conductance formulas are violated in the complicated non-symmetrical process equipment geometries and non-stationary process conditions. Modelling can also become quite difficult, especially if many different flow regimes need to be considered. Water outgassing is a critical process as it heavily influences the pumpdown time. However, our present understanding of the process is incomplete. There are two physically different models, namely the isothermal reversible adsorption and the diffusion-controlled outgassing models, to explain water outgassing. We also do not know the sticking coefficient of water on stainless steel very well. In this talk I will highlight a few outstanding vacuum gas dynamics problems from an industry perspective.

5:00pm **VT2-ThA10 Minimizing Contamination to Multilayer-Dielectric-Diffraction Gratings within a Large Vacuum System**, ***B. Ashe***, *K.L. Marshall, D. Mastrosimone, C. McAtee*, University of Rochester

The University of Rochester's Laboratory for Laser Energetics is in the final stages of constructing the OMEGA EP short-pulse, petawatt laser system. A critical component for OMEGA EP is the grating compressor chamber (GCC). This large (12,375-ft^3) vacuum chamber contains critical optics where laser-pulse compression is performed at the output of the system on two 40-cm-square-aperture, IR (1054-nm) laser beams. Critical to this compression, within the GCC, are four sets of tiled multilayer-dielectric (MLD) diffraction gratings that provide the capability for producing 2.6-kJ output IR energy per beam at 10 ps. The primary requirements for these large-aperture (43-cm x 47-cm) gratings are high diffraction efficiency greater than 95%, peak-to-valley wavefront quality of less than @lamda@/10 waves, and high laser-induced-damage threshold greater than 2.7 J/cm^2 at 10-ps measured beam normal. Degradation of the grating laser-damage threshold due to adsorption of contaminants must be prevented to maintain system performance. The presence of extrinsic contaminants (either particulate or molecular) in the vacuum system puts the MLD gratings at risk with respect to lowered damage threshold. A number of protocols have been developed and implemented at LLE to minimize MLD grating contamination and characterize the performance of the GCC vacuum chamber. In this paper, we describe the GCC vacuum chamber and component cleaning procedures, the qualification, testing methods, and studies undertaken for materials intended for use within the chamber, the use of absorptive getters to protect the gratings from molecular contamination, and the protocols necessary for the integration and operation of the MLD gratings. This work was supported by the U.S. Department of Energy Office of Inertial Confinement Fusion under Cooperative Agreement No. DE-FC52-92SF19460, the University of Rochester, and the New York State Energy Research and Development Authority. The support of DOE does not constitute an endorsement by DOE of the views expressed in this article. Key words: laser-pulse compression, vacuum chamber, cleaning, particulate contamination, molecular contamination.

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[1] Ketsdever, A.D., "Design Considerations for Cryogenic Pumping Arrays in Spacecraft-Thruster Interaction Facility", Journal of Spacecraft and Rockets, Vol 30, number 3, 400-410, 2001 .

Applied Surface Science

Room: 4C - Session AS-ThP

Aspects of Applied Surface Science II Poster Session

AS-ThP1 DNA Microarrays to Detect the Serotype of Dengue Viruses in a Large Number of Samples from Mosquitoes or Patients Collected in Mexico , *A. Diaz-Badillo,* CINVESTAV-IPN, Mexico*,* ***V. Altuzar,*** Universidad Veracruzana, Mexico*, J.G. Mendoza-Alvarez,* CINVESTAV-IPN, Mexico*, A. Cisneros,* Universidad Autonoma Benito Juarez, Mexico*, F. Jimenez-Rojas, J.P. Martinez-Muñoz,* Salud Pública y Servicios de Salud de Oaxaca, Mexico*, J.L. Herrera-Perez,* CICATA-IPN, Mexico*, C.O. Mendoza-Barrera,* Universidad Veracruzana, Mexico*, F. Sanchez-Sinencio, P. Gariglio-Vidal, M.L. Muñoz*, CINVESTAV-IPN, Mexico

Dengue is a mosquito-borne viral infection causing a major public health problem globally. Dengue virus (DENV) is the causative agent of dengue fever and dengue hemorrhagic fever and includes four distinct serotypes (DEN-1, DEN-2, DEN-3, and DEN-4). DEN-2 and DEN-3 have been associated with severe dengue disease. In this work we demonstrated a high throughput of microarrays for detection of dengue virus in serum samples from patients with a defined dengue infection from Oaxaca or in mosquito population collected across eighteen Mexican states. We have applied microarray analysis for simultaneous serotyping multiple RNA samples from human or mosquitoes through the NS3 genome. The proposed microarray method can be used for i) rapid and reliable dengue diagnosis; ii) serotyping and iii) surveillance of mosquitoes infected with dengue. Moreover by using these microarrays we have determined DEN viruses in pools of gravid females mosquitoes collected in several sites of eighteen Mexican states in 2005. Our microarrays were also useful to confirm the presence of DEN-2 in 96 serum samples, DEN-3 in three samples from Oaxaca city and one case from Juchitán, Oaxaca contained DEN-2 and -3. The microarrays quantification were validated by using RT-PCR, in fact they presented agreement in all cases excepting with those mosquito samples collected in one site of Chiapas, Oaxaca, Morelos and Nayarit. In conclusion, we show the success of applying microarrays assay to provide a consistently robust qualitative detection of dengue serotypes (DEN-1, DEN-2, DEN-3 and DEN-4) in serum samples from patients or in pools of gravid female mosquitoes collected in the field of eighteen Mexican states.

AS-ThP2 Surface Engineering with Functional Soft Materials*, M. Yan*, Portland State University

Organic and polymeric materials are effective in tailoring the chemical and physical properties of the surface layer, and to introduce functions to materials. We have developed a simple and versatile method for attaching a wide range of soft materials on solid substrates. The technique employs a photochemical coupling chemistry that is fast, efficient, and is capable of creating structures with control over density and topography.[1] Applications of this surface functionalization technique for the fabrication of nanowells,[2] carbohydrate microarrays[3] and single polymers[4] will be highlighted.

[1] Liu, L.; Engelhard, M. H.; Yan, M. "Surface and Interface Control on Photochemically Initiated Immobilization", J. Am. Chem. Soc. 2006, 128, 14067-14072.

[2] Yan, M.; Bartlett, M. "Micro/Nanowell Arrays Fabricated from Covalently Immobilized Polymer Thin Films on a Flat Substrate," Nano Lett. 2002, 2, 275-278.

[3] Pei, Z.; Yu, H.; Theurer, M.; Walden, A.; Nilsson, P.; Yan, M.; Ramström, O. "Photogenerated Carbohydrate Microarrays", ChemBioChem 2007, 8, 166-168.

[4] Liu, L.; Yan, M. "A General Method for the Covalent Immobilization of Single Polymers," Angew. Chem. Int. Ed. 2006, 45 (37), 6207-6210.

AS-ThP4 A Quantitative Model Relating Interphase Chemistry and Adhesive Fracture in Steel Cord-Rubber Composites*, G.E. Hammer*, The Goodyear Tire & Rubber Company

In steel cord-rubber adhesion testing high rubber coverage, or cohesive fracture in the rubber, is generally accepted as a necessary condition for good adhesive bonding. On the microscopic level the transition from high rubber coverage to exposed wire is a transition from fracture in the rubber to separation in the sulfide layer in the adhesive interphase. This sulfide layer is a mixture of copper(I)- and zinc sulfides. Multivariate statistical analysis of Auger depth profiles of the interphase produced chemical depth profiles from which the composition of the interfacial sulfide (percent zinc sulfide and copper(I)sulfide) can be measured. For a variety of compounds, cures, and aging conditions the rubber coverage was a function of the percent zinc sulfide, with rubber coverage dropping abruptly as the percent zinc sulfide increased from 60 to 80%; specifically the a rubber coverage of one-half the initial value appeared to correspond to a percent zinc sulfide of 75%. A mechanism has been proposed wherein the loss of adhesion was attributed to the one or both of (i) overgrowth of the bonding copper sulfide by the non-bonding zinc sulfide in the interphase, (ii) embrittlement of the sulfide by increased content of zinc sulfide.

AS-ThP5 Electronic States of Fe Atomic Chains on Pt (997) Surface*, R. Cheng*, *E. Ayieta,* Indiana University-Purdue University*, Y. Losovyi*, Louisiana State University

The study of low dimensional systems is of great interests due to their technical applications as well as the rich fundamental physics. The variety of one dimensional atomic chains can be synthesized on stepped surfaces, which provide opportunities for systematically tailoring the surface properties. The electronic structure of the high vicinal surface plays an essential role to determine the physical properties of the atomic chains as well as the surface catalysis. We have used several surface analysis techniques to study the surface of the (997) single crystal. The scanning tunneling microscopy and low energy electron diffraction results show that the surface has uniform step terrace without any reconstruction. The angle resolved ultra violet photoemission spectroscopy was performed to characterize the band structure of Pt(997) surface by using synchrotron radiation source. Then Fe were carefully deposited on to Pt(997) substrate at room temperature. The atomic resolution STM data shows that Fe atomic chains were formed along the step edges due to the step decoration. Finally angle resolved ultra violet photoemission spectroscopy was also performed to characterize the Fe atomic chains.

AS-ThP6 Using a Dual-Beam SIMS to Study Nano-scale Metallic Thin Films and Biological Samples*, H. Chen*, *T. Bunai, E.R. Tracy, W.E. Cooke, A.L. Wilkerson,* College of William and Mary*, S. Rossnagel,* IBM T.J. Watson Research Center*, D. Manos*, College of William and Mary

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) offers high sensitivity and mass resolution. It is used widely in both research laboratories and industry. While TOF-SIMS is a well established surface analyzing method, high resolution depth-profile analysis is often desired in semiconductor industry, nano-structure manufacturing and engineering. Using a TRIFT II dual-gun system, which is equipped with a Au_n^+ gun as primary beam and an Argon gun as sputter beam, we studied a series of samples that consist of multilayer, nano-scale metallic thin films. Depth profiling is carried at different sputter energies (500eV-5keV) and the resolution is compared for these different sputter energies. Using the imaging capability of TOF-SIMS, the image of the crater after sputtering is obtained and the ion mixing at interface is studied. The result is compared with TRIM simulations. One great advantage that TOF-SIMS offers over other types of mass spectroscopy like MALDI is sub-micron spatial resolution. MALDI is the primary method used in mass spectroscopic imaging of biological samples like cells and tissue sections. Though MALDI offers a wide mass range, the spatial resolution, limited by the matrix crystal size and laser beam spot size, is often tens of microns. SIMS high spatial image is a well suited complement to MALDI image. The argon sputtering, though primarily used to study inorganic samples, was recently used to expose cell inner structures for electron microscopy images. Using the dual-beam system, we studied a prostate tissue section. The sputtering rate is determined, and depth-profiles are correlated to interior cell structures in the SIMS image.

AS-ThP7 Characterization of Mobile Ions in Insulating Materials and Their Effect on Polymer Adhesion*, K.M. Stika*, DuPont*, K. Proost, A. De Backer,* DuPont-Belgium*, J.R. Marsh, D.E. Davidson, D.G. Swartzfager, K.G. Lloyd*, DuPont

Adhesion of polymers to inorganic substrates can be seriously affected by the surface and interfacial chemistry of the adjoining layers. Modification of the substrate through heating, chemical treatment, accelerated aging or environmental exposure has been shown to contribute to the ultimate adhesion performance of laminate and multilayer structures. Similarly, diffusion of ions from a glass surface with the formation of a leached ion layer under varied conditions is also a well known phenomenon. It follows that the ability to control and profile elemental composition and depth distribution of highly mobile ions in the near surface region of inorganic materials is an important tool for the fundamental understanding of polymer/inorganic adhesion. This presentation will highlight recent efforts to profile near surface mobile ions as a function of substrate aging or surface treatment and the correlation of these chemical profiles with changes in polymer/inorganic adhesion performance.

AS-ThP8 Molecular Dynamics Simulations of 30 keV and 2 keV Ga in Si, ***L.A. Giannuzzi***, FEI Company, *B.J. Garrison*, The Pennsylvania State University

Molecular dynamics simulations of 2 keV and 30 keV Ga bombardment of Si(011) at a grazing angle of 88 degrees show that the dynamics effectively follow scattering from a flat surface and that very little energy is transferred to the substrate. The inclusion of an adatom above the surface allows for the coupling of the energy of motion parallel to the surface into the substrate. The adatom and one other Si atom eject and motion in the substrate occurs down to a depth of 13 Å. These results show that some surface roughness is necessary for sputtering to occur at very grazing angles of incidence (i.e., high incident angles). Therefore, it is unlikely that focused ion beam polishing can create a non-facetted or atomically smooth surface.

AS-ThP9 Residual Stress of Focused Ion Beam-Exposed Polycrystalline Silicon, ***K. Archuleta***, University of New Mexico, Sandia National Labs, *D.P. Adams*, *M.J. Vasile*, Sandia National Labs, *J.E. Fulghum*, University of New Mexico

Focused ion beam systems are increasingly utilized to fabricate tools, instruments, sensors and devices on the micrometer and nanometer scales. It is thus critical to understand the impact of FIB bombardment on the relevant properties of different materials. Despite many investigations of implanted gallium concentrations, surface roughening and microstructural changes, few studies have quantified the residual stress that results from FIB exposure. Medium energy (30 keV) focused gallium ion beam exposure of silicon results in a compressive inplane stress with a magnitude as large as 0.4 GPa. Experiments involve uniform irradiation of thin polysilicon microcantilevers (200 µm in length) over a range of dose from 1 x 10^{16} to 2 x 10^{18} ions/cm^2. The radii of curvature of microcantilevers are measured using white light interferometry in atmosphere before and after ion beam exposure. The residual stress is determined from these radii and other measured properties using Stoney's Equation. The large residual stress is attributed to ion beam damage, microstructural changes and implantation.

AS-ThP10 Nanoindentation Study of Silicon-on-Insulator (SOI) and Strained (sSOI) Multilayers Composite Films, ***J.E. Jakes***, University of Wisconsin-Madison and USDA Forest Products Laboratory, *D.S. Stone*, University of Wisconsin-Madison, *K. Tapily*, *H. Baumgart*, Old Dominion University, *G. Celler*, SOITEC, Bernier-Grenoble, France, *A.A. Elmustafa*, Old Dominion University

Silicon-on-Insulator (SOI) technology provides an engineered composite substrate where the active top Si device layer is decoupled from the mechanical support wafer by an interspersed electrically insulating and mechanically compliant silicon oxide layer. The main application of SOI technology is found in microelectronics, where SOI offers CMOS performance enhancement with the use of an embedded oxide layer to isolate transistors from the substrate, which results in lower parasitic capacitance and reduced junction leakage and a host of other benefits. For further performance gain lattice strain can be incorporated into SOI films in order to enhance carrier mobility for MOSFETs. Bi-axially tensile strained sSOI films were obtained with a fabrication sequence of epitaxially growing 150 Å to 600 Å strained Si films on a relaxed 20% Ge containing $Si_{1-x}Ge_x$ buffer layer on a donor wafer. During epitaxy the Si lattice stretches to match the larger $Si_{1-x}Ge_x$ lattice. The larger lattice constant of Ge produces a 4.1% lattice mismatch with the Si crystal. The higher the Ge alloy concentration, the higher the embedded strain becomes. Following successful bonding of both wafers, the donor wafer was split off with the Smart Cut^{TM} exfoliation technique. The surface was then finished with an etching process to completely remove all traces of the $Si_{1-x}Ge_x$ film, resulting in a Ge-free bi-axially strained Si film on amorphous SiO_2 insulator. In this work we use nanoindentation to investigate the hardness and modulus of standard relaxed SOI and bi-axially tensile strained sSOI with Si films ranging in thickness from 10 to 60 nm and extreme strained xsSOI multilayer samples. The elastic response of the silicon-oxide-silicon substrate multilayer system to indentation can be modeled using elasticity theory, which reveals excellent agreement with the experimental results. The nanoindentation experiments detect a 5% difference in composite modulus with indent depths between 30 and 40 nm deep for 60 nm-thick tensile strained sSOI films compared to SOI films. These strained films are grown epitaxially on a $Si_{0.80}Ge_{0.20}$ buffer layer followed by wafer bonding and film exfoliation by the Smart Cut^{TM} technology. The sSOI and xsSOI thin films exhibit mean tensile stress levels of 1.3 GPa and 2.5 GPa respectively using a $Si_{0.60}Ge_{0.40}$ buffer layer.

AS-ThP11 Study of Photocatalytic Activity in the Low Temperature-Annealed TiO_2 Thin Film Prepared by Sol-Gel Technique, ***A. Majumder***, *S. Biswas*, *M.F. Hossain*, *T. Takahashi*, University of Toyama, Japan, *Y. Kubota*, University of Yokohama City, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

Semiconductor photocatalysts, particularly titanium oxide (TiO_2) with high photocatalytic activity, offers convenient route of purification of air and water and a provision of 'self-maintaining' clean surface. Several physical and chemical techniques have been used to prepare titanium dioxide thin film. Among the various techniques, the relatively simple sol-gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. However, generally post-deposition annealing at high temperature is required for achieving crystalline phase. Crystallinity is one of the key factors behind the photocatalytic activity of TiO_2, therefore achievement of better crystallinity at relatively low temperature is an important issue. In our present study, the titanium dioxide porous films were deposited on glass slides by sol–gel technique; where, an alcoholic solution of tetra-buthylorthotitane was hydrolysed in a water/alcohol/acetic acid mixture. The solution thus prepared was deposited on glass substrates. These films were transparent and crack free. All the films were annealed at different annealing temperatures, ranging from 350° C to 500°C. Sufficiently good crystalline sample was obtained by annealing at 350° C. For this present investigation; annealing temperature and number of coating layers were varied. The sol was initially characterized by DTA-TGA. The structure and optical characterizations of these films were made by X-ray diffraction and UV-Vis spectroscopy, respectively. XRD patterns of all the titanium dioxide films confirmed the anatase structure. The surface morphology of the films was observed by atomic force microscope (AFM) and scanning electron microscope (SEM). The morphology of porous titanium dioxide thin films strongly depends on annealing temperatures and number of coatings. The photocatalytic activity of the TiO_2 thin films was evaluated by the decomposition of methanol with the help of FTIR spectroscopy. It has been observed that the photocatalytic activity of the TiO_2 thin films increases with the optimization of annealing temperature as well as with the increase of the numbers of layers. The variation of photocatalytic activity with different annealing temperatures and different number of layers is interpreted in terms of different crystallinity, porosity and surface morphology.

Biomaterial Interfaces

Room: 4C - Session BI-ThP

Biomaterial Interfaces Poster Session

BI-ThP1 HAp/Chitosan Composites from Electrospinning Technique, *F. Vazquez-Hernandez*, *S.A. Lopez-Haro*, UPIITA-IPN, Mexico, ***C.O. Mendoza-Barrera***, Universidad Veracruzana, Mexico, *M.A. Melendez-Lira*, CINVESTAV-IPN, Mexico, *M.L. Albor-Aguilera*, *E. Diaz-Valdez*, FCFM-IPN, Mexico

Human bone is a hidroxyapatite HAp ($HCa_5O_{13}P_3$) and collagen based composite. Actually many methods and techniques have been developed and applied to design advanced materials for bone replacent. An stratergy to biomimic bone tridimentional structure, composition and mechanical properties is mimic it at nanoscale. In other words, selectively incorporate nano particules of apatites into a polymeric matrix by controlling structure and composition of the fibres. In this work we present the preliminary results of HAp/Chitosan composites prepared via electrospinning technique. Chitosan fibers were spun from aqueous solutions (pH= 3) and nano particles of HAp were added prior to the deposition. Prior and after the deposition the compositional and structural characteristics were verified by using scanning electron microscopy SEM, energy dispersive spectroscopy EDS, x-ray diffraction XRD, Raman spectroscopy and Fourier transform infrared spectroscopy FTIR. Energy dispersive spectroscopy and x-ray diffraction confirmed that the mineral deposits were hydroxyapatite and calcium phosphate monobasic MCP ($CaH_4\ O_8\ P_2$), both of them apatites present in bone while Fourier transform infrared studies FTIR showed the characteristic 1220-1020 cm^{-1} chitosan region in agreement with Raman results.

BI-ThP2 TOF-SIMS Imaging Study on Water Soluble and Organic Soluble CdSe/ZnS Core/Shell Quantum Dots, ***T.G. Lee***, *H. Min*, KRISS, Korea, *Y. Kim*, *S.J. Lim*, POSTECH, Korea, *D.W. Moon*, KRISS, Korea, *S.K. Shin*, POSTECH, Republic of Korea

Water-soluble CdSe/ZnS core/shell quantum dots capped by 3-mercaptopropionic acid(MPA) have been studied by using time-of-flight secondary ion spectroscopy (TOF-SIMS) imaging analysis. TOF-SIMS images provide direct evidence of local chemical information on the quantum dot surfaces. The water-soluble quantum dots can be conjugated with protein, DNA and other biomolecules, and thus be useful to applying to bioimaging and biosensing. These quantum dots were generated by converting original organic soluble ligands to MPA ligands. We characterized both surfaces of water soluble and organic soluble quantum dots and confirmed the successful exchange of ligands by using TOF-SIMS images of ligand molecules and molecular metal adducts.

BI-ThP3 The Effect of TOF-SIMS Ion Sources on the Fragmentation Pattern of Adsorbed Protein Films*,* ***S. Muramoto****,* University of Washington*, D.J. Graham,* Asemblon, Inc.*, R. Michel,* University of Washington*, M.S. Wagner,* Proctor & Gamble Co.*, T.G. Lee, D.W. Moon,* Korea Research Institute of Standards and Science*, L.J. Gamble, D.G. Castner*, University of Washington

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a powerful surface analysis technique for the characterization of organic surfaces due to its high surface sensitivity, molecular specificity, and high mass resolution. However, the fragmentation patterns of positive secondary ions from adsorbed proteins, produced by primary ion bombardment, are complex due to multiple fragments originating from each of the 20 amino acids present in proteins. Therefore, the multivariate analysis technique principal component analysis (PCA) was used to identify fragment peaks that vary significantly between spectra. This study utilized Cs^+, Au^+, Au_3^+, Bi^+, Bi_3^+, Bi_3^{++}, C_{60}^+, and C_{60}^{++} ion sources to generate mass spectra for five single-component proteins (albumin, fibrinogen, lysozyme, collagen and immunoglobulin G) adsorbed onto mica. With the use of PCA, we observed differences in fragmentation patterns among the ion sources for all proteins. However, the differences between ion sources for a given protein were smaller than the differences between different proteins. This allows the type of protein to be identified regardless of the ion source used. For each of the five proteins, the fragmentation patterns generated from Cs^+, Au^+ and Au_3^+ ions were differentiated at the 95% confidence level. For the Bi ion sources, the fragmentation patterns from the Bi^+ ions were differentiated from the fragmentation patterns from the Bi_3^+ and Bi_3^{++} ions at the 95% confidence level, but the fragmentation patterns from the Bi_3^+ and Bi_3^{++} ion sources could not be differentiated. From the PCA loadings it appears that there may be a dependency between the mass of the ion source and the number of carbon atoms in the emitted secondary ions (i.e., the Au ions may produce more smaller fragments than the Cs ions). Also, sampling depth may play a role in the observed differences between monoatomic and the cluster ion beams. The results from this study show how the combination of TOF-SIMS with PCA can be used to identify the influence of primary ion type on secondary ion fragmentation patterns.

BI-ThP4 Synthesis of CdSe Nanoparticles by Nanocaged Protein sHSP 16.5*,* ***J.-W. Park****, S.H. Moh, N.H. Kim, K.K. Kim, Y.H. Roh*, Sungkyunkwan University, Korea

Synthesis of semiconductor nanoparticles is one of the interesting research fields in nanotechnology. The semiconductor nanoparticles are applicable to various electronic device, optical devices and bio sensors. Since the energy levels of the semiconductor nanoparticles are quantized depending on their size and shape, therefore it is important to synthesize semiconductor nanoprticles with the same size and shape. Quantum-effect devices were actively investigated to solve these problems. In this study, we performed biomimetic approach to control these factors by using inorganic material (CdSe nanoparticle) and organic nanocaged proteins. Protein cage architectures can be utilized as size- and shape-constrained reaction environments for nanomaterial synthesis. Biomimetic fabrication could be performed in the optimized conditions using small heat shock protein 16.5 (sHSP16.5) mutant and ion complex of cadmium and selenium. A directed nucleation could be achieved through the specific residues on the negatively charged center domain of sHSP16.5. CdSe nanoprticles had the excellent size uniformity in the core of the mineralized sHSP16.5. For 2D array on the Si wafer, we treated chemical such as 3-aminopropyltrethoxysilane (APTES). The mineralized sHSP16.5 has highly binding affinity on the APTES treated Si wafer, which the reason is hydrogen interactions between amine group of the APTES and carboxyl group of sHSP16.5. These results give us to control arrangement of quantum dots on the Si wafer. This biomimetic approach will be possible to achieve advanced floating gate memory devices and single electron transistor in the near future.

BI-ThP5 Visible Light Activated Conjugated Polyelectrolytes as Antimicrobials*,* ***T Corbitt****, L.K. Ista, K. Ogawa, S. Chemburu, G.P. Lopez,* University of New Mexico*, K. Schanze,* University of Florida*, D. Whitten*, University of New Mexico

Conjugated polyelectrolytes (CPs) are polymers that contain ionic solubilizing groups. These materials are water soluble and feature strong visible absorption and fluorescence. Recently we have shown that CPs functionalized with cationic groups such as trimethyl ammonium (1) and diazobicyclooctane bis quaternary salt (2) polyphenyleneethynylene display efficient light-activated biocidal activity against a variety of microorganisms including Escherichia coli, Cobetia marina, Pseudomonas aeruginosa and Bacillus anthracis, Sterne spores. When bacteria are mixed with aqueous solutions of the polymers the CPs form a surface coating on the microorganism. Irradiation of the bacteria surface-coated with polymers 1 or 2 leads to efficient deactivation of the bacteria as revealed by culturing and live/dead assays. We have also demonstrated that CPs are effective against bacteria when coated at near monolayer coverage on a surface. An additional format currently under investigation involves polymers with the repeat unit of 1 grown covalently from the surface of silica nanoparticles and microspheres (SGCP). The polymer coatings of the SGCPs are more rough and appear from studies using confocal fluorescence microscopy and electron microscopy to protrude from the surface. We find that the SGCP entrap Cobetia marina; live-dead assays of entrapped bacteria kept in the dark and irradiated with visible light reveal that bacteria entrapped on the surface of a 5 micron SGCP are killed while those kept for a similar period in the dark remain viable. We are currently determining whether the light-activated pathogen killing requires molecular oxygen and, if so, whether singlet oxygen is a key intermediate. Our observation that bacteria are not only killed but also degraded suggests that singlet oxygen may subsequently generate much more powerful reactive oxygen species. Structure-property relationships are being developed to optimize the biocidal effect of specific CPs, with the ultimate objective being to develop a new class of polymer-based materials and coatings that are highly effective antimicrobial agents with broad-spectrum activity. The CPs offer advantages over low molecular weight compounds in that they are relatively stable and easily adapted to form robust coatings. Their ease in processing indicates they can be incorporated into filtration devices, foams, paints and fibers for diverse protection applications.

BI-ThP6 Determination of the Surface pK_d of Carboxylic Acid and Amine-Terminated Alkanethiols Using Surface Plasmon Resonance*,* *K.P. Fears,* ***S.E. Creager****, R.A. Latour*, Clemson University

Alkanethiol self-assembled monolayers (SAMs) are widely used as model surfaces because they form very well-characterized monolayers over a broad range of surface chemistries. An important property for SAMs with ionizable functional groups is the surface dissociation constant (pK_d), which defines the charge-density for a given pH solution. Using surface plasmon resonance (SPR) spectroscopy, we developed a method for the direct measurement of the pK_d of COOH and NH_2-SAMs by combining the ability of SPR to detect the changes in mass concentration close to a surface and the shift in ion concentration over the surface as a function of surface charged density. An analytical study was first performed to theoretically predict the general shape of the expected SPR plots by calculating the excess mass of salt ions over the SAMs as a function of the difference between the solution pH and surface pK_d. SPR studies were then conducted to measure the shift in salt concentration as a function of bulk pH, with the resulting data being used to determine the pK_d for $HS-(CH_2)_{11}-COOH$ SAMs to be 7.4 ± 0.2 (N=4, mean ± 95% C.I.) and 6.5 ± 0.4 (N=4, mean ± 95% C.I.) for $HS-(CH_2)_{11}-NH_2$ SAMs . These methods present a way to calculate the pK_d for charged SAM surfaces that is non-disruptive and minimally interactive with the surface, thus providing an accurate and direct measure of the pK_d of the surface.

BI-ThP7 Effect of PNIPAAM Chain Length on Thermal Responsive Properties and Cellular Adhesion*,* ***B.P. Andrzejewski****, J. Fenton, L.K. Ista, G.P. Lopez*, University of New Mexico

Poly(N-isopropyl acrylamide) (PNIPAAm) is one of the most extensively studied responsive materials exhibiting a thermally triggered molecular transition effecting hydration. Our poster will present work on surface grafted PNIPAAm by the controllable reaction of atom transfer radical polymerization (ATRP). We use ATRP to investigate the effects of polymer length on both thermal responsive and biological adhesion properties. X-ray photoelectron spectroscopy (XPS), contact angle measurements, ellipsometric thicknesses and biological attachment studies will be used to probe thermal responsiveness to the polymer chain length. By precisely varying the polymer length, we give insight into the chemical and physical properties of the surface that govern its thermal responsiveness and resulting cellular adhesive properties.

BI-ThP8 Universal Route for Synthesis of Protein Resistant Polymer Brushes by Surface-Initiated Atom Transfer Radical Polymerization*,* ***A. Hucknall****, A.J. Simnick,* Duke University*, B.D. Ratner,* University of Washington*, A. Chilkoti*, Duke University

The ability to resist non-specific protein adsorption is an important enabling technology for the design of biosensors and biomedical implants. We have previously shown that surface-initiated atom transfer radical polymerization (SI-ATRP) of oligoethylene glycol methacrylate (OEGMA) can be used to create exceptionally robust and non-fouling surface coatings. In our previous studies, examples of substrates modified with poly(OEGMA) brushes were limited to materials which support the formation of self-assembled monolayers (SAMs) capable of initiating SI-ATRP, such as gold, silicon and metal oxides. However, the surfaces of many technologically relevant materials, such as plastics, do not support SAM formation. This paper presents a simple method to modify the surface of virtually any material with a robust, non-fouling poly(OEGMA) brush by SI-ATRP. Surface initiator layers capable of supporting SI-ATRP were formed by two routes: (1) plasma polymerization of 2-chloroethyl methacrylate and (2) dip-coating of poly(vinylbenzyl chloride). These layers were then used to initiate SI-ATRP of OEGMA. XPS revealed that the poly(OEGMA) brushes formed by either route were indistinguishable from those formed on alkanethiol SAMs on gold. The ability of the resulting poly(OEGMA) layers to resist non-specific protein adsorption was evaluated by incubating the surfaces in undiluted fetal bovine serum for 12 hours-subsequent XPS analysis showed no detectable protein adsorption. Substrates were also incubated for 12 hours in a solution of human umbilical vein endothelial cells in serum containing media and no cell attachment was observed on the poly(OEGMA) coated substrates.

BI-ThP9 Modeling Force versus Distance Profiles of Terminally Anchored Poly (N-isopropyl acrylamide) with Self-Consistent Field Theory, ***S. Mendez***, *B. Andrzejewski, D.H. Keller, H.E. Canavan, G.P. Lopez, J.G. Curro,* University of New Mexico, *J.D. McCoy*, New Mexico Tech

Tethered polymers are widely used to control surface properties such as wettability or cell adhesion. By making thin films out of polymers that are thermo-responsive, we can modulate surface properties with changes in temperature. Specifically, we use poly(N-isopropyl acrylamide) (PNIPAM) since this exhibits lower critical solution temperature (LCST) behavior near 32°C in water. At temperatures below the LCST, the polymer is hydrated and swollen, whereas above the LCST, the polymer collapses, and when tethered, the surface becomes more hydrophobic. In the past we reported on a method of synthesizing thin films of terminally anchored PNIPAM from self-assembled monoloyers using atom transfer radical polymerization.[1] We used neutron reflectivity techniques to measure the polymer brush structure at temperatures above and below the solution LCST. To model the temperature-induced structural changes of these brushes, we employed self-consistent field (SCF) theory using as input the Flory-Huggins chi parameter extracted from the experimental polymer solution phase diagram.[2] As a continuation of that work, we used the SCF theory to calculate the force between the PNIPAM brush and a test wall as a function of wall separation distance, i.e., we generated force-distance profiles. The parameters that we varied were temperature, polymer surface coverage and molecular weight, and the interaction between the PNIPAM and the test wall. AFM techniques were employed to obtain force-distance profiles of PNIPAM samples. We found that the force-distance profiles predicted by the theory were in qualitative agreement with those from experiment. Our ultimate goal is to employ theoretical predictions to guide future efforts to optimize tethered PNIPAM for cell attachment/detachment applications.

[1] Yim et al, Macromolecules 2006, 39, 3420.

[2] Mendez et al, Macromolecules 2005, 38, 174.

BI-ThP10 Electrochemical Behavior of Electroactive Species in Nucleic Acid Monolayers of Different Chain Length, ***K. Wang***, Polytechnic University, *M.A. Gaspar,* Columbia University, *R.A. Zangmeister,* National Institute of Standards and Technology, *R. Levicky*, Polytechnic University

Monolayers of immobilized nucleic acids (DNA) are promising experimental models for investigating fundamental properties of charged polymers at solid-liquid interfaces. We have investigated the charging behavior of single-stranded DNA polyelectrolyte brushes. In this study, voltammetric behavior of hexaamineruthenium(III) chloride (RuHex) in end-tethered single-stranded DNA monolayers of different strand lengths is investigated. The surface coverage of non-labeled DNA chains was determined independently with X-ray photoelectron spectroscopy (XPS). Our results show that, for DNA chains varying from 5 to 100 thymine nucleotides, the reduction potential of RuHex^{3+} counterions associated with the DNA monolayer is predominantly a function of chain surface coverage and is rather insensitive to the chain length. However, the total charge passed to reduce the counterions to the 2+ oxidation state is predominantly a function of the total nucleotide number, given by the product of chain surface coverage and chain degree of polymerization. A model is proposed to explain the observed behavior. The dynamic evolution of the reduction peak area and potential are also investigated, providing a picture of the time dependence of the adsorption of RuHex^{3+} into the monolayers. The research provides a method to estimate the chain coverage of non-labeled, end-tethered DNA chains with various chain lengths.

BI-ThP11 Tuning the Zeta Potential of Poly-L-Lysine Substrates for the Selective Immobilization of Nanoparticles and Biomaterials, ***N. Farkas***, *J.A. Dagata,* National Institute of Standards and Technology, *K.F. Pirollo, E.H. Chang*, Georgetown University Medical Center

Colloidal systems composed of nanoparticles must be charge stabilized in order to prevent aggregation. In many applications of nanotechnology it is necessary to immobilize nanoparticles intact and dispersed on a substrate so that high-resolution imaging and characterization can be carried out. An essential first step in sample preparation therefore involves appropriately matching the zeta potential of nanoparticles in solution to the zeta potential of the substrate surface and adjusting the pH and ionic strength of the solution environment. Here we report a method for preparing patterned substrates with regions of optimally tuned surface zeta potential by combining fluid scanning probe microscopy and a recently reported surface zeta potential apparatus [P. J. Sides et al., Langmuir 22 (2006) 9765]. Specifically, we vary the zeta potential of a poly-L-lysine substrate over a range of approximately -60 mV $< \zeta < +$ 100 mV by exposure to UV/ozone and control nanoparticle adsorption from effectively zero to full monolayer coverage. Exposure through a mask produces local regions with positive and negative surface charge resulting in selective adsorption of nanoparticles. We demonstrate attachment, followed by particle size distribution, and zeta potential measurements, for hard and soft nanoparticles including 10- to 80-nm diameter gold nanoparticles and 30- to 80-nm diameter liposomes.

BI-ThP12 Chemical Characterization of Taq DNA Polymerase Adsorption on Different Surfaces, ***R. Canteri***, *R. Dell'Anna, S. Forti, L. Lunelli, L. Pasquardini, L. Vanzetti, M. Anderle, C. Pederzolli*, Fondazione Bruno Kessler-irst - Italy

PCR (polymerase chain reaction) represents the most widely used method for amplification of defined DNA sequences in medical and biological applications. The most recent innovative technologies are based on PCR reaction miniaturization. In fact, reductions in reagent consumption lower costs and increase scalability, enabling genome-wide approaches. Due to the increased surface-to-volume ratio of microchip PCR, a crucial role is played by the internal surface. Effects related to the non specific surface adsorption of PCR reagents (e.g. the replicating enzyme DNA polymerase) become significant and may reduce the efficiency of DNA amplification. In this study we investigate the Taq (Thermus aquaticus) DNA polymerase adsorption on different material surfaces, namely silicon (with different deposited oxide layer), pyrex glass, chromium nitride, cyclic olefin co-polymer (COC), polycarbonate (PC), poly(methyl methacrylate) (PMMA), and polydimethysiloxane (PDMS) surface. We carry out analyses via time of flight secondary ion mass spectrometry (ToF-SIMS), providing a physical-chemical surface picture, and via immunofluorescence by using anti-Taq DNA polymerase monoclonal antibody, giving the surface distribution and the amount of the protein. By combining these different techniques a deeper insight into the mechanisms governing the non specific surface adsorption of PCR reagents is possible.[1]

[1] This work was accomplished in the framework of LaTEMAR (Laboratorio di Tecnologie Elettrobiochimiche Miniaturizzate per l'Analisi e la Ricerca - Laboratory of Miniaturized Electrobiochemical Technologies for Analysis and Research), Centre of Excellence funded by MIUR (Italian Ministry for Education, University and Research) grants - FIRB 2003-2004 - for public/private structures involved in research fields characterized by strategic value.

BI-ThP13 Surface Chemical and Geometric Determination of Neuronal Migration on Patterned Surfaces, ***W. Wang***, *A. Natarajan, P. Molnar, S. Lambert, M. Das, M. Stancescu, N. Bhargava, J.J. Hickman*, University of Central Florida

Highly organized neuronal networks exist in the brain and are formed by appropriate neuron migration during the developmental stage. In vitro, engineering the appropriate neuron migration pathways and controlling the destination of single migrating neurons has been a challenge due to the insufficient understanding of integrated physiochemical mechanisms that regulate this process. In this work, we show that with controlled surface chemistry and proper design of pattern geometry of the substrate, single neuron migration pathways and destinations can be controlled. However, more importantly, the mechanism of this migration of how the neuron populations respond to the different surface chemistry and pattern geometry has been investigated by time lapse morphological analysis. We recorded the dynamic neuron migration that occurs during the formation of patterned two-neuron circuits using embryonic hippocampal neurons, where the somal adhesion sites, axon and dendrites outgrowth pathways are precisely determined. The cellular patterns were maintained in a defined serum free culture medium. Substrate surfaces were modified with self-assembled monolayers and patterns formed by laser ablation through a quartz photo mask. The surface chemistry was analyzed utilizing X-ray photoelectron spectroscopy and contact angle measurements. The patterns were visualized by metal deposition and optical profilometry. The neurons were characterized by static and dynamic morphological analysis and immunocytochemistry. Synaptic connections were determined by dual-patch clamp electrophysiology. The neurons were observed to migrate to designed somal adhesion sites by leading edge extension along the designed neurite pathways using a previously unknown process. After soma attachment, axon and dendrite outgrowth then continued along the designed pathways. This result will contribute to the methods of designing neuron network formation in culture, for the study of neuron migration in vitro and sensor design and fabrication.

BI-ThP14 Surface Characterisation and Biological Response of Enzymatically Tailored, Surface-Coupled Polysaccharides Pectic Hairy Regions*, ***G. Ceccone**, D. Gilliland, I. Liakos, F. Rossi,* EC-JRC-IHCP, Italy, *M. Morra, C. Cassinelli, G. Cascardo,* Nobil-Bio-Ricerche, Italy, *C. Della Volpe,* University of Trento, Italy, *R. Verhoef, H. Schols*, University of Wageningen, The Netherlands

The exploitation of the bio-active properties of polysaccharides covalently linked to materials surfaces is a rapidly growing area of biomaterials surface science. Recent findings on bioactivity of plant carbohydrate polymers are spurring an activity of biomolecular scouting and suggest that pectic polysaccharides are promising flexible molecules for novel bioactive surfaces. In this work we have investigated the properties of surface linked pectic rhamnogalacturonans(RG-I) fractions(MHRs) obtained by commercial enzyme preparations of homogenized vegetable tissue. MHRs were covalently linked to different substrates, namely polystyrene(PS), Titanium(Ti) and polycarbonates(PC) surfaces aminated by glow discharge plasma and analysed by XPS, ToF-SIMS, AFM, and contact angle measurement. Cell adhesion experiments using L-929 fibroblasts and Aortic Smooth Muscle cells(SMC) were performed to evaluate the effect of the MHRs nature on cell adhesion. Moreover, cells growth and specific alkaline phosphatase (ALP) activity of osteoblast-like SaOS2 cells were also measured. Surface analyses of different samples indicate that coupling of MHRs polysaccharides was successful for all substrates. XPS analysis of plasma amminated PS shows significant amount of N (13at%) related to the presence of amino groups. After MHRs coupling, strong increase of O/C ratio is detected, whilst nitrogen signal is still present indicating that the thickness of MHR layer is below the XPS sampling depth(<10nm).ToF-SIMS analysis supports the XPS data: amminated surfaces present CxHyN peaks expected in allylamine-like films, whilst large fragments peaks (m/z>250amu) are observed both on parent and on surface-coupled polysaccharides.AFM force-separation curves show that immobilization of MHRs significantly affects the interfacial forces with the absence of any attractive interaction until repulsive contact is reached. Results of cells experiments reveal that the structure of the immobilized MHRs (long vs short hair) has great influence on adhesion, morphology and cells enzymatic activity. In particular the long-haired MHRs are found less adhesive. Interestingly, specific ALP activity of the modified surfaces is upregulated respect to that of the control, suggesting that MHRs coated surfaces present interfacial properties suitable for osteoblast differentiation.

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BI-ThP15 Optically Responsive Nano-Composite Layers for Quantitative Label-Free Detection of Biospecific Interactions, *P. Buecker, E. Trileva, M. Himmelhaus, **R. Dahint***, University of Heidelberg, Germany

In a recent paper,[1] we presented a novel way of preparing densely packed, metal coated nanoparticle films for the label-free detection of binding events. The layer system is composed of dielectric nanoparticles, which are adsorbed onto a plain gold surface and subsequently metallized by deposition of gold colloid prior to electroless plating. Upon reflection of white light, the layers exhibit pronounced extinction peaks which shift to higher wavelengths when molecules adsorb onto the surface. For the same concentration and incubation time of octadecanethiol, an about fivefold higher red-shift of the extinction maximum was observed than reported for conventional surface plasmon resonance (SPR).[2] However, as no quantitative information existed on the amount of adsorbed molecules, which may be different for our nanoparticle layers and the plain gold surfaces used in standard SPR, no clear decision could be made regarding their sensitivity towards adsorbate layer thickness or mass density. Thus, the goal of the present study was to accurately determine the mass sensitivity of the nano-composite films in order to facilitate quantitative studies of binding events. For this purpose, self-assembled monolayers of simple and ethylene glycol terminated alkanethiols with various chain lengths were prepared on the nanoparticle coated substrates. The measured red-shift of the extinction spectrum upon molecule adsorption was related to the thickness and mass density of the films as determined by X-ray photoelectron spectroscopy. Special attention was paid to the question whether sensitivity decreases with increasing film thickness, as this could limit the use of the nanoparticle layers for biosensing applications, which often involve the detection of high molecular weight molecules. Experiments on antigen/antibody interactions show that the sensitivity factors determined for thin organic films can also be used to quantify the amount of surface bound protein in immunoreactions.

[1] R. Dahint, E. Trileva, H. Acunman, U. Konrad, M. Zimmer, V. Stadler, M. Himmelhaus, Biosensors & Bioelectronics, in press.

[2] L. S. Jung, C. T. Campbell, J. Phys. Chem. B 2000, 104, 11168-11178.

BI-ThP16 Synthesis Biocompatible Gold Nanorods, *S. Reed, **B. Ayres***, Portland State University

The ability to tune the optical properties of metal nanoparticles by changing their size and shape make them an ideal and diverse tool for biomedical applications. Challenges remain to utilizing nanomaterials for in vivo medical applications. By selecting benign compounds as synthons for nanoparticles it is predicted that toxicity can be greatly reduced. Furthermore, the resulting synthetic waste can be minimized and the process made more environmentally friendly and safe. We report nanoparticle-liposome composite materials that are stable, water soluble, and anticipated to be benign. Specifically, soy lecithin has recently been used to synthesize particles with these characteristics. These lipids are a cheap, readily available and non-toxic ligand for the synthesis of gold particles. Soy lipids form liposomes that function as nanoreactors in which particles form. We aim to change the shape and size of particles by manipulating these nanoreactors allowing for tuning of their optical properties. The optical applications of gold nanoparticles are of particular interest. Design of particles with a particular shape and size are desirable for use in vivo. Rod shaped nanoparticles absorb near infrared light that penetrates into deep tissue and presents a unique possibility to locate and treat maladies non-invasively. Using soy lecithin as a ligand, particles of a uniform size distribution can be created with reproducible results. Soy components have also shown promise for shape control of particles. Using these naturally occurring ligands, a series of gold nanoparticles have been synthesized and characterized. The resulting nanoparticles are stable for long periods with little aggregation. UV-Visible spectroscopy and transmission electron microscopy have been used to characterize size and shape of the resulting nanoparticles. It is believed a plethora of components contained in soy could also play a role in particle synthesis. We have isolated a small number of these compounds and identified them using NMR and mass spectrometry. Active components have been identified which contain linoleate tails. Ethyl linoleate has been positively identified and its ability to effect the shape of the gold nanoparticles is under study. Synthetic ethyl linoleate is being used in parallel with ethyl linoleate recovered from the soy lecithin to reveal its role in shape control of the nanoparticles as well as the rate of reaction in particle synthesis.

BI-ThP17 Surface Plasmon Resonance Microscopy Combined with a Novel Microfluidic System for High-Throughput Immunoassays, *J. Liu, M.A. Eddings, B.K. Gale, **J.S. Shumaker-Parry***, University of Utah

Surface plasmon resonance (SPR) microscopy provides quantitative, real-time information about adsorption and desorption on an SPR-active sensor surface with high spatial resolution. Label-free, high-throughput analysis of biomolecule interactions is made possible by combining patterned biomolecule immobilization with SPR microscopy. Typically, the biomolecules are immobilized ex situ using a pin-based microspotting device with many parameters that must be well-controlled in order to create an active and reliable sensor surface. We demonstrate the combination of a high-throughput microfluidic device with SPR microscopy for quantitative, in situ antibody immobilization. The microfluidic device provides 48 separate flow channels that can be used simultaneously for antibody immobilization and subsequent antibody-antigen interaction analysis. Because the biomolecules can be immobilized in situ, exposure to harsh environments can be avoided, a major benefit for protein immobilization. In addition, the biomolecule immobilization process can be monitored in real time by SPR microscopy and characterized quantitatively. Applications in immunoassay development for studying patient immunogenic response to antibody-based drugs will be described.

BI-ThP18 Characterization of Plasma Polymerized Immunosensor by XPS, SPR and ToF-SIMS, ***E.N. Newman**, F. Cheng, L.J. Gamble, K. Bomsztyk, D.G. Castner*, University of Washington

Surface treatment of polypropylene with plasma polymerized acrylic acid (PPAA) has been used to fabricate an immunosensor. This study examines both the amount and the bioactivity of the immobilized antibody. A comparison of PPAA - based strategy to the traditional coupling chemistry onto self-assembled monolayers was done using X-ray photoelectron spectroscopy (XPS) and surface plasmon resonance (SPR). XPS results for the PPAA surfaces indicate that 1) PPAA can be deposited onto various substrates (e.g., polypropylene, Si wafer and gold), 2) ~ 50% of the low-power, deposited PPAA film dissolves after soaking overnight in water, and 3) the N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide / N-hydroxysuccinimide method activates carboxyl groups at PPAA surface and allows proteins to be coupled to it. SPR provides a quantitative comparison of the amount of anti-ferritin immobilized by two strategies and the amount of ferritin the immobilized anti-ferritin binds. In addition, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to investigate the structure of the PPAA surface as well as the structure of the immobilized anti-ferritin. Our results suggest that the PPAA - based strategy improves the biological activity and stability of the immobilized antibodies.

BI-ThP19 Label-free Plasmonic Detection of Biomolecular Binding by a Single Gold Nanorod, ***G.J. Nusz****, S.M. Marinakos, A.C. Curry,* Duke University*, A.B. Dahlin, F. Hook,* Lund University, Sweden*, A. Wax, A. Chilkoti*, Duke University

We report the use of isolated gold nanorods as plasmonic transducers to detect the binding of streptavidin to biotin-conjugated nanorods on a surface in real time by tracking the wavelength shift of their resonant scattering spectrum using a darkfield microspectroscopy system. The limit-of-detection of streptavidin binding by a single biotinylated nanorod is 1 nM. An analytical model is presented that provides a rational framework from which optimal nanoparticle geometries can be predetermined for a specified detection experiment. In addition, the model provides a method for quantifying the number of molecules bound to the nanorod surface based on the resonant wavelength shift. Signal saturation occurs upon the binding of approximately 700 streptavidin molecules to the surface of gold nanorods that are immobilized on a glass substrate, with a detection limit of approximately 40 protein molecules per nanorod. The limits of molecular detection that can be theoretically achieved by a single nanorod are discussed as well as the prospects of detection of single receptor-analyte binding events in real-time.

BI-ThP20 Preparation of High Resolution SPR Imaging Microarray Using Polymeric Micropatterns, *J. Jung,* Seoul National University, Korea*, J. Yuk, K. Ha,* Kangwon National University, Korea*,* ***J. Hyun***, Seoul National University, Korea

In this paper, we demonstrate a simple method to fabricate SPR imaging microarrays using polymer micropatterns. The use of thick polymeric micropatterns in imaging SPR microarray passivates the region by removing SPR signals completely or by saturating the SPR signal far beyond the detection range in SPR imaging. Two schemes to create polymeric micropatterns on the surface were demonstrated by micropatterning a thick insulating layer before depositing a metal layer or after depositing a metal layer. A biotin-streptavidin system was successfully performed to verify the systematic binding of biomolecules and the adsorption of cell culture media on the microarrays was quantitatively characterized. This SPR microarray can be applied in a variety of areas including protein adsorption, cell research, diagnosis of diseases, and more.

BI-ThP21 Development of Metal Polymer Based Hybrid Micro Channel Network in bio-MEMS, *M. Dhayal, R.R. Pandey, S.C. Jain,* ***K.K. Saini***, National Physics Laboratory, India

In this paper development of cost effective polymeric material based micro devices using soft lithography techniques had been discussed. This includes polymer based micro fluidic devices for bioengineering applications to study the self-assembly of bio-molecules in bio-MEMS. We had investigated the effects of diffusing transition metals into soft polymer based micro channel network (MCN) to control the surface charge and chemistry. These inorganic coatings and metal particle diffused into the MCN has been derivatised with various organic functionalities. This process can lead to novel characteristics of these devices for different bioengineering applications including bio-molecules separation and controlled electro osmotic mobility.

BI-ThP22 Fabrication of Micron-sized Retroreflectors, ***T. Sherlock****, S.M. Kemper, P. Ruchhoeft,* University of Houston*, R.L. Atmar,* Baylor College of Medicine*, R.C. Willson*, University of Houston

We have fabricated micron-sized retroreflectors (structures that return incident light directly back to the source) and have shown that they are extremely bright and detectable over a large range of angles when inspected with a simple optical microscope. These retroreflectors are part of an ultra-sensitive detector platform for sensing small quantities of virus particles, bacteria, DNA, RNA, or any variety of molecules of interest. In particular, we are targeting our first generation sensor to detect Norwalk virus particles. In this proposed system, the base of the retroreflector is decorated with antibodies to the virus, and, if present, the virus particles are captured by this surface. After capture, gold nanoparticles, coated with a secondary antibody, are introduced into the system, attach to the virus, and drastically reduce the retroreflector brightness with a specific, well-understood spectral signature. If no virus is present, the reflectivity is unaffected. We have measured the reflectivity versus 40nm diameter gold nanoparticle surface density and have found a 40% reduction in signal for 100 nanoparticles per square micron when illuminated with broad-band light. The base of the retroreflector is about 4 square microns in size, yielding a detection sensitivity of hundreds of particles. Further optimization of particle size and illumination wavelength is expected to increase this sensitivity substantially. Retroreflectors are fabricated by coating a silicon wafer with 2.5 microns of polyimide and 200nm of resist. A lithography step is used to generate the retroreflector pattern as openings in the resist and a 50nm thick nickel coating is deposited using thermal evaporation. After a lift-off step, which leaves behind only the nickel that coated the base of the resist openings, the patterns are transferred into the polyimide in an O_2/CF_4 reactive ion etch, leaving the retroreflecting structure with very straight relatively smooth walls. Next, gold is evaporated to coat the base of the structure and a directional evaporation step is used to cover all but the sensor base with aluminum. The gold is selectively functionalized with amine-reactive thiol molecules which serve as a platform for attaching antibodies, oligonucleotides, or other detector molecules.

BI-ThP23 Patterning Live Bacterial Cells for Biological Applications, *Z.Y. Suo,* ***R. Avci****, P. Rugheimer, X.H. Yang, Y. Idzerda, D.W. Pascual*, Montana State University

The immobilization of live bacterial cells in a controlled fashion in well-defined patterns will have many applications in biosensors, and in biomedical and fundamental biological studies. The surface antigens, fimbriae and flagella of Salmonella typhimurium and Escherichia coli and corresponding antibodies were used to demonstrate the immobilization of live bacteria in well-defined patterns. The leashing of live bacterial cells was achieved on antibody-modified substrates of gold, silicon and glass. The tendency of bacterial cells to remain adhered (leashed) only to the antibody-modified areas was used to fabricate microarray patterns whose size can be controlled down to a micron scale. Patterns are generated with either a focused ion beam milling system or a microplotter. Cells patterned in this way retain their viability for at least six hours in a PBS buffer solution and are capable of regeneration if incubated in a growth medium. These microarray patterns can serve as prototype sensors which are able to capture targeted pathogens including bacteria, virus and proteins. For example, we have already demonstrated the use of such microarrays as a bacterial sorting system, in which a pre-targeted bacterial strain is captured and isolated from a mixed culture of microorganisms. The technique offers a reliable approach for fundamental microbiological research on the behavior of bacteria in an immobilized mode, as microorganisms respond to environ¬mental changes. For example, we observed that individual S. typhimurium cells gradually adjust their orientation from a "lying down" to a "standing up" position during regeneration, presumably trying to leave their position in search of more food. In such a struggle, immobilized cells produce a larger number of flagella as compared with planktonic cells, as confirmed by SEM and AFM studies.

BI-ThP24 A Bio-MEMS Device for Measuring Contractile Forces of Cultured Myotubes on Microfabricated Cantilevers, ***K.A. Wilson****, M. Das, P. Molnar,* University of Central Florida*, K.J. Wahl, R.J. Colton,* U.S. Naval Research Laboratory*, J.J. Hickman*, University of Central Florida

The boom in the semiconductor manufacturing industry of the past three decades has yielded a vast array of techniques for fabricating devices with micro to nano-scale features. Concomitantly, advances in biotechnology have opened new avenues for the application of these technologies in the form of gene and protein arrays, lab-on-a-chip devices and biological micro-electromechanical systems (Bio-MEMS). To date, application of these technologies has largely focused on the study of biomolecules and single cells or cell types. However, these technologies also hold great promise for the study of complex cellular and tissue interactions that are of critical importance when developing new drug therapies for disease and catastrophic injury. A tissue type of broad interest with regard to drug development and basic cell biology is skeletal muscle, which is affected by a variety of pathological conditions such as Parkinson's, ALS, and muscular dystrophy. For this reason we have developed a Bio-MEMS device based on microfabricated silicon cantilevers for the controlled, real-time interrogation of embryonic rat myotubes as a high-throughput test bed for drug discovery and basic science. The cantilevers were fabricated using standard photolithographic and micromachining techniques. The surfaces of the cantilevers were then modified using an amine-terminated alkylsilane SAM (DETA) to improve cellular adhesion, growth and differentiation. Dissociated embryonic rat myocytes were cultured for 7-10 days in a defined serum-free medium until contractile myotubes had formed. Monitoring and interrogation of the myotubes was accomplished using an AFM detection system of our own design, which consisted of a microscope, photodiode laser, position sensitive detector, field stimulation chamber, and a computer with data acquisition and analysis software. This simple system allows the real-time, high-throughput analysis of the physiological properties of the contracting myotubes. With this system we have shown the ability to selectively control the frequency and magnitude of myotube contraction as well as induce and observe physiological phenomena such as tetanus and fatigue. Contraction forces were calculated using a modified Stoney's equation for bending of a cantilever due to thin film stress. Ongoing work will allow the selective patterning and co-culture of neuronal cell types with myotubes for studying the neuromuscular junction and in vitro biological circuits.

BI-ThP25 Surface Modification and Photolithographic Patterning of Microelectrode Arrays for Cell-Based Biosensor Applications*, **A. Natarajan, N. Bhargava, P. Molnar, M. Das, J.J. Hickman*, University of Central Florida

A major research area in the field of cell-based biosensors and pharmaceutical testing is the development of functional cell-based networks and their integration with silicon-based platforms. The development of a hybrid cell-electrode system could also aid in understanding neuronal circuits, cardiac physiology and function, and the interactions between these cells. Using surface chemistry, we have developed a technique to first modify the surface of commercially available microelectrode arrays and glass using self-assembled monolayers (SAM). This is done using a cell-adhesive SAM like trimethoxysilylpropyldiethylene-triamine (DETA). Patterns are then made on the microelectrode arrays using a photolithography based method with a quartz mask that defines and guides neuron attachment and development. The patterned surface is then backfilled with an appropriate cell-repulsive SAM like perfluoroalkyltrichlorosilane (13F). The surfaces have been characterized by both X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements. Dissociated Embryonic hippocampal cells, in a serum-free medium, were cultured on these patterned microelectrode arrays in order to create neuronal networks with directed synaptic connectivity. The cells were characterized by morphological analysis as well as immunocytochemistry. The functionality of these networks was further studied using long term recording of the electrical activity of these cells in the presence and absence of toxins. We will report on the characterization of these devices as well as the methods developed for toxin detection and elucidation using these devices. We have also developed a technique to look at myocardial tissue function by manipulating surface chemistry in order to pattern and guide the growth of actively beating monolayers of neonatal rat cardiomyocytes on glass. These devices have also been characterized for their response to toxins and its effect on cardiac physiology. These hybrid systems are being used to further study basic neuronal networks and cardiac physiology properties like functional reentry. More importantly the devices are being applied to study toxic effects in pharmacological evaluation and to study disease models like Arrhythmia.

Electronic Materials and Processing

Room: 4C - Session EM-ThP

Electronic Materials and Processing Poster Session

EM-ThP1 Electrical Characteristics of Aluminum Oxide Films Deposited by Spray Pyrolysis in the Presence of Ammonia*, S. Carmona, M. Aguilar-Frutis,* CICATA-IPN, Mexico*, M. Garcia-Hipolito, J. Guzman,* IIM-UNAM, Mexico*,* ***C. Falcony***, CINVESTAV-IPN, Mexico

Aluminum oxide films deposited by ultrasomic spray pyrolysis in the presence of a mist of H2O-NH4OH show an improvement of the overall electrical characteristics. The films were deposited on (100) silicon wafers at temperatures in the range of 400 to 550 °C. Films 200 to 300 Å thick incorporated in a metal-oxide-semiconductor structure present dielectric constants of 8, interface densities of the order of 5x1010 1/eV-cm2 at midgap and a dielectric strength higher than 2MV/cm for samples deposited at 550°C. The average surface roughness for these films was of the order of 10 Å and the refraction index of about 1.6. Also the IR-transmittance spectra of these films suggest the presence of a silicon oxide interlayer for deposition temperatures above 500 °C.

EM-ThP2 The Influence of Si Content on the Work Function of WSi_x Gate Electrode*,* ***C.M. Lin****, J.-S. Chen*, National Cheng Kung University, Taiwan

Metallic gate electrodes (including metals, metal nitrides and metal silicides) are potential candidates desirable to replace the poly-Si gate electrode for reducing the gate depletion, gate resistance, and dopant penetration problems. In additional, threshold voltage modification is necessary to achieve high-performance NMOS and PMOS devices. Refractory metal silicides have received attention for decades in MOS technology. Among the various metal silicides, tungsten silicide is of particular interest due to its low resistivity, good adhesion and high-temperature stability. The variation of nitrogen content in WN_x will lead to the change of work function of W was confirmed in our previous work. In this study, we try to tune the work function of tungsten by adding Si. The W:Si ratio of WSi_x is experimentally controlled. The microstructure and the C-V curves of the ($WSi_x/SiO_2/Si$) MOS structure are measured. The work function of WSi_x films is extracted from the plot of flatband voltage versus SiO_2 thickness. For W and $WSi_{0.56}$ films, the work functions are 4.67 and 4.78 V, respectively. The correlation between work function and the materials characteristics of WSi_x films will be discussed.

EM-ThP3 Reduction of Defects at the SiO_2/SiC Interface by MeV Electron Beam Irradiation*,* ***C. Jeon****, J.H. Nam, W. Song, D.H. Oh, J.R. Ahn, C.-Y. Park,* Sungkyunkwan University, Republic of Korea*, M.-C. Jung, H.J. Shin,* Pohang Accelerator Laboratory, Republic of Korea*, Y.H. Han, B.C. Lee*, Korea Atomic Energy Research Institute, Republic of Korea

Among wide-band gap semiconductors, SiC has attracted interests in part because a stable native oxide SiO_2 can be grown only on SiC. However, metal-oxide-semiconductor field effect transistors (MOSFETs) based on SiC have shown lower electric performance than expected from bulk SiC properties.[1] The low electrical performance has been known to be related to defects at the SiO_2/SiC interface. The defects produce fixed charges and interface trap states lowering electric performance. Several experiments using x-ray photoelectron spectroscopy have shown that the defects are Si suboxides (Si^{3+}, Si^{2+}, and Si^{1+}) and Si oxycarbides (Si-C-O).[2,3] Therefore, the reduction of defect density at the SiO_2/SiC interface is one of crucial issues for device applications of the promising wide-band gap SiC. In this study, 1 MeV electron beam was irradiated on a SiO_2/SiC wafer at room temperature and ambient condition to reduce the defect density at a SiO_2/SiC interface, where a native SiO_2 film with a thickness below 1 nm was naturally grown on a 6H-SiC(0001) wafer in air. The effect of the irradiation on the SiO_2/SiC interface was investigated schematically by using synchrotron radiation scanning photoelectron microscopy with various incident photon energies (hν's). This makes it possible to measure spatially-resolved core-level spectra along directions parallel and perpendicular to a surface. Spatially-resolved Si 2p spectra show that 1 MeV electron beam irradiation reduces inevitable defects, Si suboxides (Si^{3+}, Si^{2+}, and Si^{1+}) and Si oxycarbides (Si-O-C), at the SiO_2/SiC interface with an ultrathin SiO_2 film leaving an abrupt SiO_2/SiC interface. It is meaningful that the defect reduction by the irradiation succeeds at room temperature and ambient condition. Therefore, MeV electron beam irradiation is a promising method in producing a high quality SiO_2 and an abrupt SiO_2/SiC interface.

EM-ThP4 Study on Characteristics of ZnO Thin Film by Chemical Mechanical Polishing*,* ***G.-W. Choi****, W.-S. Lee, S.-W. Park,* Chosun University, Korea*, Y.-J. Seo,* Daebul University, Korea*, Y.-K. Lee*, Chosun University, Korea

As a semiconductor material, ZnO has many useful properties such as excellent trasmittance for visible light, very high piezoelectricity and high gas sensitivity. Such properties make them well suited for the realization of many optoelectronic applications including transparent conductive oxides in display devices and solar cells, photodetectors, and transparent thin film transistors. In this paper, The electrical and the optical properties were investigated to find the optimum microstructure of ZnO thin films deposited by RF magnetron sputtering. To achieve high transmittance and low resistivity, we examined the various film deposition conditions such as deposition time, working pressure, annealing temperature, and substrate temperature. Then, electric characteristics, transmittance and surface roughness of ZnO thin films were measured by Hall effect measurement, UV-VIS spectrometer and AFM. Next, in order to improve the surface quality of ZnO thin film, we performed the chemical mechanical polishing (CMP) by change of process parameters, and compared the electrical and optical properties of the polished ZnO thin film. The thickness of ZnO films was measured by a-step. The spectral transmittance of ZnO thin films was measured in the wavelength range 200-900 nm by a UV-VIS spectrometer. This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

EM-ThP5 Characterizations of Zn(1-x)Mn(x)O Thin Film Grown by Pulsed Laser Deposition*,* ***D.-R. Liu****, C.-Y. Su*, National Applied Research Laboratories, Taiwan

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnMnO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, the

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Zn(1-x)Mn(x)O ($0.04 < x < 0.30$) thin films were grown on sapphire(0001) substrates by Nd:YAG pulsed laser deposition(PLD). The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR). Atomic force microscopy (AFM) and magnetic force microscopy (MFM) were employed to characterize the surface properties of these films. The high-resolution x-ray diffraction was used to evaluate the crystal quality of the films. The magnetic properties of the ZnMnO thin films were measured by a superconducting quantum interference device (SQUID) magnetometer. Photoluminescence (PL) spectroscopy and ellipsometer were used to characterize the optical properties. The results show that oxygen is very important for the properties of ZnMnO thin films.

EM-ThP6 Effect of Buffer Layer on InN Films Grown by UHV RF-MOMBE

W.C. Chen, C.-C. Kei, H.C. Pan, National Applied Research Laboratories, Taiwan*, S.Y. Kuo,* Chang Gung University, Taiwan*, J.S. Chen, **C.N. Hsiao***, National Applied Research Laboratories, Taiwan

InN nitride films were grown by using a metal-organic molecular beam epitaxy system. Trimethyl-indium and RF radical nitrogen were used as group III and V sources, respectively. Ga-doped ZnO and AlN buffer layers were used to improve the film quality of InN on silicon substrate. The growth rate of InN film can reach 25nm/min by using the Ga-doped ZnO buffer layer. According to X-ray diffraction and field emission transmission electron microscope results, the InN films are polycrystalline wurtzite with (0002) preferred orientation. Compared with the AlN buffer, the Ga-doped ZnO film can improve the film quality of InN. Photoluminescene result suggests that the band gap of InN film is around 0.65eV. Hall effect measurement reveals that the sheet carrier concentrations of InN film is 5 × 1017 cm-2. The growth kinetic of InN films could be controlled by adjusting the III/V ratio, RF plasma power and growth temperature.

EM-ThP7 Preparation and Characterization of HfO_2 Thin Films Prepared by Atomic Layer Deposition on Silicon

***K.T. Kim**, G.H. Kim, J.C. Woo, C.I. Kim*, Chungang University, Korea

In recent years, the continuous downward scaling of dynamic random access memory capacitors, requires exploitation of capacitive devices of advanced topology, i.e. stacked or trenched structures. In choosing the replacement high-k materials for SiO_2 for the transistor gate region several challenging factors should be taken into account such as: a) the dielectric-silicon interface quality and stability b) the relation between the dielectric constant and the energy level configurations (energy band gap) c) energy band offsets, which could lead to an increase in the leakage current d) defect density at the interface. Among the many possible candidate high-k (15-30) dielectric materials, HfO_2emerging as a promising gate dielectric material, due to its high dielectric constant and superior thermal stability on Si substrates. Moreover, the ALD (atomic layer deposition) method is preferred for obtaining these high quality high-k dielectric layers, because of its excellent thickness controllability and low thermal budget. In the present study, HfO_2 thin films were atomic layer deposited from the liquid hafnium precursor TEMA ($Hf[N(CH_3)(C_2H_5)]_4$) precursor and O_3 oxidation and were characterized using angle resolved X-ray photoelectron spectroscopy , scanning transmission electron micrscopy , and electron energy loss spectroscopy .

EM-ThP8 Characterization of Plasma Etching Induced Interface States at Ti/p-SiGe Schottky Contacts

M. Mamor, Sultan Qaboos University, Sultanat of Oman

SiGe/Si heterojunctions are particularly attractive in microelectronic and optoelectronic applications such as in heterojunction bipolar transistors, modudulated doped field effect transistors and infrared detectors. SiGe/Si heterostructures provide new possibilities to engineer the bandgap in a material compatible with mature Si technology and they are now widely used to release novel devices integrated with silicon-based circuits. Plasma etching is widely used in the semiconductor industry as it offers the capability of performing many processes in vacuum without exposing the semiconductor surface to the atmosphere. However, these plasma-etching techniques also result in lattice damage at and below the surface, which alters the electrical and optical properties of the etched semiconductor surface. We have used electrical measurements (DLTS) complemented by current-voltage (I-V) and capacitance-voltage (C-V) over a wide temperature range (100-300 K) at frequencies of 10-100KHz for assessment of the defects introduced in Si0.95Ge0.05 by argon plasma sputter etching. From DLTS, defect concentration depth profiling was extracted and revealed that the main defect introduced during argon plasma sputtering is located very close to the surface. I-V and C-V analysis shows that the electrical characteristics deviated from the ideal case and indicates the presence of lateral inhomogeneities of the barrier height, resulting from the plasma etching induced surface states at Ti/SiGe interface. From the low frequency and high frequency C-V plots, the interface states density and their energy distributions were extracted.

EM-ThP9 DC-to-RF Dispersion Effects in AlGaN/GaN HEMTs Operated Under High Stress

***P.B. Shah**, B. Huebschman, E. Viveiros, K. Kingkeo, A. Hung, K.A. Jones*, US Army Research Laboratory

Communication and radar applications place strong requirements for linearity, efficiency, gain and power handling capability on high power, high frequency AlGaN/GaN HEMT performance. In AlGaN/GaN HEMTs, the surface, interface and bulk traps have been identified as the cause of nanosecond and microsecond range drain-source current transients present during device turn-on and turn-off. These transients drain power from the source, degrade transmitted information, and affect system operating life. Therefore, it is important to understand the causes of these transients and to reduce their effects, through modeling, and characterization. We focus on physics based and emperical spice models because, once developed, these models will allow design and optimization of MMICs taking into account the transients. Both, unpassivated and AlGaN HEMTs passivated with Si3N4, and SiO2 are considered. The surface traps act as virtual gates, and to model them we are paralleling HEMT and FET models available in Agilent's ADS software with passive elements subcircuits. Adjusting the modulating pulse duty cycle, and gate and drain voltage biases have provided high-power / high-temperature operation data. Results indicate that although Si3N4 mitigates drain lag effects at low power levels , the transients still appear at higher operation power levels. Also, the transients are not as clearly related to pre- and post-kink regions on the I-V characteristics. The drain lag ratio (off state drain current overshoot value / drain current steady state value) increases with device heating due to large ID and large VDS (20V.) Furthermore, the slope of the drain current decay is also influenced by the gate bias present after the drain bias has returned to zero. Gate lag measurements on a number of AlGaN/GaN HEMTs indicate that the turn-on transient is much shorter (~35 ns) than the turn-off transient (~70 ns) and the drain-current waveform when the HEMT is switched on will have different profiles -- in some cases concave and other cases convex. Furthermore, only in some devices as the time interval with low gate bias (VGS = 0) increases, the drain current in the device's on-state increases, even if most of the turn-on pulse at the gate is applied while VDS = 0, due to carrier heating. With accurate modeling to match the DC I-V, gate lag and drain lag transients, and S-parameter device data, models were verified and used to reverse engineer the AlGaN/GaN HEMT.

EM-ThP10 Ohmic Contacts to n- and p-type GaN Based on TaN, TiN, and ZrN

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We examined the potential of transition metal nitrides as a diffusion barrier for Ti/Al-based Ohmic contacts to n-GaN and Ni/Au-based Ohmic contacts to p-GaN. The annealing temperature (600-1000°C) dependence of Ohmic contact characteristics using either Ti/Al/X/Ti/Au (n-Ohmics) or Ni/Au/X/Ti/Au (p-Ohmics) metallization schemes, where X is TaN, TiN, or ZrN, deposited by plasma-assisted sputtering were investigated by contact resistance and Auger Electron Spectroscopy (AES) measurements. For n-GaN ($n \sim 3x10^{17}$ cm^{-3}), the as-deposited contacts were rectifying and transitioned to Ohmic behavior for annealing at ≥600°C. A minimum specific contact resistivity of $\sim 6x10^{-5}\Omega.cm^{-2}$ was obtained after annealing over a broad range of temperatures (600-900°C for 60 secs), comparable to that achieved using a conventional Ti/Al/Pt/Au scheme on the same wafer. The contact morphology became considerably rougher at the high end of the annealing range. The long-term reliability of the contacts was also examined-each contact structure showed an increase in contact resistance by a factor of 3-4 over 24 days at 350°C in air. AES profiling showed that long-term aging had little effect on the nitride-based contact structure. For annealing temperatures greater than 500°C, the contacts to p-GaN ($p \sim 10^{17}$ cm^{-3}) displayed Ohmic characteristics and reached a minimum specific contacts resistance of about $2x10^{-4}\Omega.cm^2$ after annealing at 700°C for 60 s. The specific contact resistance was stable on annealing up to at least 1000°C. However, at high temperatures the morphology of the contacts became very rough and a large degree of intermixing between the metallic layers was observed. The thermal stability of these contacts were found to be superior as compared to conventional Ni/Au, which displayed poor characteristics at anneal temperatures greater than 500°C.

EM-ThP11 XPS and LEISS Study of GaAs Surface Preparation using Ammonium Hydroxide

*F.S. Aguirre-Tostado, **M. Milojevic**, S.J. McDonnell, R.M. Wallace*, University of Texas at Dallas

The use of high-mobility channel materials, such as GaAs and InGaAs in addition to high-κ dielectrics has attracted substantial interest as a means to maintain integrated circuit scaling and performance. For ultra-thin dielectric films, the quality of the high-κ/semiconductor interface plays a crucial role in determining the electrical properties of a device. GaAs surface preparation plays an important part in controlling the interfacial chemistry.[1] Previous photoemission studies[2,3] have examined the effects of etching GaAs with HCl, HF and NH4OH in a controlled atmosphere (argon,[2] nitrogen[3]). This paper examines the chemistry of the GaAs surface after a

NH 4OH-based cleaning procedure, without the use of a controlled atmosphere, for high-k dielectric deposition. In-situ anneals up to 450 ºC promote As-oxide dissociation resulting in the formation of Ga-oxide and As desorption. An in-situ bulk and interface study of sputter deposited $LaAlO_3$ on GaAs is also presented on this surface. This work is supported by the MARCO MSD Focus Center.

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EM-ThP12 Study on Scalability of MTJ Cells Using SPM, *S. Kim*, *K. Kim, I. Chung*, Sungkyunkwan University, Korea

We investigated various sizes of magnetic tunneling junction (MTJ) cells which are considered as an alternative nonvolatile storage due to its unique characteristics such as high speed, low operation voltage and high endurance. We studied switching field variations in terms of the sizes of sub-micron MTJ cells by measuring the I-V characteristics of MTJ cells and I-H loops, which was obtained by measuring the tunneling current with sweeping a magnetic field. In addition, We obtained magnetic domain images utilizing magnetic force microscope (MFM) for MTJ cells to understand the variation in I-H loop. We found that the switching field of the MTJ cell tends to increase as the size decreases due to the demagnetization field.

EM-ThP13 The Effect of Synthesis Methods on the Properties of ZnO:Ga Nanoparticle Ceramic Scintillators, *D.M. DeVito*, *B. Kensanli, B.L. Armstrong, J.O. Ramey, C.J. Rawn, J.Y. Howe,* Oak Ridge National Laboratory*, N. Giles,* West Virginia University*, L.A. Boatner, J.S. Neal*, Oak Ridge National Laboratory

A number of different radiation detection applications require scintillators with high light output, good attenuation power, low afterglow, and very fast decay times. Fast decay times are of primary importance in positron emission tomography (PET) and nuclear physics experiments. Zinc oxide doped with gallium is known for its fast scintillation properties (sub-nanosecond decay time) under a variety of excitation conditions (alpha, gamma, UV). The expanded development of synchrotron radiation for the investigation of advanced materials has only underscored the need for continued development. This work investigates the effect that synthesis method (urea precipitation, solution phase, combustion synthesis) has on gallium incorporation, particle size and distribution and resulting emission using a wide variety of analytical techniques.

EM-ThP14 Magnetic Field Dependent Electrical Properties of Vertically Grown Ni Single Nanowire, *A.-Y. Koo*, *H. Yang, C.J. Kang, Y.S. Kim,* Myongji University, Korea*, J.Y. Cho,* Korea University, South Korea*, Y.J. Choi,* Myongji University, Korea*, Y.K. Kim*, Korea University, South Korea

Magnetotransport of nickel nanowires has been widely investigated due to its potential application to magnetic memory devices. However, because of the difficulty to make a good electrical interconnects between single nanowire and metal pad, most magnetotransport studies have been performed on bundles of nanowires embedded in a template or a single nanowire with e-beam lithographically patterned metal contact. In order to overcome the averaged-out information of the bundles of nanowire and the complexity in patterning metal pads, we developed a novel and simple method to measure the magnetotransport properties of Ni single nanowire electrodeposited in an AAO template by adopting scanning probe microscopy technique. In addition to the magnetotransport properties, we studied the electrical properties of Ni single nanowire using the Electrostatic Force Microscopy (EFM) and Scanning Capacitance Microscopy (SCM). We will discuss the magnetic field dependent electrical property variation due to the crystallographic structure of Ni nanowire.

EM-ThP15 Photoluminescence Study of Silicon Nanoclusters Embedded in a SiO2 Matrix Deposited by Reactive Sputtering and Implanted with Si Ions, *J. Carrillo*, *G. Garcia,* Universidad Autonoma de Puebla, Mexico*, M. Melendez,* Centro de Investigación y Estudios Avanzados-IPN, Mexico*, W. Calleja*, Instituto Nacional de Astrofisica, Optica y Electronica, Mexico

The search for a luminescence material compatible with silicon-based integrated circuit processing technology is a need for optoelectronic applications, and has received great attention in recent years. The optical properties of silicon nanocrystals in SiO2 have been studied extensively since visible room temperature photoluminescence (PL) was first observed in such systems. Several models have been suggested in attemps to clarify the origins of the PL properties of indirect-gap group-IV semiconductor nanocrystals. For example, some researchers explain their results using a three-dimension quantum confinement model, while others believe that interface defects and emmiting centers are responsible for PL emission. In this paper, the dependence of silicon nanoclusters embedded in a Si-implanted SiO2 matrix deposited by reactive sputtering and after annealing is presented. Red photoluminescence has been observed at room temperature from deposited films and its intensity exhibits a strong dependence on the temperature and time of annealing. High - resolution transmission electron microscopy, Fourier transform infrared transmission spectra and PL results are used to discuss the emission mechanisms. We acknowledge the partial financial support of VIEP-BUAP through the project 06/EXC/06-G.

EM-ThP16 Particle Emission from Zinc Oxide during 193-nm Excimer Laser Irradiation[1], *E.H. Khan*, *S.C. Langford, J.T. Dickinson*, Washington State University

We report observations of particle and light emission from single crystal and anodic ZnO during pulsed 193-nm irradiation by quadrupole mass selected time-of-flight measurements and photoluminescence spectroscopy. The particle emissions in particular are relevant to thin film production by laser ablation deposition. At fluences between 50 and 600 mJ/cm^2, the only ion observed from single crystal ZnO at our level of sensitivity is Zn^+. The mean kinetic energy of 3.3 ± 1.6 eV is consistent with electrostatic ejection from defect sites with a net positive charge. Zinc ions absorbed on top of surface electron traps would experience a repulsive force when the underlying trap is photoionized. During prolonged irradiation, the Zn^+ intensity drops quickly, reflecting the depletion of surface defects by the emission process. Consistent with the radiation hardness of ZnO, single crystal remains transparent during prolonged irradiation. However, the sample photoluminescence evolves from greenish-blue, to deep blue, and to violet. At fluences above 600 mJ/cm^2, the Zn^+ intensities increase rapidly and other positive ions appear, including O^+ and O_2^+. Neutral O and O_2 appear, followed by neutral Zn at 775 mJ/cm^2. Analyses of the neutral time-of-flight distributions indicate effective surface temperatures near 600 K at 800 mJ/cm^2 and near 1100 K at 1.2 J/cm^2. These temperatures are well below the melting point of ZnO, suggesting that the observed neutral species are produced photochemically and desorb thermally. At these fluences, intense ion emissions persist for many thousands of laser pulses; defects consumed in the emission process are continuously replenished. Emissions from anodic black ZnO are similar to the emissions from single crystals except that comparable emission intensities are achieved at lower fluences for the black ZnO. Weak emissions are also observed from the native oxide on electropolished Zn plate.

[1] We thank Dr. L. Boatner of Oak Ridge National Laboratory for providing single crystal ZnO. This work is supported by the DOE grant DE-G03-02ER45988.

EM-ThP17 Pentacene TFTs with Ferroelectric Gate Insulators for Non-Volatile Memory Element, *W. Choi*, *S.H. Noh, J.M. Choi, D.K. Hwang, S. Im*, Yonsei University, Korea

Field effect transistors using ferroelectric materials as a gate insulator (FeFET) could be next generation-memory elements because of its attractive characteristics: non-volatile data retention, small size, non-destructive read-out, and fast programming speed. Recently, thin-film transistors (TFTs) with organic ferroelectric gate insulators have been studied since the fabrication of FeFET is possible at the low temperature compatible with glass substrates. While previous researches showed high performances in terms of good retentions and large hysteresis loop, they have some problems such as high programmable voltage (~100 V), a low mobility (~10^{-3} cm^2/V s). To overcome aforementioned drawbacks, we fabricated pentacene based FeFET with the gate insulator composed of stacking multi-layers. In this presentation, we report on the fabrication of pentacene thin-film transistor with a poly-4-vinylphenol (PVP)/ Poly(vinylidenefluoride/trifluoroethylene) (P(VDF/TrFE))/PVP triple-layer gate insulator. A triple-layer polymer gate insulator is deposited on an indium-tin oxide (ITO)/glass substrate by sequential spin-casting processes: 45 nm-thick PVP for a smoothing layer, 130 nm-thick P(VDF/TrFE) for a ferroelectric layer and 240 nm-thick PVP for a buffer layer. Each layer has own role for non-volatile memory thin file transistor. Our FeFET with the PVP/P(VDF/TrFE)/PVP triple layer exhibits a field effect mobility of 0.2 cm^2/V s at each memory state and ~15V threshold voltage shift in the transfer characteristics which originates from the polarization of the ferroelectric layer by 50V writing voltage. The retention time was measured for 10^4 second under constant read condition. More and advanced details will be discussed in coming presentation.

EM-ThP18 Flexible Organic Thin Film Transistor using Al_2O_3-PVP Nano-Composite Gate Dielectrics, *H.Y. Noh*, *Y.G. Seol, S.I. Kim, N.-E. Lee*, Sungkyunkwan University, Korea

Organic TFTs with low threshold voltage (V_T), low-leakage current, and high current on-off ratio are needed for various applications in flexible electronics. Employment of organic/inorganic nano-composite gate dielectrics may provide a low V_T and flexibility improvement in OTFT devices. For this purpose, the nano-composite gate dielectric layers composed of the PVP polymer matrix and alumina nano-particle filler were investigated in this work. Treatment of alumina nano-particles by a coupling agent was carried out for improved dispersion of the nano-particles and their chemical binding with the PVP matrix. Flexible organic thin film transistors were fabricated using pentacene semiconducting layer and electroplated nickel (Ni) gate electrode on flexible polyimide substrate. Electroplated gate electrode fabricated on the plasma-treated polyimide substrate also provides a good adhesion. PVP/Al_2O_3 nano-composite layer with different volume fractions was spin-coated. Pentacene and gold source-drain electrodes were thermally evaporated on the gate dielectric layer using a shadow mask in vacuum chamber. Leakage current of the nano-composite gate dielectric was reduced by two order magnitude compared to that of pure PVP layer for the same film thickness. Electrical measurements of the OTFT devices showed the electrical performance of a field-effect channel mobility of 0.94 cm^2 V^{-1}s^{-1}, an on/off current ratio of 10^5, a threshold voltage of -11.5V. Flexible tests indicated that the device with the nano-composite gate dielectric has the electrical performance superior to the device with pure PVP gate dielectric with repetitive cyclic bending.

EM-ThP19 Fabrication and Characterization of Pentacene Thin Film Transistor with a Polymer Insulator As Gate Dielectric*, C. Lee*, *K. Seo, J. Ko, J. Lee, I. Chung*, Sungkyunkwan University, Korea

Interfacial properties between semiconductor and insulator are critical to determine the performances of organic thin film transistors (OTFTs). In this study, we have fabricated OTFT with a back gate structure on the patterned pentacene active region. We studied the variation of electrical properties in terms of polyvinyl cinnamate (PVCN) which was used as a gate dielectric with different mole concentrations (6%, 7%, 8%). We investigated the leakage current behavior by obtaining topology and its current image simultaneously using scanning probe microscope (SPM). Also, we extracted the electrical properties such as mobility, threshold voltage VT and On/Off ratio from IDS-VDS, IDS-VGS characteristics of OTFTs.

EM-ThP20 Differentiating True Tunneling from Defect Dominated One, Using Current-Voltage Curve Fitting*, A. Vilan*, Weizmann Institute of Science, Israel

The shapes of current-voltage curves which originate from either true tunneling across the insulating film or from metallic shorts through the film (defects) are extremely similar.[1,2] While this problem is known since the 1960's,[3] there is yet no direct solution for it. An evidence for tunneling is received only by complementary observations such as characteristic vibronic features (IETS, molecules)[4] or magneto-resistance below T_c (superconductors).[2] The uncertainty regarding defect transport means that the nominal junction's geometry (namely contact area and insulator thickness) is not necessarily relevant. This motivated a search for a simplified modeling of charge transfer which avoids any prerequisite input parameters and relays solely on graphically extracted parameters. In my talk, I will show that the two popular, highly non-linear current-voltage (I-V) relations of inelastic tunneling (Simmons model[5]) and nonresonant super-exchange (Mujica-Ratner model[6]) can be reasonably approximated by simple cubic relations of two characteristic parameters: the equilibrium conductance (G_0) and the shape factor (ρ).[7] Both G_0 and ρ depend on barrier height and width while contact area contributes only to G_0. Therefore, correlating between G_0 and ρ is highly informative in evaluating the actual junction parameters. In case of defect dominated transport, the extracted contact area would be much smaller than the nominal one, providing a direct experimental indication for the quality of the junction. This approach can be extended also to the Fowler-Nordheim relations describing field emission at high bias range. The proposed analysis would be demonstrated on various experimental and simulated I-V's.

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EM-ThP21 Dye Doped Red Organic Light-emitting Diode*, L. Li*, China Aerospace and Technology Corporation No.513 Institute, China

Full color display is the goal of organic light-emitting diode(OLED), but the making of stable red organic light-emitting diodes is a great barrier in mass production of OLED and is also the most interesting study nowadays. Some red light-emitting diodes have been realized by doping a dye rubrene with different dopant concentrations in light-emitting layers, the configuration of devices is ITO/CuPc/NPB/Alq3:rubrene:DCJTB /Alq3/LiF/ Al, where NPB and Alq3 is used respectively as hole transport layer and electron transport layer. By using the theories of Forster and energy band, it is found that the main energy transfer mechanism in doped red OLED is not Forster energy-transfer but sequential carrier trapping mechanism, and rubrene can assist energy transfer from Alq3 to DCJTB more efficiently, which greatly improves the luminence efficiency and performances of devices.

EM-ThP22 Photoluminescence Characterization of Polythiophene Films Doped with Highly-Functional Molecules*, H. Kato*, *S. Takemura, H. Kobe, Y. Mori, Y. Matsuoka, Y. Watanabe, K. Shimada, T. Hiramatsu, N. Nanba, K. Matsui*, Kanto Gakuin University, Japan

Conducting polymer polythiopene (PT) films incorporated with highly-functional molecules such as copper phthalocyanine (CuPc), fullerene C60, rhodamine B and TCNQ was synthesized and characterized by photoluminescence measurements in order to fabricate organic optical hybrid materials. The electrochemical polymerization was performed in acetonitrile containing thiophene monomer and (Et)4NBF4 as a supporting electrolyte and the polymerization on an ITO substrate was conducted by applying positive voltage to the anode. The molecule was injected by electrochemical and diffusion methods. A photoluminescence emission peak was observed at 594 nm in the case of PT doped sample with CuPc by diffusion method. The emission peak was observed at 540 nm shifted to the lower wavelength in the case of electrochemically positive voltage applied sample after CuPc was diffused into the PT. Fourier transform infrared spectroscopy (FTIR) measurements suggested the partial deformation of the aromatic structure of CuPc and a polymer-CuPc linkage. Adding C60 molecules to the CuPc diffused PT sample by the diffusion method made the emission peak shift to the higher wavelength at 730 nm suggesting the molecular interaction between CuPc and C60 in the photoluminescence emission process because double emission peaks were observed at 590 and 735 nm in the case of single doping of C60. Double doping of C60 and CuPc in PT was also investigated by FTIR. In the case of single doping of C60, successive electrochemical process made the double emission peaks a single peak at 580 nm. The FTIR measurements suggested charged states of C60 or a polymer-C60 linkage. The present work clarified that the photoluminescence emission peak position varied and was controlled by electrochemically applying voltage or adding specific molecules. This work was supported by High-Tech Research Center Project aided by MEXT.

EM-ThP23 Effect of Water Immersion and Surface Compositional Profile of Photoacid Generator Molecules in Photoresist Materials*, S. Sambasivan*, *V.M. Prabhu, D.A Fischer*, National Institute of Standards and Technology, *L.K. Sundberg, R.D. Allen*, IBM Almaden Research Center

Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to quantify the surface composition and depth profiling in the top 2 to 6 nm range of photoacid generators (PAG) in thin film photoresist materials. By considering model compositional profiles, NEXAFS distinguishes the surface molar excess within the top 6 nm from the bulk. A surface enriched system, triphenylsulfonium perfluorooctanesulfonate (TPS-PFOS), is contrasted with a perfluorobutanesulfonate (TPS-PFBS) photoacid generator, which displays an appreciable surface profile within a 6 nm segregation length scale. A comparative study of the surface composition of PAG (TPS-PFOS, TPS-PFBS and TPS-Triflate) in photoresist system before and water immersion was monitored via NEXAFS. Results reveal that the loss of PAG occurs after the water immersion in all the three different PAG system examined. Detailed quantification of the PAG loss due to water immersion was seen to critically depend on the size of the PAG and its solubility in water. TPS-PFOS photoacid generator largest in size despite its least solubility in water showed the maximum loss after water immersion followed by TPS-PFBS and TPS-Triflate. These results, while applied to 193-nm photoresist materials, highlight a general approach to quantifying NEXAFS partial electron yield data and find application to immersion lithography fundamentals.

EM-ThP24 Improvement of Ferroelectric Properties of Pb(Zr,Ti)O3 Thin Film Capacitor Fabricated by Chemical Mechanical Polishing through Post Cleaning Process*, Y.-K. Jun*, *P.-G. Jung, P.-J. Ko,* Chosun University, Korea, *N.-H. Kim,* Sungkyunkwan University, Korea, *W.-S. Lee*, Chosun University, Korea

Chemical mechanical polishing (CMP) process was proposed to fabricate the ferroelectric Pb(Zr,Ti)O3 capacitor instead of plasma etching process for the vertical profile without plasma damage in our previous study. Our previous study showed that good removal rate with the excellent surface roughness compared to plasma etching process were obtained by CMP process for the patterning of Pb(Zr,Ti)O3 thin film. The post cleaning process was also one of the very important parameters influenced on ferroelectric properties of Pb(Zr,Ti)O3 thin film capacitor. The ferroelectric properties were degraded without post cleaning process. However, the optimized post cleaning process for Pb(Zr,Ti)O3 thin film was not reported. In this study, the effects on the degradation of Pb(Zr,Ti)O3 thin film capacitors of the contaminations such as slurry residues were investigated.

And the exclusive cleaning chemicals for Pb(Zr,Ti)O3 thin film were developed in this work. The improved ferroelectric properties of Pb(Zr,Ti)O3 thin film capacitor were obtained with the optimized post cleaning process after fabrication of Pb(Zr,Ti)O3 thin film capacitor by CMP process. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2006-005-J00902).

EM-ThP25 Pressure Damage to BLT Thin Film Capacitor Fabricated by Chemical Mechanical Polishing Process, ***P.-G. Jung**, Y.-K. Jun, S.-H. Shin, P.-J. Ko,* Chosun University, Korea*, N.-H. Kim,* Sungkyunkwan University, Republic of Korea*, W.-S. Lee*, Chosun University, Korea

BLT thin films have many advantages such as highly fatigue resistance, low processing temperature, and large remanent polarization for high-density ferroelectric memories. However, the problems by plasma etching in patterning process of BLT thin films such as the angled sidewall preventing the densification of ferroelectric memory and being apt to receive the plasma damage were reported. Chemical mechanical polishing (CMP) process was proposed to fabricate the ferroelectric capacitor instead of plasma etching process for the vertical profile without plasma damage. CMP characteristics were presented in E-MRS 2006 spring meeting. CMP characteristics such as the removal rate and WIWNU% were improved by the increase of CMP pressure; however, the ferroelectric properties including polarization-electric field (P-E) characteristics of BLT capacitor fabricated by CMP process with the highest CMP pressure condition were disappeared. Bi content of BLT thin film was rapidly decreased as the increase of CMP pressure surface analysis. This means that Bi was easily removed in high CMP pressure. Therefore, the CMP pressure was controlled in CMP process for BLT thin film capacitor although the removal rate of BLT thin film became lower. Ferroelectric properties of BLT thin film capacitor were recovered with the vertical sidewall without the plasma damage. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

EM-ThP26 A Study on the Electrochemical Reaction of Cu Electrode using Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) Method.*, **Y.-K. Lee**, S.-W. Park, S.-J. Han, G.-W. Choi,* Chosun University, Korea*, Y.-J. Seo,* Daebul University, Korea*, W.-S. Lee*, Chosun University, Korea

Chemical mechanical polishing (CMP) is the most commonly used planarization technique in semiconductor process for ULSI applications. As its name indicates, CMP process depending on the chemical interaction of the slurry with polishing wafer and mechanical down force applied to the wafer. Recently, the application of CMP has been especially popular in the fabrication of Copper damascene structures. However, the low-k materials at 65nm and below device structures because of fragile property, requires low down-pressure mechanical polishing for maintaining the structural integrity of under layer during their fabrication. Also, the problems faced by copper CMP process is the lower removal rate due to the low mechanical down force required by the low k dielectric and to reduce dishing and erosion. To solve these problems, in this paper, we studied electrochemical mechanical polishing (ECMP) as an epoch-making technology that uses electrical current and voltage for copper CMP process. In this experiment, 2 x 2 Cu disk of 99.99% pure was used as experimental samples in a standard two-electrode with Cu working electrode (WE), Pt counter electrode (CE). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) Method were plotted for each of the electrolyte (NaNO3) and concentration level. And then, we investigated that how this chemical affect the process of voltage induced material removal in ECMP of Copper. This work was supported by grant No. (R01-2006-000-11275-0) from the Basic Research Program of the Korea Science & Engineering Foundation and by Korea Research Foundation Grant (KRF-2006-005-J00902).

EM-ThP27 Voltage-Activated Electrochemical Reaction of Cu Electrode for Electrochemical Chemical Mechanical Polishing (ECMP) Application*, **S.-J. Han**, S.-W. Park, Y.-K. Lee, G.-W. Choi,* Chosun University, Korea*, Y.-J. Seo,* Daebul University, Korea*, W.-S. Lee*, Chosun University, Korea

The chemical mechanical polishing (CMP) process has been widely used to obtain global planarization of inter-metal dielectric (IMD) layers, inter-layer dielectric layers (ILD) and pre-metal dielectric (PMD) layers. Also, several semiconductor device and materials manufacturers have used this method. Especially, copper CMP has become an integral part of multilevel interconnection process. However, for the fabrication of 65nm and beyond technology nodes with fragile low k dielectric and copper, the down force of CMP process must be greatly reduced or eliminated to manage the low mechanical strength of low k film. To overcome these problems, we developed a new planarization technology that uses electrolyte chemistry instead of abrasive slurry. The current-voltage (I-V) curves were employed, in this paper, to evaluate the effect of electrolyte concentration on the reaction trend. From the I-V curve, the electrochemical states of active, passive, transient, and trans-passive could be characterized. The scanning electron microscopy (SEM) was used to observe the surface profile. The energy dispersive spectroscopy (EDS) spectrum was employed to analyze metallurgical components on the surface. From these analyses, it was important to understand the electrochemical mechanisms of the electrochemical chemical mechanical polishing (ECMP) technology. This work was supported by grant No. (R01-2006-000-11275-0) from the Basic Research Program of the Korea Science & Engineering Foundation and by Korea Research Foundation Grant (KRF-2006-005-J00902).

EM-ThP28 SEM Image Analysis and Resistance Measurements of Cu Via with Defects on a Test Wafer*, **S. Suzuki**, K. Umemura, T. Sunaoshi, Y. Nakano*, Hitachi High-Technologies Corporation, Japan

In LSI process, it is necessary for improvement of yield to inspect and analyze internal defects (e.g. void, etching-stop) of Cu interconnects after an electrical probing test. However, there are complicated and time-consuming procedures that consist of inspection of defects, samples making with focused ion beam (FIB) and cross section observation with scanning electron microscope (SEM). Therefore we have proposed more effective analysis system combined of SEM inspection and electrical probing equipment. This paper presents a relation between voltage contrast (VC) of SEM images and electrical resistance of via on a simple test wafer. The Via patterns of oxide (diameter of 160-300nm, depth of 500nm) were fabricated on double blanket layers which were made up of W layer (thickness of 200nm) to bring conductivity and SiO_2 layer to completely insulate from Si substrate. Next, TaN, Ta and Cu layer were buried in the via and planed with CMP at typical single damascene process. Two kinds of defects were in the via on the test wafer. With SEM inspection equipment and analyzing brightness of SEM images, these were classified into normal via and two kinds of defects via. Bright, gray and dark images of via correspond to normal, void and etch stop via respectively. Current-voltage (I-V) measurements of each via to calculate resistance were performed by electrical probing equipment with SEM, and one probe was contacted to W layer as ground line fabricated by FIB, another to Cu surface at the top of the via. First, I-V measurements were performed for normal via with a diameter of 160 - 300nm. The current, which was about 0.2mA at a voltage of 10mV, was continuous and ohmic, so it was sufficient to calculate a resistance. The resistance of several Ω was reasonable for a resistance generally performed in measurements of via chain. The resistance was in inverse proportion to the square of diameter, as expected, and its variation increased for small size via. Second, I-V measurements were performed for etch-stopped or void via with a diameter of 160nm. The resistance of void via was about 10 times of normal via and its variation was larger than variation of normal via. This suggests that variation of resistance dues to variation of void size in Cu. Furthermore, investigation of correlation between the resistance and brightness of SEM images presented numerically allows to know detailed information of defects. Finally, the combination of SEM inspection and electrical probing equipment can enable the estimate of resistance of via. In LSI process, it is possible to monitor defects directly and quantitatively by using SEM inspection equipment.

EM-ThP29 Aluminum (Al) Contaminants & Copper (Cu) Debris Control in Wire Bonding Process: A Novel Ionization Application*, **O.A. Janducayan**, G. Nuneza*, Fairchild Semiconductor Inc, Philippines

The effect of ionization is already proven over the years in so many fields and most of the positive effect of this can be manifested in the field of semiconductor. Specific in the wire bonding technology, broken welds are one of the most common failure signature in the industry today and the resolution of this failure varies depending on the failure mechanism. Ionization or the neutralization of static energy during wire bonding of aluminum wires in power packages were proven to have beneficial effects; such effects can be utilize to control metal to metal adhesion in the surrounding environment, i.e. adhesion of conductors through Copper (Cu) contaminants against another metal surface, Aluminum (Al) build up in wedge tools, etc. The neutralization of static energy during the processing of these metals can be effectively utilized to improve overall quality of the process. The framework of this paper presents a study of the beneficial effect of ionization that can contribute in the elimination of broken weld cause by the Aluminum build up and the integration feasibility of ionization application in the original equipment manufacturers Wire Bonding process.

EM-ThP30 Novel Photoresist for Improvement in Pattern Collapse on Silicon Nitride*, H.-J. Yun, **D.-Y. Kim**, Y.-G. Kwon, B.-D. Kim, Y.-H. Kim, T.-S. Kim, Y.-B. Koh*, Samsung Electronics, Korea

Silicon nitride is useful in semiconductor industry for surface passivation as a hard mask. Recently, even at optimum exposure dose (Eop), it was found that photoresist patterns collapsed on silicon nitride which underwent ashing and stripping due to former step failure. The cause of pattern collapse is thought to be adhesion insufficiency resulted from a large discordance between the surface tension of substrate and that of resist. A polymer which has hydrophilic ester moiety was synthesized, and a resist based on this polymer shows better adhesion to silicon nitride. 42 nm line and space patterns were delineated using 193nm lithography tool without pattern collapse.

Nanometer-scale Science and Technology

Room: 4C - Session NS-ThP

Nanometer-Scale Science & Techology Poster Session II

NS-ThP1 Aligned Growth of Carbon Nanotube using Protein Supramolecule, ***S. Kumagai,*** ATRL, Matsushita Electric Industrial Co., Ltd., Japan, *T. Ono,* Tohoku University, Japan, *R. Tsukamoto,* CREST, Japan Science and Technology Agency, Japan, *S. Yoshii, I. Yamashita*, ATRL, Matsushita Electric Industrial Co., Ltd., Japan

Carbon nanotubes (CNTs) have remarkable electrical, mechanical and chemical properties and are expected for broad applications in nanoelectronics. For practical applications, it is desirable to be able to synthesize a CNT in a particular location. In this study, we present novel catalytic nanoparticle (NP) positioning technique for CNT growth, which is one application of the Bio Nano Processs (BNP)[1]. We used cage-shaped protein, apoferritin (φ12nm) to synthesize homogenous catalytic φ7nm Co NPs within the cavity and the negatively charged outer surface of the apoferritin was used for electrostatic placement of the inner Co NP on Si substrate. We modified Si substrate with positively charged aminosilane molecule (3-amimopropyltriethoxysilane: APTES) and made electrostatic interaction between the ferritin and a surface-modified Si substrate place the ferritins with Co core on a Si substrate. Under appropriate ionic strength around neutral pH, negatively charged ferritins were adsorbed selectively on positively charged APTES-modified area that was fabricated on negatively charged SiO2 surface. This electrostatic adsorption method successfully worked to place the ferritins on the APTES patterns. Heat treatment under O2 gas removed outer protein shells selectively and left only Co NPs on the substrate. The substrate with NPs placed at the designed positions was set in a DC plasma chamber and heated. Firstly, the substrate was treated by H2 plasma to reduce the NPs. After the treatment, CNT growth was conducted under C2H2/H2 plasma. The SEM observation revealed that CNTs grew not on the Si substrate surface but on the NP patterned area. This indicated that the patterned Co NPs, which were synthesized through the BNP, worked as catalyst and determined CNT growth position. Here, we demonstrated novel technique for the CNT growth at the designed positions. We also have succeeded in the single NP placement by analyzing the electrostatic interaction precisely. Individual CNT growth from arranged single NPs will be realized for nanoelectronic devices such as field emission and vertical FET. Part of the experiment was done in Micro/Nanomachining Research and Education Center, Tohoku University. This study is partially supported by Leading Project of MEXT, Japan.

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NS-ThP2 Fabrication of TiN Nanopillar Field Emitters Templated by Porous Anodic Aluminum Oxide, ***T.-M. Chen***, *J.-Y. Hung, F.-M. Pan, L. Chang,* National Chiao-Tung University, Taiwan, *S.-C. Wu*, National Nano Device Laboratories, Taiwan

Anodic aluminum oxide (AAO) has been widely used as a template for fabrication of nanostructured materials. In this study, we fabricated highly ordered TiN nanopillars on the Si substrate as electron field emitters using the AAO as the template. The nanopillars showed satisfactory field emission properties because of the high aspect ratio of the nanostructure and a low work function of TiN. To prepare the AAO template, an Al film 2 μm thick was first thermally evaporated on a sputter-deposited TiN layer of 500 nm in thickness. The Al film was anodically oxidized in an oxalic acid electrolyte at room temperature, and the as-prepared AAO pore channels had a pore diameter about 60 nm. During the preparation of the AAO pore channels, the underlying TiN layer was anodically oxidized as well in the late stage of the AAO anodization, forming titanium oxide nanodots. The TiOx nanodots were then used as the hardmask for dry-etching the underlying TiN layer, thereby transferring the AAO hexagonal arrangement pattern to the TiN layer leading to the formation of the well-ordered TiN nanopillar array. The nanopillars were ~200 nm in height and ~50 nm in diameter. The TiN nanopillar field emitter had a turn-on voltage of < 5V/μm, which was defined as the voltage at which the field-emission began to exhibit linear Fowler-Nordheim field emission characteristics.

NS-ThP3 Growth and Characterization of Carbon Nanotubes on Biaxially Textured Ni Alloy Metallic Substrates without Additional Catalysts, ***C. Varanasi,*** University of Dayton Research Institute, *J. Bulmer, M. Mullins,* AFRL/PRPG, WPAFB, *J. Burke,* University of Dayton Research Institute, *J. Baca,* AFRL/PRPG, WPAFB, *L. Brunke,* University of Dayton Research Institute, *K. Yost, P. Barnes*, AFRL/PRPG, WPAFB

One of the common methods used to grow aligned CNTs on various substrates is chemical vapor deposition (CVD) using C2H2 or CH4 as precursors. In this process, the substrates are processed prior to CVD such that metallic nanoparticles such as Fe, Ni etc. are formed on the surfaces to act as catalysts during the CVD process. However, the adhesion of CNTs to the substrates has been a problem in this approach as the nanoparticles are not integrated in to the substrate. In this study, biaxially textured Ni based alloy substrates were investigated as an alternate choice of substrates where the catalyst forms an integral part of the substrate to reduce the problem of adhesion of CNTs to the substrate. A biaxially textured Ni based substrate offers a surface with a well oriented grain structure (offering uniform growth) and the defects, grain boundaries, and the precipitates of the alloying additions etc., in the materials provide the necessary nucleation sites for the CNT growth. In the present work, several biaxially textured Ni alloy based metallic substrates were investigated to grow CNTs without giving any prior catalyst treatment to the substrates. A very high density of the CNT growth was observed on these substrates when suitable conditions were used using a CVD process with C2H2 as a carbon source. In the present talk, the experimental details to prepare the textured metallic substrates and CVD growth conditions used to grow the CNTs will be discussed. In addition, the characterization of textured substrates and CNTs grown on these substrates by using various characterization tools such as orientation image microscopy, Raman spectroscopy, TEM, and SEM will be presented.

NS-ThP4 Synthesis and Characterization of $LaPO_4$:Eu Nanotubes Prepared by the Sol-Gel Template Method, ***M.J. Fisher,*** *W. Wang, P.K. Dorhout, E.R. Fisher*, Colorado State University

Flat electroluminescent, plasma, and field emission devices demand materials with better stability, brightness, and industrial processing ability. Lanthanide ions (e.g. Eu^{+3}) have sharp and intense emission lines, and exhibit high luminescence yields. Synthesis technique, particle size and heating process strongly affect the physico-chemical properties of lanthanide ion containing oxide materials. We have synthesized pure phase $LaPO_4$:Eu bulk-powders and nanoparticles via the sol-gel template method, which has a high industrial processing ability for pure-phase submicron scale materials. Materials were dried at 70 °C, and sintered at 650 °C. Powder X-ray diffraction indicates that at 70 °C the bulk powder is a mix of hexagonal and monazite phases, whereas at 650 °C the bulk-powder is a pure monazite phase. SEM showed the morphology of the nanoparticles is tubular. Luminescence spectra of both the bulk-powder and the nanotubes contain the typical Eu^{+3} peaks.[1] As the nanotubes diameter decreases from 200 nm to 20 nm, the luminescence spectrum developed a broad background. The temperature and particle size are major factors in the observed phase and luminescence properties of the materials synthesized. Site-selected excitation, energy dispersive spectroscopy, and x-ray photoelectron spectroscopy results will also be discussed.

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NS-ThP5 Carbon Nanotubes Synthesized from Electrospun Nanofiber, ***J.-Y. Hong***, *M.-H. Lee, W.C. Choi, C.-Y. Park*, Sungkyunkwan University, Korea

One-dimensional carbide materials can be synthesized using multiwalled carbon nanotubes as templates by reaction with volatile oxide and/or halide species. Nanofibers may also be used as templates to produce carbon nanotubes with catalyst by temperature reactions. Electrospinning has received steadily increasing interest due to its ability to produce nanometer-sized fibers with a high level of reinforcement. Here we introduce carbon nanotubes (CNTs) synthesized using electrospun polyacrylonitrile (PAN) nanofibers. PAN and Fe composites as a catalyst were added to dimethylformamide (DMF) and the solution was stirred magnetically until PAN was fully dissolved. The spinning dope was transferred to a glass pipette mounted vertically in the electrospinning station. A voltage of 20kV was applied to the solution to start the spinning process. And the electrospun fibers were collected in a random mat. The PAN nanofibers were stabilized for 30min at 200°C and carbonized for 1h at 700°C. Then, the nanofibers were further heated to 900°C in acetylene as the carbon source. As the results of Raman spectroscopy and HR-TEM mesurements, carbon nanotubes were synthesized, at the same time, it was confirmed that the size of CNTs varies directly as that of the electorspun nanofibers. From these results, we suggest that the size of CNTs may be controlled by the PAN concentration in the electrospun nanofibers.

NS-ThP6 Field Emission Properties of Noble-Metal Coated Carbon Nanotube-Emitters

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Because of their unique geometrical structure and high aspect ratio, many researchers have studied the potential applications of carbon nanotubes (CNTs) in field emission display and high current electron source that requires low turn on voltage, high current density and emission stability. To enhance the field emission properties of CNTs, the intertube distance, densities, alignments and work function are very important factors, so which have been extensively studied in recent years.[1-4] However, as yet, the sensible solution have not been obtained. In this study, we report the field emission properties of CNT-emitters coated with noble metals(Au, Ag, etc.) and their alloy (Ag-Cu). The vertical aligned multi wall CNTs and the sequential noble metal coating are synthesized by DC-plasma chemical vapor deposition in ambient of the mixed gas (C_2H_2 and NH_3) and DC-magnetron sputtering, respectively. The results of the field emission measurements show that the field emission properties of noble metal coated CNTs have remarkably improved in the emission current density and the turn on electric field. We can find one of the reason for the enhancement in the field emission properties from SEM images obtained from the samples before and after noble metal coating. The density of emitter can be controlled by the suitable coating conditions. Also, we can enhanced the contact resistance and the emission stability under coarse condition. We suggest that the enhanced filed emission performance of the noble metal coated CNTs emitters are attributed by the reducing the emitting sites and low work function, and low contact resistance. The details will be introduced.

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NS-ThP7 Synthesis and Control of Carbon Nanotubes using Diffusion Mechanism of Fe Catalyst

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Since electrical properties of single-walled carbon nanotubes (SWCNTs) are primarily determined by its diameter and chirality, control of diameter is the crucial issue for application of CNTs-based electronic device. Thus, the preparation of catalyst with small and uniform size is essential factor to grow the SWCNTs with narrow diameter distribution. In this work, we investigate the growth of SWCNTs with narrow diameter distribution using a sandwich-like structures (Al/Fe/Al) deposited on Si substrate by DC magnetron sputter. The Fe catalyst layer is 1nm and the Al top-layer has various thickness from 1 nm to 10 nm. All samples are pre-annealed at 800°C by furnace in Ar ambient. Then, CNTs are grown by thermal chemical vapor deposition with C_2H_2, H_2 at 850°C for 10 min. A sort of CNTs are determined using Raman spectroscopy, and after pre-annealing, the variety of catalyst size with the thickness of top-Al layer is checked by X-ray photoelectron spectroscopy, transmission electron microscopy and magnetic force microscopy. It shows that the density and the kind of CNTs are depend on the thickness of Al top-layer and pre-annealing conditions. From these results, we can consider the following: (1) The catalyst is out-diffused through the Al top-layer by pre-annealing process, and the exposed catalyst size will be controlled by the thickness of Al top-layer and the pre-annealing conditions. Thus, we can be control a sort of CNTs. (2) This technique can be used for the device application that employ SWCNTs.

NS-ThP8 Phosphorylation of Multiwalled Carbon Nanotubes

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Carbon nanotubes are among the most exciting new materials being investigated and synthesized, owing to their outstanding mechanical, electronic and optical properties.[1,2] Fore more than a decade, the translation of these properties into realistic applications has been hindered by solubility and processing difficulties.[3] Recently the development of efficient methodologies for covalent chemical modifications has raised hope for the use of these materials in various fields of application such as biosensors, vaccine and drug delivery systems, medical imaging, biomaterials, water purification[4] etc. As part of an ongoing project on the application of carbon nanotubes, we which to report here the incorporation of phosphorus moieties on the end and side walls of the multiwalled carbon nanotubes obtained through NaClO oxidation followed by condensation reactions with alkyl or aryl chlorophosphates. Characterization of the phosphorylated multiwalled carbon nanotubes has been done by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), thermal gravimetric analysis (TGA) and Raman spectroscopy. It is anticipated that these new compounds could provide interesting biological activity in biological systems, and properties that might allow their incorporation into both organic and inorganic polymer matrices.

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NS-ThP9 Ring-shaped Emission Patterns from Carbon Nanotube Films

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Field emission patterns in the shape of perfect rings were observed on the luminescent screen of a specially designed triode cell with parallel electrodes. This cell is designed for investigation of 25.5 mm diameter flat samples. During the routine I-U measurements of broad-area flat cathodes, consisting of silicon or molybdenum substrates coated with carbon nanotubes (CNTs), rings appeared sporadically as relatively stable images among other field emission patterns like lobes and daisies. Their projected size was a few mm and was thus big enough to allow providing the analysis of their details. The origin of the electrons projected onto the screen is presumably a uniformly emitting cap atop of a long single wall CNT. This is consistent with models which predict high enhancement of the electric field and a ring-shaped pattern mainly as a result of imaging on a flat screen. The macroscopic value of the electric field at which rings were recorded was between 0.7 and 2.5 V/µm. The picture brightness analysis allows estimating the current corresponding to a particular ring and its brightness profile. The current of an individual ring was in the order of 2 - 4 µA. An outstanding finding of this study is a much greater angular width of the emitted beam for most of the rings compared to those that had been observed or predicted by reported calculations. The true mechanism that causes the difference between the model and our experiment is probably related to the atomic scale phenomena not included in their calculations.

NS-ThP10 Growth of Conducting Polypyrrole on Nanometer-Scaled Holes Array by Nanosphere Lithography

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Conducting polymers are attractive materials that could be used at all levels of microelectronics as alternatives for metal and semiconductors. Particularly, polypyrrole is one of the most promising conducting polymers because of its ease of synthesis, environmental stability and higher sensitivity. Additionally, through combination with nano-fabrication, this conducting polymer will provide a valuable method of large-area, easy fabrication of nanometer-scaled conducting polymer patterns that would be useful in polymer-based electronics. In this work, we have used nanosphere lithography technique using polystyrene beads and oxygen plasma ashing technique. Using nanosphere lithography, oxygen plasma ashing and chemical vapor deposition, we could fabricate the nanometer-scaled holes (< 50 nm) array on the gold coated silicon substrate. The fabricated nanometer-scaled holes are well-ordered and have high density. The polypyrrole was successfully grown on the nanometer-scaled holes by electrochemical polymerization. We confirmed that the polypyrrole was grown toward the vertical direction of the substrate by AFM and SEM. The C-V measuring of obtained polypyrrole arrays was performed. The obtained electrical and geometrical properties of polypyrrle were superior to use electrical sensors. These results will also open the possibilities to fabricate the unique tools for the highly aligned emitters, diode and vertical-type field effect transistors.

NS-ThP11 Creating a Nano-Scale Porous Network of Porphyrin Molecules

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Molecular self-assembly is a very promising alternative for designing and fabricating new nano-scale materials in the so-called "bottom-up" approach. In addition, the possibility of creating patterns of molecular networks with predefined, well-controlled geometries that could be used as a sort of nanoporous molecular material is opening new ways to fields as different as catalysis, electronics, or information storage. In particular, porphyrin molecules are of special interest due to the main role the play in a wide variety of biological, and chemical processes, and also photovoltaic devices. In this work we report on the self-assembly of meso-tetrakis (2-4-6-trimetil) fenil porphyrin (TMsP) when vapour-deposited in UHV conditions on Cu(100). For low coverages, the porphyrins can be found isolated or forming small clusters on the surface. Intramolecular resolution allows to determine their conformation and orientation, which come dictated by the substrate, the porphyrin main axis being parallel to the Cu[110] directions. Upon increasing the coverage, the TMsP molecules self-assemble to form a square lattice. Interestingly, our calculation reveal that the intermolecular distance and relative orientation are almost independent of the substrate, indicating that the assembly process comes mainly dictated by the intermolecular forces. An open, nano-porous, square network of TMsP can also be fabricated by depositing the molecules on Cu(100) c(2 x 2) / N. This surface, formed after adsorbing < 0.5 ML of N on Cu(100) and annealing to 600 K, is composed of square N islands, ~ 5 nm wide, separated by thin Cu lines, and has been used as a template to create arrays of metallic nanostructures. When the TMsP molecules are deposited on this surface, they nucleate almost exclusively on the Cu lines, leaving empty the N islands. In this way, by carefully controlling the width of the Cu lines and the molecule coverage, a film with 5 nm wide square pores of variable density that could be use as template for the growth of other nanoparticles can be created.

NS-ThP12 Effective Model for InGaAs/GaAs Quantum Dot with Material Mixing

*I. Filikhin, M.H. Wu, V.M. Suslov, **B. Vlahovic***, North Carolina Central University

We model an InGaAs/GaAs quantum dot (QD),including the height dependence of the Ga content of the QD. The effect of material mixing on the electron energy spectra is considered, using the experimentally measured height dependence of the Ga fraction from Ref.[1] Our theoretical model is based on a single sub-band approach with an energy dependent effective electron mass. We apply an approach in which the combined effect of strains, piezoelectricity and interband interactions are simulated by an effective potential[2]. It is shown that these effects may be taken into account in an effective manner using this approach. Based on our model, we perform an analysis of the results obtained by direct treatment of strain effects in Refs.[3] ("ab initio" calculations). To prove the adequacy of our model, we compare the results obtained for energy spectra of few electrons tunnelling into InAs/GaAs QDs, with experimental capacitance-gate-voltage data[4]. We find that the effective method is valid for the case of material mixing in the InGaAs/GaAs quantum dot. In the case of a linear height dependence of the Ga fraction, the strength of the effective potential must be chosen to correspond with the averaged value for the Ga distribution function. Effects of the QD cross section and the Ga fraction distribution are studied. We also compare our results with those obtained from psuedopotential calculations[5].

This work was partly supported by the Department of Defense and NASA through Grants, W911NF-05-1-0502 and NAG3-804, respectively.

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NS-ThP13 Guide for Optical Observation of Quantum Confinement or Quantum Size Effects at Room Temperature

A.C. Diebold, University at Albany, *J. Price*, SEMATECH

Although quantum confinement effect and quantum size effects are often considered low temperature phenomena, quantum confinement has been observed by ellipsometry at room temperature. This presentation will review examples of the observation of nanoscale effects at both low and room temperature. For example, the shift in the E1 critical point of thin silicon on insulator films has been sown to be due to quantum confinement and to roughly follow a 1/L^2 trend.[1] XPS has also observed quantum size effects for multi-monlolayer Al on Si(111).[2] Often, effect are seen despite the shift being less than the thermal energy, KT. Despite this, attempts to observe theoretically predicted resonances in the IR region of thin, polycrystalline TiN films failed. Based on this information we will propose some guides for when these effects can be observed at room temperature.

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NS-ThP14 Observation of Si/Co/Cu/Co Surface and Interface Processes for Nanostructure Formation by Scanning High Electron Energy Diffraction

H. Shirinzadeh, Materials and Energy Research Center, Iran

We observe the oxidation process on clean Si surfaces using high-resolution scanning reflection electron diffraction and form nanostructures on them, through focused electron-beam (EB) induced surface reactions. Si thermal oxidation occurs layer by layer, and the interface between the oxide film (<1.5 nm thickness) and Si substrate becomes atomically abrupt. When the sample is heated to 700-800 °C, resulting in the exposure of a clean Si substrate. The typical width of the clean Si `open windows' is about 10 nm. Using selective reactions during heating after the deposition of Si and Co films on the patterned samples, Si and Co nanoislands with 25 nm size are formed on Si surfaces.

Magnetic of surface and ultrathin film.

NS-ThP15 Cerium Oxide Nanoparticles: Distinguishing Influences of Size from Chemical or Environmental Effects

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Quantum confinement is a frequently observed and potentially useful property of nano-sized particles. An increase in band gap with the decrease in particle size is the phenomena of quantum confinement, typically valid when the particle size is approximately the exciton radius. However, because small particles are highly dependent on their surface, sample history and the local environments may also alter their properties and produce effects that may be interpreted as quantum confinement. We show that cerium oxide (Ceria, CeO2) is impacted by such effects. Nanoceria is a potential material for a spectrum of applications including solid oxide fuel cells, catalysis, oxygen sensors, biomedical use, and chemical mechanical planarization. The major characteristic of ceria crucial for these applications is its oxygen storage capability (OSC). The OSC is rendered to ceria by the ability to effectively switch between the 3+ and 4+ oxidation states based on ambient conditions. In the nanoscale regime, there are a number of reports that analyzed the ceria particles synthesized under different conditions. Many authors have computed the band gap and particle size by comparing the experimental UV Vis absorbance data to the effective mass approximation (EMA) theory. While some of the researchers have hypothesized that counter acting phenomena like dielectric confinement will nullify the confinement effects in ceria, others have strongly supported the quantum confinement effect. We attribute the reason for such a discrepancy in the open literature to the differences in synthesis and characterization environments along with the agglomeration of nanoparticles. We have synthesized ceria nanoparticles in different aqueous media (DI water, poly (ethylene glycol), dextran, and glucose). The optical absorbance spectra were collected as a function of time. A careful analysis of these data has clearly indicated that the ceria nanoparticles change their oxidation state in solution with time and the rate is dependent on environment. This change in chemistry denies the possibility to use the EMA theory for the particle size interpretation from the absorbance data and also raises questions about reported band gap values. Transmission electron microscopy and X-ray photo electron spectroscopy have been used to compliment the results from UV Vis analysis.

NS-ThP16 Nanofabrication of Deep Sub-wavelength Plasmonic Waveguides for Characterization

***M. Lu**, L.E. Ocola, S. Gray, G. Wiederrecht*, Argonne National Laboratory

Conceptual plasmonic devices show promising potential in transmitting and processing light at deep sub-wavelength scale.[1] The design and fabrication of a 100-nm-wide hybrid light-bending waveguide structure is discussed. Numerical modelling using finite-difference time-domain (FDTD) algorithm shows the device has an efficient confinement that is capable of transmitting light around 90 degree corners with minimal loss (<10%). The waveguide core is made by electron beam lithography and reactive ion etching with a bilayer resist. Sharp inner corners, which is important for low loss light bending, are achieved by an effective proximity correction (PEC) during e-beam lithography. The 800-nm-thick metal cladding is then formed by a selective electroplating. The wave guide is designed for near-field scanning optical microscope (NSOM) characterization, by leaving open the top of the waveguide. Achievement of this waveguide will enable submicron optical devices without the need of photonic crystals.

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NS-ThP17 Light Emission from STM Tunneling Junction on Ag Films Grown on Si(111) Surface

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Detection of lights emitted from the STM tunneling junction has been developed as one of the local spectroscopic method to probe optical properties of surfaces. Recently, we set up the STM with light detection apparatus which uses an optical fiber for collection of the emitted light from the tunneling junction. We obtained STM-induced light emission spectra emitted from Ag surfaces grown in two different forms on a Si(111)-7x7 surface. As characterized by STM images, films with flat terraces are grown on a 7x7 surface of Si(111), while Ag clusters with varying sizes are formed on a H/Si(111)-1x1 surface. The light emission spectra shows peaks at the energy range of 2.3~2.7 eV. The peak positions in the emission spectra remain the same for different tunneling bias voltages, indicating that the emission is induced through inelastic tunneling. The detected light emission is interpreted as due to the decay of a tip-induced plasmon (TIP) which is confined between the tip and the surface. The differences in the peak position and in the energy broadening are attributed to the difference in roughness and in shape. Comparison of the two surfaces and discussion will be made based on the theory of light emission from TIP.

Plasma Science and Technology

Room: 4C - Session PS-ThP

Plasma Science and Technology Poster Session

PS-ThP1 An In-situ Diagnostic to Detect Charging during Plasma Etching, ***E.R. Ritz***, *D.N. Ruzic, R. Ramasamy*, University of Illinois at Urbana-Champaign

In plasma etching processes, especially those with high aspect ratios, it is known that defects can occur such as trenching, bowing, and twisting. These defects are particularly noteworthy in the manufacture of DRAM deep-trench capacitors. In order to investigate the role of charging on these phenomena an in-situ diagnostic was fabricated using photolithographic and deposition techniques. The device consists of a base layer of titanium with alternating layers of SiO_2 and titanium. During the construction of the device, vias are integrated into the layout, extending all the way from the top surface to the substrate. The silicon dioxide layers act as insulators to create discrete measurement layers, provided by the titanium layers. The titanium layers are attached to voltage measurement leads and can then be used to measure the build up of sidewall charging at different heights along the via when exposed to a plasma. To determine the effect of geometry, if any, on charging, several aspect ratios were used by maintaining the same device thickness but varying the diameter of the vias. The entire stack is less than one micron thick, with vias ranging in diameter from 1 micron to only 20 nanometers, thereby producing aspect ratios of 1:1 to 30:1. Results from the diagnostic will be shown for various etching recipes.

PS-ThP2 The Effect of Radio-Frequency Bias on Electron Density in an Inductively Coupled Plasma Reactor, Measured by a Wave Cutoff Probe, *M.A. Sobolewski*, National Institute of Standards and Technology, ***J.H. Kim***, Korea Research Institute of Standards and Science

Inductively coupled plasma reactors allow greater, more independent control of ion energy and ion flux than is possible in traditional capacitively coupled plasma reactors. Nevertheless, even in inductively coupled reactors, it is unlikely that perfectly independent control can be achieved. The application of radio-frequency (rf) substrate bias, which is intended to only affect ion energies, may also produce changes in the plasma electron and ion densities and the total ion flux. Such changes are generally believed to be small, but it is not clear how small. Modeling studies of inductively coupled plasmas usually do not consider these bias effects. Experimental measurements of the effect of bias on electron density have been made, using Langmuir probes or microwave interferometry, but the data reported so far are quite limited and often appear to be contradictory. The accuracy of some results may be in doubt, since measured changes are comparable in size to systematic errors present in the measurement techniques. To provide a better characterization and understanding of the effect of bias power on electron density, we performed a detailed study in Ar, CF_4, and Ar/CF_4 plasmas. We measured the electron density with a wave cutoff probe, which avoids problems with deposition and rf compensation that may affect the accuracy of Langmuir probes. The effect of rf bias on electron density was measured as a function of source power, position, pressure, bias frequency, bias amplitude, and time. At selected experimental conditions, results from the cutoff probe were compared to Langmuir probe measurements, and both showed the same effects. Two types of bias-induced changes in electron density were observed. One was a gas composition effect caused by etch or sputter products liberated from the wafer surface. The other was an electron heating effect caused by absorption of bias power by plasma electrons. Simple models of each effect were derived and shown to yield quantitative predictions in agreement with the observations.

PS-ThP3 Measurement of Ion Energy Distribution in Dual-Frequency Capacitively Coupled Plasma, ***S.-H. Seo***, *H.-S. Lee, J.-B. Lee, H.-Y. Chang*, Korea Advanced Institute of Science and Technology

The ion energy distribution in a large-area and dual-frequency capacitively coupled plasma (CCP) was measured by using two methods, the noninvasive ion energy analyzer (NIEA) and the quadrupole mass spectrometer (QMS). The argon plasma was generated by 2 and 13.56 MHz RF powers, which were separately applied to two electrodes with a diameter of 600 mm and a gap distance of 50 mm between two electrodes. The NIEA detector was installed between the matching network and the electrode at two electrodes. It was found that the the energy distribution of ions incident to the low-frequency (LF) RF electrode exhibits a characteristic distribution with a series of peaks when 2 and 13.56 MHz RF power are applied simultaneously while it exhibits a single peak distribution or a well-known double peak distribution when a single RF power is applied or it is measured at high-frequency (HF) RF electrode. Those structured ion energy distributions were observed for a variety of the power ratio of two RF powers. The QMS equipment was installed inside the LF RF electrode. And, the energy distribution of ions incident to the LF RF electrode was measured by using the QMS and was compared with the ion energy distribution measured by the NIEA. The features of the ion energy distribution were analyzed and explained by the modulation of the sheath potential by two RF frequencies, which could be measured with the high-voltage probe at the electrode.

PS-ThP4 Analysis of Plasma Electrical Characteristics during Arcing and the Development of Arcing Detector in rf Discharges, ***K.Y.H. Kim***, KAIST, Republic of Korea

Arcing phenomena have become a fatal problem in TFT-LCD fabrication, semiconductor manufacturing, PECVD, and many other processes using plasma. But it has been unknown how arcing affects electrical characteristics of plasma. We investigated the sudden-electrical perturbation of plasma by arcing. The RF electrode was dc grounded to increase plasma potential and generate arcing. We measured floating potential, RF voltage and current to analysis the plasma-electrical variation by arcing. Experimental results show that the arcing in RF discharges change suddenly electrical characteristics of plasma and that especially amplitudes of both RF voltage and current decrease during arcing. And we described experimental results (plasma-electrical variation by arcing) analytically. Finally, using the arcing variation, we developed the equipment which can detect plasma arcing by non-perturbed method. This equipment was tested in real processing reactor like as semi-conductor etcher and showed the ability of sensitive arcing-detection.

PS-ThP5 Diagnostic of Plasma Generated in Water by Time-Resolved Optical Spectroscopy, ***C. Miron***, *M.A. Bratescu, T. Ishizaki, N. Saito, O. Takai*, Nagoya University, Japan

Electrical discharges in water are used for generation of ozone, oxygen, hydroxyl radicals and other chemically active species. These reactive species leads to favorable conditions for synthesis, as well as degradation of compounds. Therefore, electrical discharges have found applications in metal nanoparticles synthesis, water disinfection, biomedical applications. Numerous works have also presented concerning the electrical behavior of water subjected to high electric fields. Despite the progress, there is not yet a complete understanding of issues relating to the breakdown initiation process and the physics of charge creation in liquids. In this study, we investigate electrical and optical properties of a discharge process in water. Time resolved optical emission spectroscopy method is used to determine the reactive species generated in the aqueous system. An electrical discharge process in ultrapure water was generated between two cylindrical electrodes in a plastic vessel. Electrodes of different diameters and materials were used in the process. The electrical discharge conditions were varied in order to determine the evolution of reactive species generated in the water. The breakdown voltage and also the electrical current applied in the discharge were observed to be modified when using different materials of the electrodes and different interelectrode gaps, thus changing the plasma behavior. The water conductivity and pH values were also changed, depending on the electrode material used in the discharge process. The time emission spectra of hydrogen, oxygen atoms and hydroxyl radicals were studied in dependence with discharge voltage, pulse width, repetition frequency. A detailed analysis of different emission lines after the ignition of the high voltage pulse was realized, with modifying the voltage, pulse width, and repetition frequency.

PS-ThP6 Diagnostics of a Microwave Plasma by Optical Computerized Tomography, ***C. Tian***, *T. Nozawa, K. Ishibasi, M. Horigome*, Tokyo Electron LTD., Japan

A Radial Line Slot Antenna (RLSA) for surface-wave-plasma at 2.45GHz is a promising candidate with respect to increased process requirements for the large-diameter plasma. Diagnostics of such a kind of plasma was performed by Optical Emission Spectroscopy (OES) under various process conditions. Time-averaged computerized tomography has been developed to obtain a sliced 2D-image for optical emission from the RLSA plasma, which gives some useful information of spatial distribution of the relative net production rate of ions and radicals. The discharge chamber is about 35 cm in diameter and 20 cm in depth with a dielectric window 3 cm thick on the top. A smart optical scanner is amounted to the observe quartz window at the plasma diffusion level. The intensity of optical emission at selected wavelength throughout OES can be reconstructed to a spatial profile of species in RLSA plasma. We performed the measurement under low-k CVD process condition for the spatial distribution of species CFx. The changes of spatial distribution of ions and radicals of CFx under different RF bias and stage temperature reveal some essential plasma dynamics relate to the property of Low-k film. It has been concluded that the optical computerized tomography provides a way for fast plasma diagnosis and efficient real time process control.

PS-ThP7 Diagnostics in a Continuous Electron Beam-Generated Plasmas, ***S.G. Walton***, *E.H. Lock, R.F. Fernsler*, Naval Research Laboratory

The US Naval Research Laboratory has developed a plasma processing system that relies on a magnetically collimated, sheet of multi-kilovolt electrons to ionize the background gas and produce a planar plasma. High-energy electron beams are efficient at producing high-density plasmas ($n_e > 10^{10}$ cm^{-3}) with low electron temperatures ($T_e < 1.0$ eV) over the volume of the beam, resulting in large fluxes of low-energy ions (< 5 eV) at surfaces located adjacent to the electron beam. Most systems under developed at NRL use a hollow cathode pulsed to high voltages to produce the electron beam, which of course, results in a modulated plasma. We have recently developed a continuous electron beam source and are investigating the plasmas produced using this source. In this work, we discuss the bulk plasma properties and the ion flux at electrodes located adjacent to the electron beam. A Langmuir probe is used to determine the plasma density and electron temperature, while an energy-resolving mass spectrometer is used to determine the ion energies and fluxes at electrodes. Together the diagnostics provide a comprehensive description of the system. These plasma parameters will be determined as a function of gas background, electron beam intensity, and electrode bias. This work was supported by the Office of Naval Research.

PS-ThP8 In Situ Plasmas Diagnostics Study of a Commercial High Power Hollow Cathode Magnetron Deposition Tool, ***C.H. Castano***, *D.N. Ruzic, B.C. Masters, M.J. Neumann, E.R. Ritz*, University of Illinois at Urbana-Champaign

A variety of plasma diagnostics can be used to study the detailed influence of parameter variation on the plasmas used for PVD and PECVD on a commercial 200mm iNOVA high power hollow cathode magnetron deposition tool. Because of the special plasma conditions, non-standard geometry, and some non-standard frequencies used, specifically designed diagnostics are preferable to commercial solutions. These diagnostics include Langmuir probe analysis for electron temperature and density, a Faraday cups to study ion energy and density, optical spectroscopy for ion species identification and energy, quartz crystal microbalances combined with electrostatic and magnetostatic filters for deposition rates and ionization fraction of the incident metal atom species. Initial results from the plasma studies will be shown and compared tto theoretical calculations for ionization fraction and efficiency.

PS-ThP9 Application of Exhaust Line OES on Plasma-less Process for Advanced Process Control, ***S. Han***, *Y.-J. Kim, S.W. Choi, W.-S. Han*, Samsung Electronics Co. Ltd, South Korea

Recently, APC(Advanced Process Control) using in_situ monitoring sensor become more important for the enhancement of production efficiency and quality control mainly FD(Fault Detection) in mass production to meet specs for reduced feature size. Moreover, it makes process development and ramp up of yield faster. So, many in_situ electrical and optical sensors are being evaluated to find more sensitive and appropriate sensor for each specific process or equipment in many chip makers. The requirements of external in_situ sensor should be low in the price to easily manipulate, small to install, and justly accurate in the detectability. Among them, exhaust line OES sensor holds limelight due to that it can be used for monitoring non plasma process as well as plasma process. In this study, it has been qualified that exhaust line OES is a best solution as a real time gas analyzer, which can monitor by_product generated from chemical reaction, which can optimize EPD (End Point Detection), pre_conditioning time like seasoning, and process drift like"first wafer effect" of many different processes. First of all, most important thing is to detect or monitor undesirable process excursion like air leak, which affects product yield.

Application of exhaust line OES on plasma_less process for Advanced Process Control Keywords: OES (Optical Emission Control), APC (Advanced Process Control), FD (Fault Detection).

PS-ThP10 Dry Etching of Extreme Ultraviolet Lithography (EUVL) Mask Structures in Inductively Coupled Plasmas (ICP), ***D.Y. Kim***, *H.J. Lee, H.Y. Jung, N.-E. Lee,* Sungkyunkwan University, Korea, *T.G. Kim, B.H. Kim, J. Ahn, C.Y. Kim*, Hanyang University, Korea

Currently, extreme ultraviolet lithography (EUVL) is being investigated for next generation lithography. Among the core EUVL technologies, mask fabrication is also of great importance. In this work, we investigated etching properties of the EUVL mask materials such as Al_2O_3 (ARC : anti-reflected coating layer), TaN (absorber layer), Ru (buffer/capping layer) and Mo/Si multi-layer (reflective layer) in inductively coupled plasmas. Etch rate and etch selectivity of the mask materials were investigated by varying the gas flow, DC self-bias voltage (V_{dc}) and top electrode power. Based on the etch results of each layer, etching of stacked mask structures were carried out. The Al_2O_3 ARC layer could be etched with the etch selectivity close to 0.5 over the TaN absorber layer. The ARC/TaN stack could be etched with a high etch selectivity over the Ru buffer/capping layer.

PS-ThP11 Multi-Level Resist Employing Physical-Vapor Deposited Amorphous Carbon, ***H.T. Kim***, *B.S. Kwon, N.-E. Lee, H.J. Cho, B.Y. Hong*, Sungkyunkwan University, Korea

In this study, we investigated the fabrication process of multi-level resist (MLR) based on thin physical-vapor deposited (PVD) amorphous carbon (α-C) layer. Due to difficulty of patterning PVD α-C with a very high plasma resistance, etching characteristics of PVD α-C layer with the SiO_2 hard-mask were investigated in a DFS-CCP (dual-frequency superimposed capacitively coupled plasma) etcher by varying the process parameters such as different high-frequency/low-frequency combination (f_{HF}/f_{LF}), HF/LF power ratio (P_{HF}/P_{LF}), O_2 and N_2 flow rates in $O_2/N_2/Ar$ plasmas. The results indicated an increased etch rate of PVD α-C for the higher f_{HF}/f_{LF} combination and for the increased low-frequency power (P_{LF}). And the etch rate of PVD α-C was initially increased and then decreased with increasing the N_2 flow rate in $O_2/N_2/Ar$ plasmas. Application of PVD α-C layer as a mask for etching of the TEOS-oxide in the stack of ArF PR/BARC/SiO_2/PVD α-C/TEOS-oxide/Si indicated a possibility of using a very thin PVD α-C layer as a mask layer in the MLR structure.

PS-ThP12 Plasma and Electrical Characteristics of an Internal Linear Inductively Coupled Plasma Source for Flat Panel Display Processing, ***J.K. Park***, *J.H. Lim, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Inductively coupled plasmas (ICP) have been investigated for the processing of semiconductors and flat panel display devices as one of the high density ($10^{11} \sim 10^{12}$ cm^{-3}) and low gas pressure plasma sources. Especially, ICP was the most attractive among the high density plasma sources due to the advantages of simple physics and a simple source structure requiring no external magnetic field. In fact, as the plasma sources for the dry etching, even though capacitively coupled plasma (CCP) sources are currently utilized for the etching of thin film transistor-liquid crystal display (TFT-LCD) devices, to improve the throughput of the TFT-LCD device processing, high density plasma sources are preferred compared to the conventional CCP sources due to their higher processing speed. In this work, an internal-type antenna (double-comb type antenna) was used as an inductively coupled plasma (ICP) source for an extremely large area (2,300 mm x 2,000 mm) processing and its plasma and electrical characteristics were investigated using a Langmuir probe and an impedance probe, respectively. Also, the etch characteristics of the photoresist (PR), such as the etch rates and etch uniformities on the large area substrate by oxygen plasma were investigated. The results showed a strong dependence of the plasma characteristics such as plasma density and uniformity on the antenna arrangement, and, for an optimized condition, the PR etch uniformity less than 13% could be obtained within the substrate area.

PS-ThP13 Characterization of a High-Temperature Flowing Oxygen Plasma Afterglow, ***N.D. Vora***, Vanderbilt University, *D.A. Pejakovic, J. Marschall,* SRI International, *B.R. Rogers*, Vanderbilt University

In the last decade there has been a renewed interest in developing ultra high temperature ceramic composites (UHTCs) as potential construction materials for parts of sharp leading edge hypersonic space vehicles. Oxygen atoms are known to play an important role in this application environment. Oxidation properties of UHTCs have been traditionally studied either in thermal furnaces which provide negligible dissociation of oxygen molecules or in arc-jet tests which dissociates all of them. To attain partially dissociated oxygen environments at low pressures and high temperatures which are better representative of the application environment, we are using a flow reactor downstream to a microwave discharge. To quantify the effect of oxygen atoms on the oxidation mechanism it is necessary to characterize the flow and oxygen plasma afterglow chemistry that the sample is exposed to during oxidation. This work discusses computational and experimental characterization of the reactor over a range of process conditions. There is a lot of uncertainty in the kinetic data available in the literature for high temperature oxygen plasma afterglow chemistry. Sensitivity analysis of the reaction chemistry will be carried out to determine the dominant reaction in the plasma afterglow at relevant pressure and temperature conditions. The output from this model, specifically the oxygen atom concentration reaching the sample, will serve as an input for the subsequent modeling of the oxidation mechanism in the materials oxidized using this set-up. Thus this characterization effort will help in better understanding the high temperature oxygen plasma afterglow chemistry and also the quantitative effect of atomic oxygen on the oxidation properties of various materials.

PS-ThP14 Performance Characteristics of Inductively Coupled rf Ion Source for Low-energy Neutral Beam, ***M. Park***, KAIST, South Korea

Low-energy neutral beam sources are very promising candidates for the next-generation nano-processing. To realize high-flux low-energy neutral beam, we have developed a novel 13.56 MHz radio frequency inductively coupled ion source. Argon ion beam velocity distributions were measured by dye laser-induced fluorescence technique and compared with electrostatic retarding field analyzer(RFA). We describe the extraction system which enables our ion beam source to have high ion beam current densities at very low energy (<50 eV) region without broadening of beam divergence or energy in comparison with conventional ion beams. Synchronized Pulse biasing technique is applied when operating SF_6 pulsed plasma.

PS-ThP15 Residue-free High Dose Ion-Implanted Resist Removal using a High Power O_2/N_2 Plasma Jet, *M. Bhargava,* University of Houston*, A.K. Srivastava,* Axcelis Technologies*, W. Donner, **J.C. Wolfe***, University of Houston

The complete, damage-free and efficient removal of high dose ion-implanted (HDI) photoresist is one of the most challenging issues in integrated circuit manufacturing. The problem arises because a crust of implanted metal ions and vitrified carbon forms on the resist surface that is much less reactive to plasma ashing chemistries than unimplanted resist. The throughput limitation implied by this intrinsically low ash rate is compounded by the need to limit the wafer temperature to avoid popping, the explosive ejection of macroscopic crust particles due to thermally induced volatilization of the unimplanted resist layer beneath the crust. This paper describes the application of a high power O_2/N_2 plasma system to ashing of HDI photoresist. Reactant gas (typically O_2:N_2=9:1) is activated by a 2.5 kW, 2.45 GHz surface wave discharge in an air cooled quartz process tube 6 mm in diameter. The directional flow (3slm) of process gas at 80 Torr pressure produces a plasma jet that emerges from the end of the discharge tube and impinges on a scanning wafer. The wafers are held by a vacuum chuck and rastered by an in-vacuum motor assembly at speeds up to 105 cm/s. The jet, about 1 cm in diameter, carries a thermal power of 500 W. Test wafers (200 mm) were coated with 1.0 µm thick I-line resist and implanted with an arsenic dose of $5x10^{15}/cm^2$ at 40 keV and hard-baked at 120 °C. In our approach, the jet delivers hot, reactive species to the resist surface while the wafer temperature is held below the hard-bake temperature to prevent popping. Remarkably, it is then possible to selectively remove the crust from the unimplanted layer. Once the crust is removed, the base resist is rapidly ashed with a high temperature (low speed) scan. A light haze is formed on the wafer surface due to the reaction of atmospheric water vapor with the As_2O_3 particles that form during the ash process. This haze can be completely removed with a DI water rinse, after which, SEM and XPS analysis indicates no ash residues. Charge damage, interface trap density, and stress induced leakage were shown to be at or below values for the other commercial plasma ashing tools, which are known to provide damage-free ashing solutions. Silicon loss studies, in progress, will be reported at the conference. A conservative estimate of time-to-clear for a 300mm, 2-jet system is about 80s.

PS-ThP16 Study of Tungsten Oxidation in Low-Temperature Plasma Processing, ***S. Xu**, L. Diao*, Mattson Technology Inc.

As the device feature size of integrated circuit continues to be scaled down, metal or polysilicon/metal stack has been used as gate electrode for transistor formation. Among different metals investigated, tungsten meets various requirements and is gradually adopted for 45nm and below nodes. However, tungsten can be oxidized easily when exposed to oxygen plasma during process, leading to degradation of device performance. One example is post-implantation photoresist stripping in oxygen plasma where tungsten oxidation results in gate profile distortion and critical dimension change. Although an effective approach to solve this problem is available by using an oxygen-free reducing gas, such chemistry usually gives a very low photoresist removal rate and poor process uniformity. The second example is selective polysilicon oxidation over tungsten after gate etching to anneal etching damage where metal oxidation is difficult to be prevented with the presence of oxygen. The current common approach is using water vapor and hydrogen mixture to do thermal oxidation, but the process requires very high temperature and tends to cause contamination issue. In this paper, a detailed and systematic work has been conducted to study the tungsten oxidation in oxygen and oxygen-containing gases in an inductively-coupled plasma reactor operating at low temperature. By using various surface analytical methodologies, the oxidation of tungsten surface has been characterized and the oxide thickness has been measured. The dependences of tungsten oxide growth or tungsten loss on various process conditions, including RF power, pressure, temperature and exposure time, and process chemistry have been investigated. The experimental results show that tungsten oxidation occurs very fast at the top surface, but the oxide growth is mostly controlled by a few process parameters. The extent of tungsten oxidation is also found to change significantly with plasma chemistry and can be varied through post-treatment. Based on this work, mechanism of tungsten oxidation in high-density plasma has been discussed. Optimized process regime and chemistry have been identified to greatly reduce or even suppress tungsten oxidation for different process applications.

PS-ThP17 Stabilization of Ion-beam in Hall-type Plasma Processing Device, ***F. Furukawa***, Japan Aerospace Exploration Agency

Hall-type plasma processing device, whose ionization/acceleration mechanisms are extremely same as magnetron, has great expectations as ion beam source for nano/micro processing. Plasma magneto-hydrodynamic(MHD) instability, however, causes at high-voltage mode operation of DC regime. In particular, large-amplitude instability in the tens of kHz has been a serious problem that should be solved to improve the operational stability and the device system durability. So we propose a hall-type plasma processing device with new design concepts that is capable of solving simultaneously the instability and the accelerator core overheating. The technologies for this concept are as follows: 1) To increase neutral species velocity-inlet in acceleration channel by preheating propellant at its conduit line inside accelerator system could bring about the lower amplitude. 2) This method of preheating propellant through circularly propellant conduit line inside propulsion system cools the device system, and produces the higher thrust and specific impulse with hardly changing thrust efficiency at the same time. 3) Furthermore, to select Boron-Nitride and Al2O3 as wall material of ionization- and acceleration-zone in acceleration channel respectively having different secondary-electron emission-coefficient could achieve the higher-efficiency and -durability. The hall-type beam accelerator designed using these technologies, which have high convergence and stabilization of high-power beam at a low-price, becomes a enhanced ion beam source. Verification of these reduction technologies is conducted through numerical analysisand experimental data: The dependencies of both performances (ion generation-/acceleration-efficiency/ energy-efficiency/propulsion-utilization efficiency) and instability amplitude/frequency on various parameters (discharge voltage/neutral species temperature/magnetic field profile) are estimated using unsteady numerical analysis and experimental data. Besides in order to clarify the physical mechanism of the technologies a new physical parameter ‘equilibrium length of ionization-zone’ is introduced. Also the spatiotemporal variations of plasma properties and electromagnetic field for the optimum operation are examined in the acceleration channel at the peculiar times in instability-cycle.

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PS-ThP18 Computational Investigation of Volume Discharge in a Nitrogen Laser, *S.M. Karabanov, V.A. Korotchenko, **D.V. Suvorov***, Ryazan State Radio Engineering University, Russia

The laser on the basis of the second positive nitrogen system is one of the most powerful sources of UV–radiation (wave-length – 337 nanometers). The central disadvantage of a nitrogen laser obstructing to average power increase, is its low (0.1-0.3 %) efficiency. Influence of rate of interelectrode voltage rise and value peak capacity on energy of pulse radiation and pumping efficiency is investigated in the present work by means of numerical simulation for the nitrogen laser with transversely pumped and the capacitive energy storage. It is shown, that the rate increase of interelectrode voltage rise augments radiation pulse energy. It is caused by increase of the attainable overvoltage degree and energy accumulated in capacity. Simultaneously time of discharge formation and duration of impulse pumping decrease that leads to increase of radiation pulse energy. Existence of the optimum rate of interelectrode voltage rise is determined at which peak pumping efficiency is reached. At large values of rise rate the pumping efficiency decrease is explained by increase of reduced electric field intensity and primary energy input displacement from processes of excitation to ionization. On the one hand peak capacity increase leads to raise of energy entered into discharge that leads to inversion increase, and on the other hand - impulse pumping duration increases, that reduces inversion. Results of calculation show, that to increase pumping efficiency of the laser it is advisable to reduce peak capacity value at simultaneous increase of its charge voltage in order to keep its accumulated energy. The obtained results indicate the possibility of considerable increase of the nitrogen laser efficiency by providing of optimized pumping conditions.

PS-ThP19 Ionization Comparisons Through Filtered High Power Pulsed Magnetron Sputtering, ***S.R. Kirkpatrick**, J. Li, S.L. Rohde*, University of Nebraska-Lincoln

Various High Power Pulsed Magnetron Sputtering (HIPIMS) voltage levels are compared in terms of their equivalent ionization potentials using a "filtered" HIPIMS source and monitoring of a pair of quartz crystal monitors. One monitor is mounted in front of the cathode; the other is mounted perpendicular to the cathode, at the end of a coil similar to those used in filtered arc systems. A ninety degree open coil ion filter was placed 4cm from the target surface. Relative ionization rates for various applied voltages and materials are estimated through the ratio of deposition on each crystal monitor. Deposition rates for copper and titanium are observed on the "filtered" monitor both when the coil is on and off for comparison. Depositions were performed using pressures ranging from 3 to 5mTorr, and rates were found at the end of the ion filter to be more than double those of the unfiltered region. These results indicate that very high levels of ionization and directed deposition can be achieved using HIPIMS sources.

PS-ThP20 Study of Micro-Trenching and Bowing with a Dry Etching Profile Simulator in a High-Density, Low-Pressure Plasma, ***J. Saussac***, *J. Margot*, Université de Montréal, Canada, *M. Chaker*, INRS, Canada

Sub-micron technologies are crucial for present and future communication systems. The complexity of device fabrication processes requires a deep understanding of the fabrication issues, especially when dealing with new materials and complex device geometry. Plasma etching is one of the necessary tools to realize such devices. Numerical simulations are of great interest for providing insights into the physics underlying plasma etching processes and are therefore helpful for optimizing the experimental conditions. In this work, we propose a 2-dimensional plasma etching simulator. According to our cellular approach, each cell is characterized by its state, namely etched, unetched, mask, mask surface and material surface. This state evolves according to the interaction between the cell and the incident particles. Monte-Carlo methods are used to define particle trajectories and the nature of interacting particles (ion or neutral). The etched profiles achieved from our numerical simulations favorably compare with those corresponding to various experimental conditions (physical sputtering, ion-assisted etching, mask geometry and angular ion distribution) as found in the literature. In particular, micro-trenching and bowing of the side-wall for Si and SiO_2 are observed. The validation of our numerical approach through this comparison enables us to further apply it for more complex materials of interest for photonic applications, such as VO_2 and $SrTiO_3$. The next step in this study will be to examine the role of plasma parameters on the etching characteristics of such materials, in order to optimize profile accuracy (low micro-trenching, low bowing and large aspect ratio).

PS-ThP21 Effect of a High Negative DC Bias Voltage Applied on an Electrode Immersed in an Inductively Coupled Plasma, ***A. Ranjan***, University of Houston, *L. Chen*, Tokyo Electron U.S. Holdings, *D.J. Economou, V.M. Donnelly*, University of Houston

A biased electrode immersed in a plasma has been used to control the plasma parameters by various researchers. For example, Coburn and Kay[1] and Xu et al[2] inserted a separate positively biased electrode into a plasma, to control the plasma potential, and the energy distribution of ions extracted from the plasma. Here, we report the effects of applying a high negative DC bias voltage on an electrode immersed in an inductively coupled plasma. Plasma properties with the DC voltage ON and OFF were measured using a Langmuir Probe. Superposition of a high negative DC voltage was found to change the electron energy distribution function (EEDF) and the plasma density significantly. Plasma density increased by 25%-250% by the application of high DC voltage of -900 V at 100 mTorr and rf power of 2000-800 W. These changes can have dramatic effects on plasma chemistry. It is expected that this imposed DC bias technique will provide an additional variable to control the etch rate and pattern profile in microelectronics fabrication.

[1] J. W. Coburn and E. Kay, J. Appl. Phys., 43, 4965 (1972).

[2] L. Xu, D. J. Economou, V. M. Donnelly and P. Ruchhoeft, Appl. Phys. Lett., 87, 041502 (2005).

PS-ThP22 Planar Laser-Induced Fluorescence Measurements in an Inductively Coupled Plasma Reactor, ***B. Jacobs***, *W. Gekelman*, University of California - Los Angeles, *M. Barnes*, Intevac Corporation, *P. Pribyl*, University of California - Los Angeles

Planar Laser-Induced Fluorescence (LIF) measurements of ion velocity distribution functions have been made in an inductively coupled plasma reactor with a pulsed plasma source. Vertical and radial velocities have been measured at thousands of spatial locations within a plane, and the LIF data has been calibrated to a 96 GHz microwave interferomter. The ion behavior in the presheath region above the wafer is investigated in particular.

PS-ThP23 Exotic Shapes of Gold Nanoparticles Synthesized with Plasma in an Aqueous Solution, ***J. Hieda***, *M. Oda, N. Saito, O. Takai*, Nagoya University, Japan

Plasma materials processing in liquid phase has a potential of an industrial process for metal nanoparticles since this process would realize extremely rapid reaction under a high pressure. Moreover, this method does not require a reducing agent to fabricate metal nanoparticles from the solution containing metal ion and extraction process of residues. In our previous study, gold nanoparticles were successfully synthesized with discharge in an aqueous solution. In this study, we reported the shape change of the nanoparticles fabricated with discharge in the aqueous solution. In order to obtain various shapes of nanoparti1cles, the amount of additives in the solution was changed. Gold nanoparticles were synthesized through reduction with a discharge in the aqueous solution containing chlorauric acid as metal source. Gelatin was added to the aqueous solution as a stabilizer. Electric conductivity of the solution was varied from 500 to 2500 μS/cm in order to obtain suitable condition for generation of discharge by the addition of KCl. The discharge was generated by a pulsed power supply. The applied voltage and the pulse width were ca. 1600 V and 2 μs, respectively. The gold nanoparticles were observed by transmission electron microscopy (TEM) and analyzed by energy dispersive X-ray spectroscopy (EDS). Plasmon band of the gold nanoparticles were measured by ultraviolet-visible spectroscopy (UV-Vis). TEM images show the presence of exotic shapes of gold nanoparticles, that is, triangle sheet, pentagon, hexagon and so on. The exotic shapes were generated when the concentration of KCl became higher. The synthesis of nanoparticles using other surfactants (e.g. CTAB) with discharge was also demonstrated. These results suggested that the shapes of the nanoparticles strongly depend on KCl or surfactant concentrations in the solution.

Surface Science

Room: 4C - Session SS-ThP

Surface Science Poster Session

SS-ThP1 Amplified Optical Switching of Surface Wettability through Tailored Morphologies, ***D. Yang***, *P. Aella, A. Garcia, D. Gust, M.A. Hayes*, Arizona State University, *S.T. Picraux*, Los Alamos National Laboratory

We report the tailoring of surface roughness to significantly amplify light-induced contact angle switching and wettability of surfaces functionalized with the photochromic azobenzene molecules. Potential applications of controlled surface wettability for microfluidic systems include delivering analyses in lab-on-a-chip environments, bio-assay in drug discovery, and chemical analyses. Transporting increasingly smaller volumes of water is an important task in miniaturized microfluidic systems. However traditional mechanical approaches do not scale well to smaller volumes due to the increased importance of interfacial forces relative to inertial forces. Thus alternative methods to control liquid interactions with surfaces and to drive droplet motion are needed. We have previously demonstrated large photo-induced switching of contact angles (10-12 degrees) for water and other fluids on azobenzene-functionalized smooth Si surfaces. With these surfaces we find one can reversibly switch the surface wettability and in cases of sufficiently low hysteresis move liquid droplets by light-induced gradients in the surface tension. In this work, we extend these studies to the design of surface morphologies for increasing the effectiveness of photo-induced switching of surface wetting. We have fabricated ordered arrays of micrometer sized pillars (heights and spacing ~ 5 to 50 μm) on Si substrates. We also have prepared novel surfaces using CVD vapor-liquid-solid growth to fabrication surfaces with various lengths of Si nanowires (~50-100 nm in diameter) and combinations of nanowire-micropillar structures to form hierarchical arrays. By combining surface roughness with photochromic azobenzene monolayers, we demonstrate the amplification of the light-induced switching angle by up to a factor of 2 compared to smooth surfaces. Particularly effective amplification is found for hierarchical nanowire-micropillar designed surfaces. We discuss how such amplification enables increased control of surface wettability and droplet manipulation by optical means.

SS-ThP2 Surface Bonding Effects in Nanoparticles, ***H.H. Farrell***, *C.D. Van Siclen, D.M. Ginosar, L.M. Petkovic*, Idaho National Laboratory, *R.D. Parra*, DePaul University

The nature of the bonding at surfaces has a profound effect on their properties. Current models for the cohesive energy of nanoparticles generally predict a linear dependence on the inverse particle diameter, 1/r, for low aspect-ratio (spherical) clusters.@super1-4@ Although this is generally true for metals, we have recently found that for the Group IV semiconductors, C, Si and Ge, this linear dependence does not hold.@super5. Instead, using first principles, density functional theory calculations to calculate the binding energy of these materials, we find a roughly quadratic dependence on the inverse of the particle size. Similar results have also been obtained for the metallic Group IV elements Sn and Pb and for Mg, another "poor" metal.@super5@ This result is in direct contradiction to current assumptions. Further, as a consequence of this quadratic behavior, the melting point of these materials will not be linear in 1/r, but will experience less suppression than experienced by metal nanoparticles with comparable bulk binding energies. Similarly, the vapor pressure of semiconductor nanoparticles will rise more slowly with decreasing size than would be expected. This non-linearity also affects sintering or Ostwald ripening behavior of these nanoparticles as well as other physical properties that depend on the nanoparticle binding energy. The reason for this variation in size dependence involves the covalent nature of the bonding in semiconductors, and even in the "poor" metals. New work on other materials, including compound semiconductors and oxides will also be presented.

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[2] See, for example, W. H. Qi, M. P. Wang, M. Zhou, and W. Y. Hu, J. Phys. D: Appl. Phys. 38, 1429 (2005), and references therein.

[3] See, for example, Chang Q. Sun, H. L. Bai, S. Li, B. K. Tay, C. Li, T. P. Chen, and E. Y. Jiang, J. Phys. Chem. B 108, 2162 (2004), and references therein.

[4] See, for example, M. Wautelet, J. P. Dauchot, and M. Hecq, J. Phys.: Condens. Matter 15, 3651 (2003), and references therein.

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SS-ThP3 Initial Adsorption of Yttrium on Si(001) 2X1 Surface, *S.Y. Chiam*, Imperial College London, Singapore, *A.C. Huan*, Institute of Materials Research and Engineering, Singapore, *W.K. Chim*, National University of Singapore, *J. Zhang*, Imperial College London, Singapore, *J.S. Pan*, Institute of Materials Research & Engineering, Singapore

Initial adsorption sites of metal on Si is an increasingly important area of research especially for growth of thin films for low dimensional devices. Growth and simulation of heterojunction thin films on Si often require a more detail information about the position and bonding of the adatom. For instance, study of Sr with experimental and theoretical methods have lead to a better understanding of Sr adatom's preferred environment and gave insights into subsequent growth of epitaxial thin film, in particular, SrTiO3. In this work, we have investigated the initial adsorption of transition metal yttrium (Y) on Si(001). Y although formally a transition metal, have very similar valence electronic properties with the lanthanide family, including lanthanum. In Si based electronics, yttrium silicide, yttrium silicate and yttrium oxide are all potential thin films for source-drain contacts, infrared-detectors, and gate dielectrics. Furthermore, information about Y adsorption sites can aid in the design and growth of ternary or quaternary oxides (eg. LaYAl2O3). We have examined the real-time deposition of Y on Si(001) 2X1 by mounting a EFM evaporator source on the STM chamber. Therefore, we have observed the deposition of sub-monolayer coverage of Y atom on the same area of clean Si image thereby reducing any errors that might arise from adsorption of other species in UHV. Our work shows that yttrium adsorbs primarily on dimer bond instead of the cave site as predicted from a theoretical simulation of La on Si(001). We've examine the possible structure for such an adsorption and discuss about its stability and its bonding character using both STM and UPS.

SS-ThP4 Site Specific Chemisorption of Cl on Si(114), *R.E. Butera*, *A. Agrawal*, *J.H. Weaver*, University of Illinois at Urbana-Champaign

The dissociative chemisorption of Cl on Si(114) was studied at room temperature using scanning tunneling microscopy (STM). Si(114) is a stable, planar, single-domain, high-index surface composed of rebonded atoms, dimers, and tetramers each aligned in rows along [-110]. STM imaging shows preferential Cl-termination of rebonded atom and dimer sites over tetramer sites. Moreover, the prevalence of specific chlorinated tetramer configurations reveals that dissociation is sufficiently exothermic that Cl can interrogate the potential energy landscape to find a local minimum. A 10 minute anneal at 550 K facilitates diffusion and allows the system to reach the equilibrium configuration. Sequential exposure and annealing cycles reveal a coverage-dependent site occupancy dictated by surface π-bonding. This study provides the necessary starting point for a thorough investigation of the structural implications of halogen etching where we find preferential desorption and novel pattern formation.

SS-ThP5 Irreversible Structural Transformation of Si(114)-2x1 Induced by Subsurface Carbon, *G. Duvjir*, *H. Kim*, *J.M. Seo*, Chonbuk National University, Korea

From the previous STM studies of Si(114)-2x1, it had been reported that its pure and reconstructed surface (A-phase) is composed of rebonded restatom(R), tetramer(T), and dimer(D) rows. Recently, during annealing Si(114) near 1300C, we have found carbon-induced Si(114)-2x1 surface (B-phase) whose reconstruction is composed of T, T and D rows. Such a B-phase turns out to be induced by bulk carbon impurity segregated to surface and trapped at the subsurface. Once the surface changes from A-phase to B-phase, it does not return to A-phase by any kind of annealing process. The portion of B-phase relative to A-phase can also be increased by C2H2 adsorption on the clean substrate held at 500 C up to 100 percent. When the surface of B-phase is used as a substrate during Si-homoepitaxy or Ge-epitaxy, the overlayer thickness increases by two layers, differently from one-layer growth mode on the substrate of A-phase. It can be concluded that carbon having a stable subsurface site induces the anisotropic compressive stress on the surface, which results in insertion of Si-dimer to R row to form T row. The potential of this B-phase for application as a template is in its thermal stability and homogeneity since A-phase always has B-phase impurity even in the clean surface.

SS-ThP6 Evidences of Two Commuting Chain Structures Existing on Si(5 5 12)-2x1, *H. Kim*, *H. Li*, *G. Duvjir*, *J.M. Seo*, Chonbuk National University, Korea

From STM/STS studies of the reconstructed Si(5 5 12)-2x1 surface, it has been found that its atomic structure of the unit-cell consists of four kinds of 1-D structures: honeycomb(H) chain, π-bonded chain, dimer-adatom(D/A) row, and tetramer(T) row. One (5 5 12) period is composed of three subunits, (337) unit with a D/A row [D(337)], (337) unit with a T row [T(337)], and (225) unit with both a D/A and a T row. Two kinds of adjacent subunits, T(337)/D(337) and D(337)/(225), are divided by H chains, while one kind of adjacent subunits, T(337)/(225), is divided by a π-chain. Existence of two chain structures has been confirmed as follows: (1)In the empty-state topographic image, H-chain has 2x periodicity along the chain due to buckling, while π-chain with missing atom defects has 1x periodicity. (2)From local STS measurement, the empty-state onset of π-chain is 0.5 eV smaller than that of H chain. (3)Exposed benzene molecule adsorbs selectively on π-chain. (4)In the homoepitaxy on Si(5 5 12)-2x1 at 550C, the first chain grown on D/A row is π-chain. Two chain structures commute with each other depending upon the external stresses perpendicular to the chain, which is the same for two row structures, D/A and T rows. These results indicate that, although numbers of consisting atoms and dangling bonds(DBs) of two different chains are identical, different DB directions induced by tensile stresses perpendicular to the chain result in such a distinct reactivity.

SS-ThP7 In-induced Atomic Chains on the Stepped Si Surface : In/Si(557)1x3, *I. Song*, *J.H. Nam*, *M.K. Kim*, *C.-Y. Park*, *D.H. Oh*, *J.R. Ahn*, Sungkyunkwan University, Korea

We have investigated the In-induced one-dimensional (1D) surface reconstruction on the Si(557) surface using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). One-dimensional electron systems have showed exotic phenomena such as Jahn-Teller distortion, non-Fermi liquid behavior, and Peierls instability.[1] Recently, stepped Si surfaces have attracted much attention as templates for formation of one-dimensional structures. Some examples that have been extensively studied are the Au/Si(553), Au/Si(557), Pb/Si(557) surfaces.[2] The In-induced 1D structure on the Si(557) surface was prepared by depositing In on the RT Si(557) surface and subsequent annealing at 500 °C. LEED show the In-induced surface reconstruction to have 1×3 phase, where the direction of the ×3 period is perpendicular to the step direction. In STM images, we found two kinds of atomic wires located at the step edge and within the terrace, respectively. The atomic chain within the terrace has obviously ×3 period along the chain direction, while the atomic chain at the step edge seems to have ×1 period along the chain direction. The atomic chains on the In-induced Si(557)1×3 is quite similar with those on the Au/Si(557) surface.[3] We will explain the In-induced Si(557)1×3 surface in comparison with the Au/Si(557) surface.

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SS-ThP8 Ozone Oxidation of Self-Assembled Monolayers on Silicon Surfaces, *T.M. McIntire*, University of California, Irvine, *A.S. Lea*, *P.L. Gassman*, Pacific Northwest National Laboratory, *Q. Li*, KLA-Tencor Corporation, *O.S. Ryder*, *B.J. Finlayson-Pitts*, University of California, Irvine

Airborne particles have well-documented effects on human health, visibility and the chemistry of the atmosphere. A major area of concern, but also largely uncertain, is the impact of particles on global climate. A significant part of this uncertainty is the lack of understanding of the nature of the organic component. This deficiency includes the chemical speciation and the distribution of the organics between the surface and the bulk of liquid particles, as well as changes due to oxidation during transport in the atmosphere. In this work, the formation of large organic aggregates has been observed from the ozone oxidation of unsaturated alkene self-assembled monolayers (SAMs) on solid silica surfaces. Ozonolysis of terminal alkene SAMs of 3- and 8-carbon lengths, as proxies for organic-coated airborne dust particles, leads to the formation of large hydrophobic aggregates which do not increase the uptake of water as previously assumed. These SAMs were generated on silicon substrates and reacted at room temperature with gaseous ozone. A combination of experimental techniques, atomic force microscopy, scanning electron microscopy, Auger microprobe, time-of-flight secondary ion mass spectrometry, and transmission FTIR, were used to study the surface composition and morphology after oxidation. Large (micron-size) organic aggregates formed on the surface while the surrounding substrate became depleted of carbon and exposed the original substrate. This highly unusual result establishes that the mechanism of ozonolysis of alkene SAMs involves polymerization, likely induced by secondary reactions of the Criegee intermediate (CI). For that reason, formation of polymers under atmospheric conditions may be more common than previously recognized. The uptake of water was not increased upon oxidation of these films, in contrast to current expectations. Implications for SAM reactions and stability in air, ozonolysis of alkenes on surfaces, and for the oxidation of alkenes on airborne dust particles are discussed.

SS-ThP9 Thermal and Non-thermal Interactions of MEA on Si(100), ***B. Forster***, *S. Yeninas, J. Thompson, J.H. Craig, Jr., J. Lozano*, Bradley University

We have used several surface analysis techniques to study the adsorption dissociation, and desorption of monoethylamine (MEA) on Si(100) surfaces. Thermal processes were studied using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). Non-thermal processes using electron irradiation of MEA/Si(100) at 100 K were studied using HREELS TPD, x-ray photoelectron spectroscopy (XPS), and electron stimulated desorption (ESD). Our data indicated low temperature electron-induced dissociation of MEA, deposition of nitrogen, and formation of silicon nitride.

SS-ThP10 Adsorption Studies of Trisilylamine on the Si(100) Surface, ***B. Bush***, *A. Marquis, O. Egwu, J.H. Craig, K. Roos, J. Lozano*, Bradley University

Trisilylamine $(SiH_3)_3N$ is the silicon analog to the carbon-containing molecular species trimethylamine $(CH_3)_3N$. The fundamental structural difference between these amines is the planar backbone exhibited by TSA. The Si_3N backbone is the same structure which occurs in silicon nitride Si_3N_4. Little fundamental work has been reported on the adsorption properties of TSA on the Si(100) surface. We report on the results of a series of adsorption studies of TSA on the Si(100) surface at 100K using XPS, UPS, HREELS, and TPS to elucidate the dissociation pathways and bonding of the TSA molecule on the surface. Results of electron bombardment studies to remove hydrogen ligands from the adsorbed species will also be discussed. Preliminary STM images of very low coverage adsorption of TSA on the Si(100) surface will also be presented and discussed.

SS-ThP11 STM Study of Niobium Deposited on Si(111) Surface, ***H. Suh***, *Y. Kuk*, Seoul National University, Korea

Superconductivity in low dimensionality has been attracting attentions of many researchers due to its technological and scientific importance. While it is well known that superconductivity is suppressed as the dimensionality is reduced, the conditions and criteria for the dimensionality still remain questionable. Scanning Tunneling Microscopy is a powerful tool for studying both topographies and local electronic structures in nanometer scale. To explore superconductivity at reduced dimensionality, we studied Nb deposits on Si surfaces. Nb, which has the highest superconducting transition temperature among elemental superconductors and has various compounds with even higher transition temperatures, was e-beam evaporated onto Si(111) surface and annealed. The surface was characterized with Scanning Tunneling Microscope (STM) and local electronic structures of the deposited Nb was studied with Scanning Tunneling Spectroscopy (STS).

SS-ThP12 STM Study of Submonolayer of Au Adsorption on Si (111)-(7x7) Surface and Influence of Substrate Temperature, ***H. Shim***, *L. Zhang, Y. Kim, G. Lee*, Inha University, South Korea

Adsorption of submonolayer Au on Si (111)-(7x7) surface at different substrate temperature was investigated using STM. At room temperature deposition, the Au adsorption on Si (111)-(7x7) typically features coexistence two species, high-lighted triangles and clusters confined within half-unit cells. The high-lighted triangles are dominant at a very low coverage, but give way to clusters with various sizes as the coverage increases. Slightly heating the substrate (below 150 C) during deposition also decreases the number of the highlighted triangles. The clusters, mostly confined within half unit cells for the deposition at substrate temperatures below about 350 C, coalesce to cover the borders of the half unit cells when substrate temperature increases. Vacancies and disorders are created near the clusters, suggesting the incorporation of Si atoms into the clusters at the heated substrate. At about 550 C deposition, the Au adsorption leads (5x2) reconstruction in the form of characteristic island-hole pairs on terrace or only (5x2) islands at the step edge. The evolution of the Au-adsorbed surfaces with substrate temperature during deposition will be discussed and compared with that of the room temperature deposition and post annealing.

SS-ThP13 Controlling and Probing Molecular Orientation and Differential Conductivity in Solid Films of Ionic Perylenebis(dicarboximide)s, ***A. Jeewandara***, *S.M. Casey*, University of Nevada, Reno

We report the control of molecular orientation and differential conductivity in solid films through self-organization and induced orientation processes. We synthesized water-soluble cationic 3,4,9,10-perylene diimide and derivatives and formed chromonic N phases (nematic lyotropic liquid crystalline phases) at room temperature upon solution concentration. Upon induced alignment (by shearing) of the chromonic N phase on a substrate and removal of solvent, anisotropic solid films of the dichroic dyes were produced. By use of a combination of polarized UV-vis and FT-IR spectroscopies, the orientation of the average molecular plane in these films was determined to be perpendicular to both the shearing direction and the substrate plane. The effect of molecular orientation on the differential conductivities in the films will be discussed.

SS-ThP14 The Molecular Scale Origins of the Surface Memory Effect, ***K. Bufkin***, *R. Adams, B.L. Johnson, D.L. Patrick*, Western Washington University

The behavior of liquid crystals (LC) at interfaces has been an important area of research for many years because of its relevance to LC device applications such as LCDs. In this research ordered monolayer films of the LC 4’-octyl-4-biphenyl-carbonitrile (8CB) on highly oriented pyrolytic graphite were investigated by scanning tunneling microscopy (STM) in order to study their disordering kinetics and to develop a better understanding of a phenomenon known as the surface memory effect. The surface memory effect occurs when a LC film retains a degree of remnant orientational order even after being heated above its isotropic transition temperature. Using STM we studied molecular-scale ordering in 8CB films heated to varying temperatures and for varying lengths of time. The results are compared to large-scale Monte Carlo simulations of a 2-dimensional Ising Model, which suggests for the first time that nearest-neighbor interactions in the isotropic phase play an important role in producing surface memory effects.

SS-ThP15 Chiral Control in Organic Monolayer Films Using Liquid Crystal Solvents, ***C. Reinhart***, *A. Morris-Cohen, D.L. Patrick*, Western Washington University

Many important chemical and physical properties of organic thin films are affected by molecular-scale order. We present investigations of a method for controlling the orientation of molecules and their chirality in monolayer films using thermotropic liquid crystal (LC) solvents and magnetic fields. Two different methods of chiral and orientational control will be discussed. The first involves an achiral set of organic compounds that, when deposited on a graphite surface, produce crystalline monolayers with non-superimposable left and right handed domains; the second set involves 3-dimensionally chiral compounds and is aimed at controlling enantiomeric excess through selective adsorption. Molecular ordering, 2D chirality and enantiomeric excess are analyzed by scanning tunneling microscopy.

SS-ThP16 Organic Semiconductor Film Growth Using Liquid Crystal Solvents, ***B.B. Ohlson***, *F.S. Wilkinson, D.L. Patrick*, Western Washington University

Organic semiconductor (OS) thin films have attracted widespread interest for their potential use in electronics, optics, information storage, photovoltaics and many other applications. Since properties such as charge transport are known to be anisotropic in most crystalline structures, having control of crystallite orientation should lead to improvements in the tunability of devices such as organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs). Furthermore, by creating films that are highly crystalline, with large grain size, and thus less potential for charge trapping at the grain boundaries, charge transport characteristics can be optimized. We present a new approach for growing OS thin films using thermotropic nematic liquid crystal (LC) solvents to deposit tetracene films with long-range uniaxial order. The LC solvent imprints its directionality onto the crystalline tetracene film as it grows, resulting in larger, highly oriented crystals. Films were deposited via atmospheric-pressure sublimation onto substrates coated by a LC layer oriented using mechanically rubbed polyvinyl alcohol (PVA). This poster will describe the effects of different processing conditions, such as LC layer thickness, substrate temperature and flux rate on film morphology and crystallinity.

SS-ThP17 Analyte Binding to CoPc: A Comparison of Analyte Binding Strength and Basicity, ***N.L. Tran***, *A.C. Kummel*, University of California at San Diego

A recent study has shown a strong correlation between analyte electron donor ability and chemiresistive Cobalt phthalocyanine (CoPc) sensor response.[1] The -H_{BF3} scale method was used as a measure of the electron pair donor ability of the 10 analytes investigated.[2] It is speculated that sensor response is dictated by the degree of charge transfer in CoPc-analyte complexes as opposed to analyte binding strength. To investigate this hypothesis, the binding strength of these electron donating analytes (acetonitrile being the weakest and triethylamine the strongest electron donor) to the Co metal of CoPc was calculated using density functional theory. Subsequently, the atomic charges of the CoPc and CoPc-analyte complex will be analyzed to measure the degree of charge transfer between the analyte and Co metal. The interaction of a neurotoxin analogue, dimethyl methylphosponate (DMMP) with CoPc is also being investigated to determine the potential for use of CoPc sensors to detect organophosphate neurotoxins. Preliminary DFT simulations show that although O_2 binding to the Co metal is weak (less than -0.1 eV exothermic), a large effect on the CoPc electronic structure and charge transfer is observed. Weak analyte-MPc binding with a large change in electronic structure are the key properties of a good sensor because a reversible absorption will result in a large change the conductivity of the MPc film.

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SS-ThP18 Ablation of Polyvinylidene Fluoride at 157-nm[1], ***J.A. Leraas***, *S.R. John, S.C. Langford, J.T. Dickinson*, Washington State University

Polyvinylidene fluoride [PVDF—$(CH\ _2CF_2)_N$] is a piezoelectric polymer employed in a variety of sensors. PVDF also possesses excellent thermal and chemical stability, which complicate the manufacture of parts with complex geometries. Structure formation by energetic radiation is potentially important to the broader application of this material. In this work, we characterize the products produced by exposing PVDF to 157-nm radiation from an F_2 excimer laser. In the early stages of irradiation, the dominant neutral product is HF, produced by photochemical excitation of side chain bonds. HF production is accompanied by the conjugation of C-C bonds and cross-linking. Given sufficient laser fluences, prolonged exposure produces bursts of positive and negative charge, neutral particles, and light. We attribute burst formation to the accumulation of conjugated carbon bonds in the near surface region. When the peak temperatures generated by successive laser pulses reach a critical level, a burst results. This unusual behavior is associated with the chemistry of the PVDF molecule. In polytetrafluorethylene, for instance, 157-nm radiation cleaves the polymer backbone to produce small fragments that are continuously removed from the target. Side chain cleavage in PVDF allows damaged material to accumulate until conditions produce a large burst of emission. The charged products accompanying a burst are strongly coupled to form a tenuous plasma, or charge cloud. The positive ions in the charge cloud have kinetic energies of 7-10 eV, consistent with electrostatic ejection from the polymer surface. We show evidence for high electron densities in the charge cloud—sufficient to neutralize most (but not all) of its positive charge. These electrons are largely confined to the charge cloud, and play an important role in generation of negative ions by dissociative electron attachment to neutral species. The relatively high velocity of the charge cloud is matched only by the fastest neutrals. Therefore only the fastest neutral particles are vulnerable to attachment. The spatial and temporal distribution of the product species have important consequences on product evolution prior to deposition. The unsteady emission intensities, with occasional large bursts, provide challenges and opportunities for the growth of PVDF films by laser ablation at 157 nm.

[1] This work was supported by the US Department of Energy under Grant DE-FG02-04ER-15618.

SS-ThP19 Ablation Mechanism In Polytetrafluoroethylene (PTFE) under 157-nm Irradiation[1], ***S.R. John***, *J.A. Leraas, S.C. Langford, J.T. Dickinson*, Washington State University

Polytetrafluoroethylene (PTFE) (C2F4)n is a model organic polymer with unique properties. In this work, we explore the mechanisms responsible for the superior etching others have demonstrated using 157-nm F2 excimer lasers. At fluences well below the threshold for plasma formation, the major neutral products are (CF2)x units. Thus decomposition is primarily from backbone scission. Mass selected time-of-flight signals for these neutral products show a fast component with energies on the order of 1.2 eV, as well as a slower, thermal component. We attribute the fast component to products formed from scission of C-C bonds due to electronic excitations along the surface. We attribute the slower component to products produced in the bulk, which then diffuse to the surface and desorb. The clean etching of PTFE at 157 nm is the result of dissociative electronic excitations. Nevertheless, analysis of the slow component indicates high surface temperatures. The F2 laser significantly heats the surface. Intense electron, positive and negative ion emissions are also observed. The high positive ion kinetic energies (3-10 eV) are consistent with an electrostatic emission mechanism. The negative ion signals are an order of magnitude weaker than the positive ions, but display similar kinetic energies (3-5 eV). We attribute negative ion formation to dissociative electron attachment of neutral monomers. This process requires high electron densities, which are observed in the cloud of positive ions. The presence of both positive and negative ions, in addition to reactive (CF2)x units, would promote the growth of high quality PTFE films by laser ablation deposition. We will briefly describe the ablation of a another fluorocarbon polymer, polyvenylidenefluoride (PVDF) (C2H2F2)n, at 157-nm. Initial exposure yields intense emissions of neutral HF due to side chain scission-in contrast to PTFE, where fragmentation is predominately due to backbone scission. The presence of hydrogen in the PVDF renders side chain bonds especially vulnerable. During prolonged irradiation, especially intense bursts of charged and neutral products accompany some laser pulses and not others. The bursts are presumably due to the accumulation of damaged material in the intervening laser pulses.

[1] This work was supported by the U.S. Department of Energy under Grant DE-FG02-04ER-15618.

SS-ThP20 Solid-Liquid Interface Engineering: Static and Dynamic Hydrophobicities on Self-assembled Monolayer Surfaces, ***N. Yoshida***, The University of Tokyo, Japan, *S. Suzuki,* Tokyo Institute of Technology, Japan, *M. Sakai, A. Hashimoto,* Kanagawa Academy of Science and Technology, Japan, *Y. Kameshima, A. Nakajima,* Tokyo Institute of Technology, Japan, *T. Watanabe*, The University of Tokyo, Japan

Wettability of solid surface has attracted much attention in many fields, from basic surface science to practical uses. Up to now, numerous studies have sought to interpret the static hydrophobicity (contact angle of a droplet and surface energy/surface tention of soild surface) in terms of the interaction between liquid and solid surface. The static hydrophobicity has been well-clarified (controlled by surface energy and morphology), however, the dynamic hydrophobicity (sliding angle and velocity of a droplet), a measure of dynamic adhesive property against water, is still in controversy. Practically, dynamic hydrophobicity does not simply depend on static hydrophobicity. Thus far, no one could completely explain a fact that hydrophobic surfaces of similar water contact angles often show quite different adhesive property against water. In this study, we successfully prepared various hydrophobic surfaces using alkyl and fluoroalkyl silanes with various adhesive properties against water in terms of solid-liquid interface engineering. We will demonstrate that the dynamic hydrophobicity, a measure of the adhesive property against water, depended on the surface morphology (even of the order of a few nanometers) and surface composition (small amount of polar groups on the surface) and that we could control it independent of static hydrophobicity.

SS-ThP21 Structural, Mechanical and Electronic Properties of Stilbene and Pentathiophene Based Molecular Monolayers, ***Y. Qi***, University of California, Berkeley, *B. Hendriksen, V. Navarro, D. Esteban, J.Y. Park, I. Ratera, J. Klopp,* Lawrence Berkeley National Laboratory, *C. Mauldin,* University of California, Berkeley, *C. Edder,* Lawrence Berkeley National Laboratory, *J. Frechet,* University of California, Berkeley, *M. Salmeron*, Lawrence Berkeley National Laboratory

The incorporation of molecules in electronic devices is promising for technological applications and a new direction in fundamental research. The structural, mechanical and electronic properties of manolayers of two molecules containing pi-systems have been studied with conducting probe atomic force microscope (CP-AFM), X-ray photoemission spectroscopy (XPS) and near edge X-ray fine structure spectroscopy (NEXAFS). One is w-(trans-4-stilbene)alkylthiol, and the other is decyl-pentathiophenyl butyric acid. We found that the w-(trans-4-stilbene)alkylthiol molecules self-assemble on Au (111) with the thiol group covalently bond to Au surfaces as confirmed by X-ray photoemission spectroscopy. The molecular film undergoes a slow structural change from a tilted to a more upright geometry, a process that can be accelerated by thermal annealing. In all cases w-(trans-4-stilbene)alkylthiol molecules show poor electrical conductivity in the vertical direction. Molecular monolayers of decyl-pentathiophenyl butyric acid were deposited on heavily doped Si (100) by the Langmuir Blodgett technique. The orientation of the molecules has been studied by NEXAFS. Current versus voltage measurements and conductivity mapping reveal a higher conductivity than that of w-(trans-4-stilbene)alkylthiol self-assembled monolayers. The friction and the conductivity were observed to strongly depend on the molecular arrangement.

SS-ThP22 Characterization of Chemically Etched Poly(tetrafluoroethylene), ***T.R. Richardson***, *F.A. Donate, C.L. Gentry, D.D. Hawn, B.J. Kern, G.E. Mitchell, G.E. Potter, C.W. Reinhardt, R.J. Wachowicz,* The Dow Chemical Co., *S. Marsh, M.E. Yevich*, Acton Technologies

Chemical etching solutions are typically employed to prepare the surface of poly(tetrafluoroethylene) for bonding to a surface. These etching solutions are based on sodium-naphthalene complexes in an aprotic organic carrier such as a glycol diether. The use of such etchants produces a chemically modified surface suitable for bonding. We employed X-ray photoelectron spectroscopy, static secondary ion mass spectrometry, and atomic force microscopy in order to understand the chemical properties of these etched surfaces. Key to this work was a procedure which utilizes macrotomy to remove thin layers of material from the surface, but these sections are obtained at a very low angle relative to the surface plane (1° or 1/2°). Using this procedure, the thickness of a layer could be "magnified" 60 or 120 times. This facilitated the use of XPS and SIMS to analyze the surface composition as a function of depth. The procedure developed produced surfaces and thin sections with no measurable smearing or contamination. The design of the apparatus resulted in production of sections or surfaces with reproducible and accurate appearance and chemistry. In this presentation we will discuss the results obtained from these low angle macrotomed surfaces, highlighting the chemistry of the surface and the modified zone. The results discussed apply to molded industrial poly(tetrafluoroethylenes).

SS-ThP23 Surface Chemistry of (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)Ru on Polycrystalline Ta, ***K.M. Thom***, *J.G. Ekerdt*, University of Texas at Austin

As device dimensions in integrated circuits scale down, there is a need to deposit ultra-thin, conformal, continuous films for various microelectronic applications. Ruthenium (Ru) thin films are promising candidates for applications such as diffusion barriers in copper metallization and capacitors in dynamic random access memories. Chemical vapor deposition and atomic layer deposition have been used to deposit Ru thin films using a variety of precursors, but the surface chemistry of these precursors is largely unexplored. This work examines the surface chemistry of (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)Ru [DER] on a polycrystalline tantalum (Ta) foil, with and without the presence of methyl iodide. X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) were used to study the adsorption and desorption behavior. Because DER was found to dissociate negligibly at room temperature and above, low temperature experiments were used to examine the interaction of the DER with the Ta foil. The DER was dosed onto Ta at 140 K and then desorbed during the TPD process; XPS spectra were taken both before and after TPD. The DER adsorbs and desorbs molecularly, although a small amount of dissociation occurs during TPD. Both XPS and TPD results indicate that the DER saturates on the surface at an exposure of about 4 Langmuir (L); no multilayers are formed. For exposures up to 0.5 L, a single TPD desorption state is observed at 272 K. As coverage increases, the single state splits into two desorption features which are centered at 264 K and 297 K at saturation. The two states are attributed to different physical states of the molecules; possibly two different molecular orientations occur on the surface. The Ru 3d$_{3/2}$ XPS feature shifts from 286.2 eV to 287.3 eV as exposure is increased from 0.1 L to saturation, a binding energy (BE) change of about 1 eV; the Ru 3d$_{5/2}$ XPS feature also shifts up by 1 eV. The BE shift with increasing coverage is consistent with the presence of two adsorbed states. Because other research has shown alkyl iodides enhance the nucleation of Ru films, methyl iodide was co-dosed into the chamber along with the DER in an attempt to promote dissociation at room temperature and above. The addition of methyl iodide enhanced the dissociation of DER as compared with the molecule alone. This talk will discuss the surface reactions of DER in the presence and absence of adsorbed iodide.

SS-ThP24 X-Ray Photoelectron Spectroscopy for Impedance Measurements, ***S. Suzer***, *H. Sezen*, *G. Ertas*, *A. Dana*, Bilkent University, Turkey

A new technique is introduced for probing charging/discharging dynamics of dielectric materials, in which X-ray photoemission data is recorded while the sample rod is subjected to 10.0 V square-wave pulses with varying frequencies in the range of 0.001 to 1000 Hz. This technique allows us to probe electrical impedance of dielectric materials. Accordingly, for a conducting graphite sample the C1s peak appears at correspondingly -10.0 eV and +10.0 eV binding energy positions (20.0 eV difference) with no frequency dependence. However, the corresponding C1s and O1s peaks of polymeric materials (PS, PMMA, and PS/PMMA blends) appear with less than 20.0 eV difference and exhibit strong frequency dependence due to charging of the polymeric films, which are faithfully reproduced by a theoretical model.[1,2] Information can be obtained from the frequency dependence of the positions, as well as the widths of the peaks. Various applications of this technique for characterization of organic (polymeric) and inorganic homogeneous and heterogeneous materials and surface structures will be presented and discussed.

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SS-ThP25 Sliding Behavior of a Water Droplet between Two Hydrophobic Coatings by Self-assembled Monolayer, ***A. Nakajima***, *S. Suzuki*, Tokyo Institute of Technology, Japan, *M. Sakai*, *A. Hashimoto*, Kanagawa Academy of Science and Technology, Japan, *N. Yoshida*, The University of Tokyo, Japan, *Y. Kameshima*, *K. Okada*, Tokyo Institute of Technology, Japan

Self-assembled monolayer (SAM) coatings of organosilanes have been widely used for surface modification of inorganic materials. We studied the sliding behavior of water droplets sandwiched between Si substrates treated by octadecyltrimethoxysilane (ODS) and fluoroalkylsilane (FAS) by changing the plates' distance (D) and droplet mass (m). The sliding angle depended on D, m, and the upper and bottom combination of the coating. The droplet between FAS coatings exhibited larger sliding angle than the ODS coating when D=1.0 mm although the FAS coating possesses higher water contact angle. The sliding behavior of water droplets sandwiched between ODS and FAS coatings was observed using a high speed camera system on a declined surface (35 degrees). The larger droplet mass and plate distance, the larger sliding acceleration. The internal fluidity in the droplet visualized by particle image velocimetry method revealed that the droplet slid down with twin flows between plates and that their border was almost the center of the plates. The water droplet sandwiched between FAS/ODS exhibited heterogeneous rolling fluid: the border of the twin flow was not the center between the plates. The magnitude of the rolling fluid depended on the surface chemical composition and the distance between two plates.

SS-ThP26 Characterisation of Self-Assembled Monolayers Using Angle Resolved XPS, ***J. Wolstenholme***, Thermo Fisher Scientific, UK, *D.J. Graham*, Asemblon, Inc., *R.G. White*, Thermo Fisher Scientific, UK

Self assembled monolayers (SAMS) are increasingly important as a means to functionalise surfaces and to control surface properties or reactivity. The length of many of the molecules used in these layers and, therefore, the thickness of the monolayers formed by them is often less than the attenuation length of the photoelectrons emitted in the XPS process. This means that the XPS technique is ideal for characterising the layers. The additional benefits coming from ARXPS are also important for the determination of layer orientation and thickness. For this work, the ARXPS data was collected in parallel over a 60 degree range, without the need to tilt the samples. This means that it is possible to collect angle-resolved XPS maps of the surface to examine the uniformity of the layers. If the layers are uniform, data can be collected as a map over a large area to minimise the X-ray flux density used in the analysis. By examining a number of samples having the same SAM at the surface, the precision of the measurements can be determined. Obviously, high precision is required if the two-dimensional uniformity is to be investigated. It will also be shown, using a range of SAM's, that the techniques developed for extracting non-destructive depth profiles from ARXPS data can be successfully applied to these materials. Results will be reported from SAMs formed from alkane thiols and from molecules containing additional functional groups.

SS-ThP27 Study of the Interplay between PDMS and Surfaces Modified with Monolayers and Small Molecules, ***L. Yang***, *F. Zhang*, Brigham Young University, *N. Shirahata*, *T. Nakanishi*, National Institute for Materials Science, Japan, *M.R. Linford*, Brigham Young University

Here we describe a method for probing the surface free energies of materials by stamping them with polydimethylsiloxane (PDMS) stamps that have also been wet with low molecular weight PDMS. Hydrophobic surfaces, e.g., alkyl monolayers with high advancing water contact angles, resist adsorption of PDMS, while PDMS adsorbs effectively onto hydrophilic or even moderately hydrophobic surfaces. For example, PDMS transfers to thin films of C60, while it does not transfer to thin films of molecules that contain long alkyl chains. In addition, PDMS transfers to hydrophilic spots patterned onto hydrophobic monolayers, but not onto the background. The degree of PDMS transfer can be used to monitor processes such as the contamination of a clean metal surface in the ambient. The PDMS transferred in these cases is easily detected by spectroscopic and imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) because of the sensitivity of this technique for this species. Wetting, X-ray photoelectron spectroscopy, and principal components analysis of the ToF-SIMS data are also employed to study this problem.

SS-ThP28 Direct Polymer Growth on Hydrogen-Terminated Silicon, ***M.R. Linford***, Brigham Young University, *N. Shirahata*, National Institute for Materials Science, Japan, *R.B. Blake*, *M.V. Lee*, Brigham Young University

When hydrogen-terminated silicon is immersed in a solution of an unsaturated monomer and a free radical initiator, a very thin, ca. 2 nm, thin polymer film grows on the surface, provided the temperature of the reaction mixture is raised to the decomposition point of the initiator. Changing the nature of the monomer, the initiator, and reaction conditions do not seem to lead to the production of significantly thicker polymer layers. However, addition of appropriate chemical reagents allows ca. 10 nm polymeric layers to be directly grown on hydrogen-terminated silicon. This method can be used in conjunction with photopatterning of hydrogen-terminated silicon, which removes hydrogen termination in certain areas on the surface and thus prevents polymer growth in these regions. Surface reactivity and patterning are confirmed by X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and atomic force microscopy.

SS-ThP30 In Situ Real-Time Grazing Incidence Study of Organic Thin Film Growth*, **A. Amassian**, V.A. Pozdin, S. Bhargava,* Cornell University*, D.-M. Smilgies,* CHESS, Cornell University*, A. Papadimitratos, S. Hong,* Cornell University*, A.R. Woll,* CHESS, Cornell University*, G.G. Malliaras, J.R. Engstrom*, Cornell University

We have performed in situ, real-time grazing incidence X-ray synchrotron measurements during the growth of organic thin films of pentacene. Experiments were carried out on films deposited from both thermal and supersonic sources on a variety of substrates (e.g., SiO_2, photoresists, polymers) and over a broad range of process parameters (e.g., growth rate, temperature, beam kinetic energy). A CCD detector captured both in-plane Bragg peaks and out-of-plane Bragg sheets, allowing us to solve the 3D structure of pentacene crystals. We reveal the formation of new polymorphs of the so-called "thin film" and bulk phases of pentacene, while in situ measurements (video to be shown)provide new insights into the initial growth of organic crystals.

SS-ThP31 Self-Assembled Monolayers of Aromatic Tellurides on Gold and Silver Substrates*, **M.T. Weidner**,* University of Washington*, A. Shaporenko,* Universität Heidelberg, Germany*, J. Müller, M. Höltig, A. Terfort,* University of Marburg, Germany*, M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) of tellurolates are promising alternatives to most frequently used thiolate-based systems. In this study we present first experimental data on SAMs of aromatic tellurolates. These SAMs were fabricated on Au(111) and Ag(111) substrates from a ditelluride precursor, bis(4'-methylbiphenyl-4-yl) ditelluride (BBPDTe) and characterized by high resolution X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. BBPDTe was found to adsorb dissociatively on both substrates, resulting in the formation of well-defined, densely packed, and ordered BPTe SAMs, with a larger molecular inclination, a lower packing density, and inferior crystallinity on Au than on Ag. However, both BPTe/Au and BPTe/Ag were not stable under ambient conditions, but underwent a rapid autooxidation, which affected exclusively the tellurolate headgroups. The BPTe molecules in the oxidized films remained, however, bound to the substrate by the terminal O atoms coordinated to the Te moieties, and the quality of the films, given by parameters such as packing density, degree of the orientational order, and average tilt angle of the SAM constituents was not noticeably affected by the autooxidation. In addition, the BPTe SAMs were compared with the analogous thiol- and selenol-based systems, and common tendencies for the different chalcogen headgroups, ranging from Te to O, were derived.

Thin Film

Room: 4C - Session TF-ThP

Aspects of Thin Films Poster Session

TF-ThP1 Ferroelectric Properties of $PbMn_{1/3}Nb_{2/3}O_3$-Pb(Zr,Ti)O_3 Thin Films Epitaxially Grown on (001)MgO Substrates*, **K. Wasa**, I. Kanno, H. Kotera,* Kyoto University, Japan*, T. Zhang, F. Li, S.-Y. Zhang*, Nanjing University, China

It is well known bulk ferroelectric oxide ceramics of modified Pb(Zr,Ti)O_3 (PZT) , $PbMn_{1/3}Nb_{2/3}O_3$- PZT, show variety of ferroelectric properties when we change the doping level of Mn and Nb. Thin films of the modified PZT will be useful for a fabrication of micro- and/or nano-level functional device including GHz electronic devices, since the co-doping of Mn and Nb to pure PZT will improve both mechanical Q values and electromechanical coupling of original PZT. However, it is not clear whether the bulk ferroelectric properties will be achieved in the ferroelectric thin films. We have tried to make epitaxial growth of thin films of the modified PZT, $xPbMn_{1/3}Nb_{2/3}O_3$- (1-x)PZT ,on (001)MgO substrates by rf-magnetron sputtering at x=0.06 and PZT(45/55). Before the epitaxial growth of the modified PZT, (001)Pt electrode with $SrRuO_3$ buffer layer was epitaxially grown on the MgO substrates by the rf-magnetron sputtering. The epitaxial temperature of the modified PZT thin films was around 600°C and the epitaxial films showed (001) single orientation of tetragonal structure. The dielectric constant of the co-doped epitaxial thin films at 1.7 μmm in film thickness was ε*=190 at 100kHz and showed sharp square shape P-E hysteresis curve with Pr=60μmC/cm^2 and Ec=110kV/cm. The bulk dielectric constant of modified PZT is ε*=300 to 400. The structural differences between bulk and thin films will cause the sharp square type P-E curve with smaller dielectric constant for thin films. The epitaxial thin films showed high piezoelectric constant, e_{31} =-4C/m^2 , which was almost the same to the highest value of piezoelectric constant observed in the pure PZT(52/48) thin films at MPB condition. The present Mn and Nb doped PZT thin films show tetragonal structure which achieves the fine interface between thin films and the substrates. Since the doping of Mn will increase the mechanical Q values, the modified PZT thin films with lower dielectric constant will be applicable for the fabrication of the nano-level functional devices including GHz film bulk acoustic resonator (FBAR).

TF-ThP2 (Dual) Ion Beam Deposition of Tantalum Pentoxide Thin Film at Room Temperature*, **W. Kulisch**, D. Gilliland, G. Ceccone, H. Rauscher, L. Sirghi, P. Colpo, F. Rossi*, Joint Research Center, Italy

Tantalum pentoxide is a material with outstanding optical (high refractive index, high transparency) and electrical properties (high dielectric constant), rendering it a promising candidate for applications in rapidly developing fields such as optics, microelectronics, and sensorics. Many modern application are based on plastic substrates such as PMMA, which in turn requires deposition at low or even room temperature. To meet this end, the deposition of Ta_2O_5 films by means of (dual) ion beam deposition at room temperature on Si, glass and plastic substrates has been investigated. A tantalum target was sputtered by Ar ions from a Kaufman source in the presence of oxygen, while the growing film was simultaneously bombarded with Ar or O ions from a plasma beam source. Films have been characterized with respect to their morphology, thickness, composition, bonding structure, and optical properties by techniques such as atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), variable angle spectroscopic ellipsometry (VASE) and UV-VIS spectroscopy. In a first step, the influence of the oxygen partial pressure on the properties of single ion beam sputtering was investigated. It turned out that the oxygen content in the films increased with the oxygen partial pressure until saturation at the stoichiometric value is reached. These films are extremely smooth (rms roughness < 0.15 nm), possess refractive indices of 2.1 or even higher and extinction coefficients lower than the detection limit of the ellipsometer (ca. 10^{-3}). In a second step, the influence of a densification of the growing films by simultaneous bombardment with either oxygen or argon ions was studied. The parameters investigated were the ion current density and the ion energy. A major aim of this study was to establish a correlation of the basic film properties, especially the bonding environment as revealed by XPS and FTIR, one the one hand, and the optical properties, on the other hand.

TF-ThP3 Characterization of Hafnium Nitride Films Deposited by Plasma ALD*, **N. Singh***, Oxford Instruments Plasma Technology, UK

Conductive hafnium nitride films have been deposited by plasma ald in the Oxford Instruments OpAL reactor. TEMAH was used as the hafnium source and nitrogen was provided from a remotely mounted inductively coupled plasma source. The influence of nitrogen-hydrogen and ammonia plasmas on film properties such as stoichiometry, refractive index, and resistivity is reported. Film thickness and refractive index were determined by ellipsometry. The resistivity was measured using a 4 point probe. The composition of the film was estimated from Auger electron spectroscopy and XRD was used to confirm the amorphous nature of the film. Depending on the plasma composition, the growth per cycle was in the range 0.7 - 1.5 Å/cycle and the refractive index varied from 1.4 - 2.3. The minimum measurable resistivity of the films was 5 μ Ω cm. Hydrogen plasma has signifcant effect on the conductivity of the deposited iflms compared to nitrogen plasma. The thickness of the films remained unchanged when left exposed to ambient air.

TF-ThP4 Al-doped ZnO (AZO) Films Deposited by Gas Flow Sputtering for Transparent Conductive Thin Films*, **H. Takeda**,* Aoyama Gakuin University, Japan*, Y. Iwabuchi, M. Yoshikawa,* Bridgestone Corporation, Japan*, Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Al-doped ZnO (AZO) has been attracted much attention as one of alternative materials to Sn-doped In_2O_3 (ITO) films. Recently, there have been strong demand for high deposition rate with stable discharge and low cost deposition systems for the various commercial applications. Gas Flow Sputtering (GFS) has two important features. The one is the possibility for very high deposition rate because of using an intense hollow cathode discharge and a large amount of sputtering gas (Ar) flow. Another is stability of the reactive sputtering process with the variation in reactive gas

(O_2) flow. Reactive sputtering is usually highly nonlinear processes for the conventional glow discharge sputtering because of the poisonings of the target surface. In the case of GFS, a large amount of Ar gas flows from the faced targets to the substrate preventing the oxidation of the target surface. AZO films were deposited by GFS on alkali-free glass (corning, #1737) without heating using two Zn-Al alloy targets (Al: 1.5 wt.%). For all the depositions, Ar gas flow and sputtering power were fixed at 1.0 SLM and 1500 W, respectively. O_2 flow was controlled from 0 to 10 sccm. The crystal structure was analyzed by X-ray diffraction (XRD). The electrical and optical properties were measured by van der pauw method and UV-IR spectroscopy, respectively. With increasing O_2, the intensity of an XRD peak of Zn metal decreased. On the other hand, ZnO XRD peaks appeared from O_2 flow of 6 sccm. All AZO films deposited over 6 sccm of O_2 exhibited a strong c-axis preferred orientation perpendicular to the substrate surface. Deposition rate was about 70 nm/min. At O_2 gas flow of 6 sccm, the AZO film showed the lowest resistivity of 9.82×10^{-4} Ω cm, Hall mobility of 10 cm^2/V s, carrier density of 5.48×10^{20} /cm^3.

TF-ThP5 Annealing and Manganese Activated Electroluminescent Characteristics of Thin Film Gallium Oxide, *J.H. Heo*, ***J.H. Kim***, Chungbuk National University, Korea

Post deposition annealing and alternating current electroluminescence of thin film gallium oxide doped with manganese (Ga_2O_3:Mn) have been studied. The Ga_2O_3:Mn films were prepared at room temperature by radio frequency planar magnetron sputtering from a 2 mol% Mn-doped Ga_2O_3 target in an oxygen-argon mixture atmosphere. The as-deposited Ga_2O_3:Mn films had an amorphous structure. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses indicated that the Ga_2O_3:Mn films began to crystallize into a monoclinic β-Ga_2O_3 phase by the post-deposition anneal at 800°C. The crystallinity of the films was continuously improved as the annealing temperature increased up to 1200°C. The polycrystalline structure was uniformly developed throughout the film by the anneal. The half-stack alternating-current thin-film electroluminescent (ACTFEL) devices were constructed using an inverted single-insulating structure, indium tin oxide (ITO)/Ga_2O_3:Mn/lead zirconate titanate (PZT)/Au on alumina (Al_2O_3) substrates. The fabricated ACTFEL devices exhibited an emission peak at around 507 nm in the green range and it was accounted for by the 3d-3d intrashell transition from the $^4T_1$ excited state level to the $^6A_1$ ground-state in divalent Mn ion. The color coordinates of the emission were x=0.197 and y=0.623 in the CIE chromaticity.

TF-ThP6 Effects of Manganese Oxide-Mixed Abrasive Slurry on the Tetra-Ethyl Ortho-Silicate Oxide Chemical Mechanical Polishing for Planarization of Inter-Layer Dielectric film in the Multilevel Interconnection, ***S.-W. Park***, *W.-S. Lee*, Chosun University, Korea, *Y.-J. Seo*, Daebul University, Korea, *G.-W. Choi, S.-J. Han, Y.-K. Lee*, Chosun University, Korea

One of the critical consumables in chemical mechanical polishing (CMP) is a specialized solution or slurry, which typically contains both abrasives and chemicals acting together to planarize films. The slurry designed for optimal performance should produce reasonable polish rates, acceptable polish rate selectivity with respect to the underlying layer, low surface defects after polishing, and good slurry stability. In single abrasive slurry (SAS), the solid phase consists of only one type of abrasive particle. On the other hand, mixed abrasive slurry (MAS) consists of a mixture of at least two types of abrasive particles, which can be chosen from inorganic (alumina, silica, ceria, zirconia, titania, manganese oxide, etc) or organic (polymeric resins) groups. In this work, in order to prepare the MAS, KOH-based fumed silica slurry of pH 11 with solid content of 13 % was diluted in de-ionized water (DIW) with 1:10 ratio. The manganese oxide (MnO2) abrasives particles were then added in the diluted silica slurry. The concentration of manganese oxide abrasive was varied from 1 wt% to 5 wt%. The surface quality after polishing is important issue in TEOS-oxide CMP. A surface with a very low scratch level is obtained by chemically modifying the abrasive surface. The particle size distribution of MAS as a function of mixed amount of manganese oxide abrasive particles was also observed a bimodal particle size distribution with the two peaks at mean aggregate particle sizes of 250 nm and 2250 nm. Formation of nanometer and large size particles is perhaps, the result of aggregation of modified manganese oxide particles. This is due to an interplay between the abrasive action of larger manganese oxide particles and chemical-tooth nature of the smaller silica particles surrounding the larger manganese oxide particles. The slurry composition is further optimized to allow an excellent polishing performance yielding good surface quality while maintaining high removal rate. In addition, it is anticipated that there were be few special slurry handling problems in a fabrication production environment because relatively benign chemistry is used. This work was supported by grant No. (R01-2006-000-11275-0) from the Basic Research Program of the Korea Science & Engineering Foundation and by Korea Research Foundation Grant (KRF-2006-005-J00902).

TF-ThP7 The Role of Nitrogen Composition in SiO_xN_y as Diffusion-Barrier Film Deposited by NH_3/SiH_4/Ar Plasma Enhanced Chemical Vapor Depositon, ***P. Thuy***, *J.H. Lee, I.K. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

For the next generation display devices, flexible display panels formed on plastic substrates are considered and one of the important issues in the flexible displays is the formation of transparent diffusion barrier on the plastic substrates or on the devices which prevents the permeation of water and oxygen to the device. In this study, SiO_xN_y thin films were deposited by plasma enhanced chemical vapor deposition (PECVD) using SiH_4/NH_3/Ar at low temperature (temperature < 50°C) and with biasing the substrate and the effect of substrate biasing and gas mixture on the film properties as a water vapor permeation barrier was investigated. The result showed that with the R ratios (R=[NH_3]/([NH_3]+[SiH_4]) from 0.4 to 0.6, nitrogen composition in the film was the highest and the roughness of the film was the lowest. Also, the water vapor transmission rate was $\leq 10^{-3}$ mg/(m^2/day). Consequently, these SiO_xN_y thin films were suitable as diffusion barriers on glass or polymer materials. In this presentation, more detailed material properties of SiO_xN_y thin films measured as a function of bias voltage and gas combination will be discussed.

TF-ThP8 Low-Temperature Formation of Polycrystalline Silicon Thin Films via Enhanced Aluminum-Induced Crystallization, ***F.W. DelRio***, *J. Lai, T.-J. King Liu, R. Maboudian*, University of California Berkeley

In the manufacture of very large scale integrated circuits and microelectromechanical systems, polycrystalline silicon (polysilicon) thin films are typically formed directly by low-pressure chemical vapor deposition at temperatures above 600 °C, using silane as the precursor gas. Such a high process temperature makes this approach unsuitable for formation of polysilicon films on low-cost glass substrates and on substrates with completed CMOS integrated circuits. To lower the thermal budget, aluminum-induced crystallization (AIC) can be used to crystallize an amorphous silicon (a-Si) film deposited at low temperature. The formation of polysilicon by AIC of non-hydrogenated a-Si relies heavily on the layer exchange of the adjacent Si and Al films. Several factors affect the exchange of the Al and Si layers, and consequently, have an impact on the characteristics of the polysilicon film. In this paper, we study the effect of silicon doping on AIC of non-hydrogenated a-Si. In particular, Al-2%Si is examined, which is commonly used in microelectronics to prevent junction spiking, hillocks, and electromigration. A series of Al-2%Si/a-Si samples are prepared in a sputtering system with multiple process chambers and annealed in vacuum at temperatures in the range of 250 to 375 °C. The silicon doping is found to enhance the crystallization process, thereby reducing the initial crystallization temperature by ~50 °C. The enhancement is attributed to the presence of Si precipitates in the Al-2%Si film, which act as nucleation sites for Si grain growth. As with the Al/a-Si system, adjacent Al-2%Si and a-Si films undergo a layer exchange during isothermal annealing, resulting in a continuous polycrystalline silicon film with good physical and electrical properties. The observed decrease in the Si_{2p} binding energy is consistent with p-type doping of the Si layer, attributed to the presence of Al in the crystallized film. Assuming an Arrhenius-type behavior for the crystallization, the activation energy for the process is found to be 0.97±0.09 eV. This value is in good agreement with the activation energy for Si diffusion in evaporated Al films, indicating that the crystallization is a diffusion-limited process.

TF-ThP10 Thermally Stable Ag Thin Film Structure Modified with Very Thin Al Layers, ***M. Kawamura***, *Y. Inami, Y. Abe, K. Sasaki*, Kitami Institute of Technology, Japan

Improvements of thermal stability of Ag thin films, featured with the lowest resistivity among all metals, have been attempted. Especially, Ag thin films on dielectric oxide layers are expected for metallization materials in future electronic devices if the improvement is achieved. One of the common ways is alloying the Ag films, but it is difficult to preserve its low resistivity due to impurity scattering effect of electrons in some cases. We show a result of structural modification, where very thin Al layers (about 1 or 3 nm of thickness) were introduced at top and/or bottom of the Ag, namely Al/Ag/Al, Ag/Al and Al/Ag structures. The Al/Ag/Al structure showed excellent stability on surface morphology and electrical resistivity even after annealing at 600°C in vacuum. It is considered that the deposited thin Al layers changed into thin Al oxide layers and resulted in capping (and/or passivation) of Ag film and better adhesion with oxide substrate. The resistivity of the film was also as low as that of bulk Ag. The Al layer at the top of Ag film showed better result than that at the bottom. Therefore, it is found that inhibition of surface diffusion of Ag films is more important to prevent agglomeration of Ag thin films. Consequently, it is found that the structural modification is very useful to obtain thermally stable Ag thin films without agglomeration even after annealing at 600°C.

TF-ThP11 Transmission Infrared Characterization of Titanium Oxide Thin Films Deposited by Atomic Layer Deposition, ***B.-C. Kang***, Sungkyunkwan University, Rep. of Korea

Metal oxide thin films have a number of perspective applications in microelectronics and sensor technology. However, there is not enough mechanistic understanding of growth chemistry during film deposition process, especially atomic layer deposition (ALD) process. We have constructed a simple ALD reactor which enables transmission infrared spectroscopy to be performed in situ on a layer-by-layer basis. In this study, ALD of TiO_2 was carried out using alternating exposures of titanium isopropoxide ($Ti(O^iPr)_4$) and water (H_2O), separated by an inert gas (e.g., N_2) purge. In situ transmission Fourier transform infrared (FTIR) spectroscopy was used to monitor the sequential surface chemistry during the $Ti(O^iPr)_4$ and H_2O exposures during ALD reaction onto the Si(100) surface. The FTIR spectra showed the growth of TiO_2 bulk vibrational modes versus number of ALD cycles. Also ex situ x-ray photoelectron spectroscopy, scanning electron microscopy and transmission electron microscopy were used to investigate the composition and detail structure of the deposited TiO_2 thin film on the Si(100) substrate.

TF-ThP12 Fabrication of CdS-based Visible Light Photocatalyst by the Use of Ammonia-Free Chemical Bath Deposition Technique, ***S. Biswas***, *M.F. Hossain, T. Takahashi,* University of Toyama, Japan, *Y. Kubota,* University of Yokohama City, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

In the recent years, utilization of a second semiconductor of lower band-gap as a sensitizer to TiO_2 attracted lot of attention as an emerging technique for preparation of visible light photocatalyst. CdS is one of the effective low band semiconductors which can be used as a sensitizer to TiO_2. However, the preparation of CdS layer by popular conventional chemical bath deposition (CBD) technique with ammonia as a complexing agent create environmental problem as large scale production causes employment of large amounts of ammonia, which is toxic, highly volatile and harmful for the environment. In this present study CdS thin films were deposited on glass substrate by ammonia free chemical bath deposition technique with Sodium citrate as a substitute to ammonia. After deposition, all the samples were annealed at 400 °C in high vacuum of 5×10^{-5} Pa for 30 min. On the top of CdS layers TiO_2 thin films were deposited by dc magnetron sputtering technique with using a mask to leave exposed CdS surface. Different samples were prepared with various amount of thiouria content for the preparation of CdS layer. The CdS thin film prepared by ammonia free recipe shows highly oriented crystallographic structure. The optical property of the CdS thin film exhibits higher red shift in compare to CdS prepared by conventional technique. Different amount of red shift has been observed with different thiouria concentrations. The photocatalytic activity was measured by decomposition of Methanol separately in UV-Vis and visible light. The surface morphology of the CdS and TiO_2 surface was studied by field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM). The result is attributed to the crystallographic structure and microstructure of both CdS and TiO_2 layers.

TF-ThP13 Study of Sol-Gel Derived TiO_2 Photoelectrode for the Fabrication of Low Cost Dye-Sensitized Solar Cells, *M.F. Hossain, S. Biswas,* ***T. Takahashi,*** University of Toyama, Japan, *Y. Kubota,* University of Yokohama City, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

Dye sensitized solar cells (DSCs) are regarded as a low cost alternative to conventional p-n junction solar cell devices. The high light-to-energy conversion efficiencies achieved with DSCs may be attributed to the nano-porous TiO_2 electrode. Among the various techniques for the preparation of TiO_2 photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates, and also it is a low temperature process. In our study, the titanium dioxide porous thin film electrodes were deposited on SnO_2: F coated glass slides by sol-gel technique; where, tetrabutylorthotitanate was used as a precursor and was hydrolyzed in a water/alcohol/amine mixture. Polyethylene glycol (PEG), with different concentrations, was added to the coating solution as a structure-directing agent, and the films thus prepared were transparent, crack free. In this present investigation, titanium dioxide thin films were prepared with different PEG concentrations and with different numbers (2-8) of coatings. The surface morphology of the films has been observed by atomic force microscope (AFM) and field emission scanning electron microscope (FE-SEM). The morphology of porous TiO_2 thin films strongly depends on the concentration of the template (PEG). The decomposition of PEG during high temperature treating is considered to be responsible for the generation of porous structure in the films as compared with TiO_2 film without addition of the polymer. It was revealed from optical study that the dye absorption increases with the increase of PEG concentration. Incident photon-to-current efficiency (IPCE) is calculated for all the solar cells with different TiO_2 thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells of TiO_2 films deposited with different PEG concentrations is discussed with the analysis of different microstructure of the TiO_2 thin films and the corresponding dye-incorporation.

TF-ThP14 Optimization of Sputter-Deposited TiO_2 Photo-Electrode for Dye-Sensitized Solar Cell, ***M.F. Hossain***, *S. Biswas, T. Takahashi,* University of Toyama, Japan, *Y. Kubota,* University of Yokohama City, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

Dye-sensitized solar cells (DSCs) have been under investigation for the past decade due to their attractive features such as high energy conversion efficiency and low production costs. The high light-to-energy conversion efficiencies achieved with DSCs may be attributed to the nano-porous TiO_2 electrode. Reactive magnetron sputtering is a very promising technique for large-area uniform coating of TiO_2 thin film and it has potential to control the crystallographic phase and micro-structure through the process of modification of different sputtering parameters. In this present study effort has been made to prepare low cost DSCs with sputter-deposited TiO_2 electrode. Nano-porous TiO_2 thin films were successfully deposited on SnO_2:F substrate by facing target reactive magnetron sputtering deposition technique with different substrate temperatures ranging from room temperature to 400° C. Low cost chlorophyllin based-dye was used along with carbon paste electrodes (CPEs) on SnO_2:F glass as a counter electrode. Incident photon-to-current efficiency (IPCE) was calculated for all the solar cells with different TiO_2 thin films to evaluate the economic viability of this technique. The amount of dye incorporation was found to be highly dependent on the microstructure and the thickness of the film, as apparent from optical measurements. The variation of photoelectric conversion efficiency of the solar cells with different TiO_2 films deposited at different substrate temperatures is discussed with the analysis of different microstructure of the TiO_2 thin films and the corresponding dye-incorporation.

TF-ThP15 Micro Structure Control of RuO2 Nanoparticle Deposition on CNTs by Cyclic Voltammetry Method, ***H.-M. Wu***, Chinese Culture University, Taiwan, *W.-T. Hong,* Institute of Materials Science and Nanotechnology, Taiwan, *L.-C. Chen*, National Taiwan University

The deposition and surface morphology of RuO2 on carbon nanotubes (CNTs) are crucial for the optimal capacitive performance of RuO2/CNTs composite supercapacitors. We investigate the effect of annealing and pulse voltage control on the microstructure of RuO2 nanoparticles during cyclic voltammetry deposition. The results have shown that the capacitance RuO2/CNTs was remarkably achieved to 225 mF/cm2 after annealed at 200? for 2 hours, and 125 mF/cm2 by applying 2 sec on time/ 5 sec off time pulse voltage for half hour, at scan rate 50 mv/sec. The micro texture of RuO2 on CNTs surface was found strongly affected by deposition condition and play a key rule of the capacitive performance.

TF-ThP16 Porosity Analysis on Supported Thin Nanoporous Films, ***K.J. Chao***, National Tsinghua University, Taiwan

Ordered nanoporous materials synthesized through surfactant templating exhibit channel structures of amorphous silicate or oxide framework, uniform apertures in the range of 2–30 nm and large surface area of ~1000 m2/g. Their intrachannel void domain provides the confined space to accommodate nanostructured molecules and clusters, and the hydroxyl groups on the intrachannel surface can be chemically modified through silynation. The applications of this type of nanoporous films are closely associated with their pore properties such as pore size and porosity as well as hydrophobicity of intrapore surface. The dielectric constant of nanoporous silica films was reported to decrease with porosity. Gas transport of these films was found to be somewhat affected by their pore size distribution. Furthermore, the uniform thickness and proper density of the nanoporous coating play key roles in its anti-reflection of light. The film texture of supported thin films was found to be affected by substrate. As those films and their substrates usually appear together in application, it is desirable to perform the characterization with on-substrate thin films instead of the films detached from their substrates. In this paper, three pore characterization techniques and their application on supported silica thin films are discussed. The porosity of nanoporous films on flat and dense substrates, including glass and silicon wafer, has been estimated from refractive index obtained by ellipsometric porosimetry and from film density and thickness obtained by specular X-ray reflectivity(XRR). After removal of organic template, such as nonionic P123 Pluronic block copolymer (EO20-PO70-EO20) and cationic surfactant CTAB (C16H33N(CH3)3Br, the intrachannel surface of nanoporous silica is rich in hydrophilic silanol groups, which can absorb water easily. The water absorbency makes the nanoporous silica difficult to maintain a constant density and low dielectric constant, especially at relative humidity > 25 %.

Therefore, it is better to perform the XRR under low humidity using an in-situ sample cell and to use the film as a low dielectric layer after hydrophobic modification. To elucidate the relationship between porosity and pore size distribution, the physical adsorption of krypton on dehydrated samples has been measured, and this technique is performed in the absence of water uptake on the hydrophilic nanoporous materials.

TF-ThP17 Silicon Carbonitrides: On the Attainability of Stable Compounds with High Nitrogen Content, ***M. Bruns,*** Forschungszentrum Karlsruhe, Germany, *M. Rudolphi, H. Baumann,* Frankfurt University, Germany, *U. Geckle*, Forschungszentrum Karlsruhe GmbH, Germany

During the last decade great efforts have been made to synthesize pure Si-C-N compounds using various precursor based techniques. These still ongoing activities were mainly stimulated by the expected attainability of materials combining the properties of silicon carbide and silicon nitride. However, most of the approaches result in compounds of deficient nitrogen content and considerable hydrogen and oxygen content, respectively. In contrast, high-purity thin films with tailored elemental composition can be achieved directly from the elements using either RF magnetron sputtering, ion implantation or the combination of both methods. In the latter cases, severalfold implantation at different energies calculated from Monte-Carlo-simulations is necessary in order to synthesize layers with homogeneous element depth-distribution up to the surface. The availability of this powerful preparation tool motivated us to study the ternary Si-C-N phase diagram in more detail. Therefore, the main stoichiometry-defining parameters for sputtering (Si/C target area ratio, N partial pressure, substrate temperature) and ion implantation (energy and fluence) have been varied systematically in order to attain a chosen composition. The chemical composition of the Si-C-N films was characterized by means of X-ray photoelectron spectroscopy (XPS). In addition, Auger electron spectroscopy (AES), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy were used to achieve a comprehensive characterization. For quantification XPS and AES data were calibrated with absolute concentration values from non-Rutherford backscattering spectrometry (n-RBS). Resonant nuclear reaction analysis (NRRA) provides non-destructive depth profiles of ^{15}N. The morphology after subsequent annealing was studied by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM).

As one prominent result the N content of 57.4 at.% required for the formation of Si-C-N compounds on the tie line Si_3N_4 - C_3N_4 cannot be reached for Si/C ratios ≤ 1, whereas stoichiometric Si_2CN_4 can be easily achieved in a reproducible manner. Obviously the compound formation does not follow a simple Si by C substitution. In conclusion these results might give reason to speculate on the attainability of pure C_3N_4.

TF-ThP18 New Method to Correlate Crystalline Orientation and Sputtering rate of Tantalum, ***C.-F. Lo***, Praxair Surface Technologies - MRC

Normally, higher target sputtering rates contribute to higher film deposition rates, which result in increased throughput. Optimizing the cathode design of sputtering tool and the sputtering parameters are common ways to increase film deposition rate. Controlling the grain orientation of the sputtered material is another possible approach to increase the deposition rate. In order to find the desired orientation for higher sputtering rates, the correlation between crystalline orientation and sputtering rate must be identified. In the past, single crystals were used to correlate the crystalline orientation and sputtering rate. This technique was time-consuming regarding sample preparation and limitations on material availability. The new method uses Electron Backscatter Diffraction (EBSD) to identify the orientation of the individual grains on a polycrystalline material prior to being sputtered. By measuring the change in eroded depth of each grain as a function of sputtering kWh, the sputtering rate is obtained, In order to gather higher grain population and ensure the eroded depth of the individual grains are measurable by a height gauge, the grain size diameter is controlled in the range of 3mm to 20mm. This study used a 4 inch diameter by 0,25 inch thickness polycrystalline Tantalum as a test sample to correlate the grain orientation and sputtering rate. By applying 1 kW power with 10 mtorr Ar pressure, the eroded depths of the individual grains at the erosion zone were measured at intervals of 5 kWh. The results showed that the (111) grain orientation has the lowest erosion rate, while the orientations with higher indices tend to be eroded faster. This study demonstrated that the relationship of crystalline orientation to sputtering rate can be easily established by sputtering polycrystalline materials with the assistance of EBSD to pre- identify the orientation of the individual grains. Copyright 2007. Praxair Surface Technologies. All rights reserved.

TF-ThP19 Combinatorial Thin Film Synthesis of Cerium Doped Lutetium Silicate (Lu2SiO5) Scintillation Materials, ***J.D. Peak****, C.L. Melcher, P.D. Rack*, University of Tennessee

Positron Emission Tomography (PET) is a widely employed medical imaging technique that possesses the advantage of being able to image metabolic activity. In PET imaging a patient ingests a radioactive tracer and gamma rays resulting from positron annihilation are detected by a circular array of single crystal scintillators coupled to photomultiplier tubes (PMT). Since the scintillator crystals are the first step in PET detection, their performance is of paramount importance in final image quality and resolution. Large scintillator crystals are often grown via time consuming processes such as the Czochralski and Bridgman crystal growth techniques. The search for new scintillator crystals can be limited by the time consuming nature of the crystal growth. In this work, we will illustrate the use of a combinatorial thin film synthesis process that is being used to explore new scintillator materials. The combinatorial synthesis process utilizes three individual rf magnetron sputtering sources which can be simultaneously powered to generate a wide composition space of binary or ternary systems. In this work, we have investigated cerium doped lutetium oxyorthosilicate (LSO) as it is currently the most widely used scintillator crystal in PET imaging and provides a good benchmark for our proposed approach. LSO thin films with a gradient of cerium doping have been deposited to investigate the effects of cerium concentration and to compare the thin film properties to those of bulk LSO crystals. We have found that the emission spectra of the thin film materials have similar characteristics compared to the bulk crystals, and the emission intensity changes with the cerium concentration. Cerium doped lutetium-silicon oxide gradients have also been grown. X-ray diffraction measurements have been correlated to the equilibrium phase diagram, and the intensity of the luminescence emission spectra have been correlated with the corresponding phases of the lutetium-silicon system. In this presentation, we will discuss the combinatorial thin film synthesis process, and will correlate the observed structural, morphological, and chemical properties of the thin films to the measured optical properties.

TF-ThP20 Electrochoromic Properties of Mg-doped Nickel Oxide Films Deposited by rf Magnetron Sputtering, ***H. Sugawara,*** Aoyama Gakuin University, Japan, *I. Yamamoto,* Nissan Motor Co., Ltd., Japan, *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Electrochromic devices have been expected as the one of the environmental technologies such as architectural "smart" windows which should have large potential to save energy. Ni oxide (NiO) films have been studied extensively as oxidation-coloring materials, which could be used as counter electrode of amorphous WO_3 films. Azens, et al. reported that heavy Mg dopings (atomic ratio of Mg/ (Ni+Mg): 44.4 %) on NiO was effective to improve optical transmittance in visible light region of 380-600 nm at the bleached state.[1] In this study, we investigated Mg doped Ni oxide films in the wide range of the doping concentration and variation of the electrochromic properties were investigated in detail. Ni oxide flims were deposited on unheated ITO-coated glass substrates by rf magnetron sputtering using NiO-MgO targets with various Mg doping concentrations (atomic ratio of Mg/ (Ni+Mg): 0, 5, 10, 20 %). Ar was used as a sputtering gas and O_2 was introduced as a reactive gas (O_2 gas composition changes from 0 % to 100 %). Total gas pressure during the depositions was maintained at 5 Pa and the film thickness was adjusted approximately to 200 nm. Crystallinity and surface morphology of the films were analyzed by X-ray diffraction (XRD) and atomic force microscope (AFM), respectively. The composition and the chemical state of the elements were analyzed by X-ray photoelectron spectroscopy (XPS). In order to analyze the electrochromic properties, the specimens were immersed in a 1M KOH electrolyte and underwent voltammetric cycling in a three-electrode arrangement with a Pt counter electrode and an Ag/AgCl reference electrode. The Ni oxide films with the proper amount of Mg doping showed higher coloration efficiency and higher transmittance at the bleached state than Ni oxide films without doping. The optimized doping concentration in this study was 5 % for the highest electrochromic performance.

[1] A. Azems, J. Isidorsson, R. Karmhag, C. G. Granqvist, Thin Solid Films, 422 (2002) 1.

TF-ThP21 Structural Characterization and Electronic Work Function of Pt-Ru Alloy Thin Films, ***A.P. Warren****, R.M. Todi, B. Yao, K.B. Sundaram,* University of Central Florida, *K. Barmak,* Carnegie Mellon University, *K.R. Coffey*, University of Central Florida

Microstructure and the electronic work function of Pt-Ru alloy thin films spanning the compositional range from pure Pt to pure Ru were investigated. Nominally 50 nm thick films were co-sputtered from elemental targets in an ultra high vacuum chamber. X-ray reflectivity and Rutherford backscattering spectroscopy were used to determine the film thicknesses and compositions. The electronic work function of the alloy film samples was determined by analysis of the capacitance-voltage characteristics of films deposited as part of a metal-oxide-semiconductor capacitor structure and found to range from 4.8 eV for pure Ru to 5.2 eV for pure Pt. To better understand the variation in work function for the intermediate compositions, a variety of characterization techniques were used. Transmission electron microscopy was used to examine the microstructure of the samples, and to assess the grain size variation. X-ray and electron diffraction were used to identify the crystalline phases present and to evaluate the extent of crystallographic texture. A notable increase in the compositional range of the hexagonal close packed (hcp) phase was observed, suggesting a metastable extension of the hcp phase stability as compared to bulk Pt-Ru alloys. The steepest change in the electronic work function for the intermediate alloy compositions coincided with a rapid change in the c/a ratio of the hcp phase.

TF-ThP22 The Importance of the Valence State of Cu in the Formation of Re-BCO using Low Pressure dc-Magnetron Sputtering, ***K. Smet,*** *R. De Gryse*, University Ghent, Belgium

In this work we propose a novel way of explaining the XRD-spectra of our rotatable dc-magnetron low pressure sputtered $YBa_2Cu_3O_{7-\delta}$ and $NdBa_2Cu_3O_{7-\delta}$ thin films. As is frequently the case at low pressure sputtering our films exhibit an expanded c-axis. This expansion is usually attributed to oxygen deficiency and/or cation-disorder in the $Re\text{-}Ba_2Cu_3O_{7-\delta}$ structure. However under certain conditions (low pressure, Cu co-sputtering, lowering deposition temperature,...) the spectra of our films not only reveal an expanded c-axis but the (00n) peaks also tend to split up, whereby one peak has the theoretical c-axis value while the other shows an enlargement. This behaviour suggests the presence of two phases in our thin films. A closer look at XRD-spectra of some of our thin films suggest that a large c-axis expansion in Cu-poor conditions might be attributed to the presence of $Y_2Ba_2O_5$. The conditions triggering the split as well as the possible presence of $Y_2Ba_2O_5$, point to the importance of the energy and/or valence state of the Cu atoms during the deposition process. Therefore in this paper we explore a possible explanation for the peak splitting in the XRD-spectra of our thin films based not only on the abundance of the Cu atoms at the substrate but also on their energy or valence state.

TF-ThP23 Chemical Mechanical Polishing Characteristics of ITO Thin Film Prepared by RF Magnetron Sputtering, ***G.-W. Choi, W.-S. Lee,*** Chosun University, Korea, *Y.-J. Seo,* Daebul University, Korea, *S.-W. Park, S.-J. Han*, Chosun University, Korea

Indium tin oxide (ITO) thin films have attracted intensive interest because of their unique properties of good conductivity, high optical transmittance over the visible region and easy patterning ability. Thin films of ITO have found many applications in anti-static coatings, thermal heater, solar cells, flat panel displays, liquid crystal displays, electroluminescent devices, sensors and organic light-emitting diodes. ITO thin film is generally fabricated by various methods such as spray, CVD, evaporation, electron gun deposition, direct current electroplating, high frequency sputtering, and reactive sputtering. In this paper, ITO films were grown on glass substrate by RF magnetron sputtering method. To achieve high transmittance and low resistivity, we examined the various film deposition conditions such as substrate temperature, working pressure, annealing temperature, and deposition time. Carrier concentration and carrier mobility of ITO thin films were measured, the transmittance of them also was done. As O2 flow rate and substrate temperature increased, the transmittance of ITO thin film increased because ITO particles formed coarse and good crystalline. Next, in order to improve the surface quality of ITO thin film, we performed the chemical mechanical polishing (CMP) by change of process parameters, and compared the electrical and optical properties of the polished ITO thin film. The thickness of ITO films was measured by ellipsometer. The electrical resistivity was measured by using the four-point probe method. . The best conditions to polish the surface of ITO thin film (which was used as the anode) smoothly were as follows: platen speed, head speed, polishing time, and slurry flow rate were 60 rpm, 60 rpm, 60 sec, and 60 ml/min, respectively. AFM analysis shows that the thin film of ITO was polished smoothly. This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

TF-ThP24 Effect of Plasma Induced Substrate Temperature Rise on AZO Thin Film Properties in ICP Assisted Bipolar Pulsed dc Magnetron Sputtering, ***W.K. Yang,*** *J.H. Joo*, Kunsan National University, Korea

To deposit Al doped Zinc oxide film on polymer substrate at room temperature, internal inductively coupled plasma assisted bipolar pulsed dc magnetron sputtering system was used. Pulse frequency was from 50kHz to 250kHz and duty ratio was between 60 - 90%. ICP was generated by a 2MHz rf generator through an L-type matching network and a ceramic shielded Cu antenna. High density plasma could heat the temperature sensitive polymer by high bombarding ion and electron energy flux. The average electron density and temperature in this experiment was 10^{11} #/cm^3 and 2 - 5 eV by Langmuir probe measurements. The distance between the magnetron sputtering target and substrate must be optimized not to give excessive heat flux to the substrate. Variable frequency pulsed dc plasmas showed wide range of shapes at the same gas pressure and power level. Up to 150kHz, the plasma region was extended as the frequency was increased. At higher frequency than 150kHz, the length of plasmas remained same. We measured the transient temperature changes in the plasma region at four different positions and will discuss the correlations between the pulse frequency and transient temperature rise of a polymer substrate.

TF-ThP25 Effect Of Sodium Addition On Cu-Poor CIGS2 Thin Film Solar Cells, ***P.S. Vasekar,*** *N.G. Dhere*, Florida Solar Energy Center

Copper-Indium-Gallium Sulfide (CIGS2) is a chalcopyrite material with a near-optimum band gap of 1.5 eV. Recent research in the CIGS2 thin film photovoltaic community is directed towards thinner films because the availability and cost of Indium are limiting factors. The required amounts of metals can be lowered by using thinner films. Initially, small sized grains are formed during the film growth. With continuing growth to larger thicknesses, more favorably oriented grains grow faster at the expense of others and coalesce to form compactly packed large-grain morphology. Hence certain thickness of a thin film is necessary so that the grains start coalescing. The solar cell performance in smaller grained chalcopyrite absorber deteriorates due to detrimental effects of the larger fraction of grain boundaries. It is essential to hasten the grain growth through coalescence to retain high-quality properties even in thinner films. Sodium may play a vital role by enhancing the atomic mobility and improving the coalescence even in thinner films. It will be interesting to study if sodium can play a role in Copper-poor CIGS2 absorbers. In Copper-rich CIGS2 precursors, increased mobility and consequently absorber phase formation is obtained due to pseudo-binary phase region. Hence Sodium may not play a vital role in Copper-rich precursors. Also Copper-rich precursors for this purpose are prepared with 40 percent excess Copper. After sulfurization, the absorber film is etched to remove the excess Copper. This may or may not lead to an exact stoichiometric Cu/In+Ga ratio of 0.92 for the absorber in addition making the film rough. Copper-poor absorber has a comparatively smooth film and better morphology after etching. This work represents a study of morphology and device properties of CIGS2 thin films with Copper-poor absorbers after Sodium is introduced on the substrate in the form of Sodium Fluoride before sputtering Copper, Indium and Gallium.

TF-ThP26 Surface Modification of Polytetrafluoroethylene by Copper Ion Implantation, ***K.-W. Weng,*** Mingdao University, Taiwan, *S. Han,* National Taichung Institute of Technology, Taiwan, *Y.-C. Chen,* National Chung Hsing University, Taiwan, *D.-Y. Wang*, Mingdao University, Taiwan

Polytetrafluorethylene (PTFE) was implanted copper by a hybrid metal plasma ion implantation (MPII) with varying ion dose. X-ray photoelectron spectroscopy (XPS) was used for the characterization of chemical structures in the ion-implanted assembly, while scanning electron microscopy (SEM) was used for the characterization of morphology. Five chemical bonds, CF_3, CF_2, CF, C-O, and elemental carbon bonds, were observed on the surface of the ion-implanted assembly. Numerous microfibers were observed on the ion-irradiated surface. Water contact angle of the ion-implanted samples increased gradually with increasing ion dose, and reached a maximum value of 103.5^0 on the surface of the sample implanted with ion dose of 3×10^{17} ion/cm^2. The decrease of microhardness at high ion dose was resulted, accounted for radiation damage. Wear resistance and resistance were also discussed in the copper modified surface.

Vacuum Technology

Room: 4C - Session VT-ThP

Vacuum Technology Poster Session (including Student Poster Competition with Cash Award)

VT-ThP1 Design and Construction of a Vacuum Tube Furnace with High Voltage Field for the Growth of Silicon Nanowires, ***C.A. Adams,*** *J.J. Register*, University of South Florida

Construction of a Vacuum Tube Furnace with High Voltage Field for the Growth of Silicon Nanowires. The goal of this project is to build a vacuum tube furnace providing up to 1150 degrees Celsius in a vacuum of approximately 30 mTorr and an electric field of 5V/µm in density to the sample. Feed and purge gasses will need to be fed through into the chamber. The tube furnace will be constructed of a ceramic cylindrical heater element mounted in a stainless steal housing with carbon board insulation surrounded. The tube will be Quartz approximately 12.5 cm diameter and 122 cm long and 2.4 cm thick with an open end and the other end reducing to a 3/8 inch tube. A stainless steal termination will be designed and built to provide a vacuum seal to the open end of the tube. This termination will use viton gasket compression seal and end in a vacuum door. All feedthroughs will take place through the side walls of the termination collar. The vacuum system will consist of a two stage mechanical pump with a foreline trap and a thermocouple vacuum gage. MKS vacuum gage and mass-flow controllers will be integrated with Labview for operational programming and data recording. Labview will also be used to record the high voltage run time and values, control and record the temperature. The furnace heater element will be powered by an Omega PID controller coupled with a SSR.

VT-ThP2 Experimental Measurements of Thermal Accommodation Coefficients for Microscale Gas-Phase Heat Transfer*, W.M. Trott, D.J. Rader, J.N. Castañeda, J.R. Torczynski, M.A. Gallis,* Sandia National Laboratories*, **L.A. Gochberg***, Novellus Systems, Inc.

An experimental apparatus is described that measures gas-surface thermal accommodation coefficients from the pressure dependence of the conductive heat flux between parallel plates separated by a gas-filled gap. Heat flux between the plates is inferred from measurements of temperature drop between the plate surface and an adjacent temperature-controlled water bath. Thermal accommodation coefficients are determined from the pressure dependence of the heat flux at a fixed plate separation. The apparatus is designed to conduct tests with a variety of gases in contact with interchangeable, well-characterized surfaces of various materials (e.g., metals, ceramics, semiconductors) with various surface finishes (e.g., smooth, rough). Experiments are reported for three gases (argon, nitrogen, and helium) in contact with pairs of 304 stainless steel plates prepared with one of two finishes: lathe-machined or mirror-polished. For argon and nitrogen, the measured accommodation coefficients for machined and polished plates are near unity and independent of finish to within experimental uncertainty. For helium, the accommodation coefficients are much lower and show a slight variation with surface roughness. Two different methods are used to determine the accommodation coefficient from experimental data: the Sherman-Lees formula and the GTR formula. These approaches yield values of 0.87 and 0.94 for argon, 0.80 and 0.86 for nitrogen, 0.36 and 0.38 for helium with the machined finish, and 0.40 and 0.42 for helium with the polished finish, respectively, with an uncertainty of ±0.02. The GTR values for argon and nitrogen are generally in better agreement with the results of other investigators than the Sherman-Lees values are, and both helium results are in reasonable agreement with values in the literature.

VT-ThP3 Sputter Deposition System for High Throughput Fabrication of Composition Spreads*, **J.M. Gregoire**, R.B. van Dover, J. Jin, F.J. DiSalvo, H.D. Abruna*, Cornell University

We describe a custom built sputtering system that can deposit composition spreads in an effectively UHV environment but which does not require the high-throughput paradigm to be compromised by a long pumpdown each time a target is changed. The system employs four magnetron sputter guns in a cryoshroud (getter sputtering) which allows elements such as Ti and Zr to be deposited with minimal contamination by oxygen or other reactive background gasses. The system also relies on custom substrate heaters to give rapid heating and cooldown. The effectiveness of the gettering technique is evaluated, and example results obtained for catalytic activity of a pseudoternary composition spread are presented.

VT-ThP4 How Does One Turn a Research-Based Molecular Beam Epitaxy System into a Reliable Training Tool?*, **M.-R. Padmore**, E.I. Altman, V.E. Henrich, F. Walker*, Yale University

Electronic devices are simultaneously decreasing in size while increasing in their importance to our everyday lives. Thin film crystalline growth is necessary for the production and integration of micro- and nanoelectronics. The Molecular Beam Epitaxy (MBE) system is one of the most widely used methods of achieving this growth. As such, it is valuable to train students in the use and applications of MBE as early as at the undergraduate level. However, in using the system to train less-experienced users, the chance of system failure increases dramatically. Thus, a system must be built which can, through the use of preventative interlocks and user-friendly interfaces, easily and cost-effectively be incorporated into an instructional setting. A major problem with many preventative measures is that they are implemented using administrative and/or procedural controls. These types of controls block the transparency of the process by not allowing the students to interact with the system itself. This system is designed to be "hands-on", allowing the trainees to see the basic science behind the technology they are using, without reducing the reliability of the system. By using engineering controls such as automatic valves and computerized shutdown interlocks, the main failures which arise from: a.) the sample transfer mechanism; b.) the ultra-high vacuum requirements; and c.) the water cooling requirements; can be avoided without severely decreasing the transparency of the system's process and with an increase in ease of use. An evaluation of the transparency, user-friendliness, and reliability of the system were conducted by allowing a small group of students of various backgrounds to perform experiments mapping out surface phase diagrams on silicon surfaces. Preliminary results of this study show that an effective set of engineering controls can be designed. The conflicting problems between transparency and reliability addressed in designing this system are not specific to Molecular Beam Epitaxy, but to any educational institution whose mission is to create reliable training tools in all fields of engineering and technology.

VT-ThP5 Vacuum Chamber Design at National Synchrotron Light Source II*, **J.-P. Hu**, H.-C. Hseuh, C. Foerster*, Brookhaven National Laboratory

National Synchrotron Light Source II (NSLS-II), proposed to be built at Brookhaven National Laboratory, will be a 3-GeV 800-meter circumference 3rd-generation synchrotron radiation facility. To provide a highly-stable and highly-focused synchrotron beam for advanced research, vacuum pressure at 10-9 Torr or below in the storage ring during normal operation is deemed critical. The approach for achieving such ultra-high vacuum would rely on the effective arrangement of non-evaporable getter strips, titanium sublimation pumps, and sputter ion pumps along the ring chamber, under proper in-situ baking and beam conditioning. The ring chamber will be made of aluminum through extrusion followed by machining, from which side-ports and ante-chamber can be precisely made to accommodate photon absorbers, lumped and distributed pumps. To test the design of the vacuum system, Monte Carlo-based Molflow and gas diffusion solver Vaccalc codes are utilized to calculate the pressure variation in channels hosting the electron beam, based on different pumping setup in models. Spare aluminum chambers of the Advanced Photon Source in Argonne Laboratory, featuring similar cross section as the NSLS-II proposed, will be used in bench test of pumping performance, thereby verifying pressure profile from code simulation. Updated design to improve ring vacuum and thus beam quality will be presented per project progress. (Work performed under auspices of the United States Department of Energy, under contract DE-AC02-98CH10886).

VT-ThP6 Viscosity and Diffusion Coefficient for a Gas Mixture Flow in a Tube, Valid Over the Whole Range of Knudsen Numbers*, **M. Vukovic***, Tokyo Electron U.S. Holdings Inc.

The viscosity and diffusion coefficients for a two-gas mixture, valid over the whole range of Knudsen numbers (Kn), are obtained by applying the generalization procedure of Beskok and Karniadakis (Microscale Thermophysical Engineering 3, 43, 1999) to the Boltzmann equation solutions of a gas mixture flow in a pipe by Sharipov and Kalempa (J. Vac. Sci. Technol. A 20(3), 814.,2002). The transport coefficients are expressed in terms their continuum limit value, multiplied by a correction factor that depends on Kn and the species masses and relative concentration. These coefficients are applied to the problem of gas counterflow in the Kn=1 range.

VT-ThP7 New Apparatus for Testing Hermetically Sealed Packages of Electronic Devices*, **M. Kinugawa**, H. Kurokawa, S. Takagi,* Mitsubishi Electric Corp., Japan*, **H. Kawata***, Wave Technology Inc., Japan

Hermetically sealed packages are widely applied to optical and high-frequency devices to maintain high reliability. The inert gasses, which are usually inserted in such packages, might contain such impurities as moisture that could damage the device. Therefore, it is crucial to know the variety and the amount of impurities in the filled gas. In this study, we show a new technique for analyzing gas in sealed packages. The advantage of our new technique is that analysis precision does not depend on package size. The testing apparatus consists of a sample chamber and an analysis chamber; they are both connected to a vacuum-tight valve and an exchangeable orifice. The analysis chamber has a quadrupole mass spectrometer and is exhausted continuously by a turbomolecular pump. The sample chamber has a rotating vacuum feedthrough that can mount several types of sample stages, a perforator, a viewport, and another pumping system. After setting sample packages on the sample stage, the sample chamber is pumped down by the pumping system. Then the pump is switched off, and the valve between the two chambers is opened, so the sample chamber will only be exhausted from the analysis chamber through the orifice. A pinhole is made on the sample package by the perforator. The gas in the sample package comes out and flows through the orifice from the sample chamber to the analysis chamber, and then the mass spectrometer in the analysis chamber detects the gas. We can get the gas composition from the integral ion intensity measured by the mass spectrometer and its ion sensitivity. The conductance of the orifice is determined by considering the sample size and the maximum vacuum pressure in the analysis chamber to keep the pressure a little lower than the working upper limit of the mass spectrometer. This technique allows accurate measurements of gas composition regardless of size package. We have already applied this technique to the development of new devices with higher reliability.

VT-ThP8 Optimization of a Multitarget Sputtering System for the Production of Magnetic Tunneling Junctions and Multilayers, *A. Chiolerio, **P. Martino***, Politecnico di Torino, Italy

Our work consists in a renovation project for an obsolete multitarget sputtering system, previously used for industrial purposes, in order to revert it to research objectives with a cost-effective operation, saving as many original components as possible. The system was equipped with a control rack, a large cylindrical vacuum chamber and a complete rotary / turbomolecular pump evacuation subsystem; substrates where inserted into a slit close to a vacuum oven by vertically lifting the whole chamber above the steel basement by means of an oleodynamic piston. The rotating oven slit was manually positioned above one of the three target sources allowing a rotation of 270°. Our newly realized system maintains the original control rack, the evacuation subsystem and the basement. A smaller cylindrical chamber has been designed in order to reduce both void spaces and evacuation time; all inner parts of the AISI 316L walls have been polished to minimize the outgassing rate while the opening is assisted by a vertical lift motor and performed only for scheduled maintenance, because a load-lock chamber is now connected to the operation chamber via a gate valve. This smaller buffer chamber has been designed either to insert and recover substrates or to serve as a second process chamber for the realization of tunneling barrier thin oxyde layers, where an oxygen line inlets the reactive gas and a sapphire window allows UV radiation to assist the critical step. Specimens are transferred to the carrying slit inside the process chamber via a magnetic manipulator; this slit is positioned above the desired sputtering source by means of an AC brushless motor operated by a remote control software. The rotating subsystem allows a full rotation (360°), the running cables being substituted by an ad hoc designed electrical rotating contact that ensures quite low electric field at contact point, no debris and appropriate friction during operation. A particular manual implementation allows one to choose between the simultaneous rotation of two coaxial axes and the movement of only one of them. The first axis is connected to the substrate slit and the other one to the shutter, which may interrupt the deposition process or interpose suitable masks to transfer geometries to the substrates. This solution ensures a higher vacuum level, with only one mechanical feedthrough, as well as much lower costs.

VT-ThP9 Influence of the Adsorption Gas on Friction Coefficient and Wear Track., ***A. Kasahara**, M. Goto, Y. Pihosh, M. Tosa*, NIMS, Japan

Surface modification of sliding motion materials is inevitable to reduce friction as well as outgassing in a vacuum. We have therefore studied the development of advanced vacuum motion materials by control of surface roughness on a submicron scale. We have successfully found that any material sheet with about 100nm-250nm surface roughness showed same friction coefficient in a vacuum as at an atmospheric pressure for Type 304 austenitic stainless steel materials and anodic oxidation processed aluminum materials. Materials with except 100nm-250nm surface roughness shows a different friction coefficient for the friction measurement in a vacuum and at an atmospheric pressure. Type 304 austenitic stainless steel sheets had a larger friction coefficient in a vacuum than at an atmospheric pressure. The anodic oxidation processed aluminum sheets had a smaller friction coefficient in a vacuum than at an atmospheric pressure. We therefore studied the relation between friction coefficient and cross-section shape of wear track depth by an atomic force microscope (AFM) Type 304 austenitic stainless steel sheets had a deeper wear track in a vacuum than at an atmospheric pressure probably because the increase in friction coefficient to the desorption of the adsorption gas as a lubricant. The anodic oxidation processed aluminum sheets had shallow wear track in a vacuum than at an atmospheric pressure probably because the adsorption force generated by the applied load was reduced by the desorption of the adsorption gas. As a result, it was thought that the absorption layer on the materials surface influenced by the surface roughness had an important role on friction.

VT-ThP10 Atomic Layer Deposition Reactor with In Situ Diagnostics for Studying Gas-Surface Interactions, *V. Rai, B.N. Jariwala, S. Agarwal*, Colorado School of Mines

In this presentation, the authors will describe the design and fabrication of a custom vacuum chamber for studying the heterogeneous surface chemistry during thin film deposition. The chamber is ideally suited for investigating the film growth mechanism during atomic layer deposition (ALD). The reactor consists of a cylindrical stainless-steel vessel, which is 10 inches in diameter, 6 inches in height. The reactor volume has been minimized to reduce the residence time of the gases to minimize the purge duration in an ALD cycle. The chamber is equipped with multiple ports for instrumentation, sample manipulation, and in situ surface and gas-phase diagnostics. The substrate is clamped to a heated plate, and the deposition temperature can be varied from 40 to 300 °C. The reactor is pumped by a 240 l/s turbomolecular pump, which provides a base pressure of 9×10^{-8} Torr. The chamber also has a parallel-plate, capacitively-coupled plasma source operating at a frequency of 13.56 MHz to generate radicals for plasma-assisted ALD. The distance between the plates can be varied from 4 cm to 9 cm using flexible linear motion bellows. The oxygen inlet into the reactor is equipped with an ozone generator to provide an alternate oxidant during metal oxide ALD. To deliver controlled amounts of low volatility precursors, we employ pressure-based mass flow controllers that require an inlet pressure of only 4 Torr and do not heat the temperature-sensitive precursors. The reactor is equipped with three in-situ diagnostic tools - (1) attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, (2) quadrupole mass spectrometry (QMS), and (3) quartz crystal microbalance (QCM). In addition, a set of ports is available for in situ spectroscopic ellipsometry. The combination of ATR-FTIR spectroscopy and QCM provide sub-monolayer sensitivity to surface adsorbates. The QMS, which is placed in a differentially pumped housing, is used to detect the surface reaction products. Specifically, we will present results from gas-surface interaction studies during the ALD of titanium dioxide using metal precursors such as titanium tetrachloride and titanium isopropoxide, and oxidants such as water, ozone, and O radicals.

VT-ThP11 A Real Time Monitoring Method on the Decomposition Degree of MOCVD Precursor through an Ultrasonic Diagnosis Method, ***J.Y. Yun**, S.W. Kang, D.J. Seong*, KRISS, S. Korea

This study proposes a method for monitoring the decomposition state of the metal-organic precursor which is used for the Metal Organic Chemical Vapor Deposition (MOCVD) system. As the precursor of MOCVD is highly likely to decompose due to the instability of its chemical structure during processing, critical problems are generated for thin film formation and its yield in this case. Although real time monitoring technology on the decomposition degree of these precursors is essential for the next generation semiconductor process, both commercialized technology and fundamental research have scarcely been accomplished. Therefore, this study endeavors for acknowledgement by the semiconductor industry with a proposal for a real time monitoring method on the decomposition degree of the precursor through an ultrasonic diagnosis method.

VT-ThP12 Development of a Static Expansion Vacuum Standard at the National Institute of Standards and Technology, ***J.H. Chow**, P.J. Abbott*, National Institute of Standards and Technology

The NIST Pressure and Vacuum Group maintains sub-atmospheric pressure standards that range from 10^{-7} to 10^{+5} Pa. These consist of orifice flow standards from 10^{-7} to 10 Pa and Ultrasonic Interferometric Manometers from 10^{-1} to 10^{+5} Pa. A new Static Expansion Standard is in development with an operating range of 10^{-3} to 10^{+3} Pa. The standard is composed of two spherical stainless-steel vessels with a volume ratio of about 100:1. The two vessels are interconnected with a stepper motor driven valve. An initial pressure of gas in the small volume is measured to high accuracy using a resonant silicon gauge and then is expanded into the evacuated larger volume. This expansion results in a pressure reduction of about 100. Further evacuation and expansion cycles are used to produce lower pressures. The system is temperature controlled to within 0.1C with a thermoelectrically cooled enclosure. This new standard provides many useful benefits: First, the Static Expansion Standard generates pressures that encompass both the orifice flow and manometry standards without relying on gas flowmeters; Second, the standard enables fast and simple calibration of spinning rotor (SRG's) and capacitance diaphragm gauges (CDG's). Currently these calibrations require a very skilled technician and are done at very high cost to customers; Third, the system allows for a convenient comparison of manometer and vacuum standards using CDG's and SRG's respectively. Work is ongoing to characterize the system, including determining the volume ratio and estimating the uncertainties.

VT-ThP13 Custom-Designed Very-High Vacuum Chamber for Growth of Large Area Silicon Nanowhiskers Arrays via an Ion-Enhanced Vapor-Liquid-Solid (VLS) Mechanism, ***M. Bettge**,* University of Illinois at Urbana-Champaign, *D. Abraham,* Argonne National Laboratory, *S. Burdin, S. MacLaren, I. Petrov, E. Sammann*, University of Illinois at Urbana-Champaign

A VHV chamber was custom-designed for experimental growth of silicon nanowhisker arrays via a novel ion-enhanced Vapor-Liquid-Solid (VLS) technique. Growth was to be carried out on a self-organized metal seed layer on a Si or SiO_2 surface. A reactive magnetron sputtering system was needed to supply atomic Si to the growth surface under concurrent high-energy ion irradiation. The successful implementation of this growth technique required sample temperature control to 450°C, a bias voltage up to 3kV, and a reactive plasma environment. Additional deposition capabilities and process controls for several inert and reactive gases were also required. The design goal was to develop an economical system using standard vacuum hardware that allowed handling of two-inch Si wafers. A wafer stage using a halogen reflector bulb for temperature control was designed to meet the requirements for whisker growth. Protection of the insulators and wafer handling proved to be especially challenging during the design of this stage. The chamber design also included capabilities for wafer storage and wafer transfer between two DC magnetron sputtering stations and a miniature evaporator custom-designed to fit a $2^{3}/_{4}$-flange. This presentation will describe the realization of the chamber design, which made possible the processing of nearly four hundred samples to date. Ultimately, this enabled the growth of aligned Si nanowhisker arrays at temperatures below 200 °C and at rates up to 200 nm/min. Growth can take place on any substrate on which a thin Si film can be deposited.

VT-ThP14 A Low Pressure Chemical Vapor Deposition (LPCVD) System Designed for Epitaxial Growth of 3C-SiC on Si, ***M.P. Orthner***, *F. Solzbacher, L.W. Rieth, E. Jung*, University of Utah

Silicon carbide (SiC) can be used as electronic material at high temperatures (>500°C) and in aggressive/corrosive gas and fluid media. Depositing thin films of 3C-SiC on Si will permit use of existing Si processing technologies on the substrate while the 3C-SiC is processed as the active layer. Cubic silicon carbide (3C) is the only polytype that can be epitaxially grown on Si. This material combination makes SiC useful in pressure sensors, accelerometers, and for encapsulation. A key problem for 3C-SiC is the number of defects formed during growth due to a 20 % lattice mismatch. The deposition of 3C-SiC on Si by low pressure chemical vapor deposition (LPCVD) has been reported using a number of different precursors and a wide range of operating conditions. Growth temperatures range from 650°C to 1400°C and pressures range from atmospheric to mTorr. An LPCVD reactor with unique hot zone geometry has been developed to achieve the required growth conditions to study the growth of 3C-SiC on Si. The system is a cold wall design using a 304 stainless steel (SS) water cooled vacuum chamber. Pressure feedback is controlled using a butterfly valve and MKS capacitance manometer down to 50 mTorr and is currently limited by the Alcatel 813B dry pump. The resistive heater is a 7" diameter graphite spiral used to heat 2", 3", 4", and 6" Si substrates. The heater is mounted 1" above the graphite wafer chuck that is rotated by a stepper motor to increase uniformity. An Omega IR2P optical pyrometer and temperature controller are used in conjunction with the 180A phase angle fired SCR to measure and control the substrate temperature. Substrate temperatures in excess of 1400°C have been achieved. A custom designed horizontal flow showerhead manufactured from 316L SS is located on the side of the wafer chuck. The gases pass horizontally over the heated Si substrates to form thin films. Silane and propane precursors are used to grow the 3C-SiC using the conventional carbonization growth technique first introduced by S. Nishino. Initial deposition of very thin (< 100nm) 3C-SiC on Si (100) substrates have been grown in the described reactor. Deposition conditions maintained a process pressure of 250 mTorr with temperatures ranging from 1200°C to 1400°C. The chemical composition, crystal morphology and surface properties were investigated in relation to the growth temperature.

VT-ThP15 Method of Diagnosing Mechanical Endurance of Dry Vacuum Pumps to High Throughput Environment, ***J.Y. Lim***, *W.S. Cheung,* Korea Research Institute of Standards and Science*, B.H. Moon,* Samsung Electronics Company, Korea*, Y.H. Shin*, Korea Research Institute of Standards and Science

Dry Vacuum Pumps are encountering rapid expansion of harsh and high throughput applications to semi-conductor/display industry. Besides their ability of making superior clean environment, they are normally exposed to clean to very harsh gas applications, thus often very easily contaminated with process byproducts in the forms of hard particles or coatings on the overall interior of the pumps. For this reason, even before installation in the process lines, detection of latent endurance for the pumps is a very important factor to diagnose primary mechanical, functional ability and internal controllable parameter settings during actual processes. With 40 to 300 slm of continuous dry air flow for one to three hours dependent on the pumping speeds, ten dry vacuum pumps carefully selected from six worldwide manufacturers were differently responded due to their internal structures, cooling systems, and breaker settings for body protection due to high temperature. Parameters such as inlet pressure, power consumption, and sound/vibration as well as parameters from SPM (single pump monitoring system) were carefully analyzed to diagnose the latent endurance of each pump. Characteristics mappings for all parameters were established for 1200 and 1800 m3/h dry vacuum pumps. In the case of total power consumption, 4 to 8 kW are manifested in range of atm. to 10-3 mbar. Dry pump body temperatures were very fluctuant in several pumps, thus minor or major modifications for their cooling systems may be necessary for those pumps. At the end of each test sequence, sudden vent test was performed to verify the pumping down characteristics as well as power consumption. Exposed to sudden avalanching mass flow, several pumps are diagnosed as relatively abnormal compared to their initial pumping down characteristics. Based on experimental results with integrated laboratory experimental system, we propose recommended characteristics design guidelines for dry vacuum pumps in the semi-conductor and display industry in the course of serial evaluation periods.

VT-ThP17 ISAC / SEBT Vacuum System at TRIUMF, *I. Sekachev,* ***D. Yosifov***, TRIUMF, Canada

SEBT is the "Super" Energy Beam Transport line connecting the medium-beta superconducting linear accelerator with the experimental hall in the ISAC-II building at TRIUMF. The SEBT vacuum system consists of five independent sub-sections comprised of nine 280 L/s (N) turbo-molecular, 5 dry mechanical pumps, 22 vacuum gauges, and 37 valves. A liquid nitrogen cooled trap and fast valve protect the Linac from pump oil migration and particular matter potentially originating from vacuum disruptions in the Experimental hall equipment. A control system with appropriate interlocks is used for system operation and protection in accordance to protocol.

VT-ThP18 In-situ Diagnosis using FT-IR Spectroscope System Installed at the Exhaust Line of the Chamber and the Characterization of Al Metal Films with a New Precursor, ***S.W. Kang***, *J.Y. Yun, D.J. Seong, Y.H. Shin,* Korea Research Institute of Standards and Science*, I.D. Yang, J.Y. Shim, J.C. Oh*, Quleap, S. Korea

In-situ Fourier transform infrared (FT-IR) spectroscope system was installed at the exhaust line of the chamber to monitor the by-products generated by gas phase reaction and surface reaction. The by-products of Al metal precursor (a new one) were changed as a function of deposition temperature and pressure and so on (deposition condition). The intensity of spectra measured at the exhaust line was also varied as a measured condition. In in-situ FT-IR spectroscopy studies vibrational spectroscopy reveals the gain and loss of the by-products as a function of the deposition condition. The behavior of the functional group (such as N-C, C-C, C-H, etc.) was monitored and from that, the temperature dependence of the film properties (ex: the film composition) could be explained. The basic properties of a new Al precursor will be introduced.

VT-ThP19 Consideration for the Role of Surface Boundary Layer and the Mechanism of Hydrogen Desorption in Stainless Steel, ***K. Akaishi***, University of Toyama, Japan

Tritium loaded stainless steel specimens of 0.5 mm thickness plate were prepared. When the specimen was chemically etched by about 70 μm in thickness,the amount of tritium trapped within the top surface was measured by β-ray induced X-ray spectroscopy technique. When the chemically etched specimen was immersed in argon gas flow in atmosphere at ambient temperature, more than 99% of tritium released from the specimen was tritiated water, HTO, and the amount of released tritium was measured as a function of time by counting technique. In this paper to evaluate quantitatively the above experimental results, a model for hydrogen transport is proposed, and results of numerical simulation for the tritium release are shown. It is demonstrated that the numerical simulation well predicts the amount of tritium released from the stainless steel specimen in the experiment. This work will be discussed as an issue of outgassing reduction in stainless steel materials.

Friday Morning, October 19, 2007

Biomaterial Interfaces

Room: 609 - Session BI-FrM

Microbioanalytical Systems

Moderator: T. Boland, Clemson University

8:00am **BI-FrM1 Tools and Platforms for Single-Cell Biology**, ***B.A. Parviz***, University of Washington **INVITED**

Genome sequence data enable global, high throughput approaches that link genomic differences to the physiological outcomes that ultimately lead to disease. However, the Achilles heel of global approaches is reliance on averaged cell populations. It is becoming increasingly clear that cells are highly heterogeneous in both gene expression and phenotype. Cellular heterogeneity confounds the interpretation of the link between genomics, phenotype, and disease and also the interpretation of response to therapeutic intervention. In fact, heterogeneity underlies most failures of current therapies for cancer. In order to realize the promise of genomics in curing major diseases, it will be necessary to elucidate pathways involved in disease at the single-cell level, to both understand and manipulate the inherent heterogeneity. The goal of the Microscale Life Sciences Center (MLSC) is to develop cutting edge technology for multi-parameter analysis of single cells, and apply this technology to the understanding of biological questions characterized by cellular heterogeneity. The current focus is on disease pathways, and the vision is to address pathways to disease states directly at the individual cell level, at increasing levels of complexity that progressively move to an in vivo understanding of disease. This presentation provides an overview of the activities in the Center and efforts undertaken to this date to develop automated platforms for trapping and manipulation of single cells, micro-scale and nano-scale photonic methods to measure cells parameters such as oxygen consumption, single-cell protein analysis, and nano-scale electronic methods to monitor extracellular molecular traffic

8:40am **BI-FrM3 Reversible Biofunctionalization and Catalytic Activity of a Metabolic Pathway Enzyme in Reusable BioMEMS Devices**, ***X.L. Luo***, *A.T. Lewandowski, G.F. Payne, R. Ghodssi, W.E. Bentley, G.W. Rubloff*, University of Maryland

We report a reversible biofunctionalization strategy for assembling a biocatalytically-active enzyme at localized sites in reusable bioMEMS devices as a first step toward an experimental platform for metabolic engineering applications, e.g. drug discovery. We prefabricate an integrated bioMEMS device and exploit a non-permanent sealing and package design which supports programmable bio-component assembly at selected sites in the completely packaged microfluidic environment. The aminopolysaccharide chitosan is utilized as the interfacial biofunctionalization material for (1) the chemical signal-guided conjugation of chitosan to a Pfs enzyme through its pro-tag, which is genetically engineered at the C-terminal of Pfs and is activated by tyrosinase for the conjugation, and (2) the electric signal-guided electrodeposition of the Pfs-chitosan conjugate to a selective electrode under negative bias in the microfluidic channel. With biofunctionalizaton complete, the Pfs-mediated enzymatic reaction is performed by introducing the substrate S-adenosylhomocysteine (SAH) into the microchannel for conversion into the products S-ribosylhomocysteine (SRH) and adenine. Reaction solutions are collected and analyzed with high-performance-liquid-chromatography (HPLC). Initial studies show that high conversions are achieved at low flow rates, while much lower conversions are achieved at high flow. After reaction, a mild acid wash removes the assembled Pfs-chitosan conjugate and thus removes the catalytic activity. Subsequent biofunctionalization with Pfs-chitosan re-establishes enzymatic activity comparable to the original, illustrating the reversibility of the enzyme assembly and the reusability of our bioMEMS. Storage in PBS buffer at room temperature for 4 days degraded the conversion efficiency only slightly, demonstrating robustness of the assembled enzyme. This work demonstrates (a) the reversible assembly of a Pfs enzyme at a specific electrode address and (b) the efficacy of the metabolic pathway enzyme Pfs in the bioMEMS: Pfs converts SAH to SRH and adenine in one step of a multi-step cell-signaling process (autoinducer-2 production), a quorum sensing phenomenon that determines pathogenicity of bacteria. These results illustrate the capability of the bioMEMS as an efficient and reusable platform in screening potential enzyme inhibitors as antimicrobial drug candidates. This work is supported in part by the Robert W. Deutsch Foundation.

9:00am **BI-FrM4 SPR Microscopy and its Applications to High-Throughput Analyses of Biomolecular Binding Events and their Kinetics**, ***C.T. Campbell***, University of Washington, *G. Kim*, Lumera Corp.

Surface plasmon resonance (SPR) sensing has long been used to study biomolecular binding events and their kinetics in a label-free way. This approach has been extended to SPR microscopy more recently, which is an ideal tool for probing large microarrays of biomolcules for their binding interactions with various partners and the kinetics of such binding. SPR microscopes now make it possible to simultaneously monitor binding kinetics on >1300 spots within a protein microarray with a detection limit of below 1 ng per cm2, or <100 femtograms per spot (< 2 million protein molecules) with a time resolution of 1 s, and spot-to-spot reproducibility within a few percent. The method is label free and uses orders of magnitude less of the precious biomolecules than standard SPR sensing. It also gives the absolute bound amount and binding stoichiometry. Experiments designed to demonstrate that this approach is capable of high-throughput kinetic studies of the binding of small (200-500 Da) ligands onto large protein microarrays will be described.

9:20am **BI-FrM5 Studies of Electroosmotic Mobilities, and Protein Adsorption in Plasma Polymerised Microchannel Surfaces**, *M. Salim, B.J. O'Sullivan, G.J.S. Fowler, G. Mishra, P.C. Wright,* ***S.L. McArthur***, University of Sheffield, UK

Miniaturisation has found its application in many biological, medical and pharmaceutical devices. Its advantages over macroscale systems include fast analysis time and lower sample consumption. These microfluidic devices use of electroosmotic flow (EOF) as the mean of fluid transport, although variations and inconsistencies in EOF may interfere with device performances. Plasma polymerisation can be used to deposit thin films of various chemical functionalities and properties. This study investigates the electroosmotic behaviour and stability of a range of different plasma polymerised and polymer grafted surfaces before and after contact with protein solutions. The results illustrate that plasma polymerised surfaces exhibit high stabilities, enabling EOF runs of more than 3 days without deterioration. Critically, EOF measurments of surfaces after contact with protein solutions illustrate significant changes in EOF with very low levels of protein adsorption. While this is detrimental to the function of the device, it does suggest that these measurements may be a sensitive probe for in channel biofouling.

9:40am **BI-FrM6 Attomolar Toxin Detection with Semi-Homogeneous Assays**, ***S.P. Mulvaney***, *K.M. Myers, P.E. Sheehan, L.J. Whitman*, Naval Research Laboratory

Assays for biomolecular detection are ideally both multiplexed and sensitive, metrics that often require conflicting solutions. For example, microarrays use spatial location for multiplexing, but target capture on the surface will ultimately be diffusion-limited. Alternatively, homogeneous assays offer very efficient target capture, but typically require multiple label types to multiplex. In our semi-homogeneous immunoassays we use microbeads for both target capture and labeling to leverage the advantages of both approaches. The sample is first mixed with secondary antibodies and microbeads that are functionalized against the secondary host. Target molecules are thereby captured onto the beads via the secondary antibodies. The target-loaded beads are then captured onto an antibody microarray, and controlled fluidic forces are applied to preferentially remove nonspecifically bound beads.[1] Finally, the remaining beads are counted to determine the target(s) concentration. Utilizing such assays, we have achieved multiplexed toxin detection, including aM detection of SEB, in <20 min in a variety of complex matrices. Micrometer-scale sensors and beads are optimal for detecting nanoscale biomolecules with practical sensitivity and speed.[2] However, the blending of micro- and nano-scales in such assays leads to some interesting relationships. In diffusion-limited, solid-phase assays, it takes hours-to-days for fM targets to accumulate on a nanosensor, but only seconds-to-minutes on a microsensor. In addition, microscale labels enable fluidic forces to be applied to achieve greater sensitivity and fewer false positives than possible with nanoscale labels. Finally, in contrast to nanoscale labels, individual microbeads can be easily detected. We believe the size mismatch between label and target contributes to the extreme sensitivity of our assays. Each microbead-label confines a very small volume beneath the contact area, thereby creating a high local concentration of target molecules and capture/label antibodies. This confinement greatly increases the effective binding constant, suppressing dissociation and detachment of the label. The relatively large bead size also contributes to the unusual log-linear dose response curves we obtain, that span up to nine orders of magnitude.

[1] Mulvaney, et al., Biosens. Bioelectron., in press.

[2] Sheehan and Whitman, Nano Lett. 5, 803 (2005).

10:00am **BI-FrM7 Affinity Capillary Electrophoresis and Other Separations on a Microfluidic Format**, ***F.A. Gomez**, A. Brown, M. Piyasena, A. Gaspar, S. Stevens*, California State University, Los Angeles **INVITED**

In this paper, we describe the design and development of novel microfluidic devices (MDs) for electrophoretic and chromatographic separations. One study details our work on through-a-chip partial filling affinity capillary electrophoresis (PFACE) to estimate binding constants of ligands to receptors using as model systems carbonic anhydrase B (CAB, EC 4.2.1.1) and vancomycin from Streptomyces orientalis. Using multilayer soft lithography (MSL), a MD consisting of fluid and control channels is fabricated from poly(dimethylsiloxane) (PDMS) and fitted with an external capillary column. Multiple flow channels allow for manipulation of a zone of ligand and sample containing receptor and non-interacting standards into the MD and subsequently into the capillary column. Upon electrophoresis the sample components migrate into the zone of ligand where equilibrium is established. Changes in migration time of the receptor are used in the analysis to obtain a value for the binding interaction. In a second study we describe the development and study of a disposable and inexpensive MD, fabricated from PDMS incorporating conventional chromatographic reversed-phase silica particles (C18) without the use of frits, permanent physical barriers, tapers or restrictors. A novel external in-line magnetic valve allows for facile packing of the particles. Clamping- and anchor-effects providing the stability and the compactness of the packing were observed. A fiber optics assembly is incorporated onto the chip for detection of species. Food dyes and cephalosporin antibiotics were used to demonstrate the chromatographic applicability of this chip-based chromatographic packing.

10:40am **BI-FrM9 Dual Magnetic-/Temperature-Responsive Nanoparticles for Microfluidic Separations and Assays**, ***J.I. Lai**, J.M. Hoffman, M. Ebara, A.S. Hoffman, P. Stayton*, University of Washington

Magnetic nanoparticle (mNP) technologies have attracted attention for diagnostic applications because mNPs display potential advantages in their diffusive and superparamagnetic properties. However, their small particle size reduces the magnetic capture efficiency. Therefore, there is a need to design mNPs that can be effectively separated without compromising their diffusive properties. Here we have developed an approach that addresses this challenge in the microfluidic channel setting by using mNPs synthesized from temperature-responsive polymeric micelles. Telechelic poly(N-isopropylacrylamide) (PNIPAAm) polymer chains were synthesized with a dodecyl tail at one end and a reactive carboxylate at the opposite end by the reversible addition fragmentation transfer technique. These PNIPAAm chains self-associate into nanoscale micelles that were used as dimensional confinements to synthesize the mNPs. The Mössbauer spectrum of the resulting mNPs shows two broad quadrupolar doublets with chemical shifts of 0.38 and 0.21 mm/s suggesting that the mNPs contain only Fe^{3+}. The X-ray diffraction spectrum confirms the mNP is γ-Fe_2O_3. The mNPs exhibit a layer of carboxylate-terminated PNIPAAm chains as a corona on the surface. The carboxylate group was used to functionalize the mNPs with biotin which was subsequently bound to streptavidin. The biotinylation increases the mNP size from 7 to 11 nm. The functionalized mNPs can be reversibly aggregated in solution as the temperature is cycled through the PNIPAAm lower critical solution temperature (LCST). The LCST of the mNP is ~ 32 °C before and after the biotinylation. While the magnetophoretic mobility of the individual mNPs below the LCST is negligible, the aggregates formed above the LCST are large enough to respond to an applied magnetic field. The mNPs can associate with biotinylated targets as individual particles, and then subsequent application of a combined temperature increase and magnetic field can be used to magnetically separate the aggregated particles onto the poly(ethylene glycol)-modified polydimethylsiloxane channel walls of a microfluidic device. When the magnetic field is turned off and the temperature is reversed, the captured aggregates re-disperse into the channel flow stream. The dual magnetic- and temperature-responsive nanoparticles can thus be used as soluble reagents to capture diagnostic targets at a specific channel position with temporal control.

11:00am **BI-FrM10 Rapid Analysis of Species Separation in Multianalyte Integrated Micro/Nano Fluidic Chips using Multivariate Image Analysis**, ***K. Artyushkova**, M. Bore, A. Evangelista-Lara, G.P. Lopez*, University of New Mexico

This study investigates the potential of multivariate methods (MVA) for identifying electrokinetic separation and estimating velocities of moving species based on analysis of imaging datasets from microfluidic and nanofluidic devices. We have developed an image analysis methodology based on MVA of temporal datasets that is capable of identifying velocities of at least two molecular species from the images where no visible separation of the species has occurred. Among multivariate analysis methods examined are Principal Component Analysis (PCA), Multivariate Curve Resolution (MCR), PARAFAC (parallel factor analysis) and Independent Component Analysis (ICA). These methods allow one to fully exploit the data by analyzing all pixels within images and using the temporal dimension, in contrast with manual methods of visual inspection of images or traditional image processing methods. The methodology has been developed and tested temporal images acquired by fluorescence microscopy capturing separation within nanochannels, microchannels and gel electrophoresis of charged dyes and model protein receptor/ligand systems.

11:20am **BI-FrM11 High Throughput Pharmacological Screening using Cell-Based Biosensors**, ***K. Varghese***, Medical University of South Carolina, University of Central Florida, *P. Molnar, N. Bhargava, M. Das,* University of Central Florida, *M.S. Kindy,* Medical University of South Carolina, *J.J. Hickman*, University of Central Florida, Medical University of South Carolina

In drug development there is a large demand for a system capable of high throughput screening, as well as stable long-term recordings. Cell-based biosensors (CBBs) have the potential to address this demand. CBBs work on the principle of a direct interface between electronics and biological cells, such that the electronics make it possible to quantify a change in the cells' immediate environment. The cell-electronics interface can be modified using different physical properties to vary the adhesive properties of cells. It then becomes possible to promote or inhibit cell adhesion, as well as support preferential attachment of one cell type over another. Cell-based electrophysiology can be broadly divided into two categories - 1) those based on intracellular potentials (e.g. use glass microelectrodes, as in patch clamping) and 2) those based on extracellular potentials. Our research focuses on the latter, wherein extracellular microelectrode arrays are used as a noninvasive and long-term approach for the measurement of biopotentials. The objective of this study is to develop a high throughput CBB where the cell-electronics interface is represented by neurons on Metal Microelectrode Arrays (MEAs). The sensor thus developed should be able to detect acute and chronic effects for a broad range of compounds, at a broad range of concentrations, on neuronal physiology. The inherent properties of this CBB also make it possible to obtain long-term recordings from the neurons. The CBB discussed here consists of a layer of cultured embryonic rat neurons on surface-modified MEAs. The interfaces were modified utilizing self-assembled monolayers and characterized utilizing XPS and contact angle measurements. This system was then used to study the time-dependant effects of Amyloid beta (a causative factor of Alzheimer's Disease) on embryonic rat neurons. Since long-term recordings were relatively easy to obtain, it was possible to observe the effects of amyloid beta, at nanomolar concentrations, over a period of ten hours or more, without cell death. A quantitative description of the effect of this compound on the neuronal system utilizing extracellular recordings will be described. The cells were also characterized by morphology as well as immunocytochemical analysis. Intracellular electrophysiological controls were also performed and will be compared to the results obtained with the solid-state devices.

Electronic Materials and Processing

Room: 612 - Session EM-FrM

Hf-based Dielectrics and Their Interfaces

Moderator: R.L. Opila, University of Delaware

8:00am **EM-FrM1 Electrical Properties of High k Dielectrics Improved by Atomic Scale Nitrogen Depth Profile**, ***W.J. Maeng**, H. Kim*, POSTECH in Korea

Nitrogen incorporation produces several benefits in the performance of high k gate oxides. However, since too much nitrogen incorporation at the interface of gate dielectric can result in device degradation, the atomic scale control of nitrogen depth profile is desirable. In this study, we have improved the electrical properties of gate oxides, including dielectric reliability and interface state density, by depth profile control using in situ nitrogen incorporation during plasma enhanced atomic layer deposition (PE-ALD). The PE-ALD HfO_2 films with oxygen plasma and PE-ALD HfO_xN_y films with N/O mixture plasma were prepared at various growth conditions, changing nitrogen profile (bottom, middle and top) and N/O flow ratio (from 0 to 4). The best electrical properties in terms of hysteresis, EOT, and interface state density were obtained when the nitrogen was incorporated in the middle of the thin film with the N/O ratio of 2, which has not been achievable by other nitridation techniques. The EOT and interface state density of middle nitridation sample was reduced to 0.95nm (HfO_2 : 1.10nm) and $0.75x10^{11}cm^{-2}eV^{-1}$ (HfO_2 : $1.20x10^{11}cm^{-2}eV^{-1}$). Also, the 50% failure electric field was improved from -10.3 MV/cm to -12.2 MV/cm.

8:20am **EM-FrM2 Effect of Annealing Temperature on the Chemical Composition, Chemical Depth Profile,and Film Morphology of High-k Gate Dielectrics by AR-XPS and AFM**, ***G. Conti***, *G. Peydaye, C.C. Wang, T. Sato, Y. Uritsky, S. Hung, P. Liu*, Applied Materials

Hf-based films are alternative gate dielectric films to SiON because of their high dielectric constant and their relatively wide band gap. These films should stay amorphous after activation annealing at T>1000 °C because grain boundaries may serve as paths of dopant diffusion. Pure HfO2 is not a good gate dielectric film because it crystallizes at a low temperature of 500 °C. In this work the effect of different annealing temperatures on chemical composition, and atomic depth profile of HfSiON films is studied by AR-XPS, AFM and TEM. HfSiON films with different N concentrations were annealed at temperatures ranging from 500C to 1050C. These films are thermally stable up to T=1000°C. AR-XPS analysis shows that Hf concentration remains constant, while the N concentration increases linearly with decoupled plasma nitridization power (DPN). All the samples show one layer of HfSiON on Si substrate with thickness of about 20Å. The AR-XPS depth profile shows that Hf and N are evenly distributed in the films, and carbon is observed as a contaminant element on the film surface. The film roughness by AFM is RMS=2Å. The temperature of T=1050C is most commonly used in the CMOS processes, because it is the temperature of Si recovery after dopants implantation. At this temperature the film should remain amorphous and thermodynamically stable. The set of films previously studied, was then annealed at T=1050C. AR-XPS analysis shows that the concentrations of both Hf and N drop significantly, while the N concentration still increases as the DPN power increases. The resulting films consist of two stacked layers of SiOx/HfSiON/Si whose total thickness ranges between of 24Å and 36Å. The AR-XPS depth profile shows that Hf is closer to the Si interface, N is buried in the middle of the film and a significant fraction of carbon is present both in the surface and in the bulk. These AR-XPS results can be explained only if crystallization occur. TEM images show the appearance of micro islands. AFM analysis shows that the film roughness increases by a factor of 20 compared to that of the film annealed at T=1000C. Based on the high film roughness, we conclude that AR-XPS technique on films at T=1050C produces meaningless results in term of composition and depth profile data. However, increasing the amount of N in the film prevents film crystallization. These films show a relative low roughness, and the AR-XPS results are similar to those of the samples annealed below T=1000C.

8:40am **EM-FrM3 Suppression of Ge-N Bonding at Ge-HfO_2 and Ge-TiO_2 Interfaces: Deposition on Nitrided Ge Surfaces, and Post-Deposition Annealing at 800°C**, ***G. Lucovsky***, *S. Lee, J.P. Long*, North Carolina State University, *J. Luening*, SSRL

Differences in length scales for nano-scale order in thin film nano-crystalline HfO_2 and TiO_2 deposited on i) remote plasma-nitrided Ge(100) substrates, and ii) Si(100) substrates with ultra-thin (~0.8 nm) SiON interfacial layers are addressed. Near edge X-ray absorption spectroscopy (NEXAS) is used to determine nano-scale order through the presence or absence Jahn-Teller (J-T) distortion removal of band-edge d-state degeneracies. These studies identify a new and novel application for NEXAS based on the resonant character of the respective N K_1 and O K_1 edge absorptions; these absorptions, respectively, provide a novel way to probe correlated changes in buried interfaces and nano-scale order for as-deposited and 800°C Ar annealed $HfO_2$and TiO_2 thin films. After an 800°C anneal, N K_1 edge spectra indicate an essentially complete elimination of interfacial GeN interfacial bonding on the Ge substrates, but no changes in SiON interfacial layer bonding on Si substrates. As-deposited films 2 nm, 4 nm and 6 nm thick on Ge and Si with interfacial transition regions do not display J-T splittings. This has been attributed to kinetically hindered nano-crystalline grain dimensions smaller than 2 nm. In contrast, after annealing, HfO_2 and TiO_2 films on Ge display spectroscopic evidence for J-T splittings, independent of film thickness. Annealed films on SiON interfaces display J-T splittings, but only for film thickness >3 nm in which grain size is not dimensionally constrained. The spectral signature of the J-T splittings for HfO_2 films on Ge is qualitatively different than for HfO_2 films SiON interfaces on Si. This is attributed to the TM oxide bonding directly to a Ge surface devoid of interfacial GeN serving as a template for mosaic in-plane controlled HfO_2 and TiO_2 grain growth to >3.5 nm. This grain size is sufficient to promote observable J-T spittings in O K_1 spectra. Equally significant, and consistent with the mosaic template description, the half-width-half-maximum of the O K_1 edge for annealed TiO_2 films is smaller for Ge substrates, 0.5 eV as compared with 0.6-0.7 eV for SiON interfaces on Si.

9:00am **EM-FrM4 Effect of Strain Localization and Percolation on Defect States by Controlled Nitrogen Incorporation in Hf Si Oxynitride Alloys**, ***S. Lee***, *G. Lucovsky, L.B. Fleming*, North Carolina State University, *J. Luning*, Stanford Synchrotron Radiation Laboratory

There are two qualitatively different ternary alloy regimes with markedly different properties that are obtained by incorporation of nitrogen in the form of Si_3N_4 bonding into TM silicates. These differentiated by i) strain localization and/or strain percolation, and more importantly iii) strain reduction associated with chemical bonding self-organizations that reduce macroscopic strain by more than compensating reductions in alloy atom entropy. In order to realize strain minimization, compositional optimization by remote plasma process processing was utilized for deposition of Hf, Ti and Hf,Ti alloy Si oxynitride dielectrics. For example, the effect of Si_3N_4 content in $(HfO_2)_x(Si_3N_4)_y(SiO_2)_{1-x-y}$ pseudo-ternary alloys has been studied spectroscopically, and also shows systematic changes in electrical properties, including reduction of electrically-active traps, and minimization of tunneling leakage. Results from soft X-ray photoelectron spectroscopy (SXPS) valence band studies indicate no detectable hole traps for Hf Si oxynitrides with Si_3N_4 content ~35 - 40%, and with equal concentrations of HfO_2 and SiO_2, ~30-32%. These alloys show no evidence for chemical phase separation, as do Hf silicates, and other Hf Si oxynitride compositions. Optimized alloys are stable to at least 1100°C annealing. Derivative near edge x-ray absorption spectroscopy (NEXAS) comparisons for O K1 edges of HfO_2 and optimized Hf Si oxynitride alloys display significantly decreases in electron trapping. The unique properties of optimized Hf Si oxynitrides are correlated with a four-fold coordination of Hf, in contrast with the 7-fold coordination of Hf in HfO_2. C-V measurements indicate a dielectric constant of ~12 in optimized Hf Si oxynitrides, and a predicted value of 16-18 in Hf,Ti Si oxynitrides. Combined with low electron trapping similar to SiO_2, and more than a 4 order of magnitude reduction in tunnel leakage, optimized TM Si oxynitride alloys are predicted to yield EOTs <1 nm, and possibly as low as 0.6 to 0.5 nm for aggressively scaled CMOS devices.

9:20am **EM-FrM5 A Comparison of the Nucleation and Growth of HfO_2 Thin Films Deposited by ALD Using TEMAH and TDMAH Precursors**, ***J.C. Hackley***, UMBC, *J.D. Demaree*, Army Research Laboratory, *T. Gougousi*, UMBC

A hot wall Atomic Layer Deposition (ALD) flow reactor has been used for the comparison of two different HfO_2 ALD chemistries: tetrakis (ethylmethylamino) hafnium (TEMAH) and H_2O, and tetrakis (dimethylamino) hafnium (TDMAH) with H_2O on H-terminated Si and SC1 chemical oxide starting surfaces. Spectroscopic ellipsometry (SE) confirms linear growth of the films with a growth rate of ~1.2 Å/cycle at 250°C for the TEMAH process, and ~1.0 Å/cycle at 275°C for the TDMAH process. Nucleation and initial growth behavior of the films were examined using x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). RBS indicates an initial 4-7 cycle nucleation barrier for the Si-H surface with both metal-organic precursors, before the growth rates on that surface match those on SC1. Steady-state coverage is attained after a ‘conditioning’ period of about 45 ALD cycles for TEMAH, as opposed to only 20 cycles with TDMAH. However, TEMAH results in a higher steady-state coverage rate of $3.1x10^{14}$ Hf/cm^2 on both starting surfaces, compared to $2.4x10^{14}$ Hf/cm^2 and $2.7x10^{14}$ Hf/cm^2 for the Si-H and SC1 surfaces with TDMAH. A comparison of the growth rate measurements with RBS and SE indicates that the HfO_2 films grown from TEMAH appear to reach about 85% of their bulk density on both starting surfaces while TDMAH results in 85% bulk density for the Si-H surface and 95% density on the SC1 surface. XPS is implemented to examine the Si/HfO_2 interfacial region for films grown on the Si-H starting surface. Angle-resolved scans ranging from 0-60° (measured from the surface normal) are taken for samples prepared with both precursors, ranging from 4-25 ALD cycles. For the TEMAH films, we detect a ~7 Å SiO_x/silicate interfacial layer which remains practically unchanged up to 50 ALD cycles as indicated by HRTEM data. In the TDMAH/H_2O process, the interface appears to be initially unstable, and the interfacial layer increases from ~6 Å at 4 cycles up to ~18 Å at 25 cycles. This unstable interface may be due to a more porous film structure, and/or the slightly higher deposition temperature than that of the TEMAH process (275 vs. 250 °C) which may enhance interface oxidation.

9:40am **EM-FrM6 Material Characteristics and Electrical Properties of Hafnium Silicate Films Synthesized by Plasma Enhanced Atomic Layer Deposition**, *J.R. Liu, R.M. Martin*, ***M. Sawkar***, *J.P. Chang*, University of California at Los Angeles

Pseudo-binary $(HfO_2)_x(SiO_2)_{1-x}$ has attracted much attention due to the interesting possibility of combining the high breakdown field of SiO_2 (E_g = 9 eV) and high dielectric constant (22~25) of HfO_2 in a complex material to keep a relatively high dielectric constant and a low leakage current.[1,2] In this work, $(HfO_2)_x(SiO_2)_{1-x}$ composite films were deposited from hafnium tetratert-butoxides (HTB) and tetraethylorthosilicate (TEOS) precursors by using an plasma-enhanced atomic layer deposition (PEALD) process. The film thickness increased almost linearly with increasing number of precursor-oxygen plasma cycles. An optimal control over the final composition was achieved by setting the deposition cycles of HfO_2 and SiO_2. Fourier Transform Infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) analysis showed that the composite films were fully oxidized. The Si-O-Hf bonds were formed in the PEALD deposited composite films. The band gap determined from the XPS O 1s plasmon loss spectrum increased from 5.6 to 5.98 eV with increasing the Si content in the as-deposited films, and it increased slightly after the composite films were annealed at 600 and 900^{o}C, respectively. Time-of-flight static secondary ion mass spectrometry (TOF-SSIMS) depth profiles showed that Hf is almost uniformly distributed throughout the films, and Hf and O exhibited a sharp decay at the Si interfacial substrate. Some Hf presence at the interface with Si could be attributed to ion beam-induced mixing of Hf into the interfacial layer. The low carbon content in these films, which is confirmed by XPS, resulted from the ambient surface contamination. The as-deposited and annealed films at 900^{o}C were determined to be amorphous by x-ray diffraction (XRD), suggesting that the introduction of SiO_2 into HfO_2 matrix prevented crystallization and kept the film amorphous at high temperature. The as-deposited $(HfO_2)_x(SiO_2)_{1-x}$ composite films showed superior electrical properties, including dielectric constants from 5.3 to 11.5 and leakage current density several orders of magnitude lower than that of SiO_2 at the same equivalent oxide thickness.

[1] R. M. Wallace and G. Wilk, MRS Bulletin, 192, 27 (2002).

[2] R. Puthenkovilakam, M. Sawkar, and J. P. Chang, Appl. Phys. Lett., 202902, 86 (2005).

10:00am **EM-FrM7 Band Alignment in Metal/Oxide/Semiconductor Stacks**

S. Rangan, *E. Bersch*, *R.A. Bartynski*, *E. Garfunkel*, Rutgers University

Understanding band alignment in a Metal/Oxide/Semiconductor (MOS) structure is both a fundamental physical chemistry challenge and a crucial technological issue for nanoelectronics as the correct band offsets across a MOS stack is essential to prevent undesirable leakage currents in device applications. A recurrent problem in the evaluation of the band offsets is the lack of reproducibility between measurements on nominally identical samples and between measurements performed using different experimental methods. In this study, we have performed ultra-violet photoemission and inverse photoemission spectroscopy measurements in the same UHV system on a variety of high-κ dielectric films (HfO_2, $Hf_{0.8}Si_{0.2}O_2$, SiO_2, Al_2O_3, ZrO_2) on different semiconductor substrates (Si, Ge, GaAs). This experimental setup allows the direct determination of band gaps, electron affinities, metal work functions, and band offsets across MOS structures. We have also explored the effect of subsequent metallization of the high-κ film in UHV with either of metals (Ru, Ti, Al) chosen for their very different work function and oxygen affinity. By examining the line shape of the shallow core levels using synchrotron radiation-excited x-ray photoemission spectroscopy, we determined the chemical state of the metal, the oxide and the substrate. Ru and Ti are found to remain metallic upon deposition on all oxide films used in this study. In contrast, strong changes in the chemistry of the entire stack are observed upon Al deposition. An Al_2O_3 interface layer is always present at the Al/Oxide interface, and evidence for reduction of the semiconductor/high-κ interface oxide is also observed. Consistent with the observed level of reactivity, our measured Metal/Oxide band offsets are in good agreement with the values predicted by the interface gap state model for as-deposited Ru and Ti. In the case of Al, owing to an additional Al_2O_3 interface layer between the oxide and the Al, our measured values are in poor agreement with the interface gap state model. This indicates that for reactive metal, the band offset is not well described by this simple model.

10:20am **EM-FrM8 Thermal Stability of Rare Earth Oxides as High-k Gate Dielectrics**

S. Van Elshocht, *C. Adelmann*, *T. Conard*, *A. Delabie*, *A. Franquet*, IMEC vzw, Belgium, *P. Lehnen*, AIXTRON, Germany, *L. Nyns*, *O. Richard*, IMEC vzw, Belgium, *J. Swerts*, ASM Belgium, *S. De Gendt*, IMEC vzw, Belgium

Chip performance has drastically increased during the past decades, pushed forward by the ITRS roadmap that projects a doubling of the amount of transistors on a chip every two years. This task has been mainly accomplished by down scaling the dimensions of the transistor, including the gate dielectric thickness down to a few atomic layers. As a result, gate leakage current densities have reached unacceptable levels. As a solution alternative gate dielectrics, replacing the standard SiON, were researched, leading to the identification of Hf-based dielectrics, recently announced to be integrated in the 45-nm technology node. Another class of alternative dielectrics that receives a lot of attention is the rare earth oxides, both as binary or ternary compounds. Rare earth oxides are being explored for their property to shift the work function of a metal gate towards n-type, which is of interest to engineer a proper transistor threshold voltage. In addition, ternary rare earth oxides have been studied because of their thermal stability that allows obtaining a material that remains amorphous during the entire CMOS process. We have studied the thermal behavior and stability of rare earth based oxides, such as Dy_2O_3, La_2O_3, $LaAlO_3$, $HfLaO_x$, and $DyScO_3$, as function of anneal temperature, time, and ambient, as well as function of their composition. Observations were made by Spectroscopic Ellipsometry, Time-Of-Flight-Secondary Ion Mass Spectroscopy, Transmission Electron Microscopy, X-Ray Reflectometry, and X-Ray Diffraction. The rare earth oxide strongly intermixes with the SiO_2 layer underneath, in agreement with the tendency of rare earth elements to form silicates.[1] More interestingly, for ternary rare earth oxides, this behavior is heavily dependent on the composition of the deposited layer. The system evolves to a stable composition that is controlled by the thermal budget and the rare earth content of the layer. Understanding this behavior is important, since it provides a better insight in the behavior of these dielectrics during the thermal treatments inherent to a CMOS process flow. Finally, as an increased Si-content, resulting from silicate formation, can increase the thermal stability of a material, proper care needs to be taken interpreting thermal stability measurements, most often based on X-Ray Diffraction.

[1] H. Ono et al., Appl. Phys. Lett., 78, 1832 (2001).

10:40am **EM-FrM9 Diffusion of La-based Layers on $HfO_2/SiO_2/Si$ Dielectric Stacks**

M.I. Medina-Montes, The University of Texas at Dallas and Cinvestav-Queretaro, Mexico, *M.V. Selvidge*, *F.S. Aguirre-Tostado,* The University of Texas at Dallas, ***A. Herrera-Gomez,*** The University of Texas at Dallas and Cinvestav-Queretaro, Mexico, *R.M. Wallace*, The University of Texas at Dallas

Although there is a consensus regarding the use of Hf-based dielectrics as an alternative to SiO_2 in MOS structures, the search for a suitable metal for n-MOS is still open. The addition of a La-based layer to $Hf_xSi_{1-x}O_2/SiO_2/Si$ dielectric stacks has proven to allow for the engineering of the work function to appropriate levels when TaN or TiN is employed as the metal gate. It has been suggested that the La diffuses into the Hf layer with thermal treatment. We performed high resolution Angle Resolved X-Ray Photoelectron Spectroscopy experiments to study the chemical depth profile distribution of $La_2O_3/HfO_2/SiO_2/Si$ dielectric stacks exposed to a nitridation treatment by NH_3 at 700°C. The expected stoichiometry and distribution of the HfO_2 and SiO_2 layers was reproduced from self consistent analysis of the ARXPS data. Regarding La, this study clearly shows that it diffuses to the top of the SiO_2 layer, and that subsequent Rapid Thermal Annealing at 1000°C for 5s does not change significantly that distribution. A similar conclusion was derived by Sivasubramani et al. from FTIR analysis.[1] In addition, back-side Secondary Ion Mass Spectroscopy results presented by Alshareef et al. are consistent with a location for La close to the HfO_2/SiO_2 interface.[2] The quantitative results for the location and amount of La, together with the associated uncertainties, will be discussed in extent in the presentation.

[1] P. Sivasubramani, T. S. Boscke, J. Huang, C. D. Young, P. D. Kirsch, S.A. Krishnan, M.A. Quevedo-Lopez, S. Govindarajan, B.S. Ju, H.R. Harris, D.J. Lichtenwalner, J.S. Jur, A.I. Kingon, J. Kim, B.E. Gnade, R.M. Wallace, G. Bersuker, B.H. Lee, and R. Jammy. VLSI (2007).

[2] H.N. Alshareef, M. Quevedo-Lopez, H.C. Wen, R. Harris, P. Kirsch, P. Majhi, B.H. Lee, R. Jammy, D.J. Lichtenwalner, J.S. Jur, and A.I. Kingon. Applied Physics Letters 89, p. 232103 (2006).

11:00am **EM-FrM10 Physical and Chemical Properties of Hf-based High-κ Dielectrics on Ge(001) for CMOS Applications**

F.S. Aguirre-Tostado, *M. Milojevic*, *S.J. McDonnell*, *M.J. Kim*, ***R.M. Wallace***, University of Texas at Dallas

The growth of High-κ dielectrics on Ge has attracted substantial interest as a means to maintain integrated circuit scaling and performance. High-κ dielectrics on Ge studies have shown promising results in terms of low equivalent oxide thickness[1] and enhanced hole mobility.[2,3,4] For MOSFET applications, the thermal stability of gate dielectrics is a requirement for an appropriate CMOS flow. This paper will describe the thermal stability studies of HfGeON gate dielectrics on Ge for several nitrogen concentrations. The structure and chemistry of the HfGeON/Ge(001) layers are studied using HRTEM, XRD and in-situ XPS and LEISS. Sputter deposited HfGeON films on atomically clean Ge epi-layers grown by MBE on Ge(001) substrates are investigated. Corresponding electrical characterization of the associated devices will also be described in view of the thermal budget where the maximum process temperature is ~500°C. This work is supported by the MARCO MSD Focus Center.

[1] C.O. Chui, S. Ramanathan, P.C. McIntyre, and K.C. Saraswat, IEEE Elec. Dev. Lett. 23, (2002) 473.

[2] C. H. Huang, et. al., in Symp. VLSI Tech. Dig., 2003, pp. 119-120.

[3] C. Chui, H. et.al., in IEDM Tech. Dig., Dec. 2002, pp. 437-440.

[4] W. P. Bai, et.al., in Symp. VLSI Tech. Dig., 2003, pp. 121-122.

Magnetic Interfaces and Nanostructures

Room: 619 - Session MI-FrM

Spin Injection, Transfer, and Tunneling

Moderator: G.J. Mankey, University of Alabama

8:00am **MI-FrM1 High-Efficiency Spin Injection through the Depleted Edge of a Magnetic Semiconductor**, ***M.E. Flatté***, The University of Iowa **INVITED**

Dilute ferromagnetic semiconductors are composed of magnetic dopants (such as Mn) that interact strongly with each other through a host nonmagnetic semiconductor (such as GaAs) over distances of order one nanometer to establish the ferromagnetic state. The interaction is mediated by holes, which at low concentrations are bound to the dopants and at high concentrations become mobile. Theoretical and experimental studies of the Curie temperature and carrier spin polarization of $Ga_{1-x}Mn_xAs$ find them to depend strongly on the hole density, and a local mean-field theory has been developed that quantitatively accounts for many of the bulk properties of these materials in terms of the mean hole density. However, the properties near the edges of magnetic semiconductors, where the carrier concentration and dopant concentration are changing rapidly over the interaction's length scale of a nanometer, cannot be accounted for within a local mean-field theory. A theory of magnetic interactions in the highly depleted regime has been built on the foundation of a quantitatively-accurate theory of the interaction energy of a single pair of widely-separated Mn dopants in GaAs. Predictions from this theory of the interaction between Mn dopants have been confirmed by experimental measurements via scanning tunneling microscopy. This theory also provides a new explanation of the origin of the unusual magnetic anisotropies in strained low-doped (even insulating) ferromagnetic $Ga_{1-x}Mn_xAs$. The resulting theory for the edges of a magnetic semiconductor suggests that the carrier spin polarization at those edges should be much larger than in the bulk of the material, and may even approach 100%. Measurements of carrier transport across highly-depleted $Ga_{1-x}Mn_xAs$ suggest that these very high spin polarizations are real, and that they may provide an alternate pathway to nearly 100% efficient spin injection.

8:40am **MI-FrM3 Spin Injection in Organic Spintronics**, ***C.-J. Sun***, Oak Ridge National Laboratory, *B. Hu*, University of Tennessee, Knoxville, *J. Shen*, Oak Ridge National Laboratory

Organic spintronics is an emerging field of nanoscale electronics involving the detection and manipulation of electronic spins in heterostructures that consist of organic and magnetic materials.[1] Compared to conventional inorganic spintronics, organic spintronics offer distinct advantages such as ease of device fabrication and intrinsic low spin scattering rate and high spin coherence over both time and distance.[2] These characteristics make organic spintronic devices plausible to operate at room temperature.[3] In this study, we fabricated spin valve devices that uses Co thin films and a manganite thin film as two ferromagnetic electrodes and an organic molecule layer as the spacer layer. A modified superconducting quantum interference device (SQUID) is used to measure local tunneling magneto-resistance (TMR) and determine spin injection efficiency as a function of thickness of Co thin films, bias voltage, and operating temperature. The mechanism of spin injection from Co thin films is addressed.

[1] Z. H. Xiong, D. Wu, Z.V. Vardeny, and J. Shi, "Giant magnetoresistance in organic spin-valves", Nature 427, 821 (2004).

[2] Alexander R. Rocha, Victor M. Garcia-Suarez, Steve W. Bailey, Colin J. Lambert, Jaime Ferrer, Stefano Sanvito, "Towards molecular spintronics", Nature Mater. 4, 335(2005).

[3] V. Dediu, M. Murgia, F. C. Matacotta, C. Taliani, S. Barbanera, "Room temperature spin polarized injection in organic semiconductor", Sol. Stat .Comm. 122, 181(2002). .

9:00am **MI-FrM4 Edge Emitting Spin-Lasers**, ***A.T. Hanbicki***, *G. Kioseoglou, O.M.J. van 't Erve, C.H. Li, I. Vurgaftman, J.R. Meyer, B.T. Jonker*, Naval Research Laboratory

Using a spin polarized current to drive a laser promises to provide threshold reduction, increased polarization of the output light, and intensity stabilization. Optically and electrically driven surface emitting lasers using InGaAs active regions have proven that indeed, spin currents can lead to threshold reduction.[1,2] We have designed and fabricated edge emitting structures based on the Fe/AlGaAs/GaAs spin injecting system to simplify and further understand this process. Samples were designed and grown to enable fabrication of either surface emitting spin-LEDs or edge emitting lasers. Specifically, a wide GaAs quantum well (QW) was grown between thick Al(35%)GaAs barriers. A 1500 Å QW serves as both a recombination region for surface emitting electroluminescence measurements and as a laser cavity for edge emitting structures. The top cladding layer is also 1500 Å, thick enough to prevent absorption by the spin injecting source, Fe, but thin enough to preserve spin injection into the recombination region. In the surface emission geometry, the behavior was similar to our standard wide-QW spin-LED structures.[3] At low temperature, emission in dominated by an H-band feature,[4] and by 20 K the emission is mainly from the bulk recombination feature. With the magnetization saturated out-of-plane, we measure electron polarizations of 24%. Cleaved cavity, gain-guided, edge emitting lasers show robust emission, however, the quality of cleaved interface greatly influences the emission spectrum.

[1] Rudolph et al., Appl. Phys. Lett. 82 (2003)

[2] Holub et al., Phys. Rev. Lett. 98 (2007)

[3] van 't Erve et al., Appl. Phys. Lett. 89 (2006)

[4] Kioseoglou et al., Appl. Phys. Lett. 87 (2005)

9:20am **MI-FrM5 High Frequency Nanoscale Spin Transfer Devices**, ***S.E. Russek***, National Institute of Standards and Technology **INVITED**

Spin transfers effects become important in multilayer magnetic devices whose dimensions are below 100 nm. The transfer of electron spin momentum can induce switching of magnetic layers or microwave precession of the magnetization. Spin transfer, coupled with giant magnetoresistance and tunneling magnetoresistance, can be used to develop new types of magnetic random access memory (SpinRAM), spin transfer nano-oscillators (STNOs), and spin transfer nano-detectors (STNDs). In this talk I will review high-speed spin transfer switching in nanoscale magnetic SpinRAM devices and the effects of thermal fluctuations and defects on the switching process. Next, I will present data on the linewidths, tunability, and phase control of STNOs, including data for both single domain oscillators and vortex oscillators. STNOs and STNDs have the advantage of small size, high tunability, broad frequency range (2 GHz to 100 GHz), and CMOS compatibility. However, there are intrinsic limitations in the linewidth due to thermal fluctuations, limitations due to the required applied fields, and limitations due to the sensitivity to nanoscale defects and patterning. I will discuss these challenges and the progress made towards making practical spin transfer devices for use in high-frequency communication and signal processing applications.

10:00am **MI-FrM7 Low Resistance Synthetic Antiferromagnet Coupled Spin Valves**, ***Z.R. Tadisina***, *S. Gupta, A. Highsmith, P. LeClair, T. Mewes, G.B. Thompson*, The University of Alabama

The magnetic properties of current-perpendicular-to-the-plane (CPP) giant magnetoresistive (GMR) spin valves employing synthetic antiferromagnet (SAF) pinning have been investigated. The standard CPP spin valve structure, with a ferromagnetic (F) layer pinned by an antiferromagnet (AF), exhibits high electrical resistance, the antiferromagnet typically being a high resistivity material. We have investigated pinning with a Co/Ru/Co SAF trilayer only, with no additional AF pinning. Elimination of the AF-induced parasitic resistance yields a higher GMR ratio. The full-film properties have been optimized using vibrating sample magnetometry (VSM) and current-in-plane (CIP) magnetotransport measurements, and related to CPP spin valve properties after patterning. A theoretical simulation of the M-H and R-H loops of the SAF-pinned spin valves is compared with these experimental results. Interlayer exchange energies for the SAF obtained from experimental measurements for the various structures were used in the theoretical simulations to improve the fit and optimize the structure. The thermal stability of various SAF structures and the corresponding SAF-pinned spin valves have also been studied and compared with those of AF+SAF-pinned and hard magnet-pinned spin valves reported on previously.[1] Structural characterization of the layers and interfaces have been carried out by high-resolution transmission electron microscopy (HRTEM). Three-dimensional atomic scale characterization of the interdiffusion between layers has been conducted using a Local Electrode Atom Probe (LEAP).

[1] "A Novel Scheme for Pinning Magnetic Layers in Current Perpendicular to the Plane Spin Valve Devices", C. Papusoi, Z. Tadisina, S. Gupta, H. Fujiwara, G.J. Mankey, and P. LeClair, presented at 53rd AVS International Symposium, San Francisco, CA, November 12-17 (2006).

10:20am **MI-FrM8 Fabrication Technology for Magnetic Random Access Memory**, ***M.C. Gaidis***, *E.A. Joseph, E.J. O'Sullivan, S. Assefa*, IBM

Magnetic Random Access Memory (MRAM) offers the potential of a universal memory – it can be simultaneously fast, nonvolatile, dense, and high-endurance. Depending on application, these qualities can make MRAM more attractive than SRAM, DRAM, flash, and hard drive memories, with a market measured in the billions of dollars. Small-scale demonstrations have realized much of the potential of MRAM, but scaling the memory to competitive sizes or embedding the memory with logic circuitry creates unique processing challenges. The building of MRAM memories in back-end-of-line (BEOL) circuitry imposes additional requirements on processes which conform to existing semiconductor fabrication facility standards. This presentation provides an overview of the basic MRAM structure and operation, followed by a discussion of MRAM-specific processing techniques and developments to obtain high yield across 200mm substrates. The potential for scaling MRAM for future generations with spin-momentum-transfer (SMT) devices will be discussed in this framework. Practical limitations on SMT scaling, and SMT adaptation of conventional MRAM processing will be reviewed.

10:40am **MI-FrM9 Beyond Fe-MgO-Fe: Alternative Barriers and Systems, *P. LeClair***, University of Alabama **INVITED**

Magnetic tunnel junctions have been an intensely active area of research since the first reliable demonstrations of tunneling magnetoresistance (TMR). However, there are only a few systems to date that experimentally show a large TMR effect at room temperature. One of the most recent and effective are ordered Fe/MgO/Fe(001) trilayers (bcc FeCo-based alloys may also be substituted for pure Fe). This system was initially predicted theoretically by Butler et al. to exhibit large TMR, and later experimentally verified by Yuasa et al and Parkin et al. The nearly four-fold improvement in magnetoresistance over earlier polycrystalline/amorphous structures has been attributed to the complex energy band matching between Fe and MgO. This promotes the tunneling of electrons from specific ("delta-1") bands in Fe(001) which exist only for majority spin electrons. The MgO tunnel barrier thereby acts as a 'spin filter.' At the most basic level, the tunneling rates for specific metallic states are controlled by the symmetry of the insulating barrier, which gives a general mechanism for large TMR. In this talk, I will try to outline the theoretical and experimental criteria for large TMR effects based on this 'spin filtering' effect, and attempt to answer the questions "Why does the Fe-MgO system work so well?" and "Is Fe-MgO a unique system?" Both experimental and theoretical considerations are crucial for realizing large TMR effects in realistic structures, and both viewpoints are necessary to explain the (initially surprising) large TMR effects in, e.g., CoFeB/ MgO/CoFeB. I will review our recent work on predicting and fabricating new TMR systems analogous to Fe-MgO-Fe, with a particular focus on alternative tunnel barriers, including organic systems. Finally, I will discuss spin-polarized tunneling characterization methods, in particular Meservey-Tedrow tunneling. This work is supported by the National Science Foundation.

11:40am **MI-FrM12 High Frequency Magnetic Properties of Amorphous and Crystalline CoFeB, *M. Pathak***, University of Alabama, *P. Janssen,* Eindhoven University of Technology, The Netherlands*, L. Wen, H. Lee, J.L. Weston, T. Mewes, P. LeClair*, University of Alabama

The recent demonstrations of extraordinarily large tunneling magnetoresistance effects in CoFeB-MgO-CoFeB trilayer structures has generated an enormous interest in the magnetic and structural properties of CoFeB alloys. In particular, the amorphous to crystalline transition plays a crucial role in realizing large magnetoresistive effects. From an application point of view (e.g., hard disk read heads), a clear understanding of the high frequency magnetic properties of these materials is required. To this end, we have studied the ferromagnetic resonance properties of CoFeB thin films up to 40GHz. We sputter deposited $Co_{56}Fe_{24}B_{20}$ films of different thickness ranging from 5nm to 40nm on oxidized Si(100) substrates, and studied the magnetization damping and crystallization as function of film thickness and annealing temperature. FMR data from 0-7 GHz were obtained using a network analyzer with both frequency and field swept, and from 7-40 GHz using rectangular shorted waveguides. FMR results suggest an increase in damping (α=0.0068 to α=0.013) with decreasing film thickness, which is more pronounced after annealing. The observed increase in coercivity with decreasing thickness after annealing (e.g. 375°C) suggests crystallization of $Co_{56}Fe_{24}B_{20}$, which is confirmed by VSM, XRD, and TEM analysis.

Nanometer-scale Science and Technology

Room: 616 - Session NS-FrM

Nanolithography and Nanoprocess Technology

Moderator: S. Pang, University of Michigan, L. Montelius, University of Lund, Sweden

8:00am **NS-FrM1 Stencil Lithography - Quick & Clean Surface Patterning at Mesoscopic Scales, *J. Brugger***, Swiss Federal Institute of Technology (EPFL), Switzerland **INVITED**

Stencil lithography is a surface patterning technique that relies on the local physical vapor deposition of material through miniaturized shadow mask membranes. It is extremely useful for the formation of patterns, mainly thin structured metal films, in situations where lithography equipment is not available or when the surfaces don't allow the chemical and thermal process steps typically involved in photolithography. Stencil lithography is scalable from mm to sub-100-nm sizes, which makes it very interesting as method for rapid-prototyping of nanostructures without the risk of contamination, and for laboratories without access to high-end nanolithography equipment. The major challenges in stencil lithography are following: i) low-cost fabrication of nanostencils, ii) optimized mechanical properties of thin membranes, iii) deposition of material on stencil membrane, iv) precise alignment of nanostencils, v) recycling of stencils. In collaboration with our project partners[1] we have recently progressed in several of the above mentioned challenges. Stencils fabrication can be based on a set of advanced silicon micro and nanomachining steps (including UV, DUV, EBL and FIB) and a combination of DRIE and wet etching. The mechanical stability of the ultra-thin low-stress silicon nitride membranes could be considerably improved by topographic reinforcement rims. Surface structures of metals (e.g. Al, Au, Bi, Cr, Ti, Cu) on various surfaces (e.g. Si, SiO2, SU-8, PDMS, PMMA, SAMs, freestanding SiN cantilevers, and curved surfaces) where systematically studied in terms of patterning accuracy. Thousands of sub-micrometer NEMS resonators were integrated in CMOS by stencil lithography and sacrificial etching. Variants of stencil methods include the local doping with ions, and local polymer etching using oxygen plasma. The talk will present the current state-of-the-art of nanostencil lithography, will highlight the strength of the method but will also discuss the current limits and challenges ahead to make it a truly reliable and scalable full-wafer nanofabrication method.

[1] Integrated Project 'NAPA' European Commission and Swiss Federal Office OFES (Contract no. NMP3-CT-2003-500120).

8:40am **NS-FrM3 Nanopatterning of Functional Polymers by Thermal Dip-Pen Nanolithography, *W.K. Lee, P.E. Sheehan,*** U.S. Naval Research Laboratory*, W.P. King,* University of Illinois, Urbana-Champaign*, L.J. Whitman*, U.S. Naval Research Laboratory

Thermal dip-pen nanolithography (tDPN) uses a heated atomic force microscope (AFM) cantilever to deposit material that is solid at room temperature. The cantilever melts the solid ink on the tip, allowing precise control over its deposition onto the surface.[1] This method for nanolithography has proven particularly effective for depositing polymers.[2] Both the polymer thickness and lateral dimensions can be controlled to nanometer tolerances by controlling the tip heating power and the writing speed. Using tDPN, controlled layer-by-layer deposition of polymer has been achieved as well as molecular alignment along the writing direction of the cantilever. Many different functional polymers have been successfully deposited on silicon oxide substrates, including those that are temperature responsive, semiconducting, piezoelectric, and light-emitting, demonstrating that tDPN is a flexible nanolithography tool for polymer deposition and patterning. We will present our characterizations of the deposited polymers and report how tDPN can be used to optimize their properties. For example, poly(N-isopropylacrylamide) [pNIPAAM] nanostructures written by tDPN undergo a hydrophilic-to-hydrophobic phase transition induced by temperature that allows the structures to controllably capture and release proteins. We use carboxylic acid functionalized pNIPAAM as a tDPN "ink" that can be grafted onto an epoxy-terminated SAM substrate. We observe the temperature-dependent phase transition by monitoring the adhesion forces of the pNIPAAM with AFM. Finally, we will describe functional polymer patterns created by tDPN in ultra-high vacuum.

[1] Sheehan, et al., Appl. Phys. Lett. 85, 1589 (2004).

[2] Yang, et al., J. Amer. Chem. Soc. 128, 6774 (2006).

9:00am **NS-FrM4 Shadow Edge Lithography for Wafer-Scale Nanomanufacturing, *J. Bai***, *J.-H. Chung*, University of Washington

Many upcoming applications, such as nanoelectronic circuitry, single-molecule based chips, nanofluidics, chemical sensors, and fuel cells, require large arrays of nanochannels and nanowires. The commercialization of these state-of-the-art nanostructure-based devices, which are far superior to the microdevices, is challenged by the patterning consistence, throughput, and cost. For the purpose, we propose the shadow edge lithography (SEL) as a silicon (Si) wafer-scale nanomanufacturing method. The shadow effect of "line-of-sight" in high-vacuum evaporation is theoretically analyzed to predict the geometric distributions of the nanoscale patterns. Nanoscale patterns are created by the shadow of aluminum (Al) edges that are prepatterned using a conventional microfabrication method. Feasibility of the method is demonstrated by the fabrication of nanoscale gaps, which are further used to fabricate either arrays of nanochannels or nanowires on 4-inch Si wafers. The fabricated nanogaps have widths ranging from 15 nm to 100 nm on the 4-inch Si wafers using an e-beam evaporator (NRC 3117, Varian Inc., Palo Alto, CA). Considering the virtual source during the e-beam evaporation, the experimental results agree well with the theoretical prediction. Furthermore, by using the height differences in the pre-patterned Al edges to compensate the geometric distributions of the shadow effect, it is found that the uniformity tolerance in nanogap width can be 2 nm or 5%

across the entire 4-inch Si wafers at a resolution down to 20 nm. Upon the nanogap fabrication, arrays of nanochannels are fabricated by reactive ion etching (RIE) using the e-beam evaporated Al layers as the etching mask; or arrays of chromium (Cr) nanowires are fabricated by depositing 15-nm Cr layer on the nanogap patterns followed by an Al lift-off. The fabricated Cr nanowires are further used as the RIE mask to produce arrays of Si nanowires on silicon-on-insulator (SOI) wafers. Our results show that that the evaporated Al layers can be used as the RIE or lift-off mask to transfer the nanoscale patterns with clear configuration and high yield. Thus, the proposed SEL provides a robust method for wafer-scale manufacturing for sub 50-nm structures, which may exceed the performance of the other nanopatterning methods. Because of the parallel processing nature of the SEL, it has a potential to become a key technology for massive nanomanufacturing with cost effectiveness.

9:20am **NS-FrM5 Conformal Intermediate Layers for Anti-Adhesive Coatings on Metal Molds**

H. Schift, Paul Scherrer Institute, Switzerland, *S. Bellini*, ETH Zürich, Switzerland, *H. Sehr*, *J. Gobrecht*, Paul Scherrer Institute, Switzerland

Stamps for nanoimprint lithography (NIL)[1] need an excellent anti-sticking surface property, which is easy to achieve with silane chemistry, if molds are made from silicon.[2] Other stamp materials, such as metals, need intermediate layers, preferably made from silicon oxide (SiO_2).[3] Then the chlorosilane group of commercially available fluorinated silanes can react with hydroxyl groups on the oxide surface under elimination of hydrochloric acid, and covalent binding can be achieved which is durable in hot embossing and injection molding processes. Two routes were developed to achieve a thin intermediate coating of stamps, one based on the thermal evaporation of Ti/SiO_2, and the other on Plasma Enhanced Chemical Vapor Deposition (PECVD) of SiO_2. Since evaporation is directed, a full conformal coverage of the surface, particularly if high aspect ratio structures need to be coated, is often only achieved with specific mounting setups or several subsequent coating steps from different directions. This is time consuming due to the evacuation steps and only results in limited thickness homogeneity. Therefore the PECVD was developed and applied on different metals (brass, nickel, steel) without the use of the Ti adhesion promoter. The process is conformal and 20 nm thick coatings can be achieved with high homogeneity. It is more flexible and can be performed within a few minutes. The most crucial point is the adhesion of the thin interlayer to the stamp surface during the demolding process. The durability of both layers was tested using different mechanical methods and coated molds were used in hot embossing and injection molding. Several thousand injection molding cycles are possible, and to date is seems that the durability of the new PECVD coating matches that of the evaporated films. This is a further step to establish anti-sticking coating techniques in high volume manufacturing of polymer parts by replication, and to enlarge the range of stamp materials used for molding and NIL.

[1] Schift H., Kristensen A., In Handbook of Nanotechnology, Vol. ed. B. Bhushan, second edition, Springer Verlag, Berlin, Germany, 239-278 (2007).

[2] Schift H., Saxer S., Park S., Padeste S., Pieles U., Gobrecht J., Nanotechnology 16, S171-S175 (2005).

[3] Park S., Schift H., Padeste C., Schnyder B., Kötz K., Gobrecht J., Microelectronic Eng. 73-74, 196-201 (2004).

9:40am **NS-FrM6 Nanoscale Electron Beam Induced Etching (EBIE)**

M.G. Lassiter, *D. Smith*, University of Tennessee, *T. Liang*, Intel Corporation, *P.D. Rack*, University of Tennessee

Traditionally, high-resolution nanomachining utilizes a gallium focused ion beam (FIB) to physically sputter away material or dissociate a precursor material to deposit material. During the process, gallium ions are implanted into the surface of the substrate and leave undesirable effects, such as reduced transmission of clear area repairs in photomasks; otherwise damaging or change the remaining material. The use of electron beam induced processes for high spatial resolution nanopatterning has recently been developed as an alternative to FIB. The electron beam induces the dissociation of a precursor gas to cause a reaction at the surface of the material. This reaction either deposits material or removes material, depending upon the precursor/substrate combination. This presentation focuses on the latter, electron beam induced etching (EBIE) of materials. Electron beam induced etching provides superior spatial resolution and can offer much better etching selectivity compared to FIB. Additionally electrons do not damage the substrate materials because of their relatively small mass compared to gallium ions. This work characterizes the process of high resolution EBIE of various relevant materials. The effects of electron beam parameters such as accelerating voltage, beam current, and the scanning parameters are investigated, as well as the relationship of the beam parameters to the gas parameters such as pressure and injection needle position. Furthermore, various precursor gases were examined, and the effects on spatial resolution, etching rate, and selectivity against other materials are determined. A 3-D Monte Carlo type simulation of the etching process has also been developed and simulation results will be compared to experimental results.

10:00am **NS-FrM7 Atomic-Scale Device Fabrication in Silicon**

M.Y. Simmons, University of New South Wales, Australia **INVITED**

One driving force behind the microelectronics industry is the ability to pack ever more features onto a silicon chip, by continually miniaturising the individual components. However, after 2015 there is no known technological route to reduce device sizes below 10nm. In this talk we demonstrate a complete fabrication strategy towards atomic-scale device fabrication in silicon using phosphorus as a dopant in combination with scanning probe lithography and high purity crystal growth. A key aspect of being able to build single atom devices is the ability to distinguish single atoms on and in the silicon surface. We demonstrate a detailed understanding of the surface chemistry to identify and control individual P atoms, using phosphine as a dopant source in silicon.[1] We can place individual phosphorus atoms in silicon at precise locations[2] and encapsulate them in epitaxial silicon with minimal diffusion and segregation of the dopants.[3] Separate studies have confirmed the range of electrical transport characteristics that can be achieved using phosphorus as a planar, buried dopant in the absence of any lithographic patterning by STM.[4] We then demonstrate that we can pattern this planar dopant layer using STM lithography and encapsulate with low temperature silicon epitaxy without lateral diffusion of the dopants out of their lithographic regions. Electrical device characteristics at low temperatures confirm the presence of the lithographic patterning as we observe a cross-over from 2D to 1D transport in the phase coherence length.[5] Using this process we have fabricated conducting nanoscale wires with widths down to ~8nm, tunnel junctions, single electron transistors and arrays of quantum dots in silicon.[6] We will present an overview of the devices that have been made with this technology and highlight some of the challenges to achieving atomically precise devices.

[1] H.F. Wilson et al., Physical Review Letters 93, 226102 (2004).

[2] S. R. Schofield et al., Physical Review Letters 91, 136104 (2003).

[3] K.E.J. Goh et al., Applied Physics Letters 85, 4953-4955 (2004).

[4] K.E.J. Goh et al., Phys. Rev. B 73, 03541 (2006).

[5] F.J. Rueß et al., Nano Letters 4, 1969 (2004).

[6] F.J. Rueß et al., Small 3, 567 (2007); Nanotechnology 18, 044023 (2007); Phys. Rev. B Rapid 85, 121303 (2007).

10:40am **NS-FrM9 Advances in Atom Beam Nanolithography: A New Exposure Tool, Masks, and Resists**

B. Craver, *H. Guo*, *A. Roy*, University of Houston, *J. Strahan*, University of Texas, *J. Reynolds*, *H. Nounu*, University of Houston, *C.G. Willson*, University of Texas, *J.C. Wolfe*, University of Houston

Atom beam lithography (ABL) is a proximity printing technique where a broad beam of energetic neutral atoms floods a stencil mask and transmitted beamlets transfer the mask pattern to resist on a substrate. ABL exposures are equivalent to those formed by ions in every respect (mass, energy, angular distribution, diffraction, scattering within the mask, resist, and wafer) except for the charge of the lithography particles. ABL images, being formed by electrically neutral particles, are completely free of charge-related artifacts that occur, often unpredictably, in ion printing due to ambient electromagnetic fields and the buildup of electrostatic charge on the mask and wafer. In this paper, we describe an integrated toolset for fabricating high density arrays with an arbitrary unit cell by atom beam lithography. The 30-50 keV exposure tool incorporates a high brightness multicusp ion source and a high pressure gas cell to convert helium ions to energetic helium atoms through charge transfer scattering. A mechanical mechanism has been developed for translating the mask image over the wafer with 1 nm precision. Nano-arrays can, thus, be fabricated using a large-area template mask consisting of a silicon membrane with a periodic array of circular openings. The mask image is translated over the wafer to create, simultaneously, an array of identical unit cells, each corresponding to an individual mask opening. Silicon stencil masks, up to 700 nm thick, are fabricated with ~50 nm openings using a magnetically enhanced, molecular bromine plasma. A plasma-deposited coating of poly(methylmethacrylate) protects the silicon membrane from ion implantation damage and thickens the mask to enhance lithographic contrast. The mask can be coated with sputtered gold to shrink the mask openings as needed for the particular application. Pattern shifts during exposure are imperceptible at the nanometer-scale. Linewidths of 25 nm have been achieved and we anticipate reporting sub-20 nm linewidths at the conference. High resolution resists with optimized sensitivity, currently under development, will be reported at the conference. Potential applications in rapid prototyping and imprint lithography template fabrication will be discussed.

11:00am **NS-FrM10 Resonances in Secondary Electron Yields from Capped Multilayer Mirrors**, ***E. Loginova***, *B. Yakshinskiy,* Rutgers University, *S. Yulin, T. Feigel,* Fraunhofer Institut (IOF), Germany, *J. Keister,* Brookhaven National Laboratory, *T. Lucatorto, C. Tarrio, S. Hill,* National Institute of Standards and Technology, *O. Dulub, U. Diebold,* Tulane University, *M. Chandok, M. Fang,* Intel Corporation, *T.E. Madey*, Rutgers University

The magnitude of secondary electron yield (SEY) at EUV wavelengths is a major factor in determining contamination rates of multilayer mirrors (MLMs) in EUV projection optics, and we have found striking resonance effects in measurements of SEY from MLMs. Low energy secondary electrons (0 to ~ 20 eV) can cause dissociation of adsorbed hydrocarbons from the background gas, and lead to carbon film growth on MLM surfaces. SEY data (electrons/photon) were measured using synchrotron radiation over the range 40 eV to 180 eV for TiO_2 and Ru single crystals (clean, O-covered, C-covered, air exposed) and compared with measurements for Mo/Si multilayer films capped by Ru, TiO_2, and RuO_2. For photon beams incident at 45 degrees, the shapes of the curves for Ru multilayers, especially the maxima at ~ 65 eV due to the Ru 4p excitation, are very similar to the data for pure Ru; such similarities are found also for a TiO_2 crystal and TiO_2-capped MLMs. Thus, the cap layer properties dominate the SEY characteristics: this agrees with theory, which predicts that a film several nm thick contributes ~90% to the SEY characteristics of the mirrors. For incidence angles close to the surface normal, and for photon energies near 92 eV (13.5 nm), dramatic energy- and angle-dependent resonances in SEY are observed for the capped MLMs, with SEYs 2 to 3 times higher than off-resonance. Calculations show excellent correlations between the photon electric field strength in the cap layers and the angular-dependent SEYs.

11:20am **NS-FrM11 Miniature Machines for Nano-Scale Research and Manufacturing: A New Model for Equipment and Instrumentation**, ***M.L. Culpepper***, Massachusetts Institute of Technology **INVITED**

Advances in nanopositioning technology make it possible to (a) increase the pace of discoveries (via instruments) and (b) improve the pace with which discoveries are manufactured and commercialized. There are a growing number of instrument/equipment applications wherein small-scale (meso- and micro-scale) nanopositioners are needed in order to achieve commercially viable speeds (kHz), resolution (Angstroms), cost ($100s) and thermal stability (Angstroms/min). New small-scale nanopositioners are emerging to meet these requirements, however there are a few technological issues that must be addressed. The purpose of this talk is to cover (i) the fundamental reasons that will compel the creation of these nanopositioners, (ii) the economic and performance benefits that they will enable and (iii) how partnerships can help to overcome the few remaining technical/ scientific issues. The import of partnerships between machine design researchers, nanofabrication process researchers, and manufacturers will be stressed as well as a plan that is focused upon creating these partnerships. The talk ends with a vision for a new class of small-scale, low-cost instrument/equipment platforms to support a new model for nano-scale research and manufacturing.

Plasma Science and Technology

Room: 606 - Session PS-FrM

Plasma-Surface Interactions III

Moderator: E.S. Aydil, University of Minnesota

8:00am **PS-FrM1 Controlling Surface States of Nanocrystalline TiO2 and its Application in Dye-Sensitized Solar Cells**, ***M. Dhayal,*** National Physics Laboratory, India, *H.B. Gu, K.H. Park*, Chonnam National University, Korea

Plasma surface modification and weak acid treatments of nanocrystalline TiO2 has been carried out to improve efficiency of dye sensitized solar cells (DSSC). The argon ions in low pressure gas discharge can modify the TiO2 surface chemistry and had increased in the proportion of Ti3+ surface states. The proportion of different surface functionalities such as alcohol/ether (C-OX), carbonyl (C=O) and C(=O)OX were also significantly changed. Similarly the acid treatment of TiO2 had also change the surface chemistry. In this study the relative change in the surface chemistry with these two different methods has been discussed. These treatments have advantages for the adsorption to dye molecules and enhancement of the photoelectric performance of DSSC. The improvement in the energy conversion efficiency of dye-sensitized solar cells (DSSCs) with controlled surface states had been investigated.

8:20am **PS-FrM2 Role of UV/VUV Radiation and Ion Bombardment in the Degradation and Roughening of Photoresist Polymers**, ***D.G. Nest***, *D.B. Graves,* University of California, Berkeley, *S. Engelmann, R.L. Bruce, T. Kwon, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park, *C. Andes,* Rohm and Haas Electronic Materials, *E.A. Hudson*, Lam Research Corp.

This study focuses on the relative roles of rare gas ion bombardment and UV/VUV radiation in photoresist (PR) polymer degradation during plasma etch and pattern transfer. We present results of a collaborative study of PR etching and roughening of current generation methacrylate-based 193 nm PR polymers and 248 nm PR. Independently controlled ion and UV sources in a vacuum beam system are used to simulate plasma-photoresist interactions, and the relative importance of UV/VUV radiation and ion bombardment during plasma etch are elucidated. The effects of ion bombardment tend to be concentrated in the near-surface layer. All PR polymers under ion bombardment appear to form a highly cross-linked near-surface layer. By contrast, the effects of UV/VUV radiation, as characterized by transmission Fourier Transform Infrared (FTIR) Spectroscopy, penetrate deeper into the bulk polymer and are more sensitive to the chemical composition of the PR polymer. Surface roughness and morphology depend on the composition of the PR as well as the ion bombardment and UV/VUV exposure protocol. Differences in polymer chemistry are correlated to surface morphological changes. Results from the vacuum beam experiments are compared to measurements made on PR exposed in plasma reactor experiments.

8:40am **PS-FrM3 About the Surface Roughness Generated by Plasma Etching Processes**, ***M. Martin***, *G. Cunge*, CNRS/LTM, France

As the critical dimension of the features decrease for each new generation of CMOS transistors, the thickness of the layers being etched also decreases. When the thickness of the layer approaches 10 nm, a new problematic is emerging: the roughness generated by the plasma etching process could become comparable to the thickness of the layer being etched potentially causing selectivity issues. In this work, we have systematically analyzed the roughness generated in c-Si (100) and in p-Silicon when etched in high-density plasmas over a wide range of conditions (pressure, rf power) using SF_6, CF_4, Cl_2 and HBr chemistries. The roughness is characterized by AFM. In this work, we demonstrate unambiguously that high-density HBr and Cl_2 plasmas DO NOT generate roughness during etching but on the contrary tend to smooth the existing surface roughness if already present. By analyzing the time evolution of the shape of self organised silicon nanopilar (patterned using diblock-copolymers), we show that the smoothening properties of etching plasmas is due to shadowing effects : the "hills" receive a high radical flux than the "valley" and are thus etched faster. In contrast, F-based plasma generates a significant surface roughness whose amplitude increases with the etching time. However, we show that the roughness formed in these conditions is generated by micromasking of silicon by AlF_x particles generated by the sputtering of the (Al_2O_3) reactor walls. A high percentage of Al is indeed detected on the surface after etching in F-based plasmas. As a matter of fact when the chamber walls are intentionally coated by a carbon layer prior to the silicon etching process (thus preventing Al sputtering), the F-based plasmas behave like the other etching chemistries investigated: they rapidly smooth any existing roughness.

9:00am **PS-FrM4 Influence of Plasma Etch Processing Parameters on Morphological and Topographic Transformations of Advanced Photoresist Materials**, ***S. Engelmann***, *R.L. Bruce, T. Kwon, R. Phaneuf,* University of Maryland, College Park, *C. Andes,* Rohm and Haas Electronic Materials, *D.G. Nest, D.B. Graves,* University of California, Berkeley, *E.A. Hudson*, Lam Research Corp., *G.S. Oehrlein*, University of Maryland, College Park

Plasma based transfer of photoresist (PR) patterns into underlying substrates is basic to micro- and nano-fabrication, but suffers from problems like introduction of surface and line edge roughness in the PR/underlying features as a result of plasma processing. In this collaboration, we seek to develop a deeper understanding of the influence of both PR materials and plasma parameters in introducing undesirable changes in PR blanket films and nanostructures. Etch rates, chemical and morphological evolution of fully formulated PR systems as well as carefully selected model polymers have been studied along with a set of sub-micron sized patterned structures using ellipsometry, atomic force microscopy, x-ray photoelectron spectroscopy, and secondary electron microscopy. The current work is designed to complement prior studies on the temporal evolution of plasma-induced PR modifications for a set of different materials processed over a limited plasma parameter range. Using an Inductively Coupled Plasma (ICP) source, a survey of the effects of bias power and voltage, source power, pressure, and feed gas composition (C_4F_8/% Ar) on 193 nm PR etching behavior and surface modifications has been undertaken. For comparison, PR modifications using discharges based on CF_4/H_2 mixtures were studied as well. The pure CF_4 discharge resulted in a relatively smooth top surface due to high removal rates. But excessive lateral etching caused tapered feature profiles. On the other hand, CF_4 discharges admixed with H_2 to improve the profile resulted in smooth top surfaces combined with low removal rates similar to C_4F_8/90% Ar. We also will present results of changes in line edge and width roughness for actual PR nanostructures, and compare these with data obtained using blanket PR films exposed using the same plasma operating conditions.

9:20am **PS-FrM5 Effect of Charging on Twisting of Extremely High Aspect Ratio Features in Plasma Etching***, ***A. Agarwal***, University of Illinois at Urbana-Champaign, *M.J. Kushner*, Iowa State University

The plasma etching of extremely high aspect ratio features (eHAR) provides challenges to maintain critical dimensions. As aspect ratios approach and exceed 100, undesirable behaviors have been observed, such as extreme tapering and twisting of features. Twisting is the sometimes sudden turning of a via or trench from the vertical to a side angle. These behaviors often occur randomly. For example, of three adjacent features, only one may display the behavior. The behaviors are also sometimes associated with location on the die, such as near an open area, or location on the wafer, being more likely near the edge of the wafer. Current theories on the source of twisting and errant behavior focus on charging effects, anisotropic ion energy distributions and the randomness of the composition of the ion and radical fluxes as the opening of the feature approaches only a few tens of nm. In this talk, processes leading to twisting of eHAR features in polymerizing (etching of SiO_2 in fluorocarbon plasmas) and in non-polymerizing (etching of Si in chlorine plasmas) chemistries will be discussed using results from a computational investigation. The Monte Carlo Feature Profile Model (MCFPM) was modified to include the effects of charging by electrons and ions, including solution of Poisson's equation and conduction current through solid materials. We found that twisting largely results from a confluence of factors, including trapping of charge in polymer, randomness in the neutralization of charge due to the stochastic-like current that enters small features and location of the feature on the die. For example, trenches adjacent to open areas are influenced by charging in the open field, an effect that diminishes with distance from the open field. The twisting effects are generally diminished but not eliminated with increasing voltage.

*Work supported Micron Technology Inc., Semiconductor Research Corporation and the National Science Foundation.

9:40am **PS-FrM6 Role of Additives (O2, CO and CO2) in NF3 Remote Plasma Etching of Si3N4**, ***J.J. An***, *H.H. Sawin*, Massachusetts Institute of Technology

In the optimization of PECVD chamber cleaning, it is important to maximize the cleaning rate and minimize the use of gases that are costly and must be treated. It is found that less than 5% of additives such as O2, CO and CO2 in NF3 plasma enhance silicon nitride etching rates particularly at lower temperatures. Using line-of-sight mass spectrometry, we have measured the atomic fluorine density and shown than it is not significantly altered by the additives. While nitric oxide (NO) generated in plasma is considered to be the main contributor of the enhancement of etching rate, its measured levels are small. Besides NO, the role of carbon containing gas products is also taken into account. While the kinetics of this effect are not yet well understood, we will present mass spectrometer results sample by line-of-sight from the plasma source, FTIR measurements of the pump exhaust, as well as etching rate variation with flow rates, pressure and sample temperature.

10:00am **PS-FrM7 Measurement of Modified Layer Formation of 193 nm Photoresist during Short Time Plasma Exposure**, ***M. Sumiya***, Hitachi High-Technologies Corp., Japan and University of Maryland, *R.L. Bruce, S. Engelmann, F. Weilnboeck, G.S. Oehrlein*, University of Maryland

The degradation of photoresists (PR) during plasma etching is one of the issues for nanoscale-fabrication. Although it has been already reported that surface roughness develops within a few seconds plasma exposure and leads to striations,[1] the mechanism of surface roughness formation during the initial stages of plasma exposure is not well understood. In this study we employed a shutter approach[2] to achieve rapidly steady-state plasma condition for processing PR surface. The time-evolutions of optical constants and thickness of the modified layer on the PR surface were obtained using 2 layer optical modeling of the ellipsometric data. The change of surface composition was observed by X-ray photoelectron spectroscopy (XPS). Remarkable differences of the etch behavior during the early etch period for different discharge conditions, i.e., ion energy, pressure and stage temperature, were observed. We found that the modified layer is formed within a few seconds and a steady-state modified layer is subsequently seen. It was revealed that these differences of etch behavior for different etch condition at the earlier etch period are due to difference of fluorination degree of the PR surface and having higher etch rate under low fluorination leads to rough surface. We also compared the etch behaviors of 193 nm PR and 248 nm PR materials. Whereas for 193 nm PR etching was observed immediately, for 248 nm PR, fluorocarbon film deposition took place at first until a fluorinated surface developed. The reason for different etch behavior of both PRs is the high oxygen content of 193 nm PR relative to that of 248 nm PR. Oxygen enhanced the etching rate of 193 nm PR during early plasma exposure when the surface roughness is introduced. Additional details on the relationship of the initial surface condition and formation of rough surface for PR materials will be discussed.

[1] X. Hua et al., J. Vac. Sci. Technol. B24(4)(2006)1850.

[2] G. S. Oehrlein, et al., J. Vac. Sci. Technol. B24(1)(2006)279.

10:20am **PS-FrM8 A Study on the Oxidation Properties of W Surface by O_2 Plasma and Reduction of WO_x Layer by H_2 Plasma in Sub 50nm Patterning Process**, ***J.K. Kim***, *B.S. Kim, S.S. Jeong, T.H. Ahn*, Samsung Electronics, South Korea

As the feature size gradually shrinks down to nano scale of sub 50nm, various metals like as W, Ti, and Co, have been introduced as a low resistance material for word line. Recently, W has become to the most powerful candidate and widely used for several applications. For the formation of W pattern, the most challenging problem is the oxidation of W surface. Generally, we treat wafer with O_2 plasma to remove the organic mask layer and polymeric residues after W etching process. W surface is oxidized to WO_x layer by reactive oxygen radicals during plasma ashing. The oxidation of W surface brings increase of pattern resistance and variation of critical dimension. In this study, we controlled the reactivity between W surface and oxygen radical varying process parameters such as radical flux, RF power and especially electrode temperature. Also, we characterized the W surface using XRR, SFX and checked the change of line resistance to compare the oxidation amount. Oxygen radicals activated moderately, could not react with W surface, while organic polymer could be sufficiently removed. Using properly activated oxygen radical, we can find the reasonable process window which is nearly free from surface oxidation and polymeric residues. Even though we find the optimum process condition, there are still thin WO_x layer after ashing. In order to remove this layer, we also investigated post treatment process using H_2 containing plasma. We found that hydrogen radical allowed a quick recovery of WO_x layer to their initial state of W. Finally, we proposed a multi-step plasma treatment process to keep W surface from oxidation during plasma ashing.

10:40am **PS-FrM9 Model Analysis of the Ion Reflection on Surfaces and the Profile Evolution during Etching of Si in Chlorine- and Bromine-Containing Plasmas**, ***S. Irie***, Kyoto University, Japan, *M. Mori, N. Itabashi*, Hitachi Ltd.,Japan, *K. Eriguchi, K. Ono*, Kyoto University, Japan

In the profile evolution during plasma etching, the reflection of energetic ions on feature sidewalls is appreciated to be important to cause profile anomalies near the feature bottom such as footing and microtrenching. We have developed a model for the feature profile evolution of Si etching in chlorine- and bromine-containing plasmas. The model incorporates an atomic-scale cellular model of surface reaction layers and Monte Carlo calculation for the trajectory of ions on feature surfaces, including their reflection on and penetration into surfaces. The model takes into account the formation of surface reaction multilayers caused by adsorption of neutrals and penetration of ions, deposition of etch products and by-products, and surface oxidation. This paper presents an investigation of effects of the energetic ion scattering on Si surfaces. In the model, the collision between ions and Si atoms on surfaces is assumed to occur, when the impact parameter is smaller than the cutoff radius; the trajectory of ions is analyzed by the Monte Carlo calculation, based on the momentum and energy conservation for an incident ion through successive two-body elastic collisions with substrate Si atoms. The impact parameter and scattering angle are calculated at each collision in the three-dimensional space. The interaction potential of Si ion is necessary for calculation, and the existing classical potential or Stilling-Weber potential is employed for the potential of Si-Cl. However, the potential of Si-Br is not well known, and so to determine the potential function for Si-Br systems, we perform ab initio quantum chemical calculations based on a density-functional method using Gaussian. Then, we analyze the scattering of Cl^+ and Br^+ ions on Si surfaces based on their potential calculated, showing that there is a difference of the scattering on Si surfaces between Cl^+ and Br^+ ions. Compared the scattering of Br^+ ions with that of Cl^+ ions, the number of Br^+ ions reflecting from Si substrates is small for all incident angle, the distribution of reflection angles is narrow, and the kinetic energy loss is rather large. The difference of the scattering on Si surfaces is attributed not only to the potential, but also to the masses of atoms. The profile simulation during etching in HBr plasmas, using the potential for Si-Br calculated, is compared with the experiments, to examine the effects of ion reflection on feature surfaces.

Surface Science

Room: 608 - Session SS1-FrM

Surface Dynamics

Moderator: A.L. Utz, Tufts University

8:00am **SS1-FrM1 Formation and Dynamics of Sputter Ripples on an Epitaxially Grown Au Surface*, K. Mitchell*,** *A. Yazdi, N. Ingle, T. Tiedje*, University of British Columbia, Canada

Under bombardment by a rastered 30keV Ga^+ ion beam, a flat epitaxially grown Au surface is found to exhibit the well known sputter ripple instability as first observed by Bradley and Harper.[1] These ripples exhibit a characteristic lateral length scale on the order of 100nm and a short-range RMS saturation height on the order of 10nm after receiving a fluence of approximately 1500 ions/nm^2. The starting surface is grown under UHV at 350°C on a freshly cleaved mica substrate resulting in a 0.5μm film with flat areas up to 8μm^2 having an RMS roughness of 0.5nm. Accurate topography data are gathered using ex situ AFM on areas exposed to increasing ion fluence to track the increase in roughness associated with the pattern formation, while in situ SEM imaging is used to observe the dynamics before and after the ripples have formed. These experimental data are compared to 2D numerical solutions of a non-linear partial differential equation which captures the essential features of height saturation, characteristic length scale and parabolic ripple shape. A state of the art fourth-order "exponential time differencing" method as perfected by Kassam and Trefethen[2] is used to advance the solution in time while high accuracy spectral methods are used to compute spatial derivatives. The equation is similar to the chaotic Kuramoto-Sivashinsky equation, but with an additional higher order non-linear term as derived by Castro and Cuerno.[3] Like the Kuramoto-Sivashinsky equation, linear terms of competing stability set the initial characteristic length and growth rate, while the non-linear terms are responsible for the height saturation and the surface shape. The additional non-linear term causes an increase in the characteristic time, length and height scales after saturation has occurred. By adjusting the strength of the new non-linear term, the solutions can be tuned to match the morphology of the experimentally observed surface. The resulting equation parameters are then able to give information about the physical constants involved in the experiment.

[1] Bradley, Harper, J. Vac. Sci. Technol. A 6,2390 (1988)
[2] Kassam, Trefethen, SIAM J. Sci. Comp. 26, 1214 (2006)
[3] Castro, Cuerno Phys. Rev. Lett. 94, 016102 (2005)

8:20am **SS1-FrM2 Charge Transfer Dynamics in Alkanethiolate Self-Assembled Monomolecular Films*, M. Zharnikov,*** Universität Heidelberg, Germany*, S. Neppl,* Technische Universität München, Germany*, A. Shaporenko,* Universität Heidelberg, Germany*, U. Bauer, D. Menzel,* Technische Universität München, Germany*, P. Kao, D. Allara,* Pennsylvania State University*, P. Feulner*, Technische Universität München, Germany

Whereas static conductance of molecules arranged in self-assembled monolayers (SAMs) has been extensively studied, less is known about the dynamics of the charge transfer in these systems. We show that the latter phenomena can be successfully addressed by resonant Auger electron spectroscopy, using the core hole clock (CHC) method. For the test system, nitrile-substituted alkanethiolate SAMs, we obtained clear, quantitative results on the characteristic transfer time of the resonantly excited electron along the molecular chain to the conductive substrate in good agreement with theory. As compared to previous studies, the charge transfer pathway in our experiment was unambiguously defined by resonant excitation of the nitrile tailgroup attached to the alkyl backbone. This particular tailgroup occurs to be a good candidate for such studies because of a suitable core hole lifetime (CLT) and the large contrast between resonant and non-resonant core decay spectra. The approach, used by us, avoids any contact and reproducibility problems and, by selection of suitable ligands with appropriate values of CLT and resonance position, spans a wide dynamic range. Extension to other functional groups is possible and promises to become a very valuable new source of information on charge dynamics in layers important for molecular electronics.

8:40am **SS1-FrM3 Dynamics of Analyte Binding onto a Metallophthalocyanine: NO/FePc*, S.R. Bishop,*** *N.L. Tran, G.C. Poon, A.C. Kummel*, University of California, San Diego

The investigation of the gas-surface reaction dynamics of NO with an iron phthalocyanine (FePc) monolayer utilizing King and Wells sticking measurements is reported. The initial sticking probability is determined to be a function of both incident molecular beam energy (0.09 - 0.4 eV) and surface temperature (100 - 300 K). NO adsorption onto FePc saturates at 3% of a monolayer (ML) at all incident beam energies and surface temperatures suggesting that the final chemisorption site is confined to the iron metal centers. At low surface temperature and low incident beam energy, the initial sticking probability is as great as 40% and decreases linearly with increasing beam energy and surface temperature. The results are consistent with the NO molecule sticking onto the monolayer FePc via physisorption to the aromatic periphery followed by diffusion to the Fe metal center. It is determined the NO molecule adsorbs to the FePc monolayer via a multiple pathway precursor-mediated chemisorption mechanism. The absorption mechanism of NO onto FePc was confirmed by control studies of NO sticking onto metal-free H_2Pc, inert Au(111), and reactive Al(111).

9:00am **SS1-FrM4 Atomic Scattering as a Probe of Polymer Surface and Thin Film Dynamics*, M.A. Freedman**,*** *S.J. Sibener*, The University of Chicago

We have studied the vibrational dynamics of self-assembled monolayers (SAMs) and polymer thin films, two complex systems of great technological interest, using the highly surface-sensitive and non-perturbative technique of low-energy helium atom scattering. While this technique has traditionally been used for single crystals and simple adsorbates on crystals, recent work in our group and elsewhere has expanded these studies to ordered organic monolayers. We have further broadened the range of studies performed with helium atom scattering to determine how much information can be gleaned from soft, disordered systems. We have shown that this technique provides a novel means for studying surface vibrational dynamics at these complex interfaces. We explored the interaction between the alkanethiol chains of the SAMs and the Au(111) substrate by investigating the energy of single phonon modes as a function of chain length. The fact that the observed phonon mode is dispersionless and exhibits no dependence on chain length indicates that the interaction between the adsorbate and substrate in the sagittal plane is dominated by single-chain harmonic-oscillator-type interactions. The energy of the single-phonon mode of decanethiol is larger than other chain lengths because its commensurate structure to the reconstructed Au(111) surface leads to stronger binding. We investigated the polymer thin film interface to determine the effect of nanoconfinement and polymer species on the vibrational dynamics. We find that helium atom scattering is a sensitive probe of the effect of nanoconfinement on the surface dynamics of poly(methyl methacrylate) (PMMA). Specifically, a reduction in the mean-square displacement derived from the elastic scattering and the reduced propensity for annihilation events in inelastic spectra indicate that thinner films are stiffer, perhaps due to substrate interactions. The inelastic spectra of PMMA, polystyrene, and polybutadiene have similar rates of intensity decay and absolute values of full width half maximum with increasing surface temperature. Deviations from a semiclassical scattering model and the linear increase in full width half maximum with increasing surface temperature indicate changes in the vibrational dynamics. We have shown that helium atom scattering is a sensitive probe of complex systems and may indeed give insight on whether the onset of glassy dynamics in the bulk affects dynamics at the topmost interface.

9:20am **SS1-FrM5 Local Electronic Properties of Molecular Assemblies at Surfaces*, J.I. Pascual*,** Freie Universität Berlin, Germany **INVITED**

The electronic properties of inorganic functional materials can be understood and predicted from a conceptual knowledge of electron dynamics. However, when organic molecules are to be used in electronic devices an atomistic picture of molecular bonding is additionally required. Local phenomenology occurring at the nanoscopic scale related with molecular chemical bonding, and hence with electronic coupling, governs many of the mesoscopic properties of organic devices. On the one hand organic-inorganic bonding can be more relevant than the molecular functionality itself. On the other, intermolecular interactions play a key role in structural organization of the molecular layer, and eventually govern the three-dimensional growth of molecular thin-films, beyond the interface limit. Our research in Berlin aims to provide a molecular scale picture about interactions occurring at the inorganic/organic interface. Our approach to this goal follows a combination of low-temperature scanning tunnelling microscopy and spectroscopy measurements with density functional theory simulations. We characterise the electronic structure of single molecules on a surface with sub-nanometer resolution in order to resolve the influence of local parameters (molecular orientation, neighbourhood, conformation,…) on its properties. Non covalent intermolecular interactions are also relevant at the inorganic interface, and may lead to the construction of three-dimensional supramolecular nanostructures with interesting electronic

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properties. In this seminar I will present several of our recent results about the electronic configuration of model molecular systems like C60, fullerene-based nanostructures and charge-transfer complexes on metal and semiconductors surfaces. The electronic configuration of the molecular ensembles will be analyzed in terms of their local neighbourhood and the degree of electronic coupling with the metal suface.

10:00am **SS1-FrM7 Reactions of Atomic Hydrogen with Self Assembled Monolayers***, **J.M. Gorham**, B. Smith, A. Stover, J.D. Wnuk, H. Fairbrother*, Johns Hopkins University

The interaction of atomic hydrogen with hydrocarbon and semi-fluorinated self assembled monolayers (SAM) has been studied in-situ using x-ray photoelectron spectroscopy (XPS) and ex-situ contact angle measurements. Results indicate that atomic hydrogen (AH) reactions with alkanethiolate SAMs are strongly dependent upon the hydrocarbon chain length. For short chained SAMs (ie. C_9 and C_{12}), AH permeates rapidly through the hydrocarbon film and reacts primarily with the native thiolate bond resulting in chain desorption, as evidenced by a simultaneous loss in both carbon and sulfur. Conversely, sulfur was removed preferentially from longer chained alkanethiolates (ie. C_{16} and C_{18}), followed by the AH mediated erosion of the hydrocarbon film. The different reaction pathways for the long and short chain SAMs are due to effect of chain length on the residence time of AH in the hydrocarbon overlayer. In contrast to the short chain SAMs, AH reactions within the hydrocarbon film become important due to the increased length of the alkyl chain. Reactions of AH with semi-fluorinated SAMs (e.g. $Si-(CH_2)_2(CF_2)_5(CF_3)$) were consistent with a kinetically controlled process initiated by H atom abstraction from C-H bonds within the SAM. Secondary reactions of the carbon-centered radicals formed in the organic film with AH leads to the desorption of fluorocarbon radicals (e.g. $CF_3(CF_2)_5$). As a result of this reaction mechanism, the rate of fluorocarbon loss from the film is proportional to the adsorbate coverage and the flux of AH. The decrease in contact angle that occurs as a result of AH exposure is directly proportional to the coverage of CF_3 and CF_2 groups, providing a convenient route to control the surface wettability and other interfacial properties. In comparison to low energy electron modification, reactions of AH with semi-fluorinated SAMs are found to be more effective in etching the organic film.

10:20am **SS1-FrM8 Misfit-Dislocation-Mediated Migration of Cu Nanostructures on Ag(111)***, **A.W. Signor**, J.H. Weaver*, University of Illinois at Urbana-Champaign

Experimental studies of island migration, an important process in crystal growth and nanostructure synthesis, have mostly been limited to homoepitaxial systems. In these systems, either diffusion or evaporation and condensation of adatoms at the island edge gives rise to motion of the entire structure, leading to size-independent barriers, and diffusivities that scale with radius according to $D \sim R^{-B}$, with B =1, 2, or 3 for the simplest cases. The present work with Cu-Ag(111), a lattice-mismatched system, provides compelling evidence for a collective mechanism involving glide of misfit dislocations. Here, the entire structure is moved by one Burger's vector b= 1/6 <211> as the dislocation nucleates and glides through the island. Scanning tunneling microscopy (STM) images show that islands with magic sizes have a propensity for defect nucleation and glide leading to enhanced mobility. Quantitative analysis of island trajectories from STM movies collected at 130-200 K yield energy barriers as low as 0.35 eV for this process, even for multilayer islands containing up to ~90 atoms. Significantly, the barriers are very sensitive to island size, and hence island diffusivities do not scale with size in the ways predicted for traditional atomistic mechanisms, greatly affecting the overall coarsening kinetics.

10:40am **SS1-FrM9 Subpicosecond Photodesorption and Photoreaction of CO on Pd(111)***, **P. Szymanski**, A.L. Harris, N. Camillone III*, Brookhaven National Laboratory

We have examined the dynamics of the desorption and oxidation of CO on a Pd(111) surface following irradiation with ~110-fs pulses of 780-nm light. For a mixed layer of CO and atomic oxygen, both the desorption of CO and the production of CO_2 exhibit superlinear dependences on the absorbed laser fluence. The fluence dependence of CO desorption at saturation coverage is unaffected by the presence of coadsorbed atomic oxygen. For both CO/Pd(111) and (CO+O)/Pd(111) systems, the probability of CO desorption increases with the initial CO coverage due to population of lower-adsorption-energy sites. Two-pulse correlation (2PC) measurements of the photodesorption yield show rapid relaxation of the excited adsorbate-substrate complex and are well explained by an electron-mediated process. The photoinduced CO_2 production in the (CO+O) mixed layer, by contrast, involves mainly CO molecules with higher binding energies. The 2PC of the CO_2 product is five times broader than that of CO, suggesting that a different effective molecule-surface coupling is responsible for the reaction compared to the desorption. Our results are consistent with a picture where strong coupling between substrate electrons and adsorbed CO leads to high transient adsorbate temperatures, which can cause a subsequent reaction with oxygen if the barrier to direct CO desorption is sufficiently high.

11:00am **SS1-FrM10 Grating-Coupled Excitation of Surface Plasmon Polariton Waves on Single Crystalline Cu(111) using Periodic Density Patterns of Rare Gas Monolayers for Adsorbate Surface Diffusion Study***, **X.D. Zhu**, Y.Y. Fei, X. Wang*, University of California at Davis

Using periodic density profiles of xenon (Xe) as thin as 1 ~ 5 monolayers, we have excited and detected grating-coupled surface plasmon polariton waves (SPPW) on Cu(111) in ultrahigh vacuum. The periodic density profiles are formed by laser-induced thermal desorption with a pair of coherent laser pulses at vacuum wavelength of 0.532 microns. The periodicity of the profiles is 5.45 microns. By illuminating the xenon-density-grating-covered Cu(111) with a converging He-Ne laser covering a span of incidence angles from 66.4° to 74.4° and detecting the oblique-incidence reflectivity difference $r_p/r_{p0} - r_s/r_{s0}$ vs. incidence angle with a multiple-element photodiode array, we observed the surface-plasmon resonance (SPR) peaked at the incidence angle of $\theta_{SPR} = 70.4°$ with a full-width at half-maximum of $\Delta_{SPR} = 0.29°$. From the resonance angle θ_{SPR} and Δ_{SPR}, we have determined the optical dielectric constant of single crystalline Cu at 633 nm to be $\varepsilon_{Cu} = -9.53 + i\ 0.142$, markedly different from the literature values for evaporated Cu films. At elevated temperatures such that a xenon density grating on Cu(111) decays in contrast, the surface plasmon resonance as measured by $r_p/r_{p0} - r_s/r_{s0}$ diminishes, reflecting the kinetic of surface diffusion of xenon on Cu(111).

11:20am **SS1-FrM11 Dynamical Study of the Elastic Forces between Dislocations in a Strained Metal Film***, **B. Diaconescu***, K. Pohl*, University of New Hampshire

Misfit dislocation networks can be used as natural templates for the growth of 2D large scale ordered arrays of clusters. The strain relaxation in metallic ultra thin films leads to the formation of large scale ordered arrays of dislocations, with unit cell sizes ranging from a few hundred to thousands of atoms. Understanding how the long-range stabilizing forces arrive from atomic interactions will provide a way of controlling the unit cell size and symmetry of the reconstructed surface. Here we show how, using atomically resolved scanning tunneling microscopy data, the dynamical evolution of vibrations of the 2D network of misfit dislocations of atomically thick Ag films on Ru(0001) can provide opportunities for measuring the long range elastic forces that stabilize the system. Fast-scanning STM data at rates of about 3 s/frame are providing a good temporal resolution of the process. In this way, an elastic constant of about 3 meV/Å^{-2} was obtained. The large size of the unit cell does not allow for full ab initio calculations, thus the experimentally determined long range stabilizing forces in such systems are related with first principles interaction parameters via 2D Frenkel-Kontorova models.

Surface Science

Room: 611 - Session SS2+EM+TF-FrM

Organic Films II: Semiconductors and C_{60}

Moderator: J.E. Reutt-Robey, University of Maryland

8:00am **SS2+EM+TF-FrM1 Unravelling Molecular Contrast Formation Obtained by NC-AFM on Titania***, **R. Bechstein**, J. Schütte, P. Rahe, A. Kühnle*, University of Osnabrueck, Germany

The (110) surface of TiO_2 constitutes an interesting model substrate for molecular adsorption studies due to its importance in applications such as organic solar cells and light emitting diodes. Several experiments revealed that organic molecules can be anchored to the surface through carboxylic groups both under ultra-high vacuum conditions[1] as well as from solution.[2] We investigated a perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI) derivative without carboxylic anchor groups by non-contact atomic force microscopy (NC-AFM) under ultra-high vacuum conditions. The molecules were deposited at room temperature onto TiO_2 (110) by evaporation from a Knudsen cell. We achieved true atomic resolution on the bare substrate as well as submolecular resolution on individual molecules. The molecules were observed to align along the [001] direction with the ability to move along this direction. They are found to be homogeneously distributed on the terraces without any tendency to cluster at step edges even at elevated temperature. Two molecular contrast modes are clearly distinguished. In one mode the molecules appear cloudy and are observed to

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be centred on top of bright rows. In the other mode the molecules are imaged with a dark bone-shaped centre and a bright rim, centred on top of dark rows. Scanning tunnelling microscopy measurements allow to conclude that the molecules are always centred on top of the bridging oxygen rows, demonstrating a contrast reversal between the two NC-AFM imaging modes. By comparing these results with previous NC-AFM studies,[3] we can assign the two modes to positive and negative terminated tips showing that in NC-AFM imaging strongly depends on the tip termination.

[1] A. Sasahara, H. Uetsuka, and H. Onishi, J. Phys. Chem. B 105, 1 (2001)

[2] C. L. Pang, T.-a. Ishibashi, and H. Onishi, Jpn. J. Appl. Phys. 44, 5438 (2005)

[3] J. V. Lauritsen, et al., Nanotechnology 17(14), 3436 (2006).

8:20am **SS2+EM+TF-FrM2 Characterization of Para-Sexiphenyl Thin Films Grown on KCl Substrates**, ***A. Andreev***, Univ. of Leoben, Austria, *A. Montaigne*, Univ. Linz, Austria, *T. Haber*, Graz Univ. of Tech., Austria, *A. Kadashchuk*, National Academy of Sci. of Ukraine, *G. Hlawacek*, Univ. of Leoben, Austria, *D.-M. Smilgies*, Cornell Univ., *R. Resel*, *A. Winkler*, Graz Univ. of Tech., Austria, *H. Sitter*, *N.S. Sariciftci*, Univ. Linz, Austria, *C. Teichert*, Univ. of Leoben, Austria

Para-sexiphenyl (6P) films grown on mica(001) and KCl(001) substrates show large morphological and optical anisotropy, which makes them attractive for nano-scale photonic devices. In this work we use Atomic Force Microscopy (AFM), electron microscopy, x-Ray diffraction (XRD), and photoluminescence (PL) in order to find the parameters controlling film morphology, structure, and quality. It is shown that the initial growth stage of 6P on KCl(001) is characterized by the formation of µm-long needles, generating a rectangular network in accordance with the substrate surface symmetry. With increasing coverage, terraced mounds composed of upright standing molecules developing between the needles are observed and subsequent growth is characterized by a coexistence of both features. It is demonstrated that both features grow directly on the substrate surface, i.e., there is no wetting layer during the deposition of 6P on KCl(001). It is also found that both needles and terraced mounds grown on KCl(001) are single crystalline, in contrast to mica(001), where different oriented 6P domains are formed inside of the chains. PL studies have shown that, as in 6P films on mica, the emission spectra contain two different components - a conventional structured spectrum due to intrinsic excitons and a broad red-shifted band ascribed to some kind of defects. The latter band most clearly can be distinguished in delayed fluorescence spectra of the studied films. It is remarkable, however, that the relative intensity of the defect band was much weaker in the films grown on KCl substrates comparing to that on mica, which corresponds well with results of morphological and structural investigations. This finding confirms the high quality of the films and implies that the defect band is rather sensitive to the structure and morphology of the films. We also discuss a correlation between growth condition of 6P and a relative intensity of the defect PL band.

8:40am **SS2+EM+TF-FrM3 A Nanoengineering Approach to Regulate The Lateral Heterogeneity of Self-Assembled Monolayers**, *J.-J. Yu*, *Y.H. Tan*, *X. Li*, University of California, Davis, *P.K. Kuo*, Wayne State University, ***G.-Y. Liu***, University of California, Davis **INVITED**

Using a scanning probe lithography method known as nanografting in conjunction with knowledge of self-assembly chemistry, regulation of the heterogeneity of self-assembled monolayers (SAMs) is demonstrated. It is known that phase segregated domains would form if SAMs are grown from thiol solutions of mixed compositions. The size and distribution of these domains depend on the interplay between reaction kinetics and dynamics, which can be regulated by varying the reaction conditions including concentration, temperature and reaction time. The reaction mechanism in nanografting, however, differs significantly from self-assembly in the conventional mix-and-grow methods. The spatial confinement in nanografting bypasses the lying-down to standing up transition process, and thus leads to a much fast kinetics. Knowledge of the reaction pathways enables development of methods for shifting the interplay between the kinetics and thermodynamics in SAM formation, and thus the heterogeneity of mixed SAMs. By varying fabrication parameters such as shaving speed, and reaction conditions such as concentration and ratio of the components, the lateral heterogeneity can be adjusted ranging from near molecular mixing to segregated domains of several to tens of nanometers.

9:20am **SS2+EM+TF-FrM5 Mechanistic Aspects of Organic Thin Film Growth from Energetic Sources: Insights from Experiment and Molecular Dynamics Simulations**, ***J.E. Goose***, *A.S. Killampalli*, *P. Clancy*, *J.R. Engstrom*, Cornell University

We have used a combination of experiments and molecular dynamics simulations to investigate the fundamental molecular mechanisms contributing to the evolution and final morphology of thin films of pentacene deposited at hyperthermal incident kinetic energies (E_i = 1-10 eV). Experimentally, using supersonic molecular beam scattering techniques and atomic force microscopy we have characterized the adsorption probability as a function of both E_i and the angle of incidence (θ_i). Interestingly, we observe differences in the dynamics of adsorption for pentacene interacting with a clean SiO_2 substrate (submonolayer growth) vs. a SiO_2 substrate covered by a pentacene thin film (multilayer growth). Specifically, for E_i greater than ~ 1-2 eV, contribution of a new mechanism for pentacene adsorbing on pentacene is implicated. To determine the nature of this mechanism, we have used the non-reactive empirical MM3 potential to model the collision of pentacene molecules with a pentacene thin film using molecular dynamics. Our simulation cell consists of ca. 100 molecules, and includes an upper terrace of 4 x n unit cells, bounded by (010) step edges. Accounting for impacts both near the middle of the terrace and near the step edge, our results from simulation for the probability of adsorption compare very well with those measured experimentally. In particular, adsorption is found to decrease with increasing E_i, and, in general, with increasing θ_i. More importantly, the simulations give us insight into nature of the events that occur at high incident kinetic energies. For thermal incident kinetic energies we observe mostly simple trapping (molecular adsorption), with near unit probability. At higher E_i of 1-5 eV, a significant fraction of molecules (~ 30%) are found to directly insert into the upper terrace, whereas a higher fraction (~ 90%) of molecules impacting near the step edge in this same energy regime also end up incorporating into the upper terrace. Indeed, direct molecular insertion into the pentacene crystal structure is the dominant interlayer process when both the molecule's orientation and incident angle are aligned normal to the surface, which leads to the formation of interstitials for the time scale of these simulations.

9:40am **SS2+EM+TF-FrM6 Growth of Pentacene Thin Films from a Supersonic Source: Unexpected Behavior in the Presence of Molecular Cluster Formation**, *A. Amassian*, *S. Hong*, *S. Bhargava*, *A.R. Woll*, *T.W. Schroeder*, *A.S. Killampalli*, *J.D. Ferguson*, *J.D. Brock*, *G.G. Malliaras*, ***J.R. Engstrom***, Cornell University

We have examined the growth of pentacene thin films on SiO_2 using supersonic molecular beam techniques and in situ real-time synchrotron x-ray scattering. At low-to-modest rates of deposition [ca. 0.001 to 0.1 monolayer(ML)/s] we observe an abrupt transition from 2D, layer-by-layer growth to 3D, islanded growth after deposition of the first few monolayers of pentacene on SiO_2. At high rates of deposition (ca. 1 ML/s), however, we find persistent 2D crystal growth, and the development of a highly textured film possessing significantly flatter and smoother surface morphology than at low rates of deposition. Concomitantly, in this regime we also observe new polymorphs of pentacene, as significant changes occur in the crystalline structure of the thin films. The transition to this anomalous, yet promising growth behavior corresponds very strongly with the onset of the formation of van der Waals clusters of pentacene within the supersonic expansion. We suggest that the presence of clusters in the incident flux acts to change the dynamics of growth due to a variety of reasons which we discuss. These findings raise the distinct possibility that organic crystals may be synthesized with ultra-flat surface morphology, making them suitable for use in a number of electronics applications where the requirement for abrupt and smooth interfaces has traditionally defaulted to the use of amorphous organic thin films.

10:00am **SS2+EM+TF-FrM7 Vibrational and Structural Investigation of Ferrocene Adsorption on Au(111) Surfaces**, ***G. Pirug***, *M. Kazempoor*, Forschungszentrum Jülich, Germany, *J. Myslivecek*, Charles University in Prague, Czech Republic, *B. Voigtländer*, Forschungszentrum Jülich, Germany

The adsorption of ferrocene ($Fe(C_5H_5)_2$) on Au(111) surfaces has been studied spectroscopically applying HREELS and XPS as well as structurally by means of LEED and STM under UHV conditions. The vibrational modes observed by HREELS indicate reversible molecular adsorption of ferrocene at temperatures of about 110 K. The corresponding frequencies are not significantly shifted with respect to IR or Raman data from solution, indicating a weak adsorbate - substrate interaction. Multilayer adsorption can be distinguished from the physisorbed first layer based on the sequential appearance and relative intensity changes of vibrational modes. In the monolayer regime vibrational modes with a perpendicular dipole moment from ferrocene molecules with an upright standing molecular axis dominate, as concluded from on- and off-specular HREEL spectra applying the surface dipole selection rules. Dissociation into cyclopentadienyl ring radicals (C_5H_5) can be excluded due to the missing related vibrational losses, such as the wagging mode expected at about 760 cm^{-1}. For multilayer coverages the orientation of the condensed ferrocene molecules is no longer exclusively perpendicular to the surface which results in the appearance of additional vibrational losses. Molecular self assembly yields a well ordered surface structure as shown by topographical STM pictures and LEED pattern.

10:20am **SS2+EM+TF-FrM8 Uncovering Molecular Dewetting: Growth and Morphology of C_{60} and PTCDA on Insulators**, ***S.A. Burke***, *J.M. Mativetsky, S. Fostner, P. Grutter*, McGill University, Canada

Despite considerable interest in recent years in the properties and structural characteristics of molecular deposits for organic based devices, there has been only limited study of growth and morphology of molecular materials on insulating substrates. The majority of traditional surface science tools are significantly hindered by the use of an insulating substrate due to complications with charging and surface damage. Over the past decade, non-contact atomic force microscopy (nc-AFM) has proven a powerful surface science tool, and is increasingly being applied to molecular studies on insulators. The power of the technique lies in its ability to image in real-space with sub-angstrom resolution as well as measure structure up to the micron scale allowing for a connection between molecular scale structures and the overall growth morphologies. The nc-AFM technique, operated in UHV, has been applied to two prototypical organic semiconductors: C_{60} and PTCDA, on two well-known insulating surfaces: KBr (001) and NaCl(001). Both systems showed island growth modes with evidence for dewetting, though the resulting morphologies differ considerably. C_{60} on both of these alkali halides forms distinctive branched island shapes. A quantitative analysis of the morphology and its connection to the underlying epitaxy will be discussed. The formation of this branched morphology appears to be a dewetting process which was observed directly in a series of nc-AFM images. The energetics of this system will also be discussed in terms of annealing and deposition onto a heated substrate. PTCDA on NaCl also undergoes a dewetting process, though in a rather different manner. At low coverages, monolayer islands are observed in a highly strained c3x3 epitaxy. However, at larger coverages these single layer islands are seen to coexist with tall crystallites exhibiting the same morphology and herringbone structure as observed for PTCDA on KBr, indicating a coverage induced dewetting transition between 0.7 and 0.8 ML. The dewetting was also induced by annealing of the single layer islands yeilding molecular crystals up to several microns long with the familiar herringbone structure of the PTCDA (102) plane. Dewetting has recently been recognized in several other organic systems as a significant factor in the growth and morphology of thin films. The examples presented here may indicate that dewetting is also an important consideration in molecule-on-insulators systems as well.

10:40am **SS2+EM+TF-FrM9 STM/STS Studies of C_{60}:Pentacene Interface Formation**, ***D.B. Dougherty***, National Institute of Standards and Technology, *W. Jin, W.G. Cullen, G. Dutton, J.E. Reutt-Robey,* University of Maryland at College Park, *S.W. Robey*, National Institute of Standards and Technology

The most efficient small-molecule organic solar cells employ heterojunctions between donor and acceptor materials.[1] In order to push the performance of such devices into a regime of cost-effective power generation, it is necessary to develop a detailed understanding of organic-organic interface morphology and its relationship to electronic band alignment. We have approached this question by studying the technologically relevant[2] system of C_{60} deposited onto pentacene, using STM/STS to provide clues to the relative importance of competing intermolecular interactions. When C_{60} is deposited onto a pentacene bilayer on a Ag(111) surface,[3] STM measurements show two unique structures in the first layer. The pentacene bilayer forms a well-ordered structure on Ag(111) with the long molecular axis nearly parallel to the surface. At the lowest coverages, C_{60} forms linear chains whose direction is templated by the underlying pentacene rows, with C_{60} molecules located between rows of pentacene molecules. The details of the observed structural arrangement are related to electrostatic interactions between C_{60} and the pentacene bilayer structure. Information on local relative band alignment for these structures is measured using constant-current distance-voltage spectroscopy.[4] The local transport gap for C_{60} linear chains is 4.4±0.2 eV compared with a gap of 3.7±0.2 eV for the surrounding pentacene bilayer. The magnitudes of the gaps are influenced by local polarization energies in each structure. At higher coverage, domains of C_{60} with no discernable long range order dominate the first layer. This disorder probably arises from frustrated intermolecular interactions between the two different chemical species. The lateral interactions between C_{60} molecules (favoring hexagonal ordering) cannot be optimized simultaneously with the comparable strength interactions between C_{60} and the underlying pentacene film (favoring an oblique unit cell). *This work has been partially supported by the Dept. of Commerce through the NIST Center of Nanomanufacturing and Metrology and the NSF-funded MRSEC via DMR-05-20471.

[1] P. Peumans, J. Appl. Phys. 93, 3693 (2003).

[2] S. Yoo et al., Appl. Phys. Lett. 85, 5427 (2004).

[3] Eremtchenko et al., Phys. Rev. B 72, 115430 (2005).

[4] S.F. Alvarado, et al., Phys. Rev. Lett. 81, 1082 (1998).

11:00am **SS2+EM+TF-FrM10 Potassium Induced Long Range Superstructure on C_{60}/Ag (111) Surface**, *C.-C. Kuo,* ***W.W. Pai***, National Taiwan University

Various long range superstructures were observed for potassium (K) doped C_{60} monolayer on Ag (111) by scanning tunnelling microscopy (STM). Pristine C_{60} monolayer exhibits a bright-dim contrast in the most stable $(2\sqrt{3}\times2\sqrt{3})$-R30 phase, whereas the molecular contrast is uniform in other metastable phases (denoted as R12 or R48 phases). Upon K doping, K segregate into compact islands at room temperature and the bright-dim contrast in the R30 phase is eliminated. Furthermore, ordered quasi-hexagonal patterns with periodicities of ~7 nm to ~40 nm appear. The ordered superstructures show distinct characteristics in each C_{60} phase. Close inspection reveals that the super lattices are not exactly hexagonal but exhibit uni-directional distortion. Therefore, the finding is perplexing as it cannot be explained by, e.g., Morie patterns. We propose that the superstructures are due to overlaying an orthorhombic one-dimensional polymerized KC_{60} phase over the hexagonal silver lattice. This is supported by high-resolution STM images showing the signature of [2+2] covalent bond formation.

11:20am **SS2+EM+TF-FrM11 Thiol-Modified Diamondoid Monolayers on Silver and Gold Studied with Near-Edge X-ray Absorption Fine Structure Spectroscopy**, ***T.M. Willey***, Lawrence Livermore National Lab., *J.D. Fabbri,* Stanford Univ., *J.R.I. Lee,* Lawrence Livermore National Lab., *P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina,* Justus-Liebig Univ. Giessen, Germany, *J.E. Dahl, R.M.K. Carlson, S.G. Liu,* MolecularDiamond Tech., *T. van Buuren,* Lawrence Livermore National Lab., *N.A. Melosh*, Stanford Univ.

Higher diamondoids, hydrocarbon cages with a diamond-like structure, have evaded laboratory synthesis and have only recently been purified from petroleum sources. Initial calculations on these unique diamond-like molecules show they may have negative electron affinity, a desirable property for electron emission. Readily available adamantane, the smallest diamondoid, can be thiolated and has shown to absorb on gold with high coverage. The availability of diamantane, triamantane, and tetramantanes opens new possibilities for surface-modification as multiple sites are available for thiol or other chemical functionalization. Surface-attached diamondoids have technological possibilities as high-efficiency electron emitters, as well as crystals for diamond growth or other nanotechnological applications, and fundamental studies of the electronic and structural properties of these molecular monolayers are a necessary precursor. We have investigated the effects of thiol substitution position, polymantane order, and metal substrate on diamondoid film morphology. Using Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) we show that the orientation of the diamondoids within each type of monolayer depends highly upon these parameters. We thus demonstrate control over the assembly, and hence the surface properties, of this exciting new class of diamond-like carbon molecules.

Thin Film

Room: 602/603 - Session TF1-FrM

Thin Films for Displays and Flexible Electronics

Moderator: M.A. Creatore, Eindhoven University of Technology, The Netherlands

8:00am **TF1-FrM1 Effects of Processing Parameters on Electroluminescence of RF Magnetron Sputter Deposited ZnS: ErF_3**, *D.M. DeVito, A.A Argun, E.S. Law,* University of Florida, *M. Puga-Lambers, M.R. Davidson,* Microfabritech, ***P.H. Holloway***, University of Florida

ZnS:ErF_3 alternating current thin film electroluminescent (ACTFEL) devices were fabricated by RF plasma magnetron sputtering. In a full factorial design-of-experiment study, increasing deposition temperature, duty cycle on the doped target and sputter gas pressure all resulted in increases in the 1.55 μm near infrared (NIR) electroluminescence (EL) irradiance at 20V above threshold (B_{20}). An increase in the EL threshold voltage (V_{th}) upon increasing the duty cycle of the undoped target was also observed. Post-deposition annealing of ACTFEL devices at 425°C for 1 hr improved the NIR EL irradiance by decreasing the F concentrations in the ZnS:Er films. The origins of these effects are discussed in terms of negative ion resputtering, surface mobility of sputtered species, crystallinity, and the effects of atomic concentration upon the EL and radiative relaxation processes. A maximum irradiance, B_{20}, of 147 μW/cm^2 is measured for the

1.55 µm NIR EL peak from a ZnS:Er ACTFEL devices produced using a deposition temperature of 150°C, a duty cycle of 75%, an argon sputtering gas pressure of 24 mTorr and post-deposition annealing at 425°C for 1 hour in nitrogen.

8:20am **TF1-FrM2 Local Compositional Environment of Er in ZnS:ErF3 Thin Film Electroluminescent Phosphors**, ***M.R. Davidson***, University of Florida, *S. Stoupin*, Illinois Institute of Technology, *D.M. DeVito*, Oak Ridge National Laboratory, *C. Segre*, Illinois Institute of Technology, ***P.H. Holloway***, University of Florida

Phosphors are wide bandgap materials that contain luminescent dopants. Excitation of the dopant can result from electron-beams (cathodoluminescence), photons (photoluminescence) or even mechanical means (piezoluminescence). We have studied the local environment of the erbium (Er3+) luminescent centers in an electroluminescent (EL) ZnS:Er phosphor. The local Er environment is critical to the efficiency and, in some cases, the emission wavelength of the phosphor. Many dopants have radiative relaxation transitions that are quantum dynamically unallowed. While these transitions may be strictly unallowed in the isolated atom, in the phosphor lattice these radiative transitions typically take place with a low probability. The excited states, therefore, must be fairly long-lived in order to allow enough time for the slow radiative transition. Defects and their associated electronic states in the vicinity of the phosphor luminescent center can act to delocalize the excited states and thus provide more effective non-radiative relaxation paths. A detailed knowledge of the local chemical and structural environment is therefore necessary in order to model the quantum efficiency of the radiative relaxation. The dependence of the local composition and order in sputter deposited thin film ZnS:ErF3 electroluminescent (EL) has been investigated using EXAFS as a function of post-deposition anneal temperature. Previous results have shown that the intensity of the EL peaks in the near infrared (1.55 µm) and visible (520 nm) both increase as the anneal temperature is increased, with the NIR intensity maximizing at an anneal temperature of 425 °C . In the as-deposited films, the entire ZnS host lattice is distorted by the presence of the Er, relative to an undoped ZnS film. The long-range crystallinity improves with increasing annealing temperature, especially for 425°C < T < 475°C, the highest annealing temperature studied. The data show that the Er atoms in the as-deposited films have a maximum of one nearest neighbor S atoms, but are surrounded predominantly by F atoms (although the presence of O atoms cannot be ruled out based on EXAFS data). Upon annealing, the spacing of the S around this complex begins to collapse and at 425°C, there is a longer range order that appears.

8:40am **TF1-FrM3 Fabrication and Characterization of Indium Zinc Oxide-Based Thin Film Transistors**, ***D.C. Paine***, Brown University **INVITED**

Active electronics implemented on cheap flexible polymer substrates offer the promise of novel display technologies, wearable electronics, large area memory, and a multitude of other, as-yet-unthought-of, applications that require low cost and high volume manufacturing. Thin film transistors (TFT's) fabricated on temperature-sensitive plastic substrates at low temperatures are the key to this technology. TFT's that use metal (In, Zn, Sn, Ga) oxide channels offer both high mobility (relative to amorphous Si) and the advantage of optical transparency in the visible regime. We report on the fabrication and performance of amorphous oxide transparent thin film transistors that use dc-magnetron sputter techniques to deposit IZO (In2O3-10wt%ZnO) at low oxygen potential (0vol%O2) for the source, drain, and gate-contact metallization and, at higher oxygen partial pressures (10 vol%O2), for the semi-conducting channel. The devices in this study were processed at room temperature except for a single 280°C PECVD deposition step to deposit a 230 nm-thick SiOx gate dielectric. The devices are optically transparent and operate in depletion mode with a threshold voltage of -5 V, mobility of 15 cm2/Vsec, an on-off ratio of >10E6 and, a sub-threshold slope of 1.2 V/decade. We show that control of oxygen in the sputter gas (0 to 30 vol %) during IZO deposition allows control of carrier density.

9:20am **TF1-FrM5 Near IR Electroluminescent Studies Of ZnS Photonic Crystal**, ***E.S. Law***, *P.H. Holloway*, University of Florida, *N. Shepherd*, North Texas State University

The effects of a photonic crystal (PC) structure on outcoupling of light from an alternating current thin film electroluminescent (ACTFEL) device are being studied. The ACTFEL device consists of a thin film of ZnS doped with erbium sputter deposited onto an aluminum-titanium-oxide (ATO) thin insulating layer on an indium-tin-oxide (ITO) transparent conducting electrode on a glass substrate. Al top electrodes are vapor deposited onto the ZnS:Er phosphor, and light is emitted through the glass substrate. ZnS:Er has strong emissions in the near IR at 1550nm, but it has been shown that much of this light is lost laterally to total internal reflection and absorption. The PC structure allows light from these lost modes to be transferred to modes that outcouple from the device. The data show that a triangular array of circles of radius and lattice spacing of 264nm and 660nm, respectively, in the ZnS:Er layer of the ACTFEL device allow coupling of horizontal modes to vertical modes. The sensitivity of this coupling to the dimensions of the PC will be reported. The PC was created with electron-beam lithography using a PMMA resist over the ZnS:Er layer of the ACTFEL device. An Ar ion etch was used to etch the triangular array of holes into the ZnS:Er layer. FOx® flowable silicon oxide was spin coated into the holes to act as the contrasting dielectric layer to the ZnS:Er layer which enables the PC effect. Finally an aluminum electrode was vapor deposited on the backside of the device. The emissions of ACTFEL devices were analyzed using an optical spectrometer. A sevenfold increase in the vertical modes of 1550nm light emission was observed from a device with a PC structure.

9:40am **TF1-FrM6 Conformal CVD of MgO from Mg(H3BNMe2BH3)2 and Water: A New Process for Dielectric Barrier Layers in Plasma Display Panels**, *Y. Yang*, ***D.Y. Kim***, *G.S. Girolami*, *J.R. Abelson*, University of Illinois at Urbana-Champaign

MgO is an attractive material for use as a dielectric barrier layer: it is a refractory oxide with a high melting point (2852 °C), high dielectric constant (9.8), wide bandgap (7.2 eV), and high secondary electron emission coefficient. These properties, combined with a good resistance to plasma erosion, make it suitable for use in AC plasma display panels, with the potential to significantly lower the firing voltage. Chemical vapor deposition affords simplicity, high deposition rate, and the ability to produce conformal coatings in deep features such as cylindrical vias. However, previous efforts to deposit MgO by CVD have not been satisfactory due to low deposition rate (~ nm/min), high deposition temperature (> 400 °C), or the presence of carbon or halogen impurities. Such issues derive from the lack of a suitable Mg-containing precursor molecule. We recently developed a completely new type of Mg precursor, bis(N,N,-dimethyldiboranamido)magnesium, here termed Mg(DMDBA)2. The vapor pressure of this precursor at room temperature is remarkably high, ~ 0.8 Torr, such that no carrier gas or heated delivery lines are required. The precursor is thermally stable but reacts readily with water to produce MgO films at temperatures as low as 225 °C. The high vapor pressure of the precursor allows us to achieve extreme conformality, e.g. a completely uniform film on a trench with depth/width ratio of 35:1, or a very rapid growth, e.g. deposition rate of a few hundred nm/min, or any compromise in between. We will present the CVD kinetics and the microstructure, crystallinity, electrical, and optical properties of MgO films grown from Mg(DMDBA)2 and H2O. Films grown at T > 500 °C on Si(100) or glass substrates are crystalline with a (002) texture; films grown at T > 400 °C are columnar; and films grown a lower temperatures are dense and smooth. The refractive index is 1.69-1.72 and the dielectric constant is 9.5, both of which are very close to the values for bulk MgO. The excellent CVD process characteristics and excellent film quality makes this an attractive new means to deposit the dielectric barrier layers in PDPs.

10:00am **TF1-FrM7 Other Impurity-co-doping Effect on the Stability of Resistivity in AZO and GZO Transparent Conducting Thin Films**, ***T. Kuboi***, *Y. Honma*, *T. Miyata*, *T. Minami*, Kanazawa Institute of Technology, Japan

It has been recently reported that the resistivity of Al-doped ZnO (AZO) and Ga-doped ZnO (GZO) transparent conducting thin films with a thickness below approximately 100 nm always increased when tested in heated high humidity environments. For the purpose of improving the resistivity stability in these films for use in heated moist environments, the effect of impurity-co-doping on the stability of resistivity was investigated for AZO and GZO transparent conducting thin films. The impurity (X)-co-doped AZO and GZO (AZO:X and GZO:X) transparent conducting thin films were prepared on glass substrates by dc (both with and without incorporated rf) magnetron sputtering, rf magnetron sputtering and pulsed laser deposition methods. AZO and GZO thin films co-doped with V or In were prepared with thicknesses in the range from approximately 20 to 200 nm at a temperature of 100-200^{o}C. The resulting thin films were investigated using micro-structural analyses such as EXAFS and TEM. The stability tests were conducted long term (up to 1000 h) in a high humidity environment (air at 90% relative humidity and 60^{o}C). It was found that the resistivity stability of AZO:V thin films was considerably improved by optimizing the content of co-doping V. In particular, AZO:V films with a thickness of 50 nm were stable enough to be acceptable for use in practical transparent electrode applications. In contrast, thin films with a thickness below approximately 30 nm were always unstable under the above test condition. The resistivity increase of films with a thickness below 30 nm is mainly attributable to carrier transport being dominated by the trapping of free electrons due to oxygen adsorption on the film surface rather than the grain boundary.

10:20am **TF1-FrM8 Sputtered In_2O_3 and ITO Thin Films Containing Zirconium**, ***T.A. Gessert,*** National Renewable Energy Laboratory, *Y. Yoshida,* Colorado School of Mines, *T.J. Coutts*, National Renewable Energy Laboratory

The deposition of high-quality tin-doped In_2O_3 (ITO) films by vacuum sputtering is well established. Nevertheless, coating specialists are keenly aware that maintaining high electrical and optical quality in a production environment represents significant challenges. ITO films with high carrier concentration and mobility generally are produced using high substrate temperature (250-350°C) in an ambient where the oxygen partial pressure is controlled to yield a slight oxygen deficiency in the film. Unfortunately, if the sputter ambient becomes too oxygen deficient, the optical transparency of the film decreases. The challenge during ITO deposition is to incorporate enough oxygen to produce films with high transparency while retaining slight oxygen deficiency to yield optimum electrical properties. In a large-area production coating system, this critical oxygen partial pressure must be achieved not only across a large deposition area, but also take into account variations such as target use, seasonal changes, and maintenance activities. Our recent investigations have identified a method to produce ITO-like films that are less sensitive to variations in the oxygen-containing deposition ambient. We are studying the effect of adding small amounts of Zr to both In_2O_3 and ITO ceramic sputtering targets. These targets are then used to produce thin films on glass substrates by r.f. magnetron sputtering. Electrical (Hall) and optical (UV-Vis-NIR spectrophotometry) analysis of these films shows that high-quality Zr-doped In_2O_3 (IZrO target = 9 wt.% ZrO_2+ 91 wt.% In_2O_3) films can be produced at high substrate temperatures (250-350°C) without adding oxygen to the sputter ambient. This result is in contrast to films produced from typical ITO targets (ITO target = 9 wt.% SnO_2+ 91 wt.% In_2O_3), where deposition in pure Ar yields films with very poor optical transparency. Films produced using a target where a small amount of Zr is added to a standard ITO target (ITO:Zr target = 1 wt.% ZrO_2+ 9 wt.% SnO_2+ 90 wt.% In_2O_3) show that the Zr addition allows for a broader range of oxygen partial pressure during deposition. We believe these results may embody significant advantages for large-area ITO film production, and could point the way toward similar benefits in other TCOs such as those based on ZnO or SnO_2 This abstract is subject to government rights.

10:40am **TF1-FrM9 Electronic and Optical Properties of TiO2-based Transparent Conducting Oxide**, ***T. Hitosugi,*** University of Tokyo, Japan, *N. Yamada, Y. Furubayashi, S. Nakao, Y. Hirose, A. Ueda,* Kanagawa Academy of Science and Technology (KAST), Japan, *T. Shimada, T. Hasegawa*, University of Tokyo, Japan

Anatase Nb-doped TiO_2 appears to be promising transparent conducting oxide (TCO) for use as a next generation transparent electrode.[1,2] We report on electric properties of transparent conducting anatase $Ti_{0.94}Nb_{0.06}O_2$ polycrystalline films on glass. The films deposited using pulsed laser deposition at substrate temperature of room temperature, with subsequent H_2-annealing at 500°C, showed resistivity of 4.5 x 10^{-4} Ωcm at room temperature, and optical transmittance of 60-80 % in the visible light region. These results indicate that anatase $Ti_{0.94}Nb_{0.06}O_2$ films have excellent potential for practical transparent conducting oxides.

[1] Furubayashi et al., Appl. Phys. Lett. 86, 252101 (2005).

[2] T. Hitosugi et al., Jpn. J. Appl. Phys. 44, L1063 (2005).

11:00am **TF1-FrM10 Reactive Sputtered SnO_2 as the Active Layer in Transparent Thin Film Transistors**, ***W.-Y. Chen,*** *J.-S. Chen*, National Cheng Kung University, Taiwan

Thin film transistors (TFTs) are the fundamental driving circuits for flat panel displays. In combination with the 'transparent circuit technology', transparent TFTs can increase the brightness and decrease the power consumption of displays. Therefore, oxide semiconductors are investigated as a substitute for the conventional amorphous silicon on TFTs because of their high optical transparency. In this work, we investigate the possibility of using reactive sputtered tin oxide (SnO_2) as the active layer in transparent TFTs. The transmittance of as-deposited SnO_2 film can reach 90%. Hall measurement shows that the SnO_2 film has higher carrier mobility than amorphous silicon. By changing the Ar/O_2 flow ratio during sputtering, the resistivity as well as the carrier mobility of SnO_2 can be varied. With an adequate preparation condition, the reactive sputtered SnO_2 film can lead to good characteristics as the active n-channel layer in transparent TFTs.

11:20am **TF1-FrM11 Electron Field Emission Study of Reactive Sputter Deposited Palladium Oxide Thin Films**, ***C.-J. Huang,*** *F.-M. Pan, T.-C. Tzeng, C.-H. Tsai*, National Chiao-Tung University, Taiwan

Palladium oxide (PdO) is a p-type semiconductor and has many technological applications, such as catalysis, photoelectrolysis, and sensors. Because it is thermally stable up to 800°C, at which the oxide decomposes, and has a relatively low work function (3.9 eV), PdO is a suitable material for field emission applications. It has been used as the electrode material in a surface conduction electron emitter display. In this study, PdO thin films 100 nm thick were prepared on the Pt bottom electrode by reactive sputter deposition and the field emission characteristics were studied. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were used to characterize the chemical composition of the PdO thin film. Under certain deposition conditions, the PdO thin film exhibited a flake-like surface structure. The morphology of the deposited PdO thin film was highly dependent on the sputter deposition conditions, such as the gas flow ratio (Ar /O_2) and the substrate temperature. According to atomic force microscopy analysis, the PdO thin film deposited at 25°C had a root-mean-square (RMS) surface roughness of ~23 nm. The flake structure had a ridge angle smaller than 60° with a height ranging from ~30 nm to 100 nm. The sharp ridge angle can enhance the electric field at the local area around the ridge during the field emission operation. The field emission property of the PdO flake structure were studied using a simple diode configuration under a vacuum condition of ~10^{-6} torr, and the turn-on field was about 8.5 V/μm at the emission current density of 10 μA/cm^2.

Thin Film

Room: 613/614 - Session TF2-FrM

Nanoparticles

Moderator: T.M. Klein, the University of Alabama

8:00am **TF2-FrM1 Preparation and Characterization of Supported Metal Sulfide Nanoclusters Using Size-Selected Deposition**, ***M.G. White,*** Brookhaven National Laboratory, *J.M. Lightstone,* SUNY Stony Brook, *P. Liu,* Brookhaven National Laboratory, *M.J. Patterson, J.C. Lofaro*, SUNY Stony Brook **INVITED**

The layered (S-M-S) structure of the bulk metal sulfides leads to unusual structures at the nanoscale (disks, fullerenes, tube) that exhibit a size-dependent band gap and/or unique catalytic properties. For example, MoS_2 is widely used as a commercial catalyst for hydrogenation and hydrodesulfurization, where it is dispersed as nanoparticles (10-30 Å) on a high surface area support. It is generally accepted that the active sites for reaction are associated with Mo atoms (with Ni/Co "promoter" atoms) located at defects or edges of the nanoparticle, however, many questions remain about the inter-relationship between nanocluster size, structure (atomic and electronic) and metal-sulfur composition, and how these physical properties influence catalytic activity. In this work, we are using mass (size) selected cluster ion beams to explore the size dependent reactivity of small nanoclusters of the early transition metal sulfides (Mo, W). Specifically, we use reactive sputtering in a magnetron source to generate gas-phase cluster cations which are then mass-analyzed to yield a beam of clusters with a precisely defined mass (size) and metal-sulfur composition. The mass-selected clusters are deposited at low kinetic energies ("soft landing") onto a solid support, e.g., Au(111) and Al_2O_3, for preparing model nanocatalysts whose properties can be studied by conventional surface science techniques. To date, we have explored the structure and stability of several prominent $Mo_xS_y^+$and $W_xS_y^+$ cluster species (x/y = 2/6, 3/7, 4/6, 5/7, 6,/8, 7/10, 8/12) in the gas phase and deposited on surfaces. These clusters are substoichiometric relative to the bulk material (sulfur to metal ratio < 2), and generally have exposed metal atoms (edge sites) that are available for adsorbate binding and reaction. Using thermal desorption (TPD) and electron spectroscopy (Auger, XPS), we have studied the reactivity and thermal stability of molybenum sulfide nanoclusters deposited on a Au(111) surface. This work was motivated by recent theoretical calculations that predict that the highly symmetric and stable Mo_4S_6 and Mo_6S_8 clusters bind to the Au(111) surface via relatively strong Au-S linkages, but with little distortion of the cluster structure. Experiments indicate that the clusters can be deposited intact, with adsorbate binding energies that depend on cluster size and atomic composition, and the presence of the Au substrate.

8:40am **TF2-FrM3 Chemical States of Sn Present in SnO2 Nanomaterial Sensors**, ***D.L. Lahr,*** *J.K. Evju, K.B. Benkstein, J.L. Hertz, S. Semancik*, National Institute of Standards and Technology

Tin(IV) oxide (SnO_2) has been studied extensively as a chemiresistive sensing material. Increasingly, it has been shown that morphologies of SnO_2 with nanoscale dimensions have improved sensing properties compared to the bulk material. We report on the observation of chemical states of tin present at the surfaces of a variety of nanoscale SnO_x materials using X-ray Photoelectron Spectroscopy (XPS). Nanoparticles, nanowires and nanostructured thin films with a nominal stoichiometry of SnO_2 actually contain a range of oxidation states of tin, from tin(IV) to tin(0), at their surfaces. Depth profiling reveals the underlying tin(IV) oxide in each of these materials, and provides information on the relative amounts of the various chemical states present as a function of depth. In addition, we present methods to control the extent of oxidation of these materials, as monitored by XPS. We propose that the relative amounts of the chemical states of tin at the surfaces of sensors composed of these materials influence their sensitivity and stability. Control of the composition of the chemical states of tin can lead to improved sensor performance.

9:00am **TF2-FrM4 New Carbon Allotropes Produced by Hydrogen Plasma Exposure of Carbon Nanotubes**, ***M.J. Behr***, University of Minnesota, *T. Singh, D. Maroudas*, University of Massachusetts, Amherst, *E.S. Aydil*, University of Minnesota

Plasma-enhanced chemical vapor deposition (PECVD) using hydrocarbons is a common technique used to grow carbon-based nanostructured materials. It has been well established that hydrogen plays a critical role in determining these materials' crystallinity. For example, PECVD of diamond films is possible only when hydrocarbon precursors are heavily diluted in hydrogen. The specific role of hydrogen in these carbon systems, however, is unknown. To investigate hydrogen's role, we have exposed multiwalled carbon nanotubes (MWCNTs) and carbon nanofibers (MWCNFs) at room temperature to atomic hydrogen produced by an inductively coupled radio frequency plasma source. We observed hydrogen-induced crystallization of MWCNTs and MWCNFs at room temperature. Nanometer-size crystals of carbon appear gradually during 2-10 hour H-atom exposure of the nanotubes. We characterized these nanocrystals using high-resolution transmission electron microscopy (HRTEM), electron diffraction, and forward recoil elastic spectrometry (FRES). HRTEM of the H-exposed material at room temperature revealed the presence of carbon nanocrystals, ~5 nm in diameter, embedded in amorphous carbon nanorods. The electron diffraction patterns and lattice spacings could not be accounted for by known crystalline phases of carbon, such as diamond and lonsdaleite, or by contaminants. However, two distinct crystalline phases are observed among a variety of others in this amorphous matrix. The observed electron diffraction patterns and lattice spacings from these two phases are consistent with a body-centered cubic (BCC) phase with lattice parameter a = 0.30 nm and a face-centered cubic (FCC) phase with lattice parameter a = 0.425 nm. The lattice parameter of the FCC phase is approximately the same as that of i-Carbon, a previously observed but unidentified phase belonging to the cubic crystal system. However, electron diffraction from i-Carbon and the FCC phase we observe do not follow the same selection rules. First-principles density functional theory calculations within the generalized gradient approximation are used in conjunction with electron microscopy to suggest possible crystal structures for these new phases. Specifically, we consider the possibility that these new ordered phases may contain hydrogen atoms in addition to carbon and examine the dependence of the structural parameters of the crystalline phases on their hydrogen content.

9:20am **TF2-FrM5 Non-Lithographic Organization of Nickel Catalyst for Carbon Nanofiber Synthesis on Laser-Induced Periodic Surface Structures**, ***Y.F. Guan***, The University of Tennessee, Knoxville, *A.V. Melechko*, Oak Ridge National Laboratory, *A.J. Pedraza, P.D. Rack*, The University of Tennessee, Knoxville

We present a non-lithographic technique that produces organized nanoscale nickel catalyst for carbon nanofiber growth on a silicon substrate. This technique involves three consecutive steps: first, the substrate is laser-irradiated to produce a periodic nanorippled structure; second, a thin film of nickel is deposited using glancing angle ion beam sputter-deposition, followed by plasma heat-treatment; and third, a catalytic dc plasma enhanced chemical vapor deposition (PECVD) process is conducted to produce the vertically aligned carbon nanofibers (VACNF). The nickel catalyst is distributed along the laser induced periodic surface structures (LIPSS), and the Ni particle dimension varies as a function of the location on the LIPSS and is correlated to the nanoripple dimensions. The glancing angle, the distance between the collimators, and the total deposition time all play important roles in determining the final catalyst size and subsequent carbon nanofiber property. Due to the gradual aspect ratio change of the nanoripples across the sample, Ni catalyst nanoparticles of different dimensions were obtained. After the PECVD process, it was observed that in order for the carbon nanofibers to grow, the nickel catalyst dimension should be larger than a certain critical value of ~ 25 nm, below which, the Ni is insufficient to sustain carbon nanofiber growth.

9:40am **TF2-FrM6 Matilda : A Mass Filtered Magnetron Nanocluster Source**, ***G.H. Kwon***, *T.M. Klein*, The University of Alabama, *W. Hale*, AJA International, Inc., *G.J. Mankey*, The University of Alabama

Matilda, a nanocluster source, consists of a cluster source, a Retarding Field Analyzer (RFA) and a Magnetic sector. A moveable AJA A310 Series 1"-diameter magnetron sputtering gun enclosed in a water cooled aggregation tube serves as the cluster source. The sputtering pressure in the aggregation tube is controlled in the range of 0.03 - 1 Torr using a mass flow controller. The mean cluster size is found to be a function of gas flow rate, sputtering power, and aggregation length. The kinetic energy distribution of ionized clusters was measured with the RFA. The RFA also serves as a high pass filter which allows only ions having a higher kinetic energy than the cluster charge times the retarding voltage to pass. A silver target was used for initial testing and cluster sizes were measured using a transmission electron microscope. At high Ar flow rates, the mean cluster size is 60 nm and for lower flow, the mean cluster size is reduced to 2 nm. Finer control of cluster size can be achieved using a mixture of He and Ar as the sputtering gas. Our results show the He gas pressure can be optimized to reduce the cluster size variations. The cluster sizes can also be selected using a magnetic sector. The sector is downstream from the RFA, and the magnetic field is applied in a direction perpendicular to the direction of ion motion. The ions are dispersed on a substrate laterally according to size. This new method of fabrication allows the study of size effects on a single substrate to increase throughput. This work was funded by the US DOE under grant number DE-FG02-01ER45867 and shared equipment from NSF-DMR-02-13985.

10:00am **TF2-FrM7 Controlled Synthesis of Single and Multi-Component Metallic and Ceramic Nanoparticles Via Matrix Assisted Pulsed Laser Evaporation**, ***A.T. Sellinger***, *E.M. Leveugle, L.V. Zhigilei, J.M Fitz-Gerald*, University of Virginia

The need to obtain nanoparticles with narrow size distributions has prompted the development of alternative processing methods. As an emerging area, laser processing has evolved into several widely accepted fields spanning from thin film growth, etching, lithography, and industrial fabrication to name a few. Within this field, the use of matrix-assisted laser processing has been successfully utilized in the deposition of soft materials in thin film form. One class of materials amenable to solution processing are acetates [$X(OAc)_2$]. Acetates are a widely favored metallorganic precursor for thin film processing on various substrates due to their decomposition behavior under ultraviolet irradiation and/or low temperature. In this research, a dry method to synthesize nanoparticles from frozen salt solutions is reported. Synthesis of Pd, Au, and Ag nanoparticles including their binary and ternary compositions were grown by photo-chemical decomposition of starting metal acetates within host matrices of chloroform and water using an excimer laser operating at 248 nm. Frozen composite targets were ablated at fluences ranging from 0.10 J/cm^2 to 1.0 J/cm^2 at a processing pressures ranging from 10 mTorr to 1 Torr. The ejected nanoparticles were deposited on continuous carbon coated and lacey carbon transmission electron microscopy grids at ambient temperature. Characterization was performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDXS). High-resolution TEM analysis showed definitive evidence of elemental composition and confirmed that the size distributions which were narrow for the Pd system which exhibited mean diameters ranging from 2 to 3 nm while the Ag and Au systems were on the order of 10 nm with evidence of large particles. Additional research concerning the growth of complex, multi-component oxide nanoparticles will be presented as time permits.

10:20am **TF2-FrM8 The Characterization of Stress Induced Crystallization of Polycrystalline Silicon Thin Film Transistor with Vertically Aligned Carbon Nanofibers**, ***J. Park***, *S.Y. Kwon*, The University of Tennessee, *S.-I. Jun*, dpiX, *A.V. Melechko, T.E. McKnight, M.L. Simpson*, Oak Ridge National Laboratory, *P.D. Rack*, The University of Tennessee

Thin film transistors (TFT) with vertically aligned carbon nanofibers (VACNF) are an attractive electronic switching device for nanoscale electroanalysis and delivering biological material into live cells. In our previous work, we have demonstrated an amorphous silicon TFT array integrated with VACNFs for delivering biological material into live cells. To enhance the device performance, we have explored a polycrystalline silicon active layer with a bottom-gate structure. For the poly silicon device, source/drain and gate metals and gate dielectric thin films were RF magnetron sputter deposited. We have examined several enhanced crystallization strategies including DC bias stress during amorphous silicon deposition and stress induced crystallization (SIC) using dielectric silicon nitride caps with relatively lower process temperature and higher crystallinity silicon than conventional annealing. The silicon films have been characterized by x-ray diffraction, scanning electron microscopy, and Raman spectroscopy. In this presentation, we will demonstrate the process flow of fabricating polycrystalline silicon with the stress effects and the characteristics of polycrystalline silicon will be discussed. Furthermore, the electrical characteristics of the TFTs with this active layer will be demonstrated.

Tribology

Room: 617 - Session TR4+SE-FrM

Friction and Wear of Engineered Surfaces Macro- to Nanoscale Approaches

Moderator: N.D. Theodore, Naval Research Laboratory, North Carolina State University

8:00am **TR4+SE-FrM1 Mechanical, Chemical, and Tribochemical Etching of Silicon Studied by Atomic Force Microscopy[1]**, ***F. Stevens***, *S.C. Langford, J.T. Dickinson*, Washington State University

Commercial silicon nitride tips for atomic force microscopy (AFM) were used as model asperities to study the mechanical and tribochemical wear of a Si(110) surface. Aqueous sodium hydroxide and tetraethyl ammonium solutions were employed as chemical etchants. Under these conditions, tip wear is a significant issue; a new tip was employed for each wear measurement. Changes in tip contact stress were estimated by characterizing tip shapes before and after wear. In basic solution, the native oxide can be patterned by the AFM tip to expose the more vulnerable underlying Si to the chemical etchant.[2] Features 20 nm deep, with lateral dimensions less than 100 nm, are readily produced. The rate of oxide wear is a strong function of force applied to the AFM tip; even at low contact forces, scanning significantly accelerates oxide wear. Initial penetration of the native oxide is not uniform and produces deep pits—presumably at pinholes or similar defects in the oxide. Once the oxide is fully penetrated in the scanned region, subsequent tribochemical etching produces depressions with flat, smooth bottoms. For a given contact force and solution, the final wear depth relative to the surrounding, chemically etched material depends only on the number of times the AFM tip has passed over the surface; changing the tip velocity has no significant effect. Thus the tribochemical component of wear is not limited by chemical reaction rates under the conditions of this work. To characterize mechanical wear apart from chemical effects, hydrogen-terminated Si surfaces were scanned in inert solutions and atmospheres; images after wear in argon show wear debris, consistent with abrasive wear. The observed abrasive wear is sufficient to account for 5-10% of the Si wear observed in the presence of basic solution. Tribochemical effects during Si wear at a contact force of 300 nN in 0.1 M NaOH can easily enhance the total etch rate by a factor of two over the sum of the chemical and mechanical wear rates.

[1] This work was supported by the US National Science Foundation under Grant CMS-0409861.

[2] S. Miyake and J. Kim, Nanotechnology 16, 149 (2005).

8:20am **TR4+SE-FrM2 New Techniques for the Quantitative Determination of nm/hr Wear Rates of Materials**, *P.R. Norton, G. Pereira,* ***Y.-R. Li,*** University of Western Ontario, Canada, *A. Lachenwitzer,* Cameco Corporation, *A. Alpas,* University of Windsor, Canada, *W. Capehart*, General Motors

Much effort has been spent on the chemical and mechanical characterization of antiwear films formed from ZDDP additives in automobile engines and on the mechanisms of their formation. By contrast, much less effort has been devoted to evaluating the wear itself. This is largely because the wear rates required in the engine are of order nm/hr, and accelerated testing under high loads is unacceptable because of the ubiquity of wear-rate transitions which make extrapolation to low loads difficult or impossible. The absence of relevant low-load (ultra-mild) wear data means that it is currently not generally possible to correlate the film characterization and wear rate studies, creating a huge gap in our understanding of wear. We are addressing this unsatisfactory situation by developing new techniques for directly measuring wear rates down to nm/hr in tests lasting a few hours. These techniques must be capable of measuring both the initial and long-term wear rates, be valid in the presence of surface films and take account of retention of material during wear. The strategy involves the implantation of Au atoms into the near-surface 100 nm region of a material (currently 52100 steel or an Al-Si alloy), and the determination of the loss of gold from the samples by means of Rutherford Backscattering (RBS) and Heavy Ion Backscattering (HIBS), and the accumulation of gold in the lubricant by Neutron Activation Analysis (NAA). The initial profiles can be either uni-modal or multi-modal with depth, to provide sensitivity to short and long-term behaviour. The analysis of both sample and lubricant/debris quantitatively accounts for all implanted gold, and the depth resolution of HIBS permits determination of the location of the residual gold in the samples.

8:40am **TR4+SE-FrM3 Nano-scale Friction and Wear of Carbon-Based Materials**, ***R.W. Carpick,*** University of Pennsylvania, *D.S. Grierson, A.R. Konicek, P.U.P.A. Gilbert,* University of Wisconsin-Madison, *A.V. Sumant, O. Auciello,* Argonne National Laboratory, *R.J. Cannara,* IBM Zürich, Switzerland, *T.A. Friedmann,* Sandia National Laboratories, *W.G. Sawyer,* Univeristy of Florida, *J.A. Carlisle*, Advanced Diamond Technologies **INVITED**

Nanostructured carbon-based materials, such as nanocrystalline diamond and atomically smooth, nanometer-thick diamondlike carbon films, have outstanding and in many cases unrivalled tribo-mechanical properties. The atomic structure of the surfaces, verified by detailed surface spectroscopy, critically affects nano-scale friction and adhesion. We will specifically discuss how hydrogen termination, sp2-content, and crystal orientation affect adhesion and friction at the nanoscale. Next, we discuss how surface spectroscopy and imaging can be simultaneously applied to study wear of carbon films using photoelectron emission microscopy (PEEM)/X-ray absorption near edge structure (XANES). From these studies we test the hypotheses of ultralow friction in these materials, specifically, the extent to which chemical passivation of dangling bonds and convertion to graphitically bonded carbon occur. Finally, we will discuss taking advantage of this knowledge for nanoelectromechanical systems and advanced nanoprobe applications.

9:20am **TR4+SE-FrM5 Wear in MEMS-Based Microball Bearings,** ***B. Hanrahan,*** *M. McCarthy,* University of Maryland, *C. Zorman,* Case Western Reserve University, *A.V. Sumant,* Argonne National Laboratory, *R. Ghodssi*, University of Maryland

PowerMEMS devices supported on microball bearings have been successfully demonstrated at low operating speeds. Continued research on the tribological properties of these support structures is necessary for the realization of robust high-speed devices. Critical dimensions need to be maintained within tight tolerances when operating high speed micromachines. The wear between stationary and moving elements must, therefore, be minimized to reduce the change in critical dimensions over the lifetime of the device. Accordingly, the mechanism of wear between silicon and hardened steel microballs is the focus of this work. Silicon test structures, 23 mm in length, were fabricated with 300 µm wide deep-etched rectangular trenches acting as housings for the microballs. The 285 µm steel balls were sandwiched between two test structures under an applied normal loading. Oscillatory motion is generated between the two structures using an externally controlled stepper motor at 400 rpm and a traveling distance of 4mm. At periodic time intervals, the test device is disassembled and inspected using an optical profilometer to determine changes in the surface topography. To the best of our knowledge, this is the first investigation of wear in MEMS-fabricated ball bearings. Initial results show both deposition and removal of material within the microfabricated trenches. At 50,000 cycles, equivalent to 200 meters of travel, an increase in average surface roughness from 7.5 nm to 30.2 nm is observed. These results suggest the adhesion and subsequent shearing of contacting materials, increasing the overall roughness. The properties of the mating materials play a critical role in determining the wear mechanism. To expand the scope of the study, solid thin film lubrication has been explored. Silicon carbide and ultra-nanocrystalline diamond are ideal candidates for wear resistant films because of their high hardness, low interfacial energy, and compatibility with MEMS fabrication processes. In our analysis we will present a detailed investigation of the wear mechanisms of steel balls on silicon with and without solid lubrication.

9:40am **TR4+SE-FrM6 Microstructure and Tribological Behavior of W-DLC Coated Rubbers**, ***Y.T. Pei***, *X.L. Bui,* University of Groningen, the Netherlands, *X.B. Zhou,* SKF Research and Development B.V., the Netherlands, *J.T.M. De Hosson*, University of Groningen, the Netherlands

W-DLC coatings have been deposited on FKM, ACM and HNBR rubbers via unbalanced magnetron reactive sputtering from a W target in C_2H_2/Ar plasma. The surface morphology and fracture cross sections of uncoated and coated rubbers are characterized with high resolution SEM. The tribological behaviors of uncoated and coated rubbers have been investigated with ball-on-disc tribotest under dry sliding against 100Cr6 ball. The coefficients of friction (CoF) of uncoated rubbers are very high ($\mu > 1$). Relatively high CoF of W-DLC coated FKM (about 0.6) is observed due to the gradual fracture and delamination of the coatings. In contrary, W DLC coated HNBR rubbers exhibit superior tribological performance with a very low CoF of 0.2-0.25 (comparable to that of Me-DLC coatings deposited on steel substrates). After 10000 sliding laps, almost no damage of the coatings is observed on the wear tracks. The micro-crack networks as deposited facilitate the flexibility of the coatings. The different surface roughness and mechanical properties of the rubber substrates explain the differences in the tribological performances of the coated rubbers. For soft and flexible substrates such as rubbers, metallic interlayer does not enhance the interfacial adhesion but negative effects are observed.

10:00am **TR4+SE-FrM7 Adaptive Tribological Nanocomposite Coatings**, ***C. Muratore***, *J.J. Hu, A.A. Voevodin*, Air Force Research Laboratory **INVITED**

Plasma processing allows precise control of the composition, microstructure and architecture of nanocomposite coating materials, enabling the design of materials that automatically adapt to variable aerospace environments, including humid and dry ambient air, space, and high temperature oxidizing conditions. Self-adaptive materials are of particular interest in tribological applications because most solid lubricants are effective in only a narrow range of ambient conditions. Thoughtful selection of multiple solid lubricant phases and the development of novel lubricant delivery mechanisms such as controlled diffusion, catalysis and chemical reactions with the surrounding atmosphere enhanced by contact between moving surfaces have recently been realized to achieve adaptation in diverse environments. For example, nanocomposite yttria-stabilized zirconia (YSZ) coatings containing Ag, Mo and other nanosized inclusions depend on temperature-activated adaptations to yield low friction (<0.2) from 25-700 °C in air. For YSZ-Ag-Mo nanocomposites, lubrication below 500 °C results from diffusion and coalescence of silver at the surface. Above 500 °C, the silver is pushed out of the wear contact, exposing a limited quantity of molybdenum in the coating to air, and initiating the controlled formation of MoO_3 and other compounds exhibiting low shear strength and thus easy sliding at high temperatures. While these adaptations at the surface reduce friction, irreversible compositional and structural changes resulting from the migration of film components can compromise the mechanical properties of the coating, thus reducing its utility over long periods at high temperature or through multiple thermal cycles. Moreover, some lubrication mechanisms occur over the entire coating surface in addition to the area experiencing wear, thus wasting the limited quantity of lubricious material stored in the coating. Coating architectures that control adaptation rates or selectively inhibit adaptation on coating surfaces unaffected by wear have been developed to increase the lifetime of adaptive tribological materials. Additionally, smart coatings with wear sensing capability have been developed to facilitate coating development and to improve reliability in critical applications.

10:40am **TR4+SE-FrM9 Hard Nanostructured Sulfur-Doped CHx-TiB2 Coatings for Improved Friction and Mechanical Performance**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

Hydrogenated amorphous carbon films are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films results in ultra-low friction performance in both dry and humid environments. However, these films have a hardness of 7 - 10 GPa and an elastic modulus around 80 GPa, which are too low for some high stress applications. Formation of nanolayer or nanocomposite coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanostructured films of sulfur-doped hydrogenated carbon and titanium diboride using dual-target magnetron sputtering. This paper will discuss the film structure and how such structure correlates with its tribological and mechanical properties.

11:00am **TR4+SE-FrM10 The Relation of Hydrogen to Superlubricity of DLC Films**, ***O.L. Eryilmaz***, *A. Erdemir*, Argonne National Laboratory

In this study, we investigated the critical role of hydrogen in friction and wear mechanisms of hydrogen-free and -poor films in dry nitrogen and high-vacuum environments. Using TOF-SIMS and XPS, we found a very important relationship between friction coefficient and the degree of hydrogenation in these films. Specifically, friction and wear test results showed that the films grown in hydrogen-free or -poor plasmas, the friction coefficients were very high (more than 0.5)and un-steady; and these films wore of very quickly during the sliding tests. However, when these films were subjected to very short-duration (a few minutes) post-hydrogen plasma treatment, their friction coefficients became very low (i.e., less than 0.1) and they were able to last very long during sliding tests. Surface analytical characterizations of the films and sliding contact surfaces were done using XPS and TOF-SIMS as well as Raman Spectroscopy and the chemical and structural findings were correlated with the tribological performance of the films. In particular, TOF-SIMS results revealed very close relationship between surface chemistry and tribological performance of DLC films.

11:20am **TR4+SE-FrM11 Friction and Wear Properties of Nanocrystalline Diamond Coatings**, ***C.C. Baker***, *N.D. Theodore*, Naval Research Laboratory, *T. Feygelson*, GeoCenters Incorporated, *J.E. Butler, K.J. Wahl*, Naval Research Laboratory

The tribological behavior of nanocrystalline diamond (NCD) coatings was studied under both unidirectional and reciprocating sliding conditions. Coatings were deposited by microwave plasma chemical vapor deposition onto Si substrates under varying growth conditions to thicknesses between 1-2 microns. Friction behavior was investigated using pin-on-flat geometry with sapphire counterfaces at average contact pressures of 0.43-0.74 GPa. Wear volumes of the ball counterface and coating wear tracks were determined with optical interferometry. Coating microstructure, chemistry, and surface morphology were examined using X-ray diffraction (XRD), micro-Raman spectroscopy, and atomic force microscopy (AFM). We have found that friction coefficients for the sapphire-NCD sliding interface are low, ranging from 0.03 to 0.1. However, there were large differences in friction run-in, with run-in from high to low friction taking between 50 to as many as 10000 cycles over a wide range of NCD deposition conditions. The role of coating microstructure, bonding chemistry, wear, and roughness of worn and unworn surfaces on run-in friction behavior of NCD will be discussed.

11:40am **TR4+SE-FrM12 Effects of Annealing on Anti-Wear and Anti-Bacteria Behaviors of TaN-Cu Thin Films**, ***J.H. Hsieh***, *M.K. Cheng, Y.K. Chang*, Mingchi University of Technology, Taiwan, *S.H. Chen*, National Chiayi University, Taiwan, *P.C. Liu*, Mingchi University of Technology, Taiwan

TaN–Cu nanocomposite films were deposited by reactive co-sputtering on Si and tool steel substrates. The films were then annealed using RTA (Rapid Thermal Annealing) at 400 ?C for 2, 4, 8 minutes respectively to induce the nucleation and growth of Cu particles in TaN matrix and on film surface. C-AFM (Conductive Atomic Force Microscopy) and FESEM (Field Emission Scanning Electron Microscopy) were used to confirm the emergence of Cu nano-particles on the surface of TaN-Cu thin films. The effects of annealing on anti-wear and anti-bacteria properties of these films were studied. The results reveal that annealing by RTA can cause Cu nano-particles with various dimensions to emerge on the TaN surface. Accordingly, hardness and friction coefficients will change, as well as the anti-bacterial behavior.

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