Applied Surface Science
Room 2005 - Session AS+BI+NS+NM-MoM
Organic Surface Modification and Nanoscale Chemical Patterning

Moderator: R. Haasch, University of Illinois, Urbana

8:00am **AS+BI+NS+NM-MoM1 Biomolecular Lithography on GaAs Surfaces***, **A. Ivanisevic,*** Purdue University **INVITED**

Atomic force microscopy (AFM) was used to fabricate well-defined peptide templates onto GaAs surfaces via Dip-Pen Nanolithography (DPN). DPN is a powerful technique to write specific organic and/or inorganic molecules onto a surface with an AFM tip. In this work, DPN was used to construct arrays of peptides with nanometer features. TAT peptides (e.g. CGISYGRKKRRQRRR) which exhibit rapid uptake in cells, were patterned onto the surface in either contact or tapping mode. Several techniques were used for the characterization of the modified surfaces: X-ray photoelectron spectroscopy (XPS), Fourier Transforms Infrared (FT-IR) spectroscopy and contact angle. Transmission FT-IR provided structural information such as peptide conformation. The complementary analysis confirmed the binding of the peptide onto the substrates and allowed to quantify the density of immobilized peptides on a given surface. Furthermore, the nanoscopic features were successfully used in recognition experiments where an RNA sequence with a loop structure, known for its specific interaction with the peptide, was tested. The results in this report indicate that one can use nanolithographic strategies to pattern GaAs surfaces, and therefore provide a proof-of-concept experiment that can be transferred in complex microfabricated semiconductor architectures.

8:40am **AS+BI+NS+NM-MoM3 The Effect of Ring Substitution Position on the Structural Conformation of Mercaptobenzoic Acid Self-Assembled Monolayers on Au(111)***, **J.R.I. Lee,*** Lawrence Livermore NAtional Laboratory*; T.M. Willey, J. Nilsson, L.J. Terminello, J.J. De Yoreo, T. van Buuren,* Lawrence Livermore National Laboratory

Mercaptobenzoic acid (MBA) is a viable alternative for preparing SAMs with carboxyl functionality. These molecules, as opposed to carboxyl-terminated alkylthiols, offer an extended pi-bonded system formed by the aryl and carboxyl groups facilitating charge transfer, and these extremely thin SAMs (< 8 Angstroms) have been shown via STM to contain a high degree of structural order. Furthermore, three different isomers of mercaptobenzoic acid may lead to differing surface properties. In this work, the orientation and bonding of self-assembled monolayers of the three positional isomers of mercaptobenzoic acid adsorbed on gold are investigated using near edge X-ray absorption fine structure (NEXAFS) spectroscopy and photoemission spectroscopy (PES). The isomer of MBA and solvent chosen in SAM preparation has considerable bearing upon film morphology. Monomers of 3- and 4-MBA assume an upright orientation on the Au substrates in monolayers prepared using an acetic acid in ethanol solvent. The aryl ring and carboxyl group of these molecules are tilted from the surface normal by a colatitudal angle of ~ 30 degrees. Preparation of 4-MBA SAMs using pure ethanol solvent, a more traditional means of synthesis, had no appreciable effect upon the monomer orientation, but S(2p) PES measurements illustrate that it results in extensive bilayer formation via carboxyl group hydrogen-bonding between 4-MBA monomers. In 2- MBA monolayers prepared using acetic acid/ethanol solvent, the monomers adopt a more prostrate orientation on the Au substrates, in which the aryl ring and carboxyl group of the molecules are tilted ~ 50 degrees from the surface normal. This configuration is consistent with an interaction between both the mercaptan sulfur and carboxyl group of 2-MBA with the underlying substrate. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Science, and performed under the auspices of the U.S. DOE by LLNL under contract No. W-7405-ENG-48.

9:00am **AS+BI+NS+NM-MoM4 XPS Analysis of Arenes and Proteins on Gold Substrates Attached by Electrochemical Reduction of Aryldiazonium Salts***, **J.L. Fenton,*** University of New Mexico*; S.M. Dirk, D. Wheeler,* Sandia National Labs*; J.E. Fulghum,* University of New Mexico

The properties of most materials can be altered by the attachment of molecules to their surface. Recent work has shown that diazonium salts can be used to attach aryl compounds to metal and semiconductor surfaces including silver, iron, platinum, silicon, and glassy carbon. Diazonium salts can be electrochemically reduced in acetonitrile leading to the attachment of aryl groups to the surface of a substrate. The attachment of aryl compounds using diazonium salts developed in our work, allows one to attach aryl compounds with different organic moieties onto metal substrates including gold. Aryl organic layers can be made of different thicknesses, and stacked structures can be created by alternating layers of molecules. This work is then expanded upon to attach proteins to metal surfaces. This approach provides a methodology to generate arrayed proteins on electrode arrays without the use of microfluidic methods such as ink jetting etc. The development of protein arrays can often provide high-throughput, quantitative measurement of receptor-ligand complexation giving an understanding of protein function, modification, and regulation. X-ray photoelectron spectroscopy (XPS) is used to deduce the different types of chemistries in single molecule samples, stacked structures, and surface tethered proteins. Angle resolved XPS is used to determine the relative location of each molecule in the stacked structures and possible orientation of proteins as well as to deduce the existence of azo linkages.

9:20am **AS+BI+NS+NM-MoM5 Challenges in the Modification and Characterization of Two- and Three-Dimensional Biointerfaces***, **M. Textor,*** ETH Zurich, Switzerland **INVITED**

Surface modifications based on biochemical or biological principles are important tools for the fabrication of biosensor chips, biomedical devices such as implants, and of drug delivery carriers. Moreover, well-designed model biointerfaces have substantially contributed in the last decade to a better insight into fundamental aspects of cell-surface interaction. An overview will be given on tools enabling the surface engineer to tailor the interface of biomaterials, with special emphasis on the approach of eliminating non-specific adsorption and adding to such a silent surface biological functionalities. Preservation of active conformation and optimum presentation (orientation, density) of surface-immobilized moieties are particular challenges in this field. Different approaches to micro- and nanopatterning of surfaces, their specific advantages/disadvantages and applications in biorelated fields are discussed. Special emphasis is placed on methods that combine top-down (e.g., lithography) and bottom-up (self-assembly) approaches. Substantial new insight into the factors that govern cell-surface interactions and cell differentiation has recently be gained by using two-dimensional (2D) patterns. There is, however, an increasing interest to explore (stem) cell development in 3D microwells with well-controlled geometry (shape/size), surface chemistry and mechanical properties (substrate stiffness). The challenges of independently tailoring chemistry and structure/topography are addressed; self-assembly techniques are in this respect particularly useful. Finally, characterization/imaging techniques that allow the monitoring of biointerface reactions in situ, in real time and quantitatively are important tools; selected methods will be presented based on highly surface- and detection-sensitive evanescent-field-based sensing.

10:20am **AS+BI+NS+NM-MoM8 Nanoscale Chemical Patterning and Architectures***, **P.F. Nealey,*** University of Wisconsin **INVITED**

Diblock copolymers are self-assembling materials consisting of two polymer chains connected at one end that tend to form ordered nanostructures, including spheres, cylinders, and lamellae, whose shape and dimensions depend on the molecular weight and composition of the polymer. Block copolymer lithography refers to the use of these ordered structures in the form of thin films as templates for patterning through selective etching or deposition. Already block copolymer lithography has been used to pattern dense periodic arrays for the applications such as quantum dots, nanowires, magnetic storage media, increased capacitance gate devices and FLASH memory. One of the current goals in block copolymer nanolithography is to reproduce many of the characteristics of the lithographic process used ubiquitously in nanomanufacturing, including pattern perfection over macroscopic areas, the ability to pattern arbitrary and non-regular geometries, dimensional control of features within exacting tolerances and margins, and registration and overlay. Two strategies will be discussed to integrate self-assembling materials into existing manufacturing practices so as to achieve molecular-level process control and the ability to produce useful architectures: directed assembly of block copolymers on topographically patterned substrates, and directed assembly of block copolymers on chemically nanopatterned substrates.

11:00am **AS+BI+NS+NM-MoM10 Tailoring of Functional Nano-Patterned Surfaces for Biosensing Applications by Combination of Plasma Processes and Electron-Beam Lithography***, F. Brétagnol, L. Ceriotti, A. Valsesia, T. Sasaki, D. Gilliland, G. Ceccone, P. Colpo,* ***F. Rossi***, JRC-IHCP-BMS, Italy

Fabrication of micro and nano-patterned surfaces with a well defined geometry and a controlled chemistry is a fundamental step for the development of bioengineered materials Micro-arranged surfaces

containing functionalities such as cell or protein adhesive in a non non-adhesive matrix provide a very useful tool in a large field of applications (tissue engineering, cell behavior investigations , artificial growth of neurons networksâ?¦) . Numerous methods have been successfully developed for the production of such surfaces including conventional photolithography, photochemistry , micro-contact printing , micro fluidic patterning . Nevertheless, the development of surfaces chemically patterned at nano scale is still a challenging issue for the implementation of new generation of miniaturized biochips and for the study of cell surface interactions. In this study, we present an innovative method for the fabrication of chemically nano-patterned surfaces. Maskless lithography based on electron-beam technique was successfully combined with plasma-based processes to create COOH terminated spots over a PEO-like matrix. Spots from micron to submicron size have been created. Quality control of the patterned surface was studied by Atomic Force Microscopy, XPS and ToF-SIMS analysis. Experiments with fluorescent proteins on the patterned surfaces exhibit a preferential adhesion on the active region showing the ability of this technique for the design of biosensing platforms.

11:20am **AS+BI+NS+NM-MoM11 Optically-Stimulated Surface Diffusion Exploited for Directed Self-Assembly on Amorphous Semiconductors***, E.G. Seebauer,* ***Y. Kondratenko****,* University of Illinois at Urbana-Champaign

Nanoscale device fabrication technologies require toolsets for miniaturization and organization of materials at nanometer dimensions. Current toolsets have developed from two diametrically opposite strategies: top-down and bottom-up. This laboratory is taking a different approach based on a new physical mechanism for photostimulated diffusion discovered here. This new strategy combines attractive features of top-down and bottom-up approaches by exploiting the self-organization capabilities latent in amorphous materials, but in a way that can be controlled by optical or electron beam exposure tools. We have developed a new surface self-assembly method at the 10-200 nm length scale using amorphous semiconducting materials. Patterned optical or electron beam exposure yields a spatially varying surface mass flux that, when performed at an annealing temperature just at the cusp of crystallization, provides the extra nudge to crystallize subcritical nuclei in regions dictated by the light flux. The full-fledged crystallites then grow by surface diffusion and Ostwald ripening until the desired fraction of the film has accreted onto the original nuclei. We have demonstrated this technique with titanium dioxide as the substrate material. This scheme should apply to a wide variety of semiconducting materials on nearly arbitrary substrates to form nanoarrays, nanowalls, and possibly three-dimensional structures. Possible applications include chalcogenide semiconductors for data storage media; nanoparticles arrays for direct use in sensors and solar cells; and semiconductor arrays for indirect use as seed layers for the subsequent deposition of sintered particle films in fabricating advanced ceramics and devices such as rechargeable batteries, solar cells, gas sensors, and photonic band gap materials in solar windowpanes.

11:40am **AS+BI+NS+NM-MoM12 Nanowires and Nanodevices via Assembly of Clusters***,* ***S.A. Brown****,* Nano Cluster Devices Ltd, New Zealand

We report the achievement of contacted electronic devices, self-assembled from atomic nanoclusters. Features of this technology, which overcomes the difficulties in the assembly of building blocks inherent to many bottom-up approaches to nanotechnology, include: Interchangeable cluster sources so as to have available a wide variety of cluster materials in a useful size range, allowing exploitation of novel structures and properties. Self-assembly methods which avoid time consuming positioning of building blocks. Use of lithographic processes which are compatible with both cluster deposition technology and standard microelectronics fabrication protocols. Understanding of basic physical assembly processes in order to predict and control device formation, including availability of suitable computer simulations. In this paper we will review the assembly methods developed, which include directed assembly in silicon V-grooves and on polymer-patterned surfaces, as well as stencilling techniques. We will then focus on the application of these techniques to one class of devices which have been realised i.e. cluster-assembled hydrogen sensors. These sensors are realised by the deposition of Pd clusters on a substrate such that one or several conduction paths are formed between a pair of contacts. The sensing principle relies on the expansion of Pd clusters and the resulting change of conductance as a result of their absorption of hydrogen and we have demonstrated very high sensitivities.

Nano-Manufacturing Topical Conference
Room 2018 - Session NM+IPF-MoM

Examples of Nanotechnology Manufacturing

Moderator: J. Randall, Zyvex Corporation

8:00am **NM+IPF-MoM1 The Economics of Matter: Nanotechnology & Scale of Manufacturing***,* ***J. Wolfe****,* Lux Capital **INVITED**

My venture partners invest in, write about, and live in the realm of mesoscale physics, or, by its more popular nomenclature, nanotechnology. Once poorly understood as an ill-defined amalgamation of disparate, atomic-level sciences, nanotechnology is now a young media darling whose time has come. Sophisticated investors and corporate executives grasp that this is no passing fad. Five years ago, we saw salient advances in materials science being neglected as the herds stampeded toward enterprise hardware and software and optical networking. We were convinced that Nicholas Negroponte would have it wrong, and that soon enough people would be trading in their bits for atoms. When our research arm, Lux Research, released its first annual "Nanotech Report" in 2001, 98 percent of Fortune 1000 executives were unable to define "nanotechnology." Today, nanotechnology has become a presidential priority, has taken center stage on CNBC, and has even surfaced as a subject of activist chatter and environmental concern. Just as plastics revolutionized the structural properties of matter - entering into industries as various as communications, electronics, food and beverage, and entertainment - now, nanoscale advances offer the ability to control the structural and functional properties of matter. This includes electric, thermal, magnetic, and optical properties, which are applicable to every industry imaginable.

8:40am **NM+IPF-MoM3 Colloidal Nanocrystals of Complex Shape: Synthesis, Properties, Applications***,* ***A.P. Alivisatos****,* Lawrence Berkeley National Laboratory and University of California, Berkeley **INVITED**

Over the last decade, there have been significant advances in the ability to prepare colloidal inorganic nanocrystals with controlled size, shape, and even interconnection (branching) and topology (hollow and nested). These materials exhibit strongly size dependent properties, but they also share many of the characteristics of inorganic solids, in terms of stability and range of properties. They can be processed in solution like polymers. They thus make attractive candidates for incorporation into a wide range of technologies, from biological labels to components in solar cells and catalysts.

9:20am **NM+IPF-MoM5 Manufacturing Nanoparticles for Applications in Society***,* ***R.W. Siegel****,* Rensselaer Polytechnic Institute **INVITED**

The past decade has seen an explosive growth worldwide in the physical, chemical, and biological synthesis and study of a wide range of nanoscale building blocks with unique properties in laboratory settings. However, before these nanoscale building blocks can significantly impact society through a wide range of novel applications, the manufacture of them needs to be scaled up to commercially viable quantities at an affordable cost. This talk will describe how one such type of nanoscale building blocks, nanoparticles, has moved from the laboratory to the marketplace, and milligrams to tons, over the past 17 years. We began making metal oxide nanoparticles via a gas-condensation physical process at Argonne National Laboratory in 1985 and in 1989 founded a company, Nanophase Technologies Corporation, to scale up production and eventually market products. Since that time, a publicly held (since 1997) business has been developed that produces commercial quantities of a variety of nanoparticles and dispersions that have found applications that benefit society in sunscreens and other health care products, polishing media for microelectronics, and nanoscale fillers for a number of plastics, among others. Nevertheless, fundamental research continues with these commercially available nanoparticles that could expand the horizons of their application space in society. Some examples from this research in our own laboratories in the National Science Foundation funded Center for Directed Assembly of Nanostructures at Rensselaer to create materials that possess enhanced mechanical, electrical, optical, and bioactive properties, and multifunctional combinations thereof, will also be presented.

10:20am **NM+IPF-MoM8 Nanotechnology and High-Efficiency Automobiles***,* ***M.W. Verbrugge****,* General Motors Research and Development Center **INVITED**

We overview a variety of nanotechnologies and associated opportunities relevant to automotive applications. A significant challenge for the automotive industry is to produce vehicles of higher energy efficiency while continuing to improve vehicle functionality. One can divide the vehicle

system into body and powertrain subsystems. This talk overviews recent developments and open questions associated with (1) structural materials for body subsystems and (2) electronic materials for energy storage and transfer. Emphasis is given to nanocomposites and surface analysis methods within the context of structural subsystems. Batteries, thermoelectric devices, and hydrogen storage media are addressed in relation to advanced propulsion subsystems.

11:00am **NM+IPF-MoM10 DNA-linked Dendrimer Nanoparticle Systems for Cancer Diagnosis and Treatment***, J.R. Baker, Jr.,* University of Michigan **INVITED**

Dendritic polymer architecture allows for the development of new therapeutics that directly target cancer cells and largely bypass healthy cells. Clusters of these polymers can be combined into more complex structures with several different subunits, each with its own function, be it targeting, imaging or therapeutics. This technology can be expanded by developing single-function dendrimer modules linked by complimentary oligonucleotides. Thus, producing multifunctional therapeutics that can be customized to a specific patient's needs.

Nano-Manufacturing Topical Conference
Room 2018 - Session NM+MS+IPF-MoA

Beyond CMOS: Emerging Materials and Devices
Moderator: C.M. Garner, Intel Corporation

2:00pm **NM+MS+IPF-MoA1 Technology Challenges: The Next 15 Years***, **P. Gargini**, C.M. Garner,* Intel Corporation **INVITED**

The semiconductor industry continues to introduce new technologies at the pace dictated by Moore's Law. The International Technology Roadmap for Semiconductors (ITRS) projects that devices can be manufactured with conventional process technology through at least 2020 even though there are significant challenges, but further extensions to extreme CMOS may require new 1D device materials. When extreme CMOS technology has reached the limits of scaling, new devices with potentially new architecture will be needed to provide continued performance improvements. For technologies beyond CMOS, research is proceeding on a number of new alternate "state" devices that would require radical materials with a silicon base. The introduction of new alternate state devices may require the introduction of new interconnect technologies and materials with nm control of properties. The challenges to driving to extreme CMOS and the options for alternate state devices will be discussed. For more information on the International Technology Roadmap for Semiconductors (ITRS): http://public.itrs.net

2:40pm **NM+MS+IPF-MoA3 Beyond CMOS - The Semiconductor Industry's Nanoelectronics Research Initiative***, H. Coufal, **J. Welser**,* Nanoelectronics Research Corporation **INVITED**

The tremendously powerful scaling of transistors, that has enabled Moore's Law for the past forty years, can not continue forever. Some of the reasons, such as the atomistic nature of matter, are obvious. Others are less obvious and will be briefly reviewed before some of the potential alternatives to charge based logic will be analyzed. Such an analysis had the semiconductor industry initiate a Nanoelectronics Research Initiative. The current status of this program will be reviewed.

3:20pm **NM+MS+IPF-MoA5 Nano Manufacturing Challenges***, **M. Mayberry**,* Intel **INVITED**

Not all "nano" is created equal. Nanostructures formed through tops down construction are widely used in the creation of electronics and have shipped in volume for several years. Nanomaterials that are formed through bottoms-up synthesis or self-assembly are at a comparably early stage in research and development. Combining the two approaches has considerable promise but also significant hurdles to overcome. To illustrate we will discuss three potential applications for nanomaterials and some of the challenges to successful implementation in manufacturing. First consider the problem of forming nanostructures as the size of the features begins to approach molecular dimensions. A 20nm wide structure would only consist of 10 resist molecules side by side if the resist molecule were 2nm in size. That introduces significant granularity which up to now has not been a key concern. This problem could be addressed by designing self-assembly molecules with the proper combination of sensitivity to illumination, chemical properties, and physical size. A second potential application is the formation of dielectrics between metal lines for interconnects. An ideal dielectric is an insulator, strong enough to withstand forces generated with temperature cycling, a barrier to migration of materials, and for performance reasons has a low dielectric constant. These could in principle be met through design of the right building blocks but there are complications with integration in the overall process flow. Finally nanodevices formed through self-assembly (ex. nanotubes) could in principle allow formation of very small devices but the challenge of precision formation, placement, and again integration are daunting. These challenges are not insurmountable but need to be addressed through the right research and development so that the promise of nanomaterials can be achieved.

4:00pm **NM+MS+IPF-MoA7 Metrology for Emerging Devices and Materials***, **E. Vogel**,* University of Texas at Dallas **INVITED**

Traditional scaling of the CMOS Field-Effect-Transistor (FET) has been the basis of the semiconductor industry for 30 years. The 15 year horizon of the International Technology Roadmap for Semiconductors (ITRS) is reaching a point which +IBw-challenges the most optimistic projections for the continued scaling of CMOS (for example, MOSFET channel lengths of roughly 9 nm).+IB0- As silicon CMOS technology approaches its limits, new device structures and computational paradigms will be required to replace and augment standard CMOS devices for ULSI circuits. These possible emerging technologies span the realm from transistors made from silicon nanowires to devices made from nanoscale molecules. One theme that pervades these seemingly disparate emerging technologies is that the electronic properties of these nanodevices are extremely susceptible to small perturbations in structural and material properties such as dimension, structure, roughness, and defects. The extreme sensitivity of the electronic properties of these devices to their nanoscale physical properties defines a significant need for precise metrology. This talk will provide an overview of emerging devices and materials, and, through example, an overview of the characterization needs for these technologies.

4:40pm **NM+MS+IPF-MoA9 Linking Proteins, Particles and Wires to make Functional Devices: Metrology, Materials and Properties***, **D.A. Bonnell**,* The University of Pennsylvania **INVITED**

Two issues that are critical, and projected to be limiting, to next generation device technology are metrology at the nanoscale and integration of diverse materials into manufactured devices. The first half of this talk will summarize advances in local measurements of properties and demonstrate new techniques that probe electronic structure and properties in nanostructures and molecular wires. These approaches will be illustrated on 3-terminal configurations that exhibit transistor or memory behavior. Opportunities for exciting advances on the horizon will be presented. The second half of the talk will present strategies for integrating a combination of metal and/or oxide nanoparticles, organic and/or biological molecules on oxide or polymeric substrates in device configurations. The processing approach, Ferroelectric Nano Lithography, induces variations in local electronic structure in substrates to direct assembly of nanostructures with diverse properties into complex patterns, thus overcoming one of the limitations of self assembly. The approach has been used to produce a molecular opto electronic switch.

Nano-Manufacturing Topical Conference
Room 2018 - Session NM+IPF-TuM

Nanotechnology and Society

Moderator: J. Murday, Naval Research Laboratory

8:40am **NM+IPF-TuM3 Nanotechnology Oversight - Managing Potential Risk in an Uncertain World*, A.D. Maynard,*** Woodrow Wilson International Center for Scholars **INVITED**

Nanotechnology has been described as a transformative technology, an enabling technology and the next technological revolution. Even accounting for a certain level of hype, a heady combination of investment, rapid scientific progress and exponentially increasing commercialization, point towards nanotechnology having a fundamental impact on society over the coming decades. However, enthusiasm over the rate of progress is increasingly being tempered by concerns over possible downsides of the technology. Real and perceived adverse consequences in areas such as asbestos, nuclear power and genetically modified organisms have engendered skepticism over the ability of scientists, industry and governments to ensure the safety of new technologies. As nanotechnology moves towards widespread commercialization, not only is the debate over preventing adverse consequences occurring at an unusually early stage in the development cycle; it is also expanding beyond traditional science-based risk management to incorporate public perception, trust and acceptance. Having appropriate oversight frameworks in place will be essential to the sustained development of nanotechnologies. These will need to address potentially new risks presented by engineered nanomaterials, and be responsive to the rapidity with which nanotechnologies are being discovered, developed and used. Existing oversight frameworks may be sufficiently robust to address new technologies with little modification, although some commentators suggest that this is unlikely. Either way, too little oversight could be as damaging to fledgling nanotechnologies as too much oversight.

9:20am **NM+IPF-TuM5 Nanoparticle Occupational Safety and Health Consortium*, M.L. Ostraat,*** DuPont Engineering Research and Technology*; K.A. Swain,* DuPont Central Research and Development*; J.J. Krajewski,* DuPont Engineering Research and Technology **INVITED**

The Nanoparticle Occupational Safety and Health (NOSH) consortium of international industrial, government and non-governmental organizations has focused research upon obtaining information on occupational safety and health associated with aerosol nanoparticles and workplace exposure monitoring and protocols. The technical goals of the consortium include 1) generating well-characterized aerosols of solid nanoparticles and measuring aerosol behavior as a function of time; 2) developing an air sampling method that can be used to conduct worker exposure assessments in workplace settings; and 3) measuring barrier efficiency of filter media to specific engineered aerosol nanoparticles. To accomplish these objectives, multiple aerosol synthesis and characterization systems have been designed to generate well-characterized aerosol nanoparticles of various chemistries < 100 nm. These aerosol nanoparticles are transported to aerosol chambers to examine aerosol behavior as a function of time, including rate of dispersion, aggregation, and particle loss for charged and uncharged aerosol nanoparticles. These aerosol nanoparticle studies form the basis for the development of a portable aerosol nanoparticle monitoring instrument which will be field tested in a wide variety of workplace environments. Through this effort, the consortium has developed instrumentation and protocols required to assess barrier effectiveness of filter media to charged and uncharged aerosol nanoparticles as a function of particle chemistry, particle size distribution, and number concentration. Work continues on identifying appropriate filter media that can be used as effective barriers for aerosol nanoparticles and establishing a knowledge base on determining specifications for using those filter media given a set of known properties about a specific nanoparticle aerosol.

10:40am **NM+IPF-TuM9 Nanotech for Environment Renaissance - Soil and Groundwater Cleanup using Reactive Nanoparticles*, W.-X. Zhang,*** Lehigh University **INVITED**

Zero-valent iron nanoparticle technology is quickly becoming a popular choice for remediation and treatment of a wide variety of common environmental contaminants in soil and groundwater. Over the three years, there are more than 30 completed and ongoing applications in North America and Europe. Nanoparticles have small sizes for effective in situ injection and dispersion and large surface areas and high surface reactivity for rapid contaminant transformation. Recent innovation in the technology and increasing supplies of nanoparticles have substantially reduced the cost of this technology for large scale applications. In this lecture, fundamental principles on nanoparticle synthesis and characterization will be highlighted. Applications of the iron nanoparticles for treatment of chlorinated organic solvents, organochlorine pesticides, PCBs, perchlorate, and hexavalent chromium will be presented. In addition, key issues related to field applications such as cost, fate/transport, and potential environmental impact will be discussed.

11:20am **NM+IPF-TuM11 Ethics between Nanoscience and Nanotechnology: Making Space for a Discussion*, A. Johnson,*** University of South Carolina **INVITED**

Much of the work in the ethical implications of science and technology is rooted in a concern over the potential and already occurring societal effects of research and the products of research. But science and technology can have profoundly different underlying assumptions about their societal interactions. Technology, or perhaps more specifically engineering, has developed a robust space for ethical discussion - a fact which underlies the recent re-orientation of engineering curriculum in the US (ABET 2000) to provide curricular support for ethics in engineering education. The ethical landscape of technology is rooted in the fact engineers unquestioning acknowledge that they produce goods for society and that those goods often have societally-transforming effects (both for good and for bad). Science has no such assumption (though individuals' beliefs may obviously differ). Many scientists believe that science can be important without any societal implications - science can be simply about knowing the unknown, without that knowledge having any societal effect. Some scientists, in their pursuit of disinterestedness, have explicitly denied the societal interactions of their work. Science, ideally in their minds, stands outside society. This strongly limits the space for ethical discussion. This position is one which has its own long history, but can be detected in Rowland's "Plea for Pure Science" to Vannevar Bush's (ironically, an engineer!) Endless Frontier to the efforts of Cold War nuclear physicists to distinguish bomb design from basic research to the Science Wars debate of the 1990s. Rather than simply cursing this position, I will address the question here of how this effects today's work at the border of science and technology, by presenting a case study on the way that researchers in nanotechnology, a field with explicit societally-transformative goals, is struggling with the pure-applied/science-technology distinction once again.

Nano-Manufacturing Topical Conference
Room 3rd Floor Lobby - Session NM-TuP

Nano-Manufacturing Poster Session

NM-TuP1 Glass Nanoimprint using Amorphous Ni-P Mold Etched by Focused Ion Beam*, **H. Mekaru,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T. Kitadani,* SAWA PLATING CO.,LTD., Japan*; M. Yamashita,* Hyogo Prefectural Institute of Technology, Japan*; M. Takahashi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

We succeeded in the glass nanoimprint of line and space patterns using an amorphous Ni-P mold. The glass-like carbon has been used as a mold material to mold not only Pyrex glasses but also quartz glasses because it's still stable in the temperature of 1650 °C. However, it is difficult to process a quartz glass substrate to arbitrary shape by machining. We thought that the amorphous Ni-P alloy is used as a mold material for the industrial glass molding. To replicate on Pyrex glasses, the mold material should endure the heating of 600 °C or more. Pyrex glasses should be able to release from the mold without a release agent. We thought that there is a possibility that the wettability between Ni and Pyrex glasses decreases if the crystal Ni layer is changed into an amorphous layer like a glass-like carbon. If Ni is electroless plated mixing suitable amount of P on a Si wafer or a Ni substrate, the Ni-P layer becomes amorphous. The ratio of appropriate Ni and P was judged from the X-ray diffraction measurement, and the optimized composition ratio of Ni-P was Ni : P = 92 wt% : 8 wt%. After electroless plated, the amorphous Ni-P layer was heat-treated at 400 °C to improve the hardness. Moreover, line and space patterns of line width less than 1 µm was etched with FIB on the mold, and the processing accuracy of the amorphous Ni-P layer was compared with the pure Ni layer. As a result, patterns of several 100 nm width can be fabricated to depth 1 µm on the amorphous Ni-P mold, and processed side walls were smooth. At pure Ni layer, the processing line was notched, and the side walls were very rough. The crystal size of the pure Ni layer was measured by the TEM observation, and the maximum crystal size was 500 nm. The crystal grain seems to hinder in the processing of the nano-pattern. Line and space patterns of the amorphous Ni-P mold was nanoimprinted on a Pyrex glass using the glass embossing device (ASHE0201) that AIST had developed.

NM-TuP2 Annealing Effect of Structural, Morphological and Optical Properties on Reactive Sputtered WO@sub3@ Films for Mediated Heterogeneous Photocatalyst*, K. Prabakar, T. Takahashi,* ***K. Takahashi****, T. Nezuka,* University of Toyama, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* University of Yokohama City, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

The WO@sub3@ mediated heterogeneous photocatalyst for the oxidation of pollutants in air would be useful study for environmental decontamination purposes. Reactive facing target sputtering method was used to deposit WO@sub3@ thin films from a metal tungsten disc in an Ar+O@sub2@ mixture gas atmosphere at different sputtering pressures. X-Ray diffraction, scanning electron microscopy, UV-vis spectrophotometer in the wavelength range 300 to 900 nm and Raman spectroscopy studies were performed to study structural, surface morphology and the optical properties of the as-deposited and annealed samples. Annealing treatments were done in oxygen atmospheres. All the as-deposited films were amorphous in structure. The films annealed at 400°C and deposited at 100 W have monoclinic crystal structure with the preferential orientation of (111) plane. As the sputtering power increases to 200 W and annealed at 400°C, a changes in the crystalline orientation of the films along the (001) direction is observed. SEM images show a denser granular structure with grains having different shapes and sizes. The WO@sub3@ films deposited at the sputtering pressure of 0.15 Pa and annealed at 400°C show the nanorods like growth from the observation of SEM images. The optical absorption edge of the as-deposited films prepared at the sputtering pressures of 0.8 - 0.15 Pa varied between 340 - 380 nm and shifted up to 470 nm when the samples are annealed at 400 °C. From the measurement of Raman spectra, it was observed that the O - W@super6+@ - O bonds, and the W@super6+@=O stretching mode of terminal atoms on the surface of WO@sub3@ microcrystalline grains. The suitability of the films for the WO@sub3@/TiO@sub2@ heterogeneous photocatalyst were analyzed and discussed.

NM-TuP3 High-K HfO@sub 2@ Nanotube Fabrication using Template Synthesis and Atomic Layer Deposition*, **I. Perez**, E. Robertson, L. Henn-Lecordier, H. Yi, S.J. Son, S.B. Lee,* University of Maryland, College Park*; G.W. Rubloff,* University of Maryland, College Park, US

In a template synthesis approach, we have exploited self-assembly which occurs during the anodic oxidation of aluminum to produce anodic aluminum oxide (AAO) membranes with high densities of cylindrical nanopores with uniform dimensions and spacing. The high aspect ratio of the pores (up to 1000:1), their nanoscale dimensions (diameters 15-100 nm), and their large area density (~10@super 11@ pores per cm@super 2@) suggest diverse applications, from nanowire and nanotube structure fabrication to gas and chemical separations, electronic nanocomponents, and nano-energy products. To achieve more precise control of nanostructure fabrication on AAO membrane templates, we have applied atomic layer deposition (ALD) to produce high-K HfO@sub 2@ nanotubes in AAO templates, which serve as scaffolds for nanofabrication of nanotubes. We then release the HfO@sub 2@ nanotubes by dissolution of the alumina template. TEM shows the HfO@sub 2@ nanotubes to have wall thicknesses 3-5 nm and lengths 2.5-3.5 µm. ALD employs alternating reactant exposures and essentially self-limiting adsorption/reaction of organometallic precursors and oxidants to achieve atomic-scale control of deposited films. With self-assembly and self-limiting reaction dominating the template and nanotube fabrication steps, this combination appears attractive to meet the future demands of nanotube manufacturing.@footnote 1@ @FootnoteText@ @footnote 1@Sponsored in part by the Laboratory for Physical Sciences.

NM-TuP4 Fabrication of Titanium Oxide Nanotubes by Anodization*, **K. Ishibashi**, H. Sato, R. Yamaguchi, Y. Kimura, M. Niwano,* Tohoku University, Japan

Dye-sensitized solar cells (DSSCs) have been an attractive device with their simple structure and cost effectiveness. DSSCs were generally constructed with a TiO@sub2n@ electrode, electrolyte containing iodine and a Pt counter electrode. It is important to adsorb a lot of dyes on the TiO@sub2n@ electrode for fabricating high-effective DSSCs and the TiO@sub2@ electrode with large surface area is required. Using the TiO@sub2@ electrode with porous structures is a solution to it. On the other hand, several groups have reported that diffusion coefficients of electron in mesoporous TiO@sub2n@ are much lower than those in the bulk crystal because of electron scattering due to grain boundaries between TiO@sub2@ nanoparticles, oxygen defects, and amorphous layers. Therefore, TiO@sub2@ nanotubes or nanowires are a promising class of materials to improve energy conversion efficiency of DSSCs because they have a large surface area comparable to mesoporous TiO@sub2@ and few grain boundaries. In fact, it was reported that the use of TiO@sub2@ nanowires improves the energy conversion efficiency. However, production of those TiO@sub2@ nanotubes requires high temperature and a reaction time of several dozens hours. In this study, we demonstrate that TiO@sub2@ nanotubes can be synthesized at room temperature for several minuets using an electrochemical process. We prepared a sheet of 99.5% Ti and anodized it at a potential of 40 V in a mixture of perchloric acid and ethanol using Pt as a counter electrode. The length and the diameter of the TiO@sub2@ nanotubes we obtained were more than 10 µmm and about 70 nm, respectively.

NM-TuP5 Fabrication of Nanometer-scale Holes Based on a Plasma Ashing and Selective Liquid Phase Deposition*, **K.S Kim**, Y. Roh,* Sungkyunkwan University, Republic of Korea

The fabrication of nanometer-scale structures such as nano-dot, nano-wires, nano-pillars, nano-holes, etc. on single crystal semiconductor surface has recently attracted growing attention in the field of semiconductor device technologies. Such nano-fabrication is important not only for further advancement of conventional ULSI technologies but also for development of new-type devices such as quantum-effect ones. Particularly, nano-hole fabrication has been demonstrated by using advanced techniques such as nano-lithography using STM, atomic hydrogen etching and aluminum etching mask. However, these techniques have time consumption problem and require high production cost. Moreover, conventional deposition processes such as E-beam evaporation and sputtering have a thermal stress problem because of high process temperature. In this work, we have used plasma down stream ashing technique and selective liquid phase deposition. Using plasma down stream ashing and selective liquid phase deposition, we could fabricate the nanometer-scale pillar structures and nano-hole, respectively. Selective liquid phase deposition method is possible to deposit silicon dioxide under 50@degree@C without damaging

the photoresist. We demonstrated less than 100 nm nano-holes and successfully reproduced in our experiment. These results may open the possibilities to fabricate the unique tools for the nanometer-scale diode, MOSFET, vertical-type field effect transistors and highly aligned emitters.

NM-TuP6 Fabrication of Binary Nano/Micro Sized Domain Composed of Alkyl and Fluoroalkylsilane Self-Assembled Monolayer*, **S.H. Lee**, T. Ishizaki, N. Saito, O. Takai,* Nagoya University, Japan

Self-assembled monolayers (SAMs) have attracted attention from a viewpoint of the functional surface modification such as physical, chemical and biological surface. In order to apply these SAMs to the practical application, it is vital to use lithography processes. Recently, several advances have been made in lithography methods for modifying functional groups on monolayer surfaces. Also, we have successfully fabricated functional surface with two different types of functional groups by modifying locally on an organosilane SAM by using vacuum ultraviolet (VUV) irradiation and scanning probe chemical conversion. However, the method was useful for specific surface functional group, the versatility was extremely low. In order to overcome the issue, it is required to establish more simple method. Here, we report a simple method to fabricate binary nano/micro sized domain composed of alkyl and fluoroalkylsilane SAM without lithography process. An octadecyltrichlorosilanes (OTS) and heptadecafluoro-1,1,2,2-tetra-hydrodecyltrichlorosilane (FOETS) were used as precursor molecules. Toluene (anhydrous, 99.8%) were used as the solvent. First, OTS-SAM domains structures were prepared on the silicon (111) substrates through a liquid phase method. In order to control the sizes of OTS-SAM domain structures, the deposition conditions were changed. The humidity and temperature conditions were changed from 5% to 50% and 5°C to 40 °C, respectively. After OTS-SAM preparation, the FOETS-SAM was prepared on the silicon oxide uncovered with OTS-SAM. The humidity and temperature conditions for FOETS-SAM were 50% and 20°, respectively. We found that the preparation conditions allowed us to control of the OTS-SAM domain size. And we confirmed that nano/micro sized domain composed of alkyl and fluoroalkylsilane SAM was formed on the silicon oxide substrate by using atomic force microscope (AFM) and Kelvin probe force microscope (KPFM).

NM-TuP7 Molecular-Beam Epitaxy of InN Quantum Dots on Nitrided Sapphire*, **Y.E. Romanyuk**,* University of California at Berkeley and Lawrence Berkeley National Laboratory, US*; R.-G. Dengel, S.R. Leone,* University of California at Berkeley and Lawrence Berkeley National Laboratory

Recent investigations suggest that the bandgap of InN is approximately 0.7 eV, rather than the previously accepted value of 1.8-2.0 eV, making InN a highly desirable component for potential band-gap-tunable optical applications. In this work, InN quantum dots (QDs) are grown by rf-plasma-assisted molecular beam epitaxy on thin nitride layers produced directly on sapphire substrates. Previous studies obtained InN QD growth on substrates or thick buffer layers of Si, GaN, and AlN. The nanostructures in this work are produced directly on nitrided c-cut sapphire substrates. The nitridation of sapphire for a period of one hour at 950°C results in the formation of a rough AlN surface layer, which acts as a very thin buffer and facilitates the nucleation of the InN QDs. A series of InN QD samples are grown at various substrate temperatures from 420°C to 500°C under slightly nitrogen-rich conditions. Ex situ AFM images reveal that the average InN growth rate is limited by the In flux on the surface, and the QD morphology depends strongly on the substrate temperature. Well-confined InN nanoislands with the greatest height / width ratio of 0.2 can be grown at 460°C. Lower substrate temperatures result in a reduced aspect ratio due to lower diffusion rate of the In adatoms, whereas the thermal decomposition of InN complicates the growth at T>500°C. The densities of separated QDs vary between 1.5x10@super 10@ cm@super -2@ and 3.0x10@super 10@ cm@super -2@ depending on the growth time. Typical island heights are 3-10 nm, and therefore, carrier confinement is expected in vertical direction in a part of the fabricated dots. For the investigation of optical properties, work is in progress to encapsulate the QDs to avoid the formation of surface states that suppress radiative recombination. The demonstration of the intrinsic photoluminescence of InN QDs would give a possibility to use InN nanostructures in photonic devices.

NM-TuP8 AFM Tip-Characterizer Fabricated from Compound Semiconductor Superlattices*, **H. Itoh**, T. Fujimoto, S. Ichimura,* RIIF-AIST, Japan

A tip characterizer for atomic force microscope (AFM) was developed to analyze the accurate tip-shape and limitation of the resolution of each tip on the cantilever. Recently, many kinds of sharp tips are supplied from many vendors, and tip radius of the conventional AFM tip is typically 10nm. It is necessary to fabricate nano-structures, which are smaller than tip radius, to carry out in situ analysis of the probe apex. Additionally, the nano-structures as a tip-characterizer must be fabricated accurately and variation of the shapes should be lower than tip radius by several times to prove accuracy of measured shape of AFM probe. A cross section of superlattices, which was made from compound semiconductor, was used to achieve accurate shape of the nano-structures. Superlattices of InGaP and GaAs were grown on the GaAs substrate. InGaP layers were controlled to be accurate thickness, which was the width of the line to characterize the tip. GaAs area was etched selectively from the cross section of the wafer. It is possible to fabricate fine lines which are thinner than 10nm. Line widths were measured by transmission electron microscopy and accuracy was measured from lattice images. Error of the twenty-nanometer-lines was less than 10% of the width and radius of the edge was lower than 3nm. Cross section of probe-tip can be measured easily from the line profile of AFM image, and it is easy to estimate deterioration of tip-shape after taking images. It is possible to estimate the deterioration of commercial tip radius in the range of 5 to 30nm, and shape of the cross section of probe-tip can be measured in the accuracy of 3nm in the range of apex radius from 10 to 30nm. This work was partially supported by Japan Science and Technology Agency.

Nano-Manufacturing Topical Conference
Room 2018 - Session NM+NS+NNT-WeM

International Developments in Nanoimprint Lithography
Moderator: S. Matsui, University of Hyogo, CREST JST, Japan

8:00am **NM+NS+NNT-WeM1 Nanoimprint: Diversity in Materials, Processes and Application***, **H. Schift,*** Paul Scherrer Institute (PSI), Switzerland*; J. Ahopelto,* VTT Centre for Microelectronics, Finland*; A. Kristensen,* Technical University of Denmark*; C.M. Sotomayor Torres,* Tyndall National Institute, Ireland*; M. Tormen,* INFM-TASC, Italy **INVITED**

Replication by molding offers more than high resolution and mass fabrication aspects. By creating a 3D structure by mechanical displacement of material, the patterning of a range of specific functional materials becomes possible, without loosing their chemical properties. Furthermore this ability can be used to fabricate complex structures, e.g. by building up devices with imbedded channels. Many of these aspects play a role within the European Integrated Project NaPa.@footnote 1@ Its aim is not only the further development of emerging nanopatterning methods, including processes, tools, and materials, but also a range of applications, which go far beyond the development of a next generation nanolithography for chip manufacturing. Nanoimprint lithography of thermoplastic materials remains the technology with the imminent highest potential, because of its ability to integrate different materials and functionalities, and by its compatibility with other mass fabrication processes such as injection molding and roll embossing.@footnote 2@ Typical applications can be seen in the topological and chemical patterning of templates for displays and cell growth, the integration of fluidic and optical functionalities in a lab-on-a-chip, and patterning of special polymers intended for polymer electronics and optics. This is achieved by using new thermoplastic polymers, or by incorporating dyes and nanoparticles with specific functionalities, e.g. for optical devices. Throughput is enhanced by using heatable stamps, and flexibility by a step and stamp approach. This toolbox, ranging from mold fabrication to analytical tools, is a prerequisite to establish nanoimprint as a future core technology in the heart of Europe. @FootnoteText@ @footnote 1@ EC-funded project NaPa (Emerging Nanopatterning Methods). URL: http://www.phantomsnet.net/NAPA/index.php.@footnote 2@ H. Schift and A. Kristensen. In Handbook of Nanotechnology, Bhushan B. ed., 2nd edition, publisher Springer Verlag, Germany (2006).

8:40am **NM+NS+NNT-WeM3 Nanoimprint Lithography: Technology, Applications and Commercialization***, **S.Y. Chou,*** Princeton University **INVITED**

Since the proposal of nanoimprint lithography (NIL) as a low-cost high-throughput sub-10-nm manufacturing method in 1995,@footnote 1@ the field has been growing rapidly in research, applications and commercialization in the past 11 years. The talk will present author's bird-eye view in these areas, as well as future potential and new directions. Particularly, the talk will address (a) NIL progresses in minimum feature size (6 nm half-pitch), printing areas (over 50 in-sq), alignment (sub-20 nm), pattern shapes (2D and 3D), materials and masks, (b) NIL applications in different disciplines, such as nanoscale electronics (nano-MOSFETs and SRAMs), photonics, displays, data storage (optical and magnetic), biotech, chemical synthesis and advanced materials, and (c) commercialization of NIL technologies. The talk will conclude that despite the success of NIL in its first 10 years, it is still just a beginning and we haven't seen anything yet! NIL will serve as an enabling ubiquitous manufacturing engine to propel future research in nanotechnology, future manufacturing of micro/nanostructures, and hence future discoveries and commercialization in nanotechnology. @FootnoteText@@footnote 1@S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett, 67 (21), 3114 (1995)

9:20am **NM+NS+NNT-WeM5 Nanoimprint and Nanopatterning in Japan***, **H. Hiroshima,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

In a while after Prof. Chou had revealed the potential of nanoimprint a decade ago, a few groups in Japan started studying on nanoimprint technology. But now many groups use nanoimprint and notice the ability. People can feel the nanoimprint fever in Japan as indicated by the nanoimprint and nanoprint technology conference (NNT) 2005 held in Nara. In Japan, many nanotechnology projects run under support by the government; however, nanopatterning using nanoimprint is strangely excluded. One of resent topics on research situation is that Nanoimprint Process Solutions (NiPS) Consortium was established in April 2005. The group of Dr. Maeda in national research institute of advanced industrial science and technology (AIST) plays a central role in the consortium and provides technical supports to the NiPS members. Another is that a nanoimprint technology study group, whose chair person is Dr. Komuro in AIST, was born in April 2006 as a valuable by-product of NNT2005. There are three powerful groups in the study group; one is the group of Prof. Matsui at university of Hyogo that shifted its focus from thermal nanoimprint to room-temperature nanoimprint; another is the group of Prof. Hirai at Osaka prefecture university that fabricates fluid devices using an improved reversal nanoimprint; and the other is our AIST group "nanoimprint manufacturing technology group" that covers high-temperature nanoimprint onto glass materials, roller nanoimprint and also UV-nanoimprint. In my presentation, I should like to introduce outlines on the activities of these groups and to show the diversity of research and development of the nanoimprint technology in Japan.

10:40am **NM+NS+NNT-WeM9 Metrology for Nanoimprint Technologies: Needs and Prospects***, **C.L. Soles**, H.W. Ro, Y. Ding, H.J. Lee, R.L. Jones, A. Karim,* National Institute of Standards & Technology **INVITED**

Nanoimprint is a next generation lithography candidate with enormous potential not just for the semiconductor industry, but also a wide range of emerging technologies. This is because nanoimprint combines a fine patterning resolution, comparable to e-beam lithography, with a high throughput and low cost tool. However, there are several aspects of the nanoimprint process that significantly differ from state of the art optical lithography currently used for high volume nanofabrication and these differences introduce new metrology challenges unique to the nanoimprint process. Equally as important, the potential increase in the pattering resolution of nanoimprint over current patterning technologies threatens to exacerbate many of the existing metrology challenges presently facing optical lithography. In this presentation we review the unique and the non-unique metrology challenges facing nanoimprint lithography. These metrology needs come from interactions with both industrial and academic practitioners of nanoimprint through international workshops and panel discussions. We will present an overview of the progress being made to meet these metrology needs. Specific examples from our own research in developing novel X-ray scattering and reflectivity measurements to facilitate the nanoimprint processes will be highlighted.

11:20am **NM+NS+NNT-WeM11 Large Area Ultraviolet Nanoimprint Lithography Applicable to Flat Panel Display***, **E.-S. Lee,*** Korea Institute of Machinery & Materials, Korea **INVITED**

Nanoimprint lithography (NIL) is known as an emerging lithography with a resolution of less than 10 nm, having a high throughput and low cost compared to the conventional photolithography. In this talk, we present very large area (> 20 inch) Ultraviolet Nanoimprint Lithography (UV-NIL) process as a breakthrough strategy for flat panel display industry. As thin film transistor liquid crystal display (TFT-LCD) manufacturers in Korea ramp up output of TV panels from advanced factories in anticipation of strong demand, the excess supply in the market is leading to steep price declines especially for TV use panels. Succeeding generation plants use larger glass substrates, thereby boosting output and helping manufacturer's lower production costs. Falling LCD panel prices may be tough for LCD manufacturers to swallow. There is something in creating profit besides investment in upgrading generation. That can only be possible by conversing process facilities to use advanced process technology. This talk will summarize activities for the development of large area UV-NIL at KIMM to date and in detail. Very large area UV-NIL process and its apparatus for the TFT-LCD pattern will be presented.

Nanometer-scale Science and Technology
Room 2016 - Session NS+NM-WeA

Nanolithography and Patterning

Moderator: S.W. Pang, The University of Michigan

2:00pm **NS+NM-WeA1 Direct Deposition of Ordered Polymer Nanostructures in UHV via thermal Dip-Pen Nanolithography***, **P.E. Sheehan**, M. Yang, A.R. Laracuent,* Naval Research Laboratory*; B.A. Nelson, W.P. King,* Georgia Tech*; L.J. Whitman,* Naval Research Laboratory

In thermal Dip Pen Nanolithography (tDPN) a heated atomic force microscope cantilever controls the deposition of a solid ink, acting like a nanoscale soldering iron. tDPN has several advantages over conventional DPN. Control over writing is greatly improved deposition may be turned on or off and the deposition rate easily changed without breaking contact with the surface. In addition, imaging with a cool tip does not appear to contaminate the surface, thereby allowing in situ confirmation of the deposited pattern. Finally, tDPN can deposit a range of materials that are immobile at room temperature from semiconductors to insulators to metals. Thermal DPN is particularly suited to the deposition of polymers. To date, mylar, MEH-PPV, and poly(3-dodecylthiophene) [PDDT] have all been successfully deposited. PDDT is of particular interest as a conducting polymer with great potential for use in organic electronic devices. Using tDPN, well-ordered PDDT nanostructures have been deposited on silicon oxide and gold surfaces with layer-by-layer thickness control. By adjusting the tip heating power and the writing speed, we can vary the polymer thickness from a single monolayer (~2.6 nm) to tens of monolayers with lateral dimensions below 100 nm. Moreover, the morphology of the nanostructure suggests that the polymer strands are aligned along the path of the AFM tip. Unlike conventional DPN inks, the low vapor pressure of solvent-free polymers allows deposition in Ultra High Vacuum (UHV). We have deposited in UHV single monolayers of highly-ordered PDDT nanostructures on clean Si(001)-(2x1). The electronic and crystallographic properties of these structures will be discussed.

2:20pm **NS+NM-WeA2 Multiplexed Electroless Nanopatterning of Metallic Arrays Via Scanning Probe Lithography***, **S.A. Backer**,* University of California, Berkeley*; M. Rolandi,* University of California, Lawrence Berkeley National Laboratory*; D. Okawa,* University of California, Berkeley*; J.M.J. Fréchet,* University of California, Lawrence Berkeley National Laboratory

Direct surface patterning of metallic species is essential for the fabrication of ever smaller nanostructures, such as electrodes, magnetic data storage devices and specific catalytic sites for localized chemical reactions. Conventional lithographic techniques based on radiation can achieve remarkable resolution and pitch. However, limitations lie in the multiplexing capabilities with the need of a separate alignment and lithography step for each metal deposited. We present a multiplexed lithographic technique based on the localized surface modification of silicon using an atomic force microscope (AFM) in fluid. The sharp tip of the AFM is used to create pinhole defects in the thin oxide present on the silicon surface. Spontaneous electroless deposition of the metal ions dissolved in the fluid occurs at the defect sites creating metallic islands as small at tens of nanometers. We demonstrate the fabrication of high pitch arrays of as many as thousands of islands of Au, Co, Sn and Fe. By consecutively exposing a sample to various metallic salts in solution, nano islands composed of different metals can be deposited in a single patterning session without needing to realign the sample or change the probe. This allows for the fabrication of multiplexed intergiditated arrays of nanostructures that could be used for orthogonal catalysis.

3:00pm **NS+NM-WeA4 High-Density Gigabit Patterning of Sub-100nm Circular Hole/Dot Arrays by Nanoimprint Lithography***, **W. Hu**,* Stanford University, U.S.A*; R.J. Wilson, L. Xu, S.J. Han, S.X. Wang,* Stanford University

High throughput and cost-effective patterning of sub-100nm periodic features is of great interest for science and engineering. In this work we present results from patterning high-density arrays of circular holes with 100nm diameters at 300nm pitch, or with 50nm diameters at 100nm pitch, throughout an area of 1 square cm. We use 75K molecular weight polymethyl methacrylate (PMMA) resist and thermal nanoimprint lithography. Several issues are addressed which arise during patterning and characterization, such as pattern distortion control during debonding and PMMA damage induced by Au metallization for scanning electron microscopy (SEM). We further demonstrate the fabrication of dense gigabit magnetic nanodot arrays using PMMA and polymethyl glutarimide (PMGI) resist bi-layers and a lift-off process. Metal residuals with different shapes are found to be associated with variable resist processing, metallization, and lift-off conditions and are removed by an ion mill process. Additionally we show that the nanodot diameter can be tuned by using oxygen plasma ashing. Finally, the magnetic properties of nanodot arrays are shown to be readily characterized by alternating gradient magnetometry (AGM).

3:20pm **NS+NM-WeA5 Advances in Nanostructure Fabrication Technology***, G. Willson, **M. Stewart**,* The University of Texas, Austin **INVITED**

The drive to manufacture cheaper and more efficient semiconductor devices has inspired remarkable improvements in imaging materials science and high resolution patterning technology for several decades. Billions of dollars have been spent in efforts to devise methods and materials that enable the printing of ever smaller transistors. Microelectronic devices in full scale production today have minimum features in the range of 70-90nm and fully functional CMOS transistors with 10nm gates have been characterized. The lithographic process that has been used to generate these "nano-structures" is becoming extremely expensive and the process window or process latitude for producing them is shrinking. The cost of the imaging process threatens the economics of the semiconductor manufacturing industry. A single efficient factory equipped to produce the next generation of devices is projected to cost as much as the gross national product of countries the size of Hungary. Imprint lithography, a lower cost, high resolution patterning technology is emerging as a potential adjunct to photolithography. Some view it as a truly disruptive patterning technology. Imprint lithography loosely defines a set of techniques that includes several forms of embossing; stamping and molding that show great promise as low cost methods for producing nanostructures. These techniques take many different forms each of which has it's own special applicability. The technique we call Step and Flash Imprint Lithography (S-FIL) is designed to allow the fabrication of high resolution, high aspect ratio images that can be aligned with precision. The process accurately replicates arbitrary shapes as small as 10nm. The process can be used to define structures with very small widths but unlike photolithography, it can be used to produce very small three dimensional structures via simultaneously controlling variations in depth. A progress report on modern patterning technologies will be presented with emphasis on imprint lithography.

4:00pm **NS+NM-WeA7 Photolithography Beyond the Diffraction Limit***, **G.J. Leggett**,* University of Sheffield, UK

A scanning near-field optical microscope (SNOM) coupled to a UV laser has been used to pattern self-assembled monolayers (SAMs) of photosensitive adsorbates. Using this approach, which we call scanning near-field photolithography (SNP), it is possible to achieve a resolution of 9 nm (nearly 15 times smaller than the conventional diffraction limit) in a SAM of alkanethiols adsorbed on gold. In conjunction with a new etchant, mercaptoethylamine in ethanol, SNP-patterned SAMs have been used as resists to fabricate gold nanostructures as small as 10 nm that have sharp edge definition. Gold nanowires, 60 nm wide, have been fabricated by selective exposure of bilayers of thiol-stabilised gold nanoparticles, followed by rinsing, in a simple two-step process. The principal criterion for achieving high resolution using SNP is the excitation of a specific photochemical reaction in a group distributed with monolayer coverage on a solid surface. This encompasses a broad range of materials. This is illustrated using monolayers of chloromethylphenyl siloxanes adsorbed on silicon dioxide, which may be selectively converted to aldehydes or to carboxylate functionalities to which biological molecules may be attached. DNA nanoarrays have been fabricated that consist of 70 nm DNA spots at 500 nm spacings. These have a density 40 000 times greater than existing DNA chips, while remaining readable by far-field optical methods. Finally we demonstrate the feasibility of carrying out nanophotolithography on aluminium surfaces. Monolayers of aryl azide terminated phosphonic acid adsorbates, which exhibit substantially enhanced ambient stability compared to alkanethiol SAMs, have been formed and selectively functionalised using SNP, in a process 50 - 100 times faster than the alkanethiol patterning process. These illustrations indicate that SNP is a powerful, flexible and straightforward technique for the execution of specific surface chemical transformations.

4:20pm **NS+NM-WeA8 SPM Nanolithography of ZrN Thin Films: Nitrogen-Enhanced Growth and Hollow Oxide Feature Formation*, N. Farkas*,** *E.A. Evans, R.D. Ramsier,* The University of Akron*; J.A. Dagata,* National Institute of Standards and Technology

A systematic study of the scanning probe microscope (SPM) oxidation of sputter-deposited ZrN thin films is presented. Based on data covering an extensive range of parameters such as exposure time, voltage, humidity and nitrogen content of the sputtering plasma, we propose a four-stage oxidation kinetics model for ZrN. We find that the heights of the oxide features are significantly larger when the films are prepared with substantial nitrogen content in the deposition plasma, whereas small nitrogen flow rates yield oxidation rates similar to Zr films. In the intrinsic part of the SPM oxidation, the oxide density increases until the volume of the oxide is about twice that of the consumed ZrN. Further oxide growth is sustainable, and in fact faster yet controlled, as the system crosses over from the space charge limited to a nitrogen-enhanced growth regime. Most striking and different from other material systems is that high-voltage SPM oxidation of ZrN generates micrometer high features that are an order of magnitude higher than the thickness of the films. Selective etching of the oxides and nitrides reveals that as the oxidation reaches the ZrN/silicon interface delamination occurs resulting in hollow oxide feature formation through stress-induced plastic flow. Interpretations of the underlying processes and film properties responsible for the unique behavior of ZrN in all regimes are provided along with an explanation for the observed non-linear voltage dependence.

4:40pm **NS+NM-WeA9 High Resolution Electron Beam Induced Etching of Extreme Ultraviolet (EUV) Lithography Mask Films*, M.G. Lassiter*,** *P.D. Rack,* University of Tennessee*; T. Liang,* Intel Corp.

The application of EUV wavelengths for lithography is emerging as a viable technology to extend the production of small feature sizes for integrated circuits and nanotechnology. In order to make EUV lithography commercially viable, production of the mask requires the repair of defects found during the mask inspection. Traditionally, the highest resolution mask repair technology involves using a focused ion beam (FIB) of Gallium ions to physically sputter away material for etching and to induce dissociation of a precursor gas to deposit material for repairs. Some of the Gallium ions are implanted into the surface of the mask and leave undesirable effects such as reduced transmission of clear area repairs in photomasks and reduced reflection of the clear area of EUV masks. The use of electron beam induced processes for the repair of EUV masks has recently been developed as an alternative to FIB repair of masks. The electron beam induces the dissociation of a precursor gas to cause a reaction at the surface of the mask. This reaction either deposits material or causes the etching of the mask material, depending upon the type of precursor used and the substrate material. This work focuses on the latter case of electron beam induced etching (EBIE). Electron beam provides superior spatial resolution than that of the FIB, so the EBIE process can be more effective in small mask feature repairs. Also, the electron beam will not damage the mask materials because of the relatively small mass of the electron and relatively low energy used in the electron beam. This work characterizes the process of high resolution EBIE of Tantalum Nitride based EUV mask films. The effects of electron beam parameters such as accelerating voltage, beam current, and the scanning parameters are investigated. Furthermore, the use of various precursor gases is examined, and the effects on spatial resolution, etching rate, and selectivity against other materials are determined.

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— F —
Farkas, N.: NS+NM-WeA8, **10**
Fenton, J.L.: AS+BI+NS+NM-MoM4, **1**
Fréchet, J.M.J.: NS+NM-WeA2, 9
Fujimoto, T.: NM-TuP8, 7
Fujishima, A.: NM-TuP2, 6
Fulghum, J.E.: AS+BI+NS+NM-MoM4, 1
— G —
Gargini, P.: NM+MS+IPF-MoA1, **4**
Garner, C.M.: NM+MS+IPF-MoA1, 4
Gilliland, D.: AS+BI+NS+NM-MoM10, 1
— H —
Han, S.J.: NS+NM-WeA4, 9
Henn-Lecordier, L.: NM-TuP3, 6
Hiroshima, H.: NM+NS+NNT-WeM5, **8**
Hu, W.: NS+NM-WeA4, **9**
— I —
Ichimura, S.: NM-TuP8, 7
Ishibashi, K.: NM-TuP4, **6**
Ishizaki, T.: NM-TuP6, 7
Itoh, H.: NM-TuP8, **7**
Ivanisevic, A.: AS+BI+NS+NM-MoM1, **1**
— J —
Johnson, A.: NM+IPF-TuM11, **5**
Jones, R.L.: NM+NS+NNT-WeM9, 8
— K —
Karim, A.: NM+NS+NNT-WeM9, 8
Kim, K.S: NM-TuP5, **6**
Kimura, Y.: NM-TuP4, 6
King, W.P.: NS+NM-WeA1, 9
Kitadani, T.: NM-TuP1, 6
Kondratenko, Y.: AS+BI+NS+NM-MoM11, **2**
Krajewski, J.J.: NM+IPF-TuM5, 5
Kristensen, A.: NM+NS+NNT-WeM1, 8
Kubota, Y.: NM-TuP2, 6
— L —
Laracuent, A.R.: NS+NM-WeA1, 9
Lassiter, M.G.: NS+NM-WeA9, **10**
Lee, E.-S.: NM+NS+NNT-WeM11, **8**
Lee, H.J.: NM+NS+NNT-WeM9, 8
Lee, J.R.I.: AS+BI+NS+NM-MoM3, **1**
Lee, S.B.: NM-TuP3, 6
Lee, S.H.: NM-TuP6, **7**
Leggett, G.J.: NS+NM-WeA7, **9**
Leone, S.R.: NM-TuP7, 7
Liang, T.: NS+NM-WeA9, 10
— M —
Mayberry, M.: NM+MS+IPF-MoA5, **4**
Maynard, A.D.: NM+IPF-TuM3, **5**
Mekaru, H.: NM-TuP1, **6**
— N —
Nakashima, T.: NM-TuP2, 6
Nealey, P.F.: AS+BI+NS+NM-MoM8, **1**
Nelson, B.A.: NS+NM-WeA1, 9
Nezuka, T.: NM-TuP2, 6
Nilsson, J.: AS+BI+NS+NM-MoM3, 1
Niwano, M.: NM-TuP4, 6
— O —
Okawa, D.: NS+NM-WeA2, 9
Ostraat, M.L.: NM+IPF-TuM5, **5**
— P —
Perez, I.: NM-TuP3, **6**
Prabakar, K.: NM-TuP2, 6
— R —
Rack, P.D.: NS+NM-WeA9, 10
Ramsier, R.D.: NS+NM-WeA8, 10
Ro, H.W.: NM+NS+NNT-WeM9, 8
Robertson, E.: NM-TuP3, 6
Roh, Y.: NM-TuP5, 6
Rolandi, M.: NS+NM-WeA2, 9
Romanyuk, Y.E.: NM-TuP7, **7**
Rossi, F.: AS+BI+NS+NM-MoM10, **1**
Rubloff, G.W.: NM-TuP3, 6
— S —
Saito, N.: NM-TuP6, 7
Sasaki, T.: AS+BI+NS+NM-MoM10, 1
Sato, H.: NM-TuP4, 6
Schift, H.: NM+NS+NNT-WeM1, **8**
Seebauer, E.G.: AS+BI+NS+NM-MoM11, 2
Sheehan, P.E.: NS+NM-WeA1, **9**
Siegel, R.W.: NM+IPF-MoM5, **2**
Soles, C.L.: NM+NS+NNT-WeM9, **8**
Son, S.J.: NM-TuP3, 6
Sotomayor Torres, C.M.: NM+NS+NNT-WeM1, 8
Stewart, M.: NS+NM-WeA5, **9**
Swain, K.A.: NM+IPF-TuM5, 5
— T —
Takahashi, K.: NM-TuP2, **6**
Takahashi, M.: NM-TuP1, 6
Takahashi, T.: NM-TuP2, 6
Takai, O.: NM-TuP6, 7
Terminello, L.J.: AS+BI+NS+NM-MoM3, 1
Textor, M.: AS+BI+NS+NM-MoM5, **1**
Tormen, M.: NM+NS+NNT-WeM1, 8
— V —
Valsesia, A.: AS+BI+NS+NM-MoM10, 1
van Buuren, T.: AS+BI+NS+NM-MoM3, 1
Verbrugge, M.W.: NM+IPF-MoM8, **2**
Vogel, E.: NM+MS+IPF-MoA7, **4**
— W —
Wang, S.X.: NS+NM-WeA4, 9
Welser, J.: NM+MS+IPF-MoA3, **4**
Wheeler, D.: AS+BI+NS+NM-MoM4, 1
Whitman, L.J.: NS+NM-WeA1, 9
Willey, T.M.: AS+BI+NS+NM-MoM3, 1
Willson, G.: NS+NM-WeA5, 9
Wilson, R.J.: NS+NM-WeA4, 9
Wolfe, J.: NM+IPF-MoM1, **2**
— X —
Xu, L.: NS+NM-WeA4, 9
— Y —
Yamaguchi, R.: NM-TuP4, 6
Yamashita, M.: NM-TuP1, 6
Yang, M.: NS+NM-WeA1, 9
Yi, H.: NM-TuP3, 6
— Z —
Zhang, W.-X.: NM+IPF-TuM9, **5**