

Monday Morning, October 19, 2015

2D Materials Focus Topic

Room: 212C - Session 2D+EM+NS+PS+SP+SS+TF-MoM

2D Materials: Growth and Fabrication

Moderator: Cory Dean, Columbia University, Peide Ye, Purdue University

8:20am **2D+EM+NS+PS+SP+SS+TF-MoM1 Growth and FTIR Characterization of 2D Hexagonal Boron Nitride on Metal Substrates.** *Boris Feigelson, V.M. Bermudez, J.K. Hite, Z.R. Robinson, V.D. Wheeler, K. Sridhara, S.C. Hernandez*, US Naval Research Laboratory

Atomically thin two dimensional hexagonal boron nitride (2D h-BN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance. The development of 2D h-BN growth is still in the early stages and largely depends on rapid and accurate characterization of the grown monolayer or few layers h-BN films.

In this work, the IR-active out-of-plane vibrational mode of 2D h-BN films grown in vertical reactor by atmospheric-pressure CVD on metal substrates (mainly Cu but also Ni) is exploited to identify 2D h-BN directly on substrates and studied both computationally and experimentally.

Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) data have been used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the $A_{2u}(\text{LO})$ vibrational mode were, for the first time, found for thin 2D h-BN films in contact with Cu and Ni [1]. To unveil the nature of the discovered sub-bands, ab-initio calculations were performed and verified using 2D h-BN films grown on various Cu substrates with varying coverage and with individual crystallites of different shapes and size up to 4 nm. It was shown that the lower-energy $A_{2u}(\text{LO})1$ sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy $A_{2u}(\text{LO})2$ sub-band around 824 cm^{-1} is related to decoupled (essentially free standing) 2D h-BN. These findings demonstrate not only a new and facile method for immediate 2D h-BN identification and characterization, but also a method that provides a simple means to characterize the degree of coupling between 2D h-BN and the substrate. This approach also provides an opportunity to determine which growth conditions lead to the absorption of foreign species on the substrate prior to the h-BN deposition and which conditions can prevent the formation of the interfacial layer between h-BN and the substrate. Such interfacial layers, like oxidized Cu, were shown to result in easily-recognizable shifts in the $A_{2u}(\text{LO})$ peak. The degree to which the interaction of the h-BN layer with the substrate is uniform and homogenous can also be assessed easily by examining the width and fine structure of the $A_{2u}(\text{LO})$ band. The developed approach can also be used to study growth and formation of h-BN/graphene and other 2D heterostructures.

References

1. B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, *Nanoscale* 7, 3694 (2015)

8:40am **2D+EM+NS+PS+SP+SS+TF-MoM2 Effect of Surface Termination on the Growth of Graphene on Cu Single Crystal Substrates.** *Tyler Mowll, E.W. Ong*, University at Albany-SUNY, *P. Tyagi*, GLOBALFOUNDRIES, *Z.R. Robinson*, College at Brockport-SUNY, *C.A. Ventrice, Jr.*, SUNY Polytechnic Institute

The most common technique for synthesizing single-layer graphene films with large lateral dimensions is chemical vapor deposition (CVD) on Cu foil substrates. The primary reasons for choosing Cu substrates are the extremely low solubility of carbon in Cu, which allows a self-limited growth of graphene, and the relatively low cost of the Cu foil substrates. However, the transport properties of the CVD grown graphene films are typically a couple of orders of magnitude lower than for graphene flakes mechanically exfoliated from graphite. One of the reasons for the reduction in transport properties is the presence of crystalline defects in the CVD grown films. These structural defects arise in part from the multidomain structure of the Cu films. In order to achieve a better understanding of the influence of the surface termination of the Cu substrate on the crystallization of graphene during the CVD growth process, a systematic study of graphene growth on Cu(100), Cu(110), and Cu(111) crystals has been performed. The growth process is performed in an ultra-high vacuum (UHV) chamber that has been modified to perform CVD growth at pressures as high as 100 mTorr. The precursor gas used is ethylene. This

growth procedure allows for the preparation of the clean surfaces in UHV, growth under typical CVD conditions, and characterization of the surface structure in UHV, without exposing the sample to atmospheric contaminants. Our results indicate that the Cu(111) surface has the lowest catalytic activity of the three surfaces for the decomposition of ethylene. In fact, the decomposition rate is so low that graphene growth is suppressed because of the sublimation of Cu at the elevated temperatures used to grow the graphene. By using an Ar overpressure, it was found that graphene could be grown on that surface. The surface symmetry of the Cu substrate has a strong influence on the rotational alignment of the graphene grains as they nucleate on each surface. For Cu(111), single-domain graphene growth can be achieved for ethylene pressures of 5 mTorr or less. For both Cu(100) and Cu(110), a minimum of two graphene domains is always observed.

9:00am **2D+EM+NS+PS+SP+SS+TF-MoM3 Thermally Annealed and Electropolished Cu Substrates for CVD Growth of 2D Materials: Graphene, h-BN and MoS₂.** *Karthik Sridhara*, Texas A&M University, *B.N. Feigelson, J.K. Hite*, US Naval Research Laboratory, *A. Nath*, George Mason University, *M. Fuhrer*, Monash University, Australia, *D.K. Gaskill*, US Naval Research Laboratory, *H. Castaneda, L.O. Nyakiti*, Texas A&M University

The growth of two dimensional (2D) materials such as graphene, hexagonal boron nitride (h-BN) and molybdenum disulphide (MoS₂) have been demonstrated by chemical vapor deposition (CVD) on polycrystalline catalytic copper substrates. These Cu foil substrates (25 μm thick) are produced by metallurgical rolling leading to the formation of irregular ridges on the foil surface along with a film of native oxide on the surface. These processing artifacts are a limiting factor for controlled and reproducible large area (several cm^2) growth of 2D materials. Greater control of growth can be achieved by controlling the density of nucleation sites and improving the catalytic activity of Cu by removing the Cu native oxide on the surface. Previous attempts to pre-treat the Cu substrate by using wet chemistry or thermal annealing to control growth has been weakly addressed.

In this work, electropolishing combined with prior thermal annealing at 1030°C for 5 hrs under H₂ is used to control the degree of roughness of cold rolled polycrystalline Cu foils, and subsequently, to explore the influence of electropolishing on the growth of 2D materials: graphene, h-BN and MoS₂. Electropolishing dissolves a thin surface layer of Cu, which contains surface defects and contaminants. This helps in decreasing the density of spontaneous nucleation sites by producing a morphologically uniform and contaminant-free surface. Secondary effects, etch pits which are ascribed to O₂ bubbling at random nucleation sites on Cu surface, are mitigated by using additives, such as acetic acid and ethylene glycol, in the H₃PO₄ electrolyte. Thermal annealing and electropolishing results in this work reveal that a roughness of $\sim 1.2\text{ nm}$ (R_a) can be achieved as measured by Atomic Force Microscope (AFM) along with a greatly planarized Cu foil. AFM will also be used to establish the Cu substrate morphology and its relationship to the growth of 2D materials. Fourier Transform Infrared, and Raman spectroscopy will be used to confirm the existence of the 2D material. Preliminary growth studies of h-BN on these high quality Cu substrates demonstrate improved growth, as assessed by the metrics of size and count of h-BN crystals from Scanning Electron Microscopy (SEM) micrographs [1]. This work will demonstrate that thermal annealing followed by electropolishing leads to optimization of Cu foil surface resulting in the larger crystal size and a reduction in nucleation sites that induce 2D material crystal growth [1].

[1] K. Sridhara. "Growth of hexagonal boron nitride on electrochemically prepared polycrystalline Cu substrates." M.S. Thesis, University of Maryland, College Park, MD, 2014.

9:20am **2D+EM+NS+PS+SP+SS+TF-MoM4 In Situ Optical Diagnostics During Molybdenum Disulfide Chemical Vapor Deposition.** *Berc Kalanyan, J.E. Maslar, W.A. Kimes, B.A. Sperling*, National Institute of Standards and Technology (NIST), *R. Tieckelmann, T. Orzali*, SEMATECH, *R. Beams, S.J. Stranick, A.V. Davydov*, National Institute of Standards and Technology (NIST)

Two dimensional (2D), layered transition-metal dichalcogenides (TMDs), e.g., MoS₂, are of increasing interest for next-generation nanoelectronic and optoelectronic devices. These materials have thickness dependent optical and electrical properties that make them suitable for a variety of applications including integrated circuits. For many applications, high volume manufacturing (HVM) of devices based on TMDs will require deposition techniques that are capable of reproducibly growing wafer-scale, 2D TMD films with monolayer control. To date, such a capability has not been widely demonstrated with typical TMD deposition processes.

This work aims to identify promising chemistries for HVM TMD chemical vapor deposition (CVD) processes. We focus on MoS₂ CVD using a variety of precursors (including organometallics, elemental sulfur, and organosulfur compounds) in a research grade single-wafer deposition system equipped with *in situ* optical diagnostics. The precursor flux is measured using optical mass flow meters installed on the delivery lines while deposition chemistry is characterized in the reactor volume above the deposition surface using *in situ* Fourier transform infrared (FR-IR) spectroscopy. As-deposited and annealed films are characterized with *ex situ* techniques, including Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy.

Stoichiometric MoS₂ films have been prepared from (η^5 -ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum and elemental sulfur. As-grown films are smooth and continuous with major MoS₂ Raman modes present. Film thickness scales approximately with Mo precursor exposure time and few-layer films can be produced using pulsed injection mode. Furthermore, optical *in situ* diagnostics allow us to relate metal precursor flux to film crystallinity and facilitate the study of precursor decomposition in the thermal boundary layer.

9:40am **2D+EM+NS+PS+SP+SS+TF-MoM5 Controlled Interfaces in 2D Materials**, *Arend van der Zande*, University of Illinois at Urbana Champaign **INVITED**

Interfaces are ubiquitous in material science and technologies. For example, grain boundaries often dominate the mechanical and electrical properties in crystalline materials, while interfaces between dissimilar materials form the fundamental building blocks to diverse technologies, such as building electrical contacts in transistors and PN diodes in solar cells. Interfaces become even more important in 2D materials such as graphene and transition metal dichalcogenides, where the lack of dangling bonds enables material stability down to a single monolayer. In this entirely surface-dominated limit, the usual rules governing 3D interface devices, such as depletion regions, break down.

In this talk, we will discuss our work on engineering in- and out-of-plane 2D materials interfaces. We will first examine the structure of atomically-thin membranes and the impact of defects such as grain boundaries on the mechanical, optical, and electronic properties. We fabricate out-of-plane interfaces by stacking 2D materials to form heterostructures, which we utilize to tailor the bandgap in 2D materials and build new optoelectronic devices such as tunable photodiodes. Looking to the future, the rapidly expanding family of 2D materials with a diverse set of electronic properties provide a promising palette for discovering emergent phenomena and a motivation for developing overarching design principles for understanding and controlling interfaces in 2D.

10:40am **2D+EM+NS+PS+SP+SS+TF-MoM8 Obtaining Clean Suspended CVD Graphene: Comparative Examination of Few Transfer and Cleaning Protocols**, *Alexander Yulav*, National Institute of Standards and Technology (NIST), University of Maryland (UMD), *G. Cheng*, *A. Hight Walker*, National Institute of Standards and Technology (NIST), *M. Leite*, University of Maryland (UMD), *A. Kolmakov*, NIST

Clean suspended graphene is used as supporting media in TEM, filtering membranes, and as electron transparent windows in ambient pressure electron spectroscopy and microscopy. CVD grown graphene is the most popular material for these applications due to its large-scale and high yield production. Multiple approaches such as sacrificial layer based methods [1] and direct transfer method on perforated carbon mesh by IPA droplet [2] have been implemented to transport graphene from copper or nickel foil onto a target substrate. However, the cleanness of the suspended graphene remains to be an issue, and controversial results on lateral size of atomically clean graphene domains have been reported [2-5]. We conduct the comparative analysis of the most widely-used CVD graphene transfer and cleaning protocols. In particular, using extreme surface sensitivity of low energy SEM, we compare the standard PMMA based approach with direct graphene transfer method. We also propose alternative graphene transfer protocol which is based on employment of polycyclic aromatic hydrocarbon (PAH) as a sacrificial layer. The advantage of PAH method over others consists in facile sublimation of sacrificial layer upon heating PAH material within moderate temperature range of 100-150 °C. All three methods of graphene transfer were compared under the same conditions followed by similar graphene cleaning procedures by platinum catalysis [4] and activated carbon adsorption [5]. Both SEM and TEM study revealed the superiority of PAH method to achieve cleaner suspended CVD graphene. We envision that novel approach of graphene transfer can be employed under conditions when exposure of the sample to moisture is prohibited such as in battery research.

[1] "Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates", Ji Won Suk *et al.*, ACS Nano, 2011, 5 (9), pp. 6916.

[2] "A direct transfer of layer-area graphene", William Regan *et al.*, Appl. Phys. Lett., 2010, 96, 113102.

[3] "Low-energy electron holographic imaging of gold nanorods supported by ultraclean graphene", Jean-Nicolas Longchamp *et al.*, Ultramicroscopy 145 (2014) 80.

[4] "Ultraclean freestanding graphene by platinum-metal catalysis", Jean-Nicolas Longchamp *et al.*, J. Vac. Sci. Technol. B 31, 020605 (2013).

[5] "Dry-cleaning of graphene", Gerardo Algara-Siller *et al.*, Applied Physics Letters 104, 153115 (2014).

11:00am **2D+EM+NS+PS+SP+SS+TF-MoM9 Low-Energy Electron Microscopy of Transition Metal Dichalcogenides Prepared by Various Methods**, *Sergio de la Barrera*, *S. Satpathy*, *R. Feenstra*, Carnegie Mellon University, *S. Wu*, *X.D. Xu*, University of Washington, *S. Vishwanath*, *X. Liu*, *J. Furdyna*, *D. Jena*, *H. Xing*, University of Notre Dame, *Y.-C. Lin*, *S.M. Eichfeld*, *J.A. Robinson*, Pennsylvania State University, *P. Mende*, Carnegie Mellon University

Recent work on two-dimensional materials has focused on transition metal dichalcogenides (TMDs), owing to their semiconducting behavior. Characterizing as-grown TMDs is crucial in improving the understanding of the effects of growth conditions, and ultimately improving material quality. Low-energy electron microscopy (LEEM) is a powerful tool for this purpose, providing real-space images with ~10 nm spatial resolution as well as selected-area low-energy electron diffraction (μ LEED) of local crystal orientation at length scales down to ~1 μ m. Additionally, by varying the incident electron beam energy, low-energy electron reflectivity (LEER) spectra are extracted.

In this work, comparative LEEM results are presented from three TMD materials: MoS₂ prepared by exfoliation (onto Si), MoSe₂ grown by molecular beam epitaxy (MBE) (on epitaxial graphene), and WSe₂ grown by chemical vapor deposition (CVD) (also on epitaxial graphene). It is found that for TMDs generally, the LEER spectra do not exhibit the oscillatory behavior (in the 0 – 6 eV range) that is seen for both graphene and hexagonal boron nitride (h-BN) for various numbers of monolayers (MLs). This lack of oscillatory behavior is interpreted as being due to the weak coupling of the interlayer states localized in between the MLs, which is itself a result of the relatively large out-of-plane lattice parameter. Nevertheless, additional "band structure" features in the LEER spectra permit clear identification of the TMD materials relative to the substrates. The exfoliated flakes are seen to extend over many 10's of μ m, the MBE-grown MoSe₂ forms a nearly continuous film, and the CVD-grown WSe₂ forms triangular islands several mm in extent. μ LEED studies of the MBE-grown MoSe₂ and CVD-grown WSe₂ reveal preferential orientation with the underlying graphene substrates.

The reduced work functions of the TMD materials relative to the underlying substrate are clearly evident in the onset voltages for the LEER spectra (i.e. the onset shifts in accordance with the local work function of the surface). Most significantly, for the WSe₂ islands, a predominant "tail" is observed in this onset, extending about 5V below the usual onset location. This tail is tentatively interpreted as arising from charging of the islands, perhaps due to polar termination at the edges of the TMD islands. Comparison of the data with simulated LEER spectra will be presented, as a test of this model for edge charge of the islands.

Work supported by the Center for Low Energy Systems Technology (LEAST), one of six SRC STARnet Centers sponsored by MARCO and DARPA, and by NSF-EFRI-1433496.

11:20am **2D+EM+NS+PS+SP+SS+TF-MoM10 Atomically-Thin 2D Layers of Group IV Semiconductors**, *Joshua Goldberger*, The Ohio State University **INVITED**

Similar to how carbon networks can be sculpted into low-dimensional allotropes such as fullerenes, nanotubes, and graphene with fundamentally different properties, it is possible to create similar "allotropes" of Ge or Sn with unique optoelectronic properties as well. Here, we will describe our recent success in the creation of hydrogen and organic-terminated group 14 graphene analogues, from the topochemical deintercalation of precursor Zintl phases, such as CaGe₂. We will discuss how the optical, electronic, and thermal properties of these materials can be systematically controlled by substituting either the surface ligand or via alloying with other Group 14 elements. Additionally, we have also developed an epitopotaxial approach for integrating precise thicknesses of Germanane layers onto Ge wafers that combines the epitaxial deposition of CaGe₂ precursor phases with the topotactic interconversion into the 2D material. Finally, we will describe

our recent efforts on the synthesis and crystal structures of Sn-containing graphane alloys in order to access novel topological phenomena predicted to occur in these graphanes.

Energy Frontiers Focus Topic

Room: 211B - Session EN+AS+EM+NS+SE+SS+TF-MoM

Solar Cells I

Moderator: Jason Baxter, Drexel University, Chintalapalle Ramana, University of Texas at El Paso

8:20am **EN+AS+EM+NS+SE+SS+TF-MoM1 Elevated Temperature Phase Stability of CZTS-Se Thin Films for Solar Cells**, *E. Chagarov, K. Sardashti*, University of California at San Diego, *D.B. Mitzi*, Duke University, *R.A. Haight*, IBM T.J. Watson Research Center, *Andrew C. Kummel*, University of California at San Diego

Density-functional theory simulations of CZTS, CZTSe and CZTS_{0.25}Se_{0.75} photovoltaic compounds have been performed to investigate stability of CZTS_{0.25}Se_{0.75} alloy vs. decomposition to CZTS, CZTSe and other secondary compounds. The Gibbs energy for vibration contribution was estimated by calculating phonon spectra and thermodynamic properties at finite temperatures. It was demonstrated that CZTS_{0.25}Se_{0.75} alloy is stabilized not by enthalpy of formation but by vibration and mixing contributions to the Gibbs energy. A set of phase diagrams was built in multidimensional space of chemical potentials at 300K and 900K temperatures to demonstrate alloy stability and boundary compounds at various chemical conditions. The Gibbs energy gain/loss for several decomposition reactions was calculated as a function of temperature with/without Cu/Zn intermixing and vibration contributions to the Gibbs energy demonstrating CZTS_{0.25}Se_{0.75} that even defect-free (no Cu/Zn intermixing) CZTS_{0.25}Se_{0.75} can be stable at typical processing temperatures.

8:40am **EN+AS+EM+NS+SE+SS+TF-MoM2 Chemical and Electrical Characterization of Polycrystalline CZTS,Se and CIGS,Se Grain Boundaries by NanoAuger and Kelvin Probe Force Microscopy (KPFM)**, *Kasra Sardashti*, UC San Diego, *P.D. Antunez*, *R.A. Haight*, IBM T.J. Watson Research Center, *A.C. Kummel*, UC San Diego

Polycrystalline Copper-zinc-tin-sulfide/selenide (CZTS,Se) compounds have received wide research interest due to their potential as inexpensive absorber materials composed of earth-abundant elements. Photovoltaic devices fabricated on CZTS,Se have reached conversion efficiencies of 12.6%. One of the key parameters to further boost the conversion efficiency is to control the concentration of recombination sites at the surface, secondary phase interfaces and in the grain boundaries. To determine the presence of secondary phases on the surface and composition of grain boundaries, this work has employed Auger nanoprobe electron spectroscopy (NanoAuger) with 8nm lateral resolution combined with high resolution ambient Kelvin Probe Force Microscopy (KPFM) with dual-lock-in setup. NanoAuger was performed in planar and cross-sectional modes on CZTS,Se surfaces before and after top surface oxide removal by NH₄OH clean. Elemental maps before and after NH₄OH clean show Sn-/O-rich and Cu-poor grain boundaries suggesting that grain boundaries are terminated by tin-oxide (SnOx). Secondary phases such as SnSe and ZnSe were observed in the cross-sectional maps. Kelvin probe force microscopy (KPFM) on the cleaned surfaces showed that SnOx-terminated grain boundaries have 80-200 mV larger work function than grains, resulting in upward band bending between grains and grain boundaries. The upward band bending accompanied by the large valence band offset between the SnOx and CZTS,Se lead to relatively large energy barriers for both electrons and holes to travel into the grain boundaries and recombine. Comparison with the elemental maps for CIGSe (with device efficiencies as high as 18%) revealed the absence of the grain boundary oxide passivation.

9:40am **EN+AS+EM+NS+SE+SS+TF-MoM5 Spin Coating Thin Film CZTS for Efficient, Low-Cost Solar Cells on Flexible Glass Substrates**, *D. Kava*, *J. Galindo*, *C.O. Sana*, *S. Shahriar*, *Deidra Hodges*, University of Texas at El Paso

Photovoltaic's contribution to energy production continues to grow as costs continue to decrease. As silicon cells approach their limits, other materials are emerging. The development of Cu₂ZnSnS₄ (CZTS) thin film solar cells using non-vacuum liquid-based spin coating techniques have been previously investigated. The focus of this paper is the optimization of p-type CZTS thin film solar cells onto flexible substrates. Flexible solar panel costs are higher than their traditional counterparts. CZTS currently reports only a 3.2% efficiency on flexible glass, while the record for CZTS on non-

flexible substrates is 12.6%. The cells are created using a single solution ink sol-gel method. All metals are dissolved in a single step prior to deposition onto substrates (nickel foil and corning willow glass) as a thin film. Corning Willow glass is a new material introduced recently to the market, while nickel is a inexpensive flexible reflective foil. The Corning Willow glass is coated with a molybdenum layer as a reflective back contact layer. By using a single step and a solution deposition method, lower production cost are achievable. For thin film deposition, we used a non-vacuum spin coater (WS650 spin processor, Laurell Technologies) with an optimized spin coat programming. Annealing took place under vacuum in a RTP furnace while time, temperature and ramp functions were varied. The other layers of the device consists of cadmium sulfide n-type window layer and a zinc oxide doped with aluminum transparent top contact layer. Characterization and analysis of the thin films were performed using Raman spectroscopy, scanning electron microscope (Zeiss NEON 40), X-ray diffraction (Philippus X'Pert), profilometer (Veeco Dektak 150), UV-Vis-NIR Spectrophotometer (Cary 5000), Hall Effect measurement system (HMS3000) and a point probe (Lucas Labs) measurements. Results show CZTS thin film solar cells on flexible glass is obtainable.

10:00am **EN+AS+EM+NS+SE+SS+TF-MoM6 Band Gap Profile of Cu(In,Ga)(Se,S) 2 Thin Films via High-Resolution Reflection Electron Energy Loss Spectroscopy**, *Sung Heo*, *H.I. Lee*, *J.B. Park*, *G.S. Park*, Samsung Advanced Institute of Technology, Republic of Korea, *D.H. Lee*, *J.G. Nam*, Samsung, Republic of Korea, *H.J. Kang*, Chungbuk National University, Republic of Korea, *B.D. Choi*, Sungkyunkwan University, Republic of Korea

Cu(In,Ga)Se₂ (CIGS)-based solar cells was investigated with an aim of enhancing cell performance because these cells provided high conversion efficiency at relatively low cost. The efficiency of CIGS cells has recently approached 19.7% at small sizes. In general, Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)₂(CIGSS) composition profiles are double-graded, and they can improve the open-circuit voltage (V_{oc}) and the efficiency of solar cells because band gaps increase toward both the surface (i.e., with the increase of sulfur) and the bottom (i.e., with the increase of gallium). It is important to accurately measure the band gap at the top and the bottom of the CIGSS cell. Nevertheless, the band gap profile measurement of the CIGSS as a function of depth is challenging.

In this study, we obtained the depth profile of the CIGSS cell using the quantitative Auger Electron Spectroscopy method, for which the relative sensitivity factor was corrected using the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. We also measured the band gap directly using high-resolution reflection electron energy loss spectroscopy (HR-REELS) with a monochromatic electron gun, which has low electron energy at 300 eV.

For the direct measurement of a band gap profile, HR-REELS spectra were obtained as a function of depth during Ar ion sputtering at 3.0 kV. The band gap profile shows a double-graded band gap as a function of depth. The band gap values are 1.32 eV at the surface (E_{g1}), 1.08 eV at the depth between 0.3 and 0.7 μm (E_{g min,position}), and 1.50 eV at the depth of about 2.2 μm (E_{g2}), respectively. Our findings suggest a new analytical method which directly determines the band gap profile as function of depth.

10:40am **EN+AS+EM+NS+SE+SS+TF-MoM8 Spatial Atmospheric ALD of Zinc Oxysulfide Buffer Layers for CIGS Solar Cells**, *C. Frijters*, *P.J. Bolt*, *P. Poodt*, *Andrea Illiberi*, Solliance/TNO, Netherlands

Copper Indium Gallium di-Selenide (CIGS) solar cells are a promising approach in photovoltaic technology, having low production costs, high conversion efficiencies (> 20%), as well as the possibility to manufacture them on flexible substrates. State-of-the-art in CIGS solar cells manufacturing is to use a stack of CdS, intrinsic ZnO (*i*-ZnO) and an Al-doped ZnO TCO on top of the CIGS film. Replacement of CdS by a non-toxic Cd-free layer with wider band gap (> 2.4 eV) would *a*) decrease the production cost by avoiding the expensive treatment of toxic wastes and *b*) increase the overall cell efficiency by enhancing the quantum efficiency in the blue range. Moreover, the use of a "soft" and highly conformal deposition technique is preferred to improve the electrical properties of the buffer layer/CIGS interface.

In this paper we present spatial atmospheric atomic layer deposition of a Zn(O,S) buffer layer as CdS replacement for CIGS solar cells. Spatial ALD is emerging as an industrially scalable deposition technique at atmospheric pressure which combines the advantages of temporal ALD, i.e. excellent control of film composition and uniformity on large area substrates, with high growth rates (up to nm/s). Films are grown by sequentially exposing the substrate to oxygen and sulfur precursors (H₂O, H₂S) and the zinc metal precursor (i.e., DEZn). By controlling the kinetics of surface reactions between evaporated precursors and reactive sites at the film surface, the composition of Zn(O,S) can be precisely tuned. The incorporation of S into

ZnO results in a bowing of the band gap in the range from 3.3 eV (ZnO) to 2.7 (S/O+S ~ 0.5) and 3.4 eV (ZnS), as measured by spectrophotometry. The morphology of the Zn(O_{x-1}S_x) films varies from polycrystalline (for 0<x<30 and 70<x<100) to amorphous (30<x<70), as measured by X-ray diffraction. CIGS solar cells with a Spatial ALD Zn(O,S) buffer layer show an increased spectral response around 400 nm compared to solar cells with a CdS buffer layer. The solar cells with the Zn(O,S) buffer layer had an efficiency of 15.9 %, compared to 15.5 % for the reference solar cells with a CdS buffer layer.

11:00am **EN+AS+EM+NS+SE+SS+TF-MoM9 Deep Level Electron Traps in Epitaxial CuInSe₂ Probed using Photo-Modulated X-ray Photoelectron Spectroscopy**, *Nicole Johnson*, University of Illinois at Urbana-Champaign, *P. Aydogan*, Bilkent University, Turkey, *A. Rockett*, University of Illinois at Urbana-Champaign, *S. Suzer*, Bilkent University, Turkey

Performance in a variety of electronic devices is largely controlled by minority carrier charge capture on point defects. To date there is no experimental method to directly identify these point defects in a chemically specific fashion. Photo-modulated X-ray Photoelectron Spectroscopy (XPS) utilizes the chemical and charge sensitivity of XPS to identify changes in peak shape due to changing atomic charge state from capture of light-generated minority carriers. Epitaxial thin films of CuInSe₂ (CIS) were chosen as a case study for this technique because their defect chemistry is still relatively unknown as compared to traditional solar cell materials. The 500-1000nm thick films were grown by a hybrid sputtering and evaporation technique on GaAs(001) substrates at 600-700°C. Aligned surface morphology features matching the substrate geometry in scanning electron microscopy (SEM) images indicate epitaxial growth, which was confirmed by x-ray diffraction (XRD). A layer of CdS was deposited on the CIS via chemical bath deposition to protect the CIS surface from oxidation in storage and to duplicate the heterojunction used in solar cells. Prior to loading in the XPS, the CdS was etched off to expose a Cd doped CIS surface for analysis. The photo-modulated XPS used monochromatic AlK α x-rays with a 532 nm laser as the illumination source. Under illumination, each film constituent was observed to exhibit unique binding energy shifts. Based on their peak shifts relative to the surface photovoltage profile, Cd and In were found to be right at the surface while Cu and Se were deeper into the film, consistent with a Cd-doped, In-rich surface. The technique is therefore shown to provide a chemically-sensitive depth profile non-destructively that can be obtained even on a relatively rough sample. Additionally, shape changes in the Se 3d doublet spectra indicate electron capture in a deep trap state that is likely due to cation vacancies. Measurements at varying temperatures indicate air-induced surface recombination states are passivated by annealing at 80C, allowing the surface photovoltage to persist. At 230C, an irreversible change happens in the surface properties such that the surface photovoltage gets much smaller and reverses sign. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).

11:20am **EN+AS+EM+NS+SE+SS+TF-MoM10 The Role of ZnTe Buffer Layers on the Performance and Stability of CdTe Solar Cells**, *Jiaojiao Li*, Colorado School of Mines, *A. Abbas*, Loughborough University, UK, *D.M. Meysing*, *J.D. Beach*, *D.R. Diercks*, Colorado School of Mines, *M.O. Reese*, *T.M. Barnes*, National Renewable Energy Laboratory, *C.A. Wolden*, Colorado School of Mines, *J.M. Walls*, Loughborough University, UK

The use of ZnTe buffer layers at the back contact of CdTe solar cells has been credited with contributing to recent improvements in both record cell efficiency and module stability. To better understand the underlying reasons high resolution transmission microscopy (HR-TEM) and atom probe tomography (APT) were used to study the evolution of the back contact region before and after rapid thermal activation of this layer. During activation the 150 nm ZnTe layer, initially nanocrystalline and homogenous, transforms into a bilayer structure consisting of an amorphous region in contact with CdTe characterized by significant Cd-Zn interdiffusion, and a crystalline layer that shows evidence of grain growth and twin formation. This graded layer may passivate interface defects and account for the improved open circuit voltage and fill factor that accompanies the RTP activation step. Copper, co-evaporated uniformly within ZnTe, is found to segregate dramatically after rapid thermal activation, either collecting near the ZnTe|Au interface or forming Cu_xTe clusters in CdTe at defects or grain boundaries near the interface. Further examination of the Cu_xTe clusters revealed that they are encased in a thin layer of Zn, and it is postulated that this structure may limit the extent of diffusion into CdTe and play an important role in device stability.

11:40am **EN+AS+EM+NS+SE+SS+TF-MoM11 The Performance and Durability of Broadband Anti-Reflection Coatings for Thin Film CdTe Solar Cells**, *G. Womack*, *P.M. Kaminski*, *John Walls*, Loughborough University, UK

Light reflection from the glass surface of a photovoltaic (PV) module is a significant source of energy loss for crystalline silicon and all types of thin film PV devices. The reflection at the glass and air interface accounts for ~4% of the total energy. Single layer anti-reflection coatings using magnesium fluoride or porous silica with sufficiently low refractive index have been reported but these are only effective over a narrow range of wavelengths. In this paper we report on the design, deposition and testing of multilayer broadband anti-reflection coatings that reduce the weighted average reflection over the wavelength range used by thin film CdTe devices to ~1.22% resulting in a useful 3.6% increase in photocurrent. In this study we have used multilayer stacks consisting of silica and zirconia layers deposited using a reactive magnetron sputtering process. Details of the stack design, sputtering process parameters and the optical and micro-structural properties of the layers are provided.

Thin film CdTe devices pose a special problem because the anti-reflection coating is applied to one side of the glass while device layers are deposited directly on to the opposite glass surface in the superstrate configuration. In thin film CdTe production, the glass is exposed to high temperature processes during the absorber deposition and during the cadmium chloride activation treatment. If glass pre-coated with a broadband anti-reflection coating is to be used then the coating must withstand temperatures of up to ~550°C. Surprisingly, our studies have shown that multilayer silica/zirconia anti-reflection coatings on soda lime glass remain unaffected by temperatures up to 600 °C at which point mild crazing is observed. This is an important observation since it means that low cost glass which is pre-processed with a broadband anti-reflection coating by glass manufacturers is potentially useable in thin film CdTe module production

Accelerating Materials Discovery for Global Competitiveness Focus Topic

Room: 114 - Session MG+BI+MS+NS+TF-MoM

Development of Novel Materials

Moderator: Talat Rahman, University of Central Florida

9:00am **MG+BI+MS+NS+TF-MoM3 Molecular Engineering of Dyes for Dye-Sensitized Solar Cells via Rational Design**, *Jacqueline Cole*, University of Cambridge, UK **INVITED**

Dye-sensitized solar cells (DSCs) have unique attributes that afford them prospective applications as smart windows - windows in buildings that generate electricity from sunlight. This electricity will be fed into a local grid that will create sustainable buildings for future cities.

Materials discovery of new DSC dyes is one of the remaining bottlenecks to technological progress of smart windows. This talk shows we are attempting to overcome this materials bottleneck via two complementary routes to molecular design: (i) a 'top down' approach that uses large-scale data mining to identify brand new classes of DSC dyes [1]; (ii) a 'bottom up' approach that computationally transforms well-known non-DSC dyes into suitable DSC dyes [2,3].

The 'top down' approach involves large-scale data-mining to search for appropriate dye candidates [1]. Here, structure-property relationships for DSC dyes have been codified in the form of molecular dye design rules, which have been judiciously sequenced in an algorithm to enable large-scale data mining of dye structures with optimal DSC performance. This affords, for the first time, a DSC-specific dye-discovery strategy that predicts new classes of dyes from surveying a representative set of chemical space. A lead material from these predictions is experimentally validated, showing DSC efficiency that is comparable to many well-known organic dyes.

The 'bottom up' approach concerns case studies on families of well-known laser dyes that are transformed into functional DSC dyes using molecular engineering [2,3]. The underlying conceptual idea is to implement certain electronic structure changes in laser dyes, using molecular engineering, to make DSC-active dyes; while maintaining key property attributes of the laser dyes that are equally attractive to DSC applications. This requires a concerted experimental and computational approach; results predict new dye co-sensitizers for DSC applications.

References

[1] J. M. Cole, K. S. Low, H. Ozoe, P. Stathi, C. Kitamura, H. Kurata, P. Rudolf, T. Kawase, "Data Mining with Molecular Design Rules Identifies New Class of Dyes for Dye-Sensitized Solar Cells" *Phys. Chem. Chem. Phys.* 48 (2014) 26684-90

[2] S. L. Bayliss, J. M. Cole, P. G. Waddell, S. McKechnie, X. Liu, "Predicting solar-cell dyes for co-sensitization", *J. Phys. Chem. C* 118 (2014) 14082-14090

[3] F. A. Y. N. Schroeder, J. M. Cole, P. G. Waddell, S. McKechnie, "Transforming benzophenoxazine laser dyes into chromophores for dye-sensitized solar cells: a molecular engineering approach", *Advanced Energy Materials* (2015) DOI: 10.1002/aenm.201401728

10:40am **MG+BI+MS+NS+TF-MoM8 Controlled Spontaneous Nanoscale Patterning of Nonstoichiometric Reconstructions for Catalysis and Light Harvesting**, *J.M. Martinez, D. Saldana-Greco*, University of Pennsylvania, *W.A. Saidi*, University of Pittsburgh, *J.S. Lim, Andrew Rappe*, University of Pennsylvania **INVITED**

The ability to manipulate the atomic and electronic structure and stoichiometry of surfaces is of utmost importance in optimizing heterogeneous catalysts. A critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior, under various thermal and chemical constraints. We explore the reconstruction behaviors of Ti- and Mn-based perovskite type oxides: BaTiO₃, PbTiO₃, and CaMnO₃; the former two exhibit ferroelectricity, while the latter undergoes surface-induced magnetic ordering. Due to the characteristic properties of these oxides, we investigate the effect of their switchable polarization (for ferroelectric oxides) and near surface magnetic ordering (CaMnO₃) in their surface phase evolution, in addition to the effects of temperature and the chemical potentials of their constituent elements. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active components (Ti and Mn). These reconstructions show rich bonding and structural motifs that affect the active sites' reactivity and accessibility. Furthermore, these surface transformations, as in BaTiO₃ and PbTiO₃, can be tuned with the help of an electric field. An applied electric field changes the material's polarization, which then alters the surface electronic properties, and thereby also affects their sensitivity towards stoichiometric changes. In addition to the thermodynamic understanding of the surface reconstructions, we introduce the kinetic tunability of the surface reconstruction. We demonstrate this from a particular surface phase coexistence observed in BaTiO₃, namely the *c*(2x2) and *c*(4x4), where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. Finally, based on our interest in CaMnO₃ (001) surfaces, we have started to explore the more complex CaMn₇O₁₂. The electronic properties of this oxide yield interesting physical phenomena including charge ordering, non-collinear magnetism and improper ferroelectricity. We are currently investigating the ground state non-collinear magnetic configuration in this compound and its role on the stability of the charge-ordered state.

11:20am **MG+BI+MS+NS+TF-MoM10 Developing Evolutionary Algorithms for a priori Crystal Structure Prediction and Applications towards Novel Pressure-Stabilized Materials**, *Eva Zurek*, University at Buffalo-SUNY **INVITED**

One way to accelerate the development of new materials is via *a priori* crystal structure prediction (CSP) of hitherto unknown systems, followed by the computation of their properties and determination of promising synthesis conditions. A number of algorithms designed to solve global optimization problems have recently been applied to CSP with much success, and evolutionary algorithms (EAs) have emerged as one of the most promising methods for systems where little or no experimental data is available. Therefore, we have developed the open-source XtalOpt EA for CSP as an extension to the widely used chemical builder and visualizer, Avogadro. In this talk we present new developments within XtalOpt that allow it to successfully predict the structures of crystals with larger and more complex unit cells. Furthermore, we summarize the application of XtalOpt towards the prediction of hydrogen-rich solids with unique stoichiometries that are computed to be stable at pressures that are attainable within diamond anvil cells. The influence of the structure of the hydrogenic lattice on the electronic structure and the propensity for high temperature superconductivity is discussed.

Thin Film

Room: 111 - Session TF+AS+SS-MoM

Self-Assembled Monolayers, Layer-by-Layer, etc.

Moderator: Han Zuilhof, Wageningen University, Netherlands

8:20am **TF+AS+SS-MoM1 The Effects of Embedded Dipoles in Aromatic Self-Assembled Monolayers**, *Swen Schuster*, Universität Heidelberg, Germany, *T. Abu-Husein*, Universität Frankfurt, Germany, *D.A. Egger, I. Hehn*, Graz University of Technology, Austria, *M. Kind*, Universität Frankfurt, Germany, *E. Zojer*, Graz University of Technology, Austria, *A. Terfort*, Universität Frankfurt, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) are frequently used as intermediate films to modify charge-carrier injection from metal-electrodes into an organic semiconductor. This is usually achieved by use of the terminal dipolar groups comprising the SAM-ambient interface and affecting, at the same time, the growth chemistry of the semiconductor. Here we suggest an alternative approach, viz. embedding dipolar element into the molecular backbone, which allows decoupling the dipole control and the interfacial chemistry. As molecular backbone we use oligophenyl moiety which provides a suitable structural match to most organic semiconductors. As polar unit we use pyrimidine, varying its orientation in the molecular backbone and, consequently, the direction of the embedded dipole moment. The electronic and structural properties of these embedded-dipole SAMs are thoroughly analyzed using a number of complementary characterization techniques combined with quantum-mechanical modeling. We show that such mid-chain substituted monolayers are highly interesting from both fundamental and application viewpoints, as the dipolar groups are found to induce a potential discontinuity inside the monolayer, electrostatically shifting the energy levels in the regions above and below the dipoles relative to one another. These SAMs also allow for tuning the substrate work function in a controlled manner independent of the docking and interfacial chemistry. In addition, a mixture of the embedded-dipole molecules with opposite orientations of dipoles makes possible a fine tuning of the work function between the ultimate values, associated with a particular dipole orientation. Quantum-mechanical modeling in conjunction with x-ray photoelectron spectroscopy experiments provides insight into the molecular organization of such mixed monolayers.

8:40am **TF+AS+SS-MoM2 IR Spectroscopic studies of Molecular Thin Films exhibiting Spontaneous Dipole Alignment**, *Alexander Rosu-Finsen*, Heriot-Watt University, UK, *J. Lasne*, Heriot-Watt University, France, *A. Cassidy*, *D. Field*, Aarhus University, Denmark, *M.R.S. McCoustra*, Heriot-Watt University, UK

In recent years, observations of the presence of a spontaneous and powerful static electric field within thin films of molecular solids have been reported by Field and co-workers [1]. These electric fields, which can approach 10⁸ V m⁻¹ or more, are believed to arise from alignment of the molecular dipoles in the thin films. Seeking to provide an independent means of observing this phenomenon of the "spontelectric phase", the first new electrically-unique, structural phase to have emerged in decades, we have used reflection-absorption infrared spectroscopy (RAIRS) to investigate thin films of nitrous oxide (N₂O). The presence of a static electric field within the thin film, the defining characteristic of spontelectrics, is demonstrated through the observed temperature dependence of longitudinal-transverse optical (LO-TO) splitting in RAIR spectra, using an analysis based on the vibrational Stark effect [2]. Tentative evidence for the surface-templating of the growth of the spontelectric phase will be presented from RAIRS studies of solid carbon monoxide (CO) on a range of water substrates (porous amorphous solid water, compact amorphous solid water and crystalline water) [3].

[1] Spontaneous electric fields in solid films: spontelectrics. D. Field, O. Plekan, A. Cassidy, R. Balog, N.C. Jones and J. Dunger, *Int. Rev. Phys. Chem.*, 2013, **32**, 345-392.

[2] Spontaneously electrical solids in a new light. J. Lasne, A. Rosu-Finsen, A. Cassidy, M. R. S. McCoustra and D. Field, *Phys. Rev. Lett.*, submitted.

[3] Templating dipole alignment in solid carbon monoxide on water ice surfaces. A. Rosu-Finsen, J. Lasne, A. Cassidy, D. Field and M. R. S. McCoustra, *Phys. Rev. Lett.*, in preparation.

9:00am **TF+AS+SS-MoM3 Coordination-Based Molecular Assemblies as Electrochromic Materials: Ultra-High Switching Stability and Coloration Efficiencies**^[1], *Michal Lahav*, Weizmann Institute of Science, Israel

Layer-by-Layer (LbL) deposition, combined with metal-ligand coordination, has served as a powerful tool for generating functional architectures.^[2] Such systems might find interesting applications in molecular electronics, sensor, solar cells and data storage. More significantly, owing to their interesting electrochromic (EC) behavior, they are promising candidates for use in smart windows and display devices. In this study we used a dip-coating process to generate molecular assemblies (MA) from metal polypyridyl complexes cross-linked with PdCl₂. These polypyridyl complexes are considered ideal chromophores for fabricating electrochromic materials, due to their excellent stability and light absorption that greatly depends on their oxidation state.^{[3],[4]} The number of pyridine moieties of the chromophores is varied to control (i) the materials' stability, (ii) color, (iii) redox-chemistry, and (iv) the film growth (i.e., linear vs. exponential). We also observed that minor structural differences (i.e., the pyridine-bipyridine bond order) at the molecular level become apparent when the stability and electrochromic properties are examined (Figure 1). The MAs exhibit high coloration efficiencies and are extremely stable: they are thermally robust and have exceptionally high (spectro)electrochemical activity. Furthermore, we demonstrated the formation of a first-generation solid-state set-up.^{[1],[5]}

- 1) S. Shankar, M. Lahav, M. E. van der Boom, *J. Am. Chem. Soc.* **2015**, *137*, Just Accepted Manuscript.
- 2) R. J. Mortimer, *Annu. Rev. Mater. Res.*, **2011**, 41, 241.
- 3) G. de Ruiter, M. Lahav, M. E. van der Boom, *Acc. Chem. Res.*, **2014**, 47, 3407-3416.
- 4) G. de Ruiter, M. Lahav, H. Keisar, M. E. van der Boom, *Angew. Chem., Int. Ed.* **2013**, 52, 704-709.
- 5) M. E. van der Boom, M. Lahav, S. Shankar, US Patent 61/906,565, **2013**.

9:20am **TF+AS+SS-MoM4 New Approaches to the Preparation of Well-defined Metal Films on Top of Self-assembled Monolayers**, *Michael Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can be potentially used as ultrathin insulating dielectric layers or intermediate films in different electronic and spintronic devices. Whereas the bottom electrode in such assemblies is represented by the metal substrate, the top electrode should be prepared at the SAM-ambient interface. Regrettably, the formation of a well-defined metal film on top of the SAMs is a non-trivial task, since the metal atoms deposited onto the SAM-ambient interface do not stay there, but penetrate into the monolayer and diffuse to the metal substrate following a strong thermodynamical drive. Here I discuss three new approaches to suppress the above penetration and diffusion, taken a representative ferromagnetic metal, nickel, as a test adsorbate. The first approach relies on irradiation-induced cross-linking of a thiol-substituted aromatic SAM. Whereas 2D-polymerization of such a SAM prevents penetration of the metal atoms into the monolayer, the thiol groups at the SAM-ambient interface serve as nucleation centers for the growing "top" film. The second approach, relying on SAMs of perfluoroterphenyl-substituted alkanethiols, utilizes a chemical reaction between the SAM constituents and adsorbate atoms. The primary process is the Ni mediated loss of fluorine atoms followed by extensive cross-linking between the partly defluorinated molecular backbones. The stability of these backbones and the rapid development of the cross-linking are the key components to hinder the metal penetration. Finally, the penetration of deposited metal atoms into a SAM can be nearly completely inhibited by the preliminary formation of palladium-chloride seeding layer at the SAM-ambient interface. The palladium atoms in the seeding layer serve as nucleation centers for the growing metal film, staying at its bottom during the growth. In contrast, the chlorine atoms are transferred from palladium to the deposited metal, staying on the top of the growing metal film and serving as surfactants.

9:40am **TF+AS+SS-MoM5 N-Heterocyclic Carbenes as Novel Ligands for Self Assembled Monolayers on Gold**, *Cathleen Crudden*, Queen's University, Canada

INVITED

The use of N-heterocyclic carbenes (NHCs) to modify homogeneous metal catalysts is widespread, however despite the versatility of these complexes, the high metal-NHC bond strength and oxidative stability of NHC-ligated metals, and the ease of synthesis of NHCs, there have been only a handful of reports of mostly ill-defined surfaces functionalized by NHCs.

We will describe the use of NHCs to form self-assembled monolayers on gold surfaces. In particular, films prepared by the deposition of 1,3-dihydro-1,3-bis(isopropylbenzimidazol-2-ylidene), show molecular ordering on the surface and remarkable stability. They show no decomposition upon heating for 24 hrs in THF, in boiling in water for 24hrs or upon treatment

with acid (pH 2) or base (pH 12). Incredibly, they even survive largely after 24 hr exposure to hydrogen peroxide. This remarkable increase in stability relative to thiol-based SAMs will greatly increase the number of reagents and conditions to which the SAMs can be exposed.

The use of these films in SPR-based biosensing will be described, as will novel methods for the preparation of such films that can be carried out in air on the bench top.

10:40am **TF+AS+SS-MoM8 Improved Stability of Ag Thin Films due to Several Organic Surface Monolayers**, *Midori Kawamura*, Kitami Institute of Technology, Japan, *C. Kudo, T. Sasaki, Y. Abe, K.H. Kim, T. Kiba*, Kitami Institute of Technology

Due to excellent physical properties, Ag thin films have been used as low-coating, optical mirror, and so on. It is necessary to prevent degradation of the Ag films in air or humid atmosphere. For the purposes, it has been reported that several metal oxide nanolayers and organic monolayers are effective to make Ag thin films stable. Previously, we reported that modification of Ag films with 3-mercaptopropyltrimethoxysilane (MPTMS) monolayer can improve durability of the Ag films after environmental tests because strong bonds were formed between thiol moiety and Ag films, and also between silanol moiety and glass substrate. In the present study, we attempted to use other type of organic molecules, namely straight chain alkylthiols, such as 1-octadecanethiol (1-ODT), 1-dodecanethiol (1-DT) for protection of Ag film surface and compared with MPTMS.

Ag thin films (10nm) were deposited on clean glass substrates by vacuum evaporation. Then monolayer of 1-ODT and 1-DT were formed over the Ag thin films by solution method. The samples were kept in a constant temperature and humidity chamber (40 degree Celsius and 90 RH%) for a week. The electrical resistance, surface morphology, optical transmittance were measured before and after the test. Ag film without the monolayer, and that with MPTMS were also examined for comparison.

The surface roughness of the Ag film without the monolayer drastically increased from 2.7 nm to 27 nm after the test. However, the increase was within 1nm on Ag films with 1-DT and 1-ODT surface layers. These changes were smaller than that on Ag film with MPTMS surface layer. By the measurement of electrical resistivity, it was found that increase in the resistivity after the test was very much suppressed in the Ag film with these monolayers. In addition, optical transmittance measurement showed that transmittance spectrum of Ag films with these monolayers did not change after the test. These results accord with the Ag film morphology change. Consequently, excellent passivation effect of 1-DT and 1-ODT surface monolayers on Ag films was confirmed.

11:00am **TF+AS+SS-MoM9 Electronic Structures of the Biaxially-strained GaSb(111) Films**, *Takuya Hatayama*, The University of Electro-Communications (UEC-Tokyo), Japan, *A. Akaishi*, The University of Electro-Communications (UEC-Tokyo), *J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

III-V compound semiconductors have been extensively researched as alternative channel materials of complementary metal-oxide-semiconductor devices because of their superior carrier mobility^[1]. In particular, GaSb is one of the promising p-channel materials, because its hole transport properties are significantly improved compared to Si. Recently, Ohtake *et al.* have reported that high-quality GaSb films can be epitaxially grown on the Si(111) substrate using the InAs buffer layer^[2]. The lattice constant in the plane of growth for the thin GaSb epilayer inherits the lattice constant of InAs, causing an inherent strain in the GaSb film. As a result, the electronic structure of the GaSb film can be modified. In this study, we evaluate the electronic properties of the strained GaSb bulk and the (111) films, especially the band gap formation, the effective mass, and the electronic conductivity, using first-principles calculations within the density functional theory. In general, the local density approximation (LDA) is commonly applied to the exchange correlation term. However, it has been well-known that the band gap of semiconductors is significantly underestimated with LDA. In order to rectify the underestimation of the band gap and to correctly evaluate electronic dispersions at band edges, we use the hybrid functional proposed by Heyd-Scuseria-Ernzerhof (HSE06) for the exchange-correlation term^[3]. The spin-orbit interaction is also included.

We assume the biaxial strain parallel to the GaSb (111) plane. For the bulk with a direct band gap at ambient pressure, GaSb becomes an indirect band gap material under the compressive biaxial strain. The biaxial strain makes the twofold-degenerate heavy-hole and light-hole bands split into two bands at the Gamma point of the valence band. Interestingly, under the biaxial tensile strain, the effective mass of holes becomes anisotropic. We will also report on changes in electronic properties of the GaSb (111) ultrathin films under the biaxial strain.

- [1] J. A. del Alamo, *Nature* **479**, 317 (2011)

[2] A. Ohtake, T. Mano, N. Miyata, T. Mori, and T. Yasuda, *Appl. Phys. Lett.* **104**, 032101 (2014)

[3] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003); *ibid* **124**, 219906E (2006)

11:20am **TF+AS+SS-MoM10 How to Repel Polymer Adsorption on Flat Surfaces?**, *Zhanhua Wang, S.P. Pujari, M.M.J. Smulders, H. Zuilhof*, Wageningen University, Netherlands

Organic monolayers or polymer brushes, often in combination with surface structuring, are widely used to prevent nonspecific adsorption of polymeric or biological material on sensor and microfluidic surfaces. Here we show for the first time how robust, covalently attached alkyne-derived monolayers or ATRP-produced polymer brushes, with a varying number of fluorine atoms, on atomically flat Si(111), effectively repel a wide range of apolar polymers without the need for micro- or nanostructuring of the surface. We have studied the antifouling property of fluoro-hydro monolayers and of fluorine-containing polymer brushes towards a range of commonly used polymers/plastics with comparable molecular weight in non-aqueous solvent, and have investigated the effect of polymer molecular weight on the fouling behavior. These studies relied on a range of characterization methods: wettability studies, ellipsometry, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). We developed a novel surface morphology survey by AFM characterization that can accurately quantify the degree of fouling.

These studies consistently displayed that especially the mono-fluorinated (F1) monolayer shows excellent anti-fouling behavior, even more so than e.g. corresponding monolayers with perfluorinated alkyl tails. In this presentation the causes of this unprecedented and surprising finding are discussed. Second, we will focus on polymer brush properties that further reduce the adsorption of polymers. These findings and analysis offer significant potential for antifouling applications of ultrathin and covalently bound fluorine-containing coatings for a range of micro- and nanotechnological applications.

11:40am **TF+AS+SS-MoM11 Symmetric Attachment of Annulated Aromatic Hydrocarbons in Self-assembled Monolayers by Use of Oxazoles**, *C. Partes*, University of Frankfurt, Germany, *S. Schuster, T. Wächter*, University of Heidelberg, Germany, *Martin Kind*, University of Frankfurt, Germany, *M. Zharnikov*, University of Heidelberg, Germany, *A. Terfort*, University of Frankfurt, Germany

Self-assembled monolayers (SAMs) have proven to be powerful tools for tuning surface properties because of the uncomplicated method of their preparation and the high variability of their organic moieties. The suitability of SAMs in applications like, e.g., organic electronics is frequently investigated. An aim for the use of SAMs is the reduction of injection barriers that occur at the interfaces between organic semiconductors and technologically relevant substrates like gold or silicon.

A SAM ideal for this purpose should exhibit a high vertical conductivity. In view of this, we investigated several aromatic and araliphatic SAMs, e.g. terphenyl-terminated monolayers on gold [1]. In a more recent ansatz, we have examined SAMs bearing annulated moieties such as anthracene, which in contrast to oligophenyls are entirely planar [2]. However, as a consequence of the asymmetric substitution of anthracene to the thiol anchor group it is hardly possible to alter the tilt angle of these thiolate molecules within the SAMs [2].

To overcome this drawback, we extended the annulated system of the SAM-forming thiols with an oxazole unit, which allows for a quasi-symmetric attachment to the anchor group. This restores the possibility to influence the tilt angle of the aromatic units using the so-called odd-even effect in SAMs.

Here, we like to present preliminary results on preparation and structural properties of SAMs made from aromatic oxazole thiols on gold surfaces.

REFERENCES

[1] Shaporenko, A.; Brunnbauer, M.; Terfort, A.; Grunze, M.; Zharnikov, M./*J. Phys. Chem. B*/108, 14462-14469 (2004).

[2] Dauselt, J.; Zhao, J.; Kind, M.; Binder, R.; Bashir, A.; Terfort, A.; Zharnikov, M./*J. Phys. Chem. C*/115, 2841-2854 (2011).

Monday Afternoon, October 19, 2015

Energy Frontiers Focus Topic

Room: 211B - Session EN+AS+EM+NS+SE+SS+TF-MoA

Solar Cells II

Moderator: Adrie Mackus, Stanford University

2:20pm EN+AS+EM+NS+SE+SS+TF-MoA1 **Influence of Annealing Temperature in the Bulk Defect Formation in Perovskite Thin Films.** *Weina Peng, B.X. Anand, L.-H. Liu, S.C. Sampat, B.E. Bearden, A.V. Malko, Y.J. Chabal*, University of Texas at Dallas

Perovskites are emerging as front-runners for solar cell applications because of their superior optoelectronic properties. Over the past few years the grain size of perovskites has been continuously improved from several hundred of nanometers to a few millimeters which resulted in better solar conversion efficiencies. In addition to surface and grain boundary related defects, perovskites are prone to the formation of bulk defects as well. However the role of bulk defects in the determination of photovoltaic performance of perovskites is rarely explored. To this end we investigate the impact of annealing temperature on the defect density in polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films of ~ 1 micron average grain size prepared using vapor assisted solution process (VASP). The photoluminescence (PL) intensity and lifetime show systematic reduction when the annealing temperature is increased from 150°C to 200°C . A rough estimate of the defect state density obtained using fluence dependent PL measurements reveal a 5 fold increase in defect density for a 25°C increase in annealing temperature although the average grains size stays unchanged. Furthermore, surface passivation of perovskite films using Al_2O_3 via atomic layer deposition leads to an improvement in PL intensity and lifetime. But the PL quantum efficiency, as well as the lifetime, of the surface passivated 200°C annealed sample remains significantly lower than that of the un-passivated 150°C annealed sample indicating that the majority of the defects states we observe in the high temperature annealed samples originate from bulk defects. Thus the present study shows that minimizing the number of bulk defects, in addition to surface defects, is very important in the realization of highly efficient perovskite solar cells.

3:00pm EN+AS+EM+NS+SE+SS+TF-MoA3 **Tandem Solar Cells Using Perovskites, Silicon and CIGS.** *M.D. McGehee, Tomas Leijtens*, Stanford University **INVITED**

The efficiency of perovskite solar cells has soared from a few percent to over 20% in the last 3 years. They are very attractive for multijunction solar cell applications because the bandgap of perovskite semiconductors can be easily tuned in the range of 1.55 to 2.2 eV and the open circuit voltage of the cells is large. We have made highly efficient semitransparent perovskite solar cells using silver nanowire meshes as the top electrode. These cells can be used in combination with either silicon or copper indium gallium diselenide solar cells to make four-terminal and two-terminal tandems. We will also present detailed characterization of perovskite semiconductors made with different processing conditions to show what needs to be done to minimize recombination and make the solar cells stable.

3:40pm EN+AS+EM+NS+SE+SS+TF-MoA5 **Lifetime, Mobility, and Diffusion of Photoexcited Carriers in Ligand-Exchanged Lead Selenide Nanocrystal Films Measured by Time-Resolved Terahertz Spectroscopy.** *G.W. Guglietta*, Drexel University, *B.T. Diroll, E.A. Gaulding, J.L. Fordham*, University of Pennsylvania, *S. Li*, Drexel University, *C.B. Murray*, University of Pennsylvania, *Jason Baxter*, Drexel University

Colloidal semiconductor nanocrystals have been used as building blocks for electronic and optoelectronic devices ranging from field effect transistors to solar cells. Properties of the nanocrystal films depend sensitively on the choice of capping ligand to replace the insulating synthesis ligands. Thus far, ligands leading to the best performance in transistors result in poor solar cell performance, and vice versa. To gain insight into the nature of this dichotomy, we used time-resolved terahertz spectroscopy measurements to study the mobility and lifetime of PbSe nanocrystal films prepared with five common ligand-exchange reagents. Non-contact terahertz spectroscopy measurements of conductivity were corroborated by contacted van der Pauw measurements of the same samples. The films treated with different displacing ligands show more than an order of magnitude difference in the peak conductivities and a bifurcation of time-dynamics. Inorganic chalcogenide ligand-exchanges with sodium sulfide (Na_2S) or ammonium thiocyanate (NH_4SCN) show high THz mobilities above $25 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is desirable for transistors, but nearly complete decay of transient

photocurrent within 1.4 ns. The high mobility with NH_4SCN and Na_2S exchanges is more than offset by their short lifetimes and results in diffusion lengths of only ~ 200 nm. In contrast, ligand exchanges with 1,2-ethylenediamine (EDA), 1,2-ethanedithiol (EDT), and tetrabutylammonium iodide (TBAI) show $\sim 5\times$ lower mobilities but much longer carrier lifetimes, with $\sim 30\%$ of photoexcited carriers remaining for >10 ns. The long lifetimes with EDA, EDT, and TBAI yield diffusion lengths of at least 500 nm, which is approaching the film thickness desired for strong light absorption in solar cells. This bifurcated behavior may explain the divergent performance of field-effect transistors and photovoltaics constructed from nanocrystal building blocks with different ligand exchanges.

4:00pm EN+AS+EM+NS+SE+SS+TF-MoA6 **iCVD Synthesis and Integration of Poly(vinylpyrrolidone) and Poly(4-vinylpyridine) as Polymer Electrolytes in Dye Sensitized Solar Cells.** *Yuriy Y. Smolin, S. Janakiraman, A.J. Sauter, M. Soroush, K.K.S. Lau*, Drexel University

Initiated chemical vapor deposition (iCVD) is used to synthesize and integrate poly(4-vinylpyridine) (P4VP) and polyvinylpyrrolidone (PVP) as polymer electrolytes within the mesoporous TiO_2 photoanode of dye sensitized solar cells (DSSCs). DSSCs with conventional liquid electrolytes are prone to leakage and evaporation, which hinders DSSC durability and field implementation. In addition, liquid electrolytes lead to significant electron recombination within the cells that limit DSSC performance. In contrast, polymer electrolytes do not suffer from the practical disadvantages and could potentially enhance the cell's I-V behavior.

However, in order to enable good contact between the TiO_2 electrode and the polymer electrolyte, a major obstacle is the difficulty in achieving good pore filling of the polymer into the mesoporous TiO_2 layer. Mesoscale pore diameter, high aspect ratio, and tortuous pore structure of the photoanode along with liquid surface tension, poor wettability, and solute steric hindrance make pore filling extremely limited when using liquid techniques. This leads to poor electrical contact and lower efficiency. To overcome the challenges of pore filling, we directly synthesized polymer electrolytes inside the pore volume of the photoanode using the solvent-free technique of iCVD. iCVD relies on the vapor delivery of monomer and initiator, which facilitates infiltration into the porous TiO_2 substrate, and by controlling the relative rates of diffusion and surface polymerization through iCVD process parameters, uniform and conformal growth of polymer is achieved. The pore filling of the polymer electrolyte into 5–10 μm photoanodes using iCVD is typically 90–100% which is significantly better than that achievable with liquid techniques like spin coating.¹

In this work, we will show that iCVD P4VP and PVP polymer electrolytes can be effectively integrated within TiO_2 mesoporous photoanodes to produce enhanced DSSCs. By varying the polymer electrolyte chemistry including the use of a crosslinking agent during iCVD to stabilize the resulting polymer structure, DSSC I-V characteristics, such as open-circuit voltage, short-circuit current density and fill factor, are tuned.² To gain a better understanding on the effect of the polymer electrolyte, experimental techniques such as linear sweep voltammetry, intensity modulated spectroscopy, and impedance spectroscopy are used. Mathematical modeling of DSSC behavior is also performed to relate these experimental observations with the dynamics of the operation of the cell.

1. S. Nejadi and K. K. S. Lau, *Nano Lett.*, 2010, 11, 419-423.

2. Y. Y. Smolin et al., *J. Power Sources*, 2015, 274, 156-164.

4:20pm EN+AS+EM+NS+SE+SS+TF-MoA7 **Interfacial Effects on Device Performance in Organic Solar Cells.** *Huanxin Ju, J.F. Zhu*, University of Science and Technology of China, *D.S. Ginger*, University of Washington

The better understanding of the underlying mechanisms is essential for the further development of highly efficient organic photovoltaics (OPVs) devices. In this paper, the transient photovoltage (TPV) and charge extraction (CE) measurements in combination with the synchrotron radiation photoemission spectroscopy (SRPES) were used to gain insights into the correlation between the microscopic interfacial properties and macroscopic device performance. The OPV devices based on PCDTBT: PC_{70}BM with Ca interlayer were studied as a reference system to investigate the interfacial effects on device performance. The charge carrier decay dynamics demonstrated that the device with the Ca interlayer exhibited a lower recombination constant (k_{rec}) than that only with the Al cathode at a given charge carrier density (n). In addition, the interfacial energy band structures indicated that the strong dipole moment produced by the Ca interlayer can facilitate electron extraction as well as drive hole away at the cathode/polymer interface, resulting in retarding interfacial recombination losses. Finally, we examined the device performance with the Ca interlayer to find that the efficiency is improved by 28% as compared to that without

the Ca interlayer, which shows good correlation with the observed interfacial properties.

4:40pm **EN+AS+EM+NS+SE+SS+TF-MoA8 Tungsten-Titanium Mixed Oxide Thin Films for Improved Structural and Optical Properties for Solar Driven Applications**, *Mirella Vargas*, The University of Texas at El Paso, *N.R. Murphy*, Air Force Research Laboratory, *R.V. Chintalapalle*, The University of Texas at El Paso

Tungsten oxide (WO₃) is a well-established n-type semiconductor possessing unique optical and electronic properties. WO₃ has become the most interesting inorganic material for electrochromic applications due to the reversible spectral absorption properties associated with WO₃. WO₃ thin films and nanostructures exhibit an optical band gap that permits efficient use of the solar spectrum including absorption in the blue part of the visible region and the ultraviolet region, as well as a high transmission region that extends from the near-infrared (IR) to the visible spectrum. Coupled with good electronic transport properties, photosensitivity, and chemical integrity, WO₃-based materials are attractive for applications related to sustainable energy production including energy efficient windows and architecture, photoelectrochemical (PEC) water-splitting, photocatalysis and solar cells. Anion or cation doping into WO₃ has been extensively studied as this offers the opportunity to tailor the transport properties that may influence the efficiency of solar driven devices. Titanium doping into WO₃ has proven to enhance the electrochromic response and the cyclic lifetime by a factor of five in PEC devices. In the present case a systematic investigation of progressively increasing the Ti content in the W-Ti target for reactive sputtering has been employed to tune the structure, chemistry, and properties of the films. Tungsten-titanium (W-Ti) mixed oxide thin films were fabricated using reactive sputtering of W-Ti alloy targets with Ti content ranging from 0 to 30 wt.%. X-ray photoelectron spectroscopy confirms the existence of W and Ti in their highest oxidation states of +6 and +4, respectively. Quantification of binding energy shifts for W and Ti core-level transitions confirms the formation of WO₃-TiO₂ composite oxide films. Optical analyses made from spectrophotometry measurements indicate a decrease in band gap with a discrete amount of Ti incorporation. The band gap decreases with increasing Ti from 3.0 eV to 2.5 eV. Such films are expected to have the possibility for tuning the electrical conductivity while retaining the optical transparency to make them efficient for photoelectrochemical cells and photovoltaics.

5:00pm **EN+AS+EM+NS+SE+SS+TF-MoA9 Potential Resolution to the "Doping Puzzle" in Pyrite FeS₂**, *X. Zhang, M. Li, L. O'Brien, J. Walter, M. Manno, F. Mork, J. Kakalios, Eray Aydil, C. Leighton*, University of Minnesota

In principle, pyrite FeS₂ is one of the most suitable photovoltaic materials for sustainable low-cost, large-scale solar cell manufacturing because it has high absorbance in the visible and comprises earth-abundant inexpensive elements. However, current efficiencies of solar cells based on pyrite FeS₂ have not exceeded 2.8%. Early research on this material concluded that unintentionally doped FeS₂ thin films are p-type and subsequent solar cell work evolved based on this presumption. In fact, it is now widely accepted that FeS₂ thin films almost always exhibit p-type conduction even though single crystals are typically found to be n-type. This discrepancy between single crystals and thin films is perplexing and to date this puzzle remains unexplained. In this talk we reexamine the conclusion that undoped FeS₂ films are predominantly p-type and provide an explanation for this "doping puzzle" in pyrite. Using a combination of Hall effect, thermopower, and temperature-dependent resistivity measurements on a large set of well characterized single crystals and thin films, we show that the widely accepted predominant p-type behavior in pyrite films may, in fact, be an artifact of hopping conduction and should be revisited. Specifically, both Hall effect and thermopower measurements establish that all of our high-mobility (>1 cm²V⁻¹s⁻¹) films and single crystals are n-type. Temperature-dependent resistivity measurements on these high mobility films and crystals establish diffusive electronic transport. We find that films with lower mobility (4x10⁻³-1 cm²V⁻¹s⁻¹) also show n-type Hall effect but exhibit a p-type Seebeck coefficient, leading to a discrepancy in the measured carrier type. Temperature-dependent resistivity measurements on these intermediate mobility films show a transition from diffusive to hopping transport. Finally, both Hall and Seebeck coefficients are strongly suppressed and invert in the lowest mobility thin films (<4x10⁻³ cm²V⁻¹s⁻¹) indicating apparent p-type conduction. Temperature-dependent resistivity measurements establish unambiguous hopping behavior in these lowest mobility films. Based on this evolution of Hall and Seebeck coefficients with carrier mobility, and the well-known suppression of the Hall and Seebeck effects in conductors with hopping electronic transport, we conclude that the apparent crossover from n-type to p-type with decreasing mobility is, in fact, an artifact of hopping conduction.

Work supported by the NSF under DMR-1309642, in addition to the University of Minnesota NSF MRSEC under DMR-1420013.

5:20pm **EN+AS+EM+NS+SE+SS+TF-MoA10 Interparticle Contact Radius and Electron Transport in Thin Films Comprised of Nanocrystals**, *Elijah Thimsen, D. Lanigan*, Washington University, St. Louis

Thin films comprised of nanocrystals are being explored for a variety of applications that involve electron transport. For traditional applications such as photovoltaic solar cells, the goal is often to utilize solution processing to make an inexpensive thin film that essentially behaves as a bulk material with diffusive transport. For other applications, such as neuromorphic computing, variable range hopping (VRH) transport is more desirable because it enables a given nanocrystal to have orders of magnitude more nearest neighbors than it physically touches. It is of paramount importance that the structure-property relationships that control electron transport mechanism be elucidated. Previous work has demonstrated that interparticle separation distance affects charge carrier mobility. However, for films comprised of nanocrystals that are physically touching, what is the effect of contact radius? In this work, we present a systematic experimental study of the effect of interparticle contact radius on the electron transport mechanism in thin films comprised of heavily-doped ZnO nanocrystals embedded in Al₂O₃. As the contact radius increased, the electron transport mechanism crossed over from VRH to diffusive conduction. For large contact radius between nanocrystals, the room-temperature electron mobility in the film approached the local mobility within a nanocrystal, approximately 10 cm² V⁻¹ s⁻¹. The conclusion is that for nanocrystals that are physically touching, the interparticle contact radius determines the transport mechanism. With the ability to control the electron transport mechanism in films comprised of ZnO nanocrystals, we performed an exploratory study of the Hall effect in these materials. Hall effect measurements are of great utility and are routine for determining charge carrier mobility and type, but the interpretation of data for materials that exhibit VRH has been difficult in the past. For well-connected ZnO nanocrystals that exhibit diffusive conduction, the Hall coefficient was independent of temperature, as expected for the high doping level. Alternatively, for films with small contact radius between nanocrystals, which exhibited a VRH transport mechanism, we observed an anomalous behavior of the Hall coefficient at low temperature (100 to 200 K). Surprisingly, for films that exhibited VRH, the magnitude of the Hall coefficient increased exponentially with decreasing temperature, in stark contrast to the conventional wisdom that the Hall effect is suppressed for VRH.

Accelerating Materials Discovery for Global Competitiveness Focus Topic

Room: 114 - Session MG+2D+MI+NS+TF-MoA

Design and Discovery (Bio and Other Interfaces)

Moderator: Sean Jones, National Science Foundation (NSF), Lynnette Madsen, National Science Foundation (NSF)

3:00pm **MG+2D+MI+NS+TF-MoA3 Rational Accelerated Design of Polymer Dielectrics**, *Rampi Ramprasad*, University of Connecticut
INVITED

To date, trial and error strategies guided by intuition have dominated the identification of materials suitable for a specific application. We are entering a data-rich, modeling-driven era where such Edisonian approaches are gradually being replaced by rational strategies which couple predictions from advanced computational screening with targeted experimental synthesis and validation. Consistent with this emerging paradigm, we propose a strategy of hierarchical modeling with successive down-selection stages to accelerate the identification of polymer dielectrics that have the potential to surpass 'standard' materials for a given application. Specifically, quantum mechanics based combinatorial searches of chemical space are used to identify polymer repeat units that could lead to desirable dielectric properties, followed by configurational space searches to determine the 3-dimensional arrangement of polymers (and their properties) built from the desirable repeat units. Successful synthesis and testing of some of the most promising identified polymers and the measured attractive dielectric properties (which are in quantitative agreement with predictions) strongly supports the proposed approach to material selection.

3:40pm **MG+2D+MI+NS+TF-MoA5 Method to Make a Stable Copper-Carbon Alloy**, *Ivan Shchelkanov, D.N. Ruzic, I. Jasiuk*, University of Illinois at Urbana Champaign

Modern industry demands advanced materials with enhanced properties. To expand a range of available materials the covetic alloy is studied. Covetic is a novel alloy invented and patented by Third Millennium Metals, LLC

(TMM). This is a new hybrid material made of a carbon and a metal, where the carbon forms a super lattice structure inside a metal. The base metal can be copper, aluminium, lead, tin or other low-melting point metals. In normal conditions the metal does not wet and does not form chemical bond with the carbon. However, the amount of carbon in the covetic alloy exceeds carbon solubility in the metal by several orders of magnitude. Such a composition is achieved by supplying a current to a volume of molten metal while it is being blended with micron size carbon particles. The alloy is prepared in vacuum.

The process of covetic formation is influenced by chemical composition of the base metal, a cast volume temperature change rate, external electric and magnetic fields, compound viscosity, surface and interphase tension coefficient, density, and thermal and electric conductivities of the metal and carbon particles. A part of the process of covetic alloy formation, which involves carbon particles dissolving, can be compared to phenomena occur in dust plasma. This assumption provides a possibility to visualise processes of microparticles spatial distribution and decomposition into single atoms with subsequent formation of a carbon super lattice inside the metal lattice.

The current work focuses on: the electric current influence on the alloy structure formation and carbon atoms distribution inside the metal; copper covetic hardness, conductivity, and tensile strength change as a function of carbon composition; and a phenomenological model for covetic alloy formation.

4:00pm MG+2D+MI+NS+TF-MoA6 Development of Nanoporous Solid Phase Microextraction (SPME) Fibers by Sputtering. *Matthew Linford, C.V. Cushman, B. Singh, A. Diwan*, Brigham Young University

Solid phase microextraction (SPME) is a solventless, fast, easy and relatively inexpensive sample preparation technique that integrates sampling, extraction and preconcentration of samples such as food, waste water, air, and biological fluids in one step. However, commercial SPME coatings may be expensive, show relatively short lives, extract limited numbers of compounds, and have relatively low thermal and mechanical stability. The aim of this study is to develop an SPME device that is thinner, robust, long lasting, has higher mechanical strength, greater thermal and solvent stability, and is devoid of the other drawbacks of commercial coatings. We describe a new method for the preparation of nanoporous SPME coatings via the oblique-angle sputtering of silicon and subsequent functionalization with silanes. The thickness of the sputtered coatings was controlled by varying the sputtering time. To increase the density of -OH groups on the surfaces, the coatings were treated in piranha solution and then reacted with n-octadecyldimethylmonomethoxysilane to render the surfaces hydrophobic. The coatings were robust and were characterized at each step in the process using XPS, water contact angle goniometry, spectroscopic ellipsometry, and scanning electron microscopy. Our sputtered, silanized fiber yielded comparable and/or better extraction efficiencies than a commercial 7 μm PDMS fiber, especially for higher molecular weight species. In the case of a series of primary alcohols, and aldehydes, our fiber outperformed the commercial PDMS fiber by a factor of 2 - 3. In the evaluation of two real world samples: a sea water extract and beer, our fiber showed unique selectivity. Our 1.1 μm fiber yielded comparable signals to 65 μm PDMS-DVB and 85 μm CAR-PDMS commercial fibers for higher molecular weight analytes. For a ~2.2 μm fiber, the performance of our fiber increased substantially.

Thin Film

Room: 111 - Session TF+2D+MG+NS-MoA

ALD, CVD, MLD, and PLD on Special Materials

Moderator: Giovanna Scarel, James Madison University, Mark Davidson, University of Florida

2:20pm TF+2D+MG+NS-MoA1 Optical Enhancement of Polyethylene Teraphthalate Films Modified by Organometallic Vapor Infiltration. *Halil Akyildiz*, North Carolina State University, *J.G. Simmons*, Redstone Arsenal, *H.O. Everitt*, Duke University, *J.S. Jur*, North Carolina State University

Polyethylene terephthalate is recyclable thermoplastic polymer that has wide application area including packaging, textiles and insulation applications. Due to the ring structures on the backbone of the polymer it shows weak luminescence in the blue spectrum upon UV light absorption by pi electrons. It has previously been shown that vapors of organometallic ALD precursors are able to infiltrate and react with the polymer to form organic inorganic hybrid materials. Infiltration of trimethylaluminum into PET to form polymer-alumina coordination complexes enhanced the photoluminescence and internal quantum efficiency of the material. In this

study we present how the polymer morphology (i.e. crystallinity) and the infiltration temperature are able to affect the optical properties of the resulting PET films. Four unique emission bands are observed in pristine PET films; (2) stronger emissions in high crystallinity films attributed to the crystalline regions of the polymer and (2) peaks that show stronger emission in low crystallinity films attributed to the amorphous regions. After the low temperature infiltration (60 °C) emissions attributed to the amorphous regions demonstrate increases intensity, indicating that the infiltration reaction is predominant in the amorphous regions of the polymer. After infiltration at 150 °C, a very high red shift is observed alongside a complete emission spectra changes, suggesting the reactions taking place at high temperatures are different than low temperature processing. This detailed understanding of the photoluminescence behavior of the hybrid films can provide insight for use of these hybrid materials with a bandgap ideal for unique optical applications.

2:40pm TF+2D+MG+NS-MoA2 Organic and Hybrid Organic-Inorganic Thin Film Deposition by Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation. *Adrienne Stiff-Roberts*, Duke University
INVITED

Over the past fifteen years, matrix-assisted pulsed laser evaporation (MAPLE) has been developed to deposit organic thin films[1-6], inorganic nanoparticles, and hybrid organic-inorganic nanocomposites[4, 7-9]. One variation of the MAPLE technique, resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE), reduces the laser energy (e.g., Er:YAG laser ~2.94 μm peak wavelength) in order to minimize polymer degradation. In addition, because the frequency of the IR laser energy is resonant with OH bond vibrational modes in water, a frozen emulsion (comprising a mixture of the guest material dissolved in an organic solvent and water) is used as the target. Therefore, the unique advantage of emulsion-based RIR-MAPLE is that most of the energy from the IR laser is absorbed by water in the frozen emulsion, which evaporates and gently transfers the guest material to the substrate with minimal solvent exposure and degradation.

In the case of hybrid organic-inorganic nanocomposites, inorganic nanoparticles are embedded in a polymer matrix to achieve specific materials properties or functionality; however, nanoparticles that are mixed with a polymer in solution tend to aggregate due to a polarity difference with polymers[10]. In contrast, RIR-MAPLE is fundamentally different from solution processing and reduces nanoparticle phase segregation by eliminating the need to co-dissolve nanoparticles and polymers into a single common solvent; and by depositing the nanoparticles and polymers in a relatively dry state.

We will demonstrate the capability of RIR-MAPLE to deposit continuous nanoparticle films with the same optical properties as nanoparticles in solution and to minimize nanoparticle phase segregation in hybrid films. We will also demonstrate hybrid organic-inorganic thin films deposited by RIR-MAPLE for application to solar cells. This work is supported in part by ONR.

References

1. Pique, A., et al., *Thin Sol Films*, 1999. : p. 536-541.
2. Bubb, D.M., et al., *J of Appl Phys*, 2002. (12): p. 9809-9814.
3. Toftmann, B., et al., *Thin Sol Films*, 2004. : p. 177-181.
4. Hunter, C.N., et al., *Surface & Coatings Technol*, 2008. (3-4): p. 300-306.
5. Sellinger, A.T., et al., *Thin Sol Films*, 2008. (18): p. 6033-6040.
6. Ge, W., et al., *Colloids Surf B Biointerfaces*, 2014. : p. 786-92.
7. Pate, R., et al., *Thin Sol Films*, 2009. (24): p. 6798-6802.
8. O'Malley, S.M., et al., *J Phys Chem C*, 2014. (48): p. 27911-27919.
9. Gyorgy, E., et al., *J Phys Chem C*, 2011. (31): p. 15210-15216.
10. Huynh, W.U., et al., *Adv Mat*, 1999. (11): p. 923-927.

3:40pm TF+2D+MG+NS-MoA5 Integrating Ultrathin ALD/ALE Films with 1D and 2D Materials to Enable New Device Structures. *Virginia Wheeler*, N. Nepal, U.S. Naval Research Laboratory, *A. Nath*, George Mason University, *A.D. Koehler*, *Z.R. Robinson*, *J.K. Hite*, *K.M. Daniels*, *M.A. Mastro*, U.S. Naval Research Laboratory, *E. Self*, *P. Pintauro*, Vanderbilt University, *J.D. Caldwell*, *R.L. Myers-Ward*, *D.K. Gaskill*, *C.R. Eddy Jr.*, U.S. Naval Research Laboratory
INVITED

As device features continue to approach nanoscale dimensions, requisite structures continually grow in complexity often resulting in 3D architectures, nanowires, and/or 2D van der Waals materials. This reduction in size leads to new phenomena, such as quantum confinement effects in electronics or strong localization of light in nanophotonics, which can potentially enable new devices. Realization of novel device structures that exploit these effects requires integration of scalable thin films of various electronic materials onto nanostructures. Atomic layer deposition (ALD) is

the preferred method to conformally coat nominally planar as well as complex, high surface area nanostructures with abrupt interfaces, wafer-scale uniformity, and angstrom-scale control of thickness. Additionally, ALD is a low temperature process which allows incorporation with many temperature sensitive nanostructure materials that are not compatible with other deposition techniques. Alternatively, a slightly higher deposition temperature can facilitate atomic layer epitaxy (ALE) of crystalline thin films with all the same beneficial characteristics of ALD. However, the inert nature of 1D and 2D materials often inhibit direct application of ALD/ALE films with desired coverage and uniformity. In this work, we will discuss crucial aspects of ALD/ALE growth, such as surface functionalization and *in situ* nucleation sequences, required to obtain uniform, conformal films on nanostructured substrates.

The essential requirements for integration of ALD/ALE layers with 1D and 2D materials will be evaluated through several case studies including: 1) integration of III-N films on graphene for a hot-electron transistor; 2) coating of carbon fibers for battery and electrode applications; and 3) functional oxide layers on SiC nanopillars to modify their optical response for several potential devices. The substrates in these cases have varying degrees of surface reactivity, so we will address the need for and our current *ex situ* and *in situ* approaches to obtaining sufficient reactivity between the substrate and ALD precursors. Moreover, it was found that ALD parameters (temperature, pulse and purge durations, etc.) impact the effectiveness of uniform, conformal coating of these structures. Other factors, such as sample suspension, are sometime critical to overcoming these limitations while still operating in ALD/ALE windows. Initial devices results will be presented, when appropriate, to demonstrate the feasibility of the integration of ALD thin films in new device structures.

4:20pm **TF+2D+MG+NS-MoA7 Development of the Optical Properties of Silicon Rich Oxide Films Growth by CVD Techniques for Possible Photovoltaic Applications**, *Karim Monfil-Leyva*, Benemérita Universidad Autónoma de Puebla, Mexico, *A.L. Muñoz-Zurita*, Universidad Politécnica Metropolitana de Puebla, Mexico, *E. Ojeda-Durán*, *A. Benítez*, *J. Carrillo-López*, *J.A. Luna-López*, *R.C. Ambrosio-Lázaro*, Benemérita Universidad Autónoma de Puebla, Mexico

Currently, electronics and semiconductor studies have focused a great effort to overcome the intrinsic disadvantages of bulk-Si to develop optoelectronic devices. In particular, the Silicon Rich Oxide (SRO) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or silicon-based light emitters. SRO can be deposited by several chemical vapor deposition techniques like Low Pressure Chemical Vapor Deposition (LPCVD) or Hot Filament Chemical Vapor Deposition (HFCVD). Silicon excess in SRO films obtained by LPCVD can be controlled by pressure ratio $R_o = N_2O/SiH_4$. Meanwhile, silicon excess in SRO films obtained by HFCVD can be controlled by changing the hydrogen flow (H_F).

In this work, we report a study of the optical and structural properties of thin SRO films obtained by LPCVD and HFCVD. Silicon excess was changed by the pressure ratio R_o in the range of 15 and 45 (SRO15 to SRO45) and H_F was changed between 25 and 75 sccm. SRO LPCVD films were annealed at 1100 °C. Ellipsometry and step measurements were applied to calculate thickness and the refractive index. Fourier transform infrared (FTIR) measurements were obtained from SRO films to confirm a change on stoichiometry. Absorbance spectra of SRO films showed rocking and bending vibration modes similar to stoichiometric silicon dioxide but an asymmetric stretching mode revealed the non-stoichiometric nature of our semiconductor films. SRO films by LPCVD showed a strong photoluminescence (PL) at room temperature (RT) on two bands, a blue band from 400 to 550 nm or a red band from 575 nm to 875 nm depending on R_o . Blue and red emission bands were related to donor acceptor decays between traps promoted by defects. SRO films by HFCVD also showed a red band from 500 to 1100 nm (depending on the H_F) and this emission was attributed to defects produced by the transport of the precursors. SRO films showed suitable optical properties for possible photovoltaic applications.

5:00pm **TF+2D+MG+NS-MoA9 Radical-Enhanced Atomic Layer Deposition Enabled Multiferroic Composite Synthesis**, *C. Pham*, *Jeffrey Chang*, *J.P. Chang*, University of California at Los Angeles

Multiferroic materials, which exhibit controllable magnetic (ferroelectric) behavior via electric (magnetic) field, are of great interest due to their wide spectrum of new device applications such as non-volatile memory devices. Unfortunately, such behavior is extremely rare in natural single-phase systems. Furthermore, the properties of the few single phase multiferroic materials are too insignificant to be integrated into current device designs. Therefore, alternative strategies involving composite materials are proposed to combine the ferroelectricity and magnetism of different materials, achieving multiferroic behavior. By utilizing piezoelectric and magnetostrictive effects in different material phases, a strain-mediated approach shows great promise for applications. In such a strategy, the interface area per volume, as well as the material crystallinity of each

constituent, will greatly influence composite properties. The conformal and high quality film growth with atomic layer deposition (ALD) shows great potential for enabling the multiferroic composites described above.

In this work, lead-free ferroelectric/antiferromagnetic BiFeO₃ (BFO) and ferrimagnetic CoFe₂O₄ (CFO) thin films were grown on SrTiO₃ (001) (STO) substrate by radical enhanced ALD (REALD) using metalorganic precursors, Bi(tmhd)₃ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), Co(tmhd)₂, and Fe(tmhd)₃. The use of oxygen radicals as an ALD oxidant provides extra process flexibility. Film crystallinities and properties were studied under different conditions. The BFO films showed epitaxial single crystalline growth in a (001) pseudocubic orientation after annealed at 650 °C while the CFO films are polycrystalline due to the lattice mismatch between the film and substrate (~ 1% for BFO and ~7% for CFO). The piezoelectric properties of BFO films were confirmed using PFM while weak ferromagnetic behavior was also observed. Tunable CFO magnetic properties were shown using thickness-related strain relaxation over the range of 5~90 nm.

Synthesis of multiferroic composites was enabled by REALD. When fixing the total thickness at 40nm, 2-2 BFO/CFO nanolaminate composites with an increasing number of sub-layers showed a controllable competition between magnetic and shape anisotropy. 0-3 CFO/PZT composites were enabled by growing conformal CFO ALD films onto mesoporous PZT medium. SEM confirmed the gradual and conformal coating with increasing ALD cycles. It was found that the pore necks limit the incorporation of CFO inside the mesoporous media as it blocks precursor penetration. The volumetric magnetic properties were found to exceed the values found in literature with 0-3 configurations.

5:20pm **TF+2D+MG+NS-MoA10 Plasma Enhanced Deposition of Nanocrystalline Silicon Thin Films from SiF₄ by RF-PECVD and MDEC: Key Aspects of Growth Dynamics**, *JK. Wang*, *P. Bulkin*, *I. Florea*, *J.L. Maurice*, *Erik Johnson*, LPICM-CNRS, Ecole Polytechnique, France

For the growth of thin-film hydrogenated silicon by low temperature plasma-enhanced chemical vapor deposition (PECVD), SiF₄ has recently attracted interest as a precursor for numerous reasons, most importantly due the resilient optoelectronic performance of the resulting layers and devices, even when grown in a slightly oxygen-contaminated growth environment. Nevertheless, many questions remain concerning the critical factors determining the quality of hydrogenated microcrystalline silicon (μc-Si:H) thin films grown from this precursor.

To advance knowledge on this subject, we present studies performed on two very different types of PECVD reactor: a standard capacitively coupled RF-PECVD reactor, using a process gas mixture consisting of Ar/SiF₄/H₂ and at deposition rates up to 4A/s, and a matrix-distributed electron cyclotron resonance (MDEC) PECVD reactor operating at much lower pressures but achieving a higher deposition rate (8 A/s) and using simply an SiF₄/H₂ mixture. In doing so, we reveal key details concerning the growth process. We underline recently obtained results concerning three critical experimental findings about the use of SiF₄ as a growth precursor: (1) the importance of temperature for high-deposition rate, low-pressure conditions, (2) the vital role of ion bombardment energy on the quality of growth, and (3) the vastly increased challenge of the nucleation process when using high-density plasma processes. The films generated in these studies have furthermore been studied by cross sectional HR-TEM, revealing more specific details about the changing nature of the films during growth, and the dependence of these dynamics on the maximum ion energy impinging on the surface. These studies - along with residual gas analysis studies and optical emission spectroscopy results - allow us to examine the precise growth mechanism of such films when using an SiF₄/H₂ mixture.

Tuesday Morning, October 20, 2015

2D Materials Focus Topic

Room: 212C - Session 2D+EM+NS+SS+TF-TuM

Optical and Optoelectronic Properties of 2D Materials

Moderator: Andrea Young, University of California at Santa Barbara

8:00am **2D+EM+NS+SS+TF-TuM1 The Tri-Angular Lattice Exciton (3ALE) Model: Exciton Physics at the Atomic Scale**, *F. Tseng*, NRC Research Associate, *E. Simsek*, George Washington University, *Daniel Gunlycke*, Naval Research Laboratory

Descriptions of excitons in pristine semiconducting crystals usually rely on the hydrogen model adopted for excitons. Owing to the weak screening in monolayer transition-metal dichalcogenides, however, the electron and hole separation in the strongest bound excitons is on the atomic scale, necessitating atomistic treatment. In this presentation, we present a minimalistic exciton model that accounts for the lattice and the spin-orbit and exchange interactions, thus making this model appropriate across the spectrum from Wannier to Frenkel excitons. Using this model, we show that the exciton lifetimes could be extended by transitioning the excitons into excitonic dark states. Longer exciton lifetimes could make these materials candidates for applications in energy management and quantum information processing.

This work has been funded by the Office of Naval Research (ONR), directly and through the Naval Research Laboratory (NRL). E.S. and F.T. acknowledge support from NRL through the ONR Summer Faculty Program and the NRC Research Associateship Program, respectively.

8:20am **2D+EM+NS+SS+TF-TuM2 Opposite Dependence of Microwave-Induced vs. Field-Induced Imaging Contrast in NV-based Fluorescence Microscopy as Function of Optical Excitation**, *Etienne Goovaerts*, *S.K.R. Singam*, University of Antwerp, Belgium, *M. Nesladek*, Hasselt University, Belgium, *M. Giugliano*, University of Antwerp, Belgium

The charged nitrogen-vacancy (NV⁻) center is a remarkable defect in diamond which allows interrogation of spin state through its fluorescence. Among the proposed applications, background-free imaging based on fluorescent nanodiamond (FND) was demonstrated [1-3]. The FNDs emission can be discriminated from spurious fluorescence by switching on resonant microwaves (MW) and/or a static magnetic field [1-3], as demonstrated in cells [1] and potentially in small animals [2]. It is now important to understand the origin of the contrast in either of these approaches, and the optimal experimental parameters.

NV defects in single-crystal diamond as well as in FNDs were excited by a 532nm laser through the microscope objective. A compact spectrometer combined with appropriate filters allowed to measure the NV⁻ and NV⁰ emission. MW-induced contrast is achieved using a broadband circular antenna (i.d. 1mm) on a printed plate, and for field-induced contrast we use a small-sized permanent magnet (~300mT). They are placed closely behind the sample with in each case the magnetic field component along the optical axis of the objective.

For shallow implanted NV in (100) diamond as well as for FNDs the fluorescence is quenched by application of either resonant MWs or static field, with contrast levels systematically higher in the single crystal case than for deposited nanoparticles. The contrast values were measured for laser powers covering 6 orders of magnitude. After an initial rise at very low excitation (max. 13% in crystal, 7% in FND), the MW-induced contrast significantly decreases at higher laser powers. In parallel, field-induced contrast increases from about 12% to values of 38% and 20% for the single crystal and FNDs. This is described under steady state conditions using a 5-level model that includes radiative and nonradiative decay and ground state spin relaxation. The MW-contrast results from induced spin transitions in the triplet ground state while the field effect relies on state mixing within the ground and the excited triplets which change the decay rates. The analysis also shows that the applied excitation rates runs through 3 regimes from below the spontaneous relaxation rate, via an intermediate regime, to above the decay rate of the intermediate singlet.

This work demonstrates the advantages of field-induced contrast microscopy over the MW-induced approach. These become particularly important at high excitation rates which are more often applied in confocal microscopy.

[1] R. Igarashi, et al, Nano Lett. 2012, **12**, 5726

[2] A. Hegyi, E. Yablonovitch, Nano Lett. 2013, **13**, 1173

[3] R. Chapman, T. Plakhoitnik, Opt. Lett. 2013, **38**, 1847

8:40am **2D+EM+NS+SS+TF-TuM3 2D Materials and Heterostructures for Applications in Optoelectronics**, *Thomas Mueller*, Vienna University of Technology, Austria **INVITED**

Two-dimensional (2D) atomic crystals are currently receiving a lot of attention for applications in (opto-)electronics. In this talk I will review our research activities on photovoltaic energy conversion and photodetection in 2D semiconductors. In particular, I will present monolayer p-n junctions, formed by electrostatic doping using a pair of split gate electrodes, and MoS₂/WSe₂ van der Waals type-II heterojunctions. Upon optical illumination, conversion of light into electrical energy occurs in both types of devices. I will present measurements of the electrical characteristics, the photovoltaic properties, and the gate voltage dependence of the photoresponse. In the second part of my talk, I will discuss photoconductivity studies of MoS₂ field-effect transistors. We identify photovoltaic and photoconductive effects, which both show strong photoconductive gain. We envision that the efficient photon conversion, combined with the advantages of 2D semiconductors, such as flexibility, high mechanical stability and low costs of production, could lead to new optoelectronic technologies.

9:20am **2D+EM+NS+SS+TF-TuM5 Excitations and Ultrafast Charge Response in Bilayer Transition-Metal Dichalcogenides**, *Volodymyr Turkowski*, *T.S. Rahman*, University of Central Florida

We analyze the absorption spectrum and ultrafast charge dynamics in bilayer 2L-MoS₂, 2L-MoSe₂ and MoS₂-WS₂ systems by using time-dependent density functional theory in the density-matrix representation. In particular, we calculate the values of the binding energies of excitons in these structures for both intra- and inter-layer electron-hole excitations and demonstrate that, similar to the case of a single layer, these energies can be as large as hundred(s) of meVs. We also analyze the ultrafast dynamics of the electrons, holes and excitons in the photoexcited bilayers. We pay special attention to the ultrafast hole transfer in these systems and find transfer times of the order 100fs, in agreement with the experimental finding for the MoS₂-WS₂ system. We perform a detailed *ab initio* study of the spatially- and time-resolved charge density in the systems during the hole transfer and conclude that sulfur and selenium orbitals play an important role in the process. Finally, we discuss possible applications of the results in light harvesting technologies.

Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

9:40am **2D+EM+NS+SS+TF-TuM6 Automatic Localization and Identification of 2D-Material Flakes by Spectroscopic Imaging Ellipsometry**, *Sebastian Funke*, *P.H. Thiesen*, Accurion GmbH, Germany, *G. Greg Hearn*, Accurion Inc.

With the rising of 2D materials in surface sciences, the localization of mono- to few-layers of 2D materials, such as graphene, Molybdenum disulfide, hexagonal boron nitride is a time consuming task. With the help of imaging spectroscopic ellipsometry flakes of 2D materials can be found and its layer numbers can be differentiated.

Therefore a spectroscopical mapping of the sample is done. At selected wavelengths nulling ellipsometry for each pixel in the field of view is done to measure Δ/Ψ . The measurement of all pixels is done simultaneously. To cover larger areas than the field of view a XY-patterning is done automatically. For each XY-position spectroscopic Δ/Ψ maps are obtained. Every pixel of a Δ/Ψ map represents the spectroscopic angle Δ/Ψ respectively. By comparing the spectral Δ/Ψ values for each pixel with the ellipsometric model of e.g. graphene monolayer, flakes of graphene monolayers on the sample can be found. To ensure, that only flakes are found, a grid with a threshold is used. The threshold indicates the number of pixels in the grid that need to fit to the model.

In the talk we present the capability of imaging ellipsometry to localize and identify monolayer to few-layers of 2D Materials. Flakes of MoS₂ with a size smaller than 10 μm can be localized. Monolayer of graphene can be distinguished from bilayers of graphene. To improve the time factor, the use of a Scheimpflug corrected objective is presented. Further investigations on different 2D materials, e.g. h-BN and the implementation of a Raman System is in progress.

11:00am **2D+EM+NS+SS+TF-TuM10 Systematic Hydrogen Intercalation of Epitaxial Graphene for THz Plasmonics, Kevin Daniels,** National Research Council postdoc working at NRL, *A. Boyd*, American Society for Engineering Education postdoc working at NRL, *R.L. Myers-Ward, D.K. Gaskill*, Naval Research Laboratory

Epitaxial growth of graphene via sublimation of silicon and graphitization of carbon atoms from silicon carbide (SiC) is ideal for large scale manufacturing of plasmonic devices but due to partially covalent bonding between the SiC (0001) substrate and the first carbon layer (6√3 buffer layer), the high room temperature mobility necessary for THz plasmonics is reduced significantly compared to exfoliated graphene. The objective of this work is to improve THz response of EG by increasing the mobility and carrier concentration of graphene through hydrogen intercalation where the Si atoms covalently bound to the buffer layer are satisfied by hydrogen atoms and create quasi free standing graphene.

Epitaxial graphene was grown from 6H-SiC (0001) in an Aixtron/Epigress VP508 horizontal hot-wall reactor, etching in H₂ during temperature ramp to 1570°C and growing graphene in Ar ambient at 1580°C. H-intercalation of EG was carried out in the same reactor at 1050°C with a flow of 80slm of H₂ and chamber pressure of 900mbar for 15-75 minutes. Morphology of the quasi-free standing graphene was observed by AFM and SEM. Raman spectroscopy using a 532nm laser (9.6mW) and spot size of 0.3μm were used to take 80x10μm maps of each sample where release of the buffer layer is observed, with broadening of the 2D peak full-width-half-max (FWHM) before and after H-intercalation is observed on the graphene terraces and step edges. Number of monolayers before and after H-intercalation was determined by XPS.

From SEM, AFM, Raman and Hall we observe changes in degree of hydrogen intercalation with respect to time. Large areas of partially intercalated EG is observed at 15 minutes which confirmed by a mix of charge carriers and reduced carrier mobility at ~250cm²/Vs. At 30 minutes some graphene terraces remain coupled to the SiC substrate with carrier mobility ~2250cm²/Vs. From 45, 60 and 75 minutes the buffer layer becomes mostly quasi free standing with small spots possibly coupled to the substrate as observed in the SEM with mobilities of ~3900, ~4000 and ~3700cm²/Vs respectively. Measurements of the resulting THz transmission spectra are currently underway to determine if the increase in mobility and carrier concentration results in narrower THz response.

11:20am **2D+EM+NS+SS+TF-TuM11 Determining the Optical Properties of Exfoliated 2D Molybdenum Disulfide on Various Substrates with Imaging Spectroscopic Ellipsometry, Peter H. Thiesen,** Accurion GmbH, Germany, *S. Funke*, HAWK, Germany, *B. Miller, E. Parzinger*, TU München, Germany, *G. Hearn*, Accurion Inc., *A.W. Holleitner, U. Wurstbauer*, TU München, Germany

Ellipsometry is a non-destructive optical method for determining film thickness and optical properties. It measures the change in the state of polarization of the light reflected from the film interfaces. Imaging ellipsometry, which combines the power of ellipsometry with microscopy, has overcome the limitation of poor sample lateral resolution found in conventional non-imaging ellipsometers. The enhanced spatial resolution of imaging ellipsometers potentially expands ellipsometry into new areas of microanalysis, microelectronics, and bio analytics.

Molybdenum disulfide is a layered transition metal dichalcogenide. From the point of current research, 2D-nano materials based on MoS₂ are very promising because of the special semiconducting properties. The bulk material has an indirect 1.2 eV electronic bandgap, but single layer MoS₂ has a direct 1.8 eV bandgap. The monolayer can be used in prospective electronic devices like transistors (MOSFETs) or photo detectors.

Wavelength spectra of ellipsometric parameters Delta and Psi of the MoS₂ monolayers and multilayers were recorded as well as microscopic maps. In case of Sapphire, The psi maps at wavelength of higher energies than the bandgap show a clear contrast between the monolayer and the substrate and at lower energies there is no contrast between the monolayer and the substrate, but the multilayer areas still show a clear contrast-making the unique properties of MoS₂ monolayers directly visible. The advantage of imaging ellipsometry is the visualisation of the shape of the monolayer and the opportunity to classify the homogeneity of the optical properties of the microcrystallite. To quantify the optical properties, different approaches of optical modelling will be discussed.

11:40am **2D+EM+NS+SS+TF-TuM12 Nonlinear Optical Spectroscopy of 2D Semiconductor Monolayers, Xiaobo Yin,** University of Colorado Boulder **INVITED**

Transition metal dichalcogenide (TMDC) monolayers have recently emerged as an important class of two-dimensional semiconductors with

potential for electronic and optoelectronic devices. Unlike semi-metallic graphene, layered TMDCs have a sizeable bandgap. More interestingly, when thinned down to a monolayer, TMDCs transform from indirect-bandgap to direct-bandgap semiconductors, exhibiting a number of intriguing optical phenomena such as valley-selective circular dichroism, doping-dependent charged excitons and strong photocurrent responses. Using nonlinear optical spectroscopy, we probe experimentally the evidence of a series of excitonic dark states as well as structural symmetry in single-layer WS₂ and MoS₂.

Thin Film

Room: 111 - Session TF+EM+MI+MS-TuM

ALD for Alternative Devices

Moderator: Paul Poodt, Solliance/TNO, Richard Vanfleeter, Brigham Young University

8:00am **TF+EM+MI+MS-TuM1 FAST-ALD™ with Close Proximity (CP) Plasma for Low Temperature Applications: Nano-Composite Layer (NCL) Stacks for Flexible Substrates, SangIn Lee, Veeco** **INVITED**

The stress of the film is an important factor in mechanical stability and reliability of the devices, especially flexible electronic applications and microelectro-mechanical systems (MEMS), because it causes mechanical cracks, delamination and degradation in reliability of the device. Moreover, mechanical integrity of nano-scaled devices requires not only the physical properties of the individual films such as thermal expansion coefficient and elastic modulus, but also integral structural properties such as interface adhesion, and therefore residual stress of the film need to be managed.

Veeco's proprietary ALD technology, Fast Array Scanning Technology (FAST-ALD™) with Close-Proximity (CP) Plasma, has unique characteristics that are differentiated from other spatial ALD technologies. CP-plasma in FAST-ALD™ provides very uniform radical streams onto the substrate without plasma-induced damages and substrate heating enabling FAST-ALD™ to provide plasma-ALD films and stable polymeric MLD films from CP Plasma which cannot be obtained from conventional plasma process, for high-quality films at extremely low temperature for use in stress-sensitive device applications such as low-k films on Si wafers or flexible functional films on plastic substrates.

Stresses in inorganic ALD layers can be offset by either carbon-incorporated dielectric (CID) interlayers or polymeric MLD interlayers. The relative percentage of the inorganic ALD film to CID interlayer can be changed to tailor the stress of the stacked film to the device requirements. In this experiment, the combinations of an inorganic dielectric layer (Al₂O₃) with CID interlayers as part of nano-laminates, obviously in the same philosophy with polymeric MLD interlayers, nano-composite layer (NCL) stacks were deposited at 80°C to control the stress of the stacks from tensile to compressive state and vice versa, by changing the thickness and atomic content of Al₂O₃ layer and materials. By changing the ratio of the thickness in NCL stacks, 4:2 stacked film (4 Al₂O₃ layers and 2 CID layers as a sub-stack) and 1:1 stacked film (1 Al₂O₃ layer and 1 CID layer as a sub-stack) with total 30nm thickness show very low tensile stress and compressive stress of +58MPa and -89MPa, respectively, indicating the potential application of these free standing film stacks to nano-scaled devices and/or environmentally sensitive devices. NCL stack shows higher immunity to cracks and competitive barrier properties than that of the single ALD layer. NCL concept approaches can be applied to semiconductor in low-k pore sealing and oxidation barrier in the backend-of-line (BEOL) and cutting-edge devices with flexible substrates.

8:40am **TF+EM+MI+MS-TuM3 Atmospheric Roll-to-Roll Spatial Molecular Layer Deposition for flexible barriers, Fieke van den Bruele, F. Grob, P. Poodt,** Holst Centre / TNO, Netherlands

Proper encapsulation of devices such as OLEDs and thin-film photovoltaics is critical, as exposure to moisture from the ambient will degrade these devices, reducing their efficiency, lifetime, or even lead to failure altogether. Especially for OLEDs, the barrier requirements are very challenging, with a Water Vapor Transmission Rate < 10⁻⁶ g/m²/day. To achieve these very low WVTRs, very high quality barrier layers are required, being pinhole free over the entire device area. Encapsulation of flexible devices is even more challenging as the encapsulation should not affect the device flexibility too much.

The recent development of roll-to-roll and large-area Spatial ALD technology has spurred the interest in ALD for encapsulation and barriers. Thin layers of inorganic material (10-20 nm) made with (spatial) ALD have sufficiently low intrinsic WVTR but often do not meet the requirements for

barriers because they are very sensitive to particles and roughness that lead to defects. Thick inorganic films are less sensitive to particles, but suffer from stress and can have a limited flexibility. Various flexible thin film encapsulation techniques have been recently developed, often combining one or more thin inorganic diffusion barrier layers (e.g. SiN_x , Al_2O_3) with an organic layer that acts as stress relief layer but has no additional barrier functionality. One of those proposed interlayers for stress relief and flexibility are organic materials deposited through Molecular Layer Deposition (MLD). A well-studied example are the Alucones, prepared by reacting trimethyl aluminum with an alcohol. There are several reports on the barrier properties of Al_2O_3 – Alucone multilayer stacks, but the results seem to be inconclusive.

Assessing the flexibility these MLD layers are is not straightforward as measuring the mechanical properties of these very thin layers is difficult. We use a simple, qualitative method to test the flexibility of these MLD layers, by combining bending test with a polymer etch test to visualize cracks and other defects in the MLD film caused by bending. Preliminary results show that the flexibility of MLD layers, like their organic counterparts, largely depend on film thickness and can suffer from instability.

The next step in making MLD barriers is upscaling towards large-area and roll-to-roll production. We will present the results of our atmospheric roll-to-roll spatial MLD of alucones on polymer foils. Furthermore, an outlook to full-industrial scale R2R ALD/MLD production of barriers will be discussed.

9:00am **TF+EM+MI+MS-TuM4 Low Temperature, Temporal and Spatial Atomic Layer Deposition of TiO_2 using Titanium Tetra-isopropoxide as Precursor, Morteza Aghaee**, Eindhoven University of Technology, Netherlands, *P.S. Maydannik*, Lappeenranta University of Technology, Finland, *P. Johansson*, Tampere University of Technology, Finland, *M. Creatore*, Eindhoven University of Technology, Netherlands, *T. Homola*, *D.C. Cameron*, Masaryk University, Czech Republic, *J. Kuusipalo*, Tampere University of Technology, Finland

Spatial atomic layer deposition (S-ALD) is a technique which has been shown to lead to high quality moisture barrier films (e.g. Al_2O_3) in a roll-to-roll process¹. However, TiO_2 is expected to outperform Al_2O_3 because of its higher stability against long-term degradation than Al_2O_3 . For high throughput S-ALD at low temperature, highly reactive precursors with high vapour pressure are necessary. Titanium chloride is typically used but has the disadvantages of residual chlorine incorporation in the film and generation of corrosive by-products. Titanium tetra-isopropoxide (TTIP) is a valid alternative because of its high vapour pressure at room temperature compared to other titanium organometallic compounds². TTIP has not previously been used as a precursor for S-ALD.

In this work, a preliminary investigation has been carried out on the temporal ALD approach consisting of alternating exposure of a polyethylene naphthalate (PEN) substrate to the precursors TTIP and water, ozone or oxygen-fed plasma. The deposition was carried out at a substrate temperature of 80-120°C. The highest growth rate (0.056 nm/cycle) and refractive index (2.33) values have been obtained by using an O_2 -fed plasma. The water vapour transmission rates have been found to be lower than $5 \times 10^{-4} \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ at 38°C, 90% RH conditions for a film thickness of 20 nm. For the water process, WVTR values were found to be in the range of 10^{-3} for a 40 nm film.

Based on these results, a low pressure S-ALD process was developed using a Beneq TFS200R system. Titanium dioxide films were successfully deposited by TTIP and water as S-ALD precursors in the same temperature range as temporal, and their properties were characterised in terms of growth per cycle, refractive index and chemical composition. The growth rate saturated at precursor exposure time of 230 ms at every deposition temperature, which was slightly higher than the growth rate in temporal ALD mode at the same temperature range. Similar properties (refractive index and chemical composition) to temporal ALD have been obtained by adopting S-ALD.

¹ P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Soderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro, and X. Zeng, *J. Vac. Sci. Technol. A* **32**, 051603 (2014).

² M. Aghaee, P. S. Maydannik, P. Johansson, J. Kuusipalo, T. Homola, M. Creatore, D. C. Cameron, Submitted to *J. Vac. Sci. Technol.* (2015)

9:20am **TF+EM+MI+MS-TuM5 Spatial Atomic Layer Deposition into Flexible Porous Substrates, Kashish Sharma**, University of Colorado at Boulder, *D. Routkevitch*, *N. Varaksa*, In Redox, *S.M. George*, University of Colorado at Boulder

Spatial atomic layer deposition (S-ALD) is important for ALD commercialization. S-ALD has been successfully demonstrated on flat

substrates. In this work, S-ALD was examined on flexible porous substrates using anodic aluminum oxide (AAO) membranes and Li ion battery electrodes. The AAO membranes were coated with ZnO ALD using diethylzinc and ozone as the reactants. The Li ion battery electrodes were coated with Al O ALD using trimethylaluminum and ozone as the reactants. These experiments utilized a rotating cylinder reactor for S-ALD that is scalable to roll-to-roll operation [K. Sharma et al., 01A132 (2015)].

ZnO S-ALD into the pores of AAO membranes depends on gas transport that is determined by the pore diameter, pore aspect ratio and reactant pulse duration. The reactant pulse duration is defined by the substrate speed in S-ALD. Different reaction conditions and AAO membrane characteristics were explored using energy dispersive spectroscopy (EDS) to measure the Zn coverage profiles. Substrate speeds were defined by rotating cylinder rates of 10, 100 and 200 revolutions per minute (RPM). The AAO pore diameters were 50, 100 and 150 nm.

For AAO pore lengths of 10 microns, the EDS analysis revealed that uniform Zn coverage profiles were obtained at 10 RPM. The Zn coverage profiles were less uniform at higher RPM values and smaller pore diameters. These results indicate that S-ALD into porous substrates is feasible. However, the uniformity of the ALD coverage will depend on reaction parameters and the characteristics of the porous substrate. In addition, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Li ion battery electrodes on flexible metal foil were coated with Al_2O_3 ALD using the S-ALD reactor at 10-100 RPM. Initial coin-cell testing has demonstrated that enhanced capacity stability of these cathode electrodes is obtained after 2-5 Al_2O_3 ALD cycles.

9:40am **TF+EM+MI+MS-TuM6 Accurate Precursor and Reactant Delivery for Quantitative Atomic Layer Deposition, Masafumi Kikano**, Stanford University, *M. Nagase*, *N. Ikeda*, Fujikin Incorporated, Japan, *P.C. McIntyre*, Stanford University

Atomic layer deposition (ALD) has been widely discussed in the literature from various points of view. Typically, the amount of the precursor and reactant supplied into the ALD chamber is dictated only by controlling valve operation time, and is not quantitatively defined. To achieve a more quantitative ALD process, we have developed new flow rate control system (FCS) which can accurately dose precursor and reactant into an ALD reactor. This FCS consists of an orifice plate, pressure sensor, thermal sensor, and piezo control valve. It can be heated to 250°C to achieve sufficient vapor pressure for most precursors used in ALD of various inorganic compounds and elements. The FCS controls the flow rate under critical expansion conditions (or choked flow conditions); the flow rate through the orifice is proportional only to the upstream pressure of the orifice.[1,2] The piezo control valve accurately controls the upstream pressure and, thus, the flow rate. This mode of operation makes it possible to control the dosing of precursor and reactant by simply operating an endpoint valve placed close to the ALD reactor, because the upstream pressure is controllable whether the gas flow is running or not.

We have demonstrated an ALD process with trimethylaluminum (TMA) and water vapor (H_2O) reaction for Al_2O_3 deposition using the FCS to accurately control dosing into the ALD reactor. Excellent uniformity and reproducibility of deposition, and high quality dielectric properties of the resulting Al_2O_3 films have been achieved. The critical doses of TMA and H_2O into the chamber have been found to achieve surface saturating ALD of Al_2O_3 on a silicon substrate.

[1] A. Guthrie, R. K. Wakerling, "Vacuum Equipment and Techniques" McGraw-Hill book company, Inc., pp17, (1949)

[2] R. H. Perry, D. Green, "Perry's Chemical Engineers' Handbook, Sixth Edition" McGraw-Hill Co., pp5-14, (1984)

11:00am **TF+EM+MI+MS-TuM10 ALD for Capacitor Technologies, Ramakrishnan Rajagopalan**, *C. Randall*, The Pennsylvania State University

INVITED

Atomic layer deposition (ALD) is a powerful processing technique that can be used to modify interfacial processes occurring in electrochemical capacitors. Charge storage mechanism in electrochemical capacitors is either due to electrostatic double layer formation or pseudocapacitive faradaic interactions at electrode/electrolyte interfaces. The talk will present an overview of our efforts in developing pseudocapacitive vanadium oxide thin films using ALD approach on high surface area carbon electrodes. The deposition process is dependent upon the carbon properties such as surface functionalization and porosity. We will report our investigation of deposition of ALD films on nanostructured carbon electrodes with controlled porosity in mesopores (<20 nm) to ultramicropore (0.8 nm to 2 nm) ranges. ALD also facilitates the possibility of combining electrochemical effects with dielectric effects. ALD of dielectrics such as Al_2O_3 on electrodes used in aqueous, organic and lithium based electrolytes can mitigate the issues relating to electrochemical stability due to solvent decomposition reactions and leakage performance with limited effect on the ESR performance of the capacitor. There is also possibility of designing

novel solid state capacitor structures that synergistically integrates the electrical double layer interactions due to ions with dielectric energy storage.

11:40am **TF+EM+MI+MS-TuM12 Compositionally and Functionally Graded Hybrid Layer for High-Performance Adhesion**, *Yichuan Ding, R.H. Dauskardt*, Stanford University

Reliable bonding of organic/inorganic interfaces continues to be one of the most important challenges in multilayer devices including microelectronic, photovoltaic and display technologies. Hybrid molecular materials which contains both organic and inorganic components has been shown to be well suited for bonding organic/inorganic (metals, metal-oxides, nitrides, ...) interface, mitigating moisture degradation and even stress migration. The hybrid films (less than 100nm) made of two primary precursors, an epoxysilane and a zirconium alkoxide, have been deposited via solution based synthesis, with low cost and high throughput. By optimizing sol-gel chemistry and processing conditions, we achieved an impressive tenfold improvement in interfacial adhesion at the epoxy/Si substrate interface, and have proven the suppression of moisture degradation at the interface.

In this work, we emphasized on our newly developed spray deposition technique with more versatility and better suited to large-scale manufacturing. We utilized both bilayer coating and dual-sources spray strategies to create highly compositionally and functionally graded hybrid film compared with films achieved via traditional dip-coating. XPS depth profiling shows highly graded hybrid films with independent compositional control within 80nm can be achieved via spray coating in the dry regime. We took advantage of the compositional control brought by spray coating to unravel the structure-property relationships in the multi-functional hybrid films by varying components/parameters to fine tune the molecular structure of the resulting film and relate that to its properties obtained from our advanced thin-film mechanical testing techniques together with other chemical characterization techniques (XPS, FTIR, NMR and GCMS). The evolution of the hybrid molecular network during film process and how molecular level details of the hybrid film has a large effect on its mechanical properties were better understood.

Tuesday Afternoon, October 20, 2015

2D Materials Focus Topic

Room: 212C - Session

2D+EM+MC+MI+NS+SP+SS+TF-TuA

Electronic and Magnetic Properties of 2D Materials

Moderator: Thomas Mueller, Vienna University of Technology, Austria, Xiaobo Yin, University of Colorado Boulder

2:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA1 Direct Capacitive Probe of Isospin Order in Graphene Bilayers, Andrea Young**, University of California at Santa Barbara **INVITED**

Bilayer graphene is a highly tunable electronic system in which electric fields can be used to control both the carrier density as well as the electronic structure. Like its monolayer cousin, the bilayer graphene Landau levels are characterized by approximate spin and valley degeneracy; unlike monolayer, however, the three dimensional structure of the bilayer allows control of the sublattice splitting with a perpendicular electric field. This feature has been used extensively to probe the phase diagram of interacting electrons, particularly within the zero energy Landau level, revealing a number of interacting states characterized by spin and/or valley order. Typically, however, the spin or valley order is inferred indirectly by varying conjugate fields and inferring the order from the resulting changes in conductivity. Here I will describe a technique capable of resolving layer-polarization directly through high sensitivity capacitance measurements. The measurements confirm the known features of the bilayer graphene phase diagram, while revealing several new phases and a series of sharp features associated with phase transitions between states of different layer polarization. These features suggest a new mechanism for inversion symmetry breaking in Bernal stacked bilayer graphene.

3:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA3 Patterning Hydrogenated Graphene via Electron Beam Irradiation, Woo-Kyung Lee, K.E. Whitener, J.T. Robinson, P.E. Sheehan**, Naval Research Laboratory

We demonstrate that electron-beam irradiation selectively removes hydrogen atoms from hydrogenated graphene (HG) prepared by the Birch reduction.¹ Hydrogen removal can pattern the surface with two different functionalities. First, we show that partially-hydrogenated graphene (Phg) on a SiO₂ substrate is ferromagnetic, and that the local magnetic strength can be tuned using e-beam irradiation. An e-beam lithography system enables us to modulate or eliminate the permanent magnetization over a large area to produce a patterned magnetic array. Secondly, since removal of the hydrogens converts the highly electrically insulating HG back into conductive graphene, we can write chemically isolated, dehydrogenated graphene nanoribbons (GNR) as narrow as 100 nm. These GNRs have a low sheet resistance ($\geq 31.5 \text{ K}\omega/\square$), only 10x that of the pristine graphene, and their Dirac points before and after e-beam irradiation appear at comparable gate voltages.

1. W.K. Lee et al., *Advanced Materials*, 27, 1774 (2015).

3:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA4 Large-Area Low-Pressure Synthesis of Single-Layer MoS₂ Films and Schottky-Barrier Formation upon Metal Deposition, Michael Gomez, J. Martinez, M. Valentin, L. Bartels**, UC Riverside

Using a high vacuum CVD process we are able to synthesize large area monolayer MoS₂ films. Organic chalcogen precursors are released into the growth chamber and react with a Mo filament creating films up to 2cm² in size that are uniform and free of oxides. The films have pronounced photoluminescence intensity and are in Raman spectroscopy indistinguishable from exfoliated material. Metal contact formation to these films was investigated under UHV conditions utilizing X-Ray Photoelectron Spectroscopy. These measurements permit us to follow the formation of a Schottky Barrier with increasing metal film thickness on the Angstrom scale. We utilize core level spectroscopy to indicate the evolution of the MoS₂ valence band under metal deposition.

4:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA7 Accelerating the Discovery of Alternative Fuel Catalysts through Intelligent Computational Framework, Altaf Karim**, COMSATS Institute of Information Technology, Pakistan **INVITED**

In today's modern world of high performance computing, properties of materials can be predicted with high accuracy before these materials are

ever made. In this scenario my focus has been on the development of state of the art computational framework based on intelligent/ smart self-learning algorithms for the design and discovery of catalytic materials. By giving some examples, I will describe how this enterprise of the predictive multi-scale modeling/simulation has been passing through the stages of its evolution and how these complex algorithmic species integrated themselves into an intelligent python, which is helping scientists design & discover new materials for alternative fuel catalysis. In practice, our computational framework develops databases of candidate catalysts. Further this framework enables a set of algorithms to screen across a broad range of multi metallic catalytic materials with variable reactivity, selectivity, and stability while searching for materials with desired combination of properties required for the optimal catalytic performance for alternative fuel production. I would also explain that how our computational tools in catalyst design deal with the multi-component microstructures of catalysts composed of multi-element nano chunks. In order to tune up the rate limiting processes we can take advantage of the multi-element nano chunks. For example, on many catalytic surfaces the diffusion is rate limiting process for larger organic molecules. To enhance the diffusion such molecules on such surfaces, nano chunks of other materials (on which the diffusion of the organic molecules is comparatively higher) can be integrated in the catalyst's surface, which improves the overall performance of the catalyst in terms of overall reactivity and also selectivity. In addition to that our tools also help us to filter out, from the databases, stable multi-component microstructures of artificially engineered catalysts.

5:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA9 Probing Massive Dirac Electrons in Bilayer Graphene, Feng Wang**, University of California at Berkeley **INVITED**

Electrons in monolayer graphene are described by massless Dirac electrons, which exhibit unique quantum phenomena due to the pseudospin and Berry phase of the massless electrons. In this talk, I will discuss our effort in probing massive Dirac electrons in gapped bilayer graphene. In particular, I will discuss the topologically protected 1D conducting channel at the domain boundary of AB-BA bilayers, which can be attributed to the quantum valley Hall edge states in gapped bilayer graphene.

5:40pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA11 Combining Photoemission and Photoluminescence Microscopy to Study Substrate Transfer Process Effects in Chemical Vapor Deposited MoS₂ Monolayers, Olivier Renault, M. Frégnaux**, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *J. Bleuse*, Univ. Grenoble-Alpes & CEA-INAC, France, *H. Kim*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *D. Voiry, M. Chhowalla*, Rutgers University
Within the perspective of integrating two-dimensional transition metal dichalcogenides (2D TMDs) such as molybdenum disulfide (MoS₂), into devices, it becomes of utmost importance to assess the influence of each step of the device fabrication process on the optical and transport properties of the MoS₂ single layer (1L) domains. Particularly at the deposition stage the properties may be influenced by substrate effects [1], and later, transfer processes may further alter the desired properties of TMDs. This requires effective microscopic characterization techniques.

We present a characterization method combining photoemission microscopy (XPEEM and Kpeem) and photoluminescence microscopy to compare the structural, optical and electronic properties of both as-deposited and transferred MoS₂ 1L domains onto different substrates. XPEEM is used with laboratory sources in both direct space imaging for work function and core-level mapping [2] and particularly in the momentum microscopy mode (k-PEEM) to perform parallel angular imaging and retrieve the band structure in a one shot experiment [3]. Micro-photoluminescence spectroscopy at low (5K) and room temperature is used to detect the specific radiative recombination that occurs in MoS₂ 1L (direct band gap semiconductor behavior) and to evidence the eventual presence of midgap states caused by process-induced defects. The results of both characterization techniques will be presented for MoS₂ 1L domains transferred onto silica and gold substrates highlighting the roles of substrate nature (metal or insulant), surface roughness, and the presence of structural defects whether induced by the preparation process or intrinsic such as grain boundaries.

[1] Jin et al. Phys. Rev. Lett. 111 (2013), 106801.

[2] Kim, Renault, et al. Appl. Phys. Lett. 105 (2014) 011605.

[3] Mathieu et al., PRB 83 (2011) 235436.

Batteries and Supercapacitors**Moderator:** Elijah Thimsen, Washington University, St.

Louis, Andrew C. Kummel, University of California at San

Diego

2:20pm EN+EM+NS+SE+SS+TF-TuA1 Behavior of Layered Cathode**Materials: A Route to Higher Energy Density for Li-Ion Batteries, Marca Doeff, F. Lin, Lawrence Berkeley National Laboratory, I. Markus, Lawrence Berkeley Lab, University of California, Berkeley** **INVITED**

The most promising cathode materials for Li-ion batteries geared towards vehicular applications are the so-called NMCs ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$), based on cost and performance considerations. NMCs exhibit a slightly sloping voltage profile in lithium half-cells, with typical utilizations significantly lower than the theoretical capacity of about 280 mAh/g. An attractive strategy for increasing the energy densities of devices meant for traction applications would be to cycle NMCs to a higher potential than is currently used (usually about 4.3V vs. Li^+/Li) so that more lithium can be extracted and cycled. For this approach to be viable, the cathodes must exhibit excellent structural stability and good reversibility over a wide composition range. Our recent work has been directed towards understanding the high-potential behavior of NMCs, using an array of synchrotron x-ray techniques as well as transmission electron microscopy. These techniques show that surface reconstruction to rock salt and spinel phases occur during high voltage cycling, and result in impedance rises and apparent capacity losses. The degree to which this occurs is a function of how the material is made and its electrochemical history. Partial substitution of Ti for Co in NMCs not only increases the capacities obtained during cycling to 4.7V in lithium half-cells compared to baseline materials, but appears to improve the cycling behavior as well. First principles calculations show that the aliovalent substitution lowers the voltage profile slightly. This allows a greater amount of lithium to be extracted and cycled below 4.7V, resulting in higher practical capacities. The Ti-substitution also delays the formation of rock salt during charging, resulting in better capacity retention. These observations suggest that optimizing the synthesis and judicious substitution can mitigate deleterious structural changes of the NMCs due to high potential operation in Li-ion cells. These strategies should be combined with those designed to prevent side reactions with electrolytic solutions during high potential operation, such as new electrolytic solutions with improved oxidative stability, or atomic layer deposition coatings on electrode surfaces, to further ensure stable cycling.

3:00pm EN+EM+NS+SE+SS+TF-TuA3 Next-Generation Electrolytes for Lithium-Ion Batteries, Sarah Guillot, University of Wisconsin -**Madison, M. Usrey, A. Pena-Hueso, Silatronix, Inc., R.J. Hamers, University of Wisconsin-Madison and Silatronix, Inc.**

Current-generation electrolytes for lithium-ion batteries are limited in electrochemical stability and thermal stability. Over the last several years, researchers at University of Wisconsin and at Silatronix, inc. have developed several new generations of electrolytes based upon incorporation of organosilane groups into the molecular structure. A recently developed class of compounds shows unprecedented enhancements in performance, including the ability to cycle full cells over 400 times at 70 degrees C, and the ability to reduce or eliminate "gassing" at cathode surfaces. In this talk we will discuss the molecular structure of these organosilane-based compounds, quantitative measurements of the decomposition pathways, and the resulting mechanistic insights into the molecular properties that give rise to their outstanding performance characteristics.

3:20pm EN+EM+NS+SE+SS+TF-TuA4 Physico-Chemical Properties of Polyamidoamine Dendrimer-Based Binders for Carbon Cathodes in Lithium-Sulfur Batteries, Manjula Nandasiri, P. Bhattacharya, A. Schwarz, D. Lu, Pacific Northwest National Laboratory, D.A. Tomalia, NanoSynthons LLC, W.A. Henderson, J. Xiao, Pacific Northwest National Laboratory

Lithium-sulfur (Li-S) batteries are one of the most promising energy storage systems, offering up to five-fold increase in energy density as compared with state-of-the-art lithium-ion batteries to meet the growing demand for environmentally benign energy storage devices with high energy density, low cost, and long life time. For practical applications, high sulfur (active material) loading ($> 2 \text{ mg/cm}^2$) within the carbon cathode in Li-S batteries is essential. Most reports on engineered cathode materials for Li-S batteries are based upon low sulfur loadings (typically $\sim 1 \text{ mg/cm}^2$), which are impractical and often give misleading results. It is unknown how these novel engineered cathodes behave under high sulfur loading conditions. The

binder is perhaps the most critical material in achieving a high sulfur loading in carbon cathodes. We have recently used dendrimers with various surface chemistries as functional binders in Li-S cells with SuperP-carbon/S as the cathode material. Even without engineering the cathode, very favorable cycling stability and electrolyte wetting were obtained with these binders. It was attributed to the high density of surface functional groups on the dendrimers, high curvature of the binder and its porosity, and the interactions between the large number of basic nitrogen and oxygen atoms on the dendrimers and lithium polysulfides.

Here, we will discuss the fundamental properties of dendrimers as aqueous binders for Li-S battery cathodes and compare their performance with other aqueous, commonly used linear polymeric binders such as styrene butadiene rubber (SBR) and sodium carboxyl methyl cellulose (CMC). Specifically, generation 4 polyamidoamine (PAMAM) dendrimers with hydroxyl (OH), 3-carbomethoxypropylidone (CMP), and sodium carboxylate (COONa) surface functional groups served as good, electrochemically stable binders at high S loadings ($\sim 3\text{-}5 \text{ mg/cm}^2$) with initial capacities ($> 1000 \text{ mAh/g}$). In comparison to CMC-SBR binder-based electrodes which failed at high C-rates (0.2C) after 40 cycles, dendrimer-based binders showed a capacity retention of $>85\%$ for more than 100 cycles. It was also observed that acidic groups and all- NH_2 surface groups are poor binders, whereas binders with COO^- and neutral surface groups (OH, CH_3) show better performance. X-ray photoelectron spectroscopy was used to identify different surface functional groups in these dendrimers and understand their interactions with SuperP-carbon/S cathode. In addition, a detailed physico-chemical characterization using IR spectroscopy and XANES/EXAFS will be presented to substantiate the superior dendrimer-carbon/S interactions.

4:20pm EN+EM+NS+SE+SS+TF-TuA7 The Road beyond Lithium Batteries is Paved — In Three Dimensions — With Rechargeable, Dendrite-Free Zinc, Debra Rolison, J.F. Parker, C.N. Chervin, I.R. Pala, M.D. Wattendorf, J.W. Long, U.S. Naval Research Laboratory **INVITED**

Lithium-ion batteries dominate the energy-storage landscape, but do so with the ever-present threat of thermal runaway and conflagration courtesy of flammable electrolytes and oxygen-releasing electrode materials. Fortunately, Zn-based batteries offer a compelling alternative grounded in the innate safety and cost advantages of aqueous electrolytes augmented by the high earth-abundance of Zn and the high energy density of Zn-based batteries (comparable to Li-ion). Traditional Zn-based batteries provide suboptimal utilization of the zinc (typically $<60\%$ of theoretical capacity) and poor rechargeability—thanks to the complex dissolution/precipitation processes that accompany Zn/Zn^{2+} cycling of conventional powder-bed Zn electrode structures in alkaline electrolyte. We address these limitations by redesigning the zinc anode as a porous, 3D-wired "sponge" architecture. Zinc sponge electrodes achieve $>90\%$ Zn utilization when discharged in primary Zn-air cells, retaining both the 3D framework of the Zn sponge and an impedance characteristic of the metal thanks to an inner metallic core of 3D zinc. When cycled in Ag-Zn and Ni-Zn cells, the Zn sponges retain monolithicity and reveal uniform deposition of charge/discharge products at the external and internal surfaces, even to deep depth-of-discharge of the zinc. These results show that all Zn-based chemistries can now be reformulated for next-generation rechargeable, Li-free batteries

5:00pm EN+EM+NS+SE+SS+TF-TuA9 Porous Silicon Electrochemical Capacitor Devices for Integrated On-Chip Energy Storage, Donald Gardner, C.W. Holzwarth III, Y. Liu, S. Clendenning, W. Jin, B.K. Moon, Z. Chen, E.C. Hannah, T.V. Aldridge, Intel Corp, C.P. Wang, C. Chen, Florida International University, J.L. Gustafson, Intel Corp

Integrated on-chip energy storage is increasingly important in the fields of internet of things (IoT), energy harvesting, and sensing. Silicon is already the materials of choice for the integrated circuits found in every IoT device; however, the efforts to integrate electrochemical (EC) capacitors on a silicon die have been limited. Unlike batteries, EC capacitors are electrostatic devices and do not rely on chemical reactions enabling cycle lifetimes of $>1\text{M}$. This is especially important for off-power-grid IoT devices where difficulty associated with regularly replacing the batteries of billions of devices is prohibitive. This work demonstrates electrochemical capacitors fabricated using porous Si nanostructures with extremely high surface-to-volume ratios and an electrolyte. Devices were fabricated with tapered channels sized from 100 nm at the top to 20 nm and with aspect ratios greater than 100:1. Surface coatings were necessary for long-term stability because unpassivated silicon structures react with the electrolytes. To obtain uniform coatings using stop-flow atomic layer deposition (ALD), efficient surface reactions are needed between high volatility, low molecular weight, small molecular diameter precursors without chemical vapor deposition side reactions. TiCl_4 and NH_3 precursors were found to coat porous Si with TiN uniformly. Measurements of coated P-Si capacitors reveal that an areal capacitance of up to 6 mF/cm^2 can be achieved using 2 μm deep pores, and scales linearly with depth with 28 mF/cm^2 measured for

12 μm deep pores. Three-terminal CV measurements with EMI-BF₄ ionic electrolyte were used to examine the stability of different pore sizes and TiN coating thicknesses. Pores with an average 50 nm width and 100:1 aspect ratio were stable to ± 1.2 V when cycled at 10 mV/s and stable to ± 1.0 V when cycled at 1 mV/s. Different ionic liquids were studied to determine the ionic liquid best suited to TiN coated porous Si including TEA-BF₄/AN, EMI-BF₄, EMI-Tf, and a 3M EMI-BF₄/propylene carbonate (PC) mixture. Using impedance spectroscopy, the time constant for a 2 μm deep porous Si EC capacitor with a high conductivity TiN coating was found to be 17.6 ms which is fast enough that this can be used for applications involving AC filtering for AC-DC conversion. Measurements of volumetric energy density versus power density of porous Si devices versus other devices show several orders of magnitude higher energy density than electrolytic capacitors with a similar voltage range. These results are also between one to two orders of magnitude higher than other studies utilizing porous silicon and are comparable to commercial carbon-based EC capacitors.

5:20pm EN+EM+NS+SE+SS+TF-TuA10 **Investigations of Magnesium Stripping and Deposition using Operando Ambient Pressure X-ray Photoelectron Spectroscopy**, Yi Yu, Lawrence Berkeley National Laboratory, Q. Liu, Shanghai Tech University, China, B. Eichhorn, University of Maryland, College Park, E.J. Crumlin, Lawrence Berkeley National Laboratory

Since the first demonstration of rechargeable magnesium battery, magnesium metal has been considered as an attractive battery anode due to its high volumetric energy density, high negative reduction potential, natural abundance in the earth crust, and relatively good safety features due to its dendrite-free formation. Although it is well accepted that the dissolution and plating of metal plays an important role in the electrochemical properties related to the discharge and charge of the battery, the nature of metal-electrolyte chemical and electrochemical interaction is still not fully established. In an effort to elucidate the interfacial electrochemical mechanisms, we present the studies of magnesium deposition and stripping using *operando* ambient pressure X-ray photoelectron spectroscopy (AP-XPS). Synchrotron X-rays at the Advanced Light Source, Lawrence Berkeley National Laboratory and our 'tender' X-ray AP-XPS endstation allow for probing the liquid-solid interface at pressures up to 20 Torr. Cyclic voltammetry is employed to examine the reversibility of electrochemical magnesium deposition. This talk will provide details on how *operando* AP-XPS coupled with electrochemistry allows for studying electrochemical processes of magnesium deposition and stripping at the liquid-solid interface and yields chemical information relevant to real-world applications.

5:40pm EN+EM+NS+SE+SS+TF-TuA11 **Atomic Layer Deposition of Solid Electrolytes for Beyond Lithium-Ion Batteries**, Alexander Kozen, G.W. Rubloff, University of Maryland, College Park **INVITED**

Solid Li-based inorganic electrolytes offer profound advantages for energy storage in 3-D solid state batteries: (1) enhanced safety, since they are not flammable like organic liquid electrolytes; and (2) high power and energy density since use of the 3D geometry can maximize the volume of active material per unit area, while keeping the active layer thickness sufficiently small to allow for fast Li diffusion. The quality of thin solid electrolytes is currently a major obstacle to developing these solid state batteries, restricting electrolyte thickness to >100 nm to control electronic leakage, consequently slowing ion transport across the electrolyte and impeding 3-D nanostructure designs that offer high power and energy.

Furthermore, the ion-conducting, electron-insulating properties of solid electrolytes are promising for their use as protection layers on metal anodes (e.g., Li, Na, Mg) and on cathodes in proposed "beyond-Li-ion" battery configurations such as Li-NMC, Li-O₂, and Li-S to prevent electrolyte breakdown.

Atomic layer deposition (ALD) is well suited to the challenge of solid electrolytes, providing ultrathin, high quality films with exceptional 3-D conformality on the nanoscale. We have developed a quaternary ALD processes for the solid electrolyte LiPON, exploiting *in-operando* spectroscopic ellipsometry and *in-situ* XPS surface analysis for process development. ALD LiPON has tunable morphology, and a nitrogen-dependent tunable ionic conductivity as high as 3.5×10^{-7} s/cm.

We explore the potential of ALD solid electrolytes for the fabrication of solid, 3D microbatteries, as well as the use of thin ALD solid electrolyte coatings on metal anodes to improve interfacial stability against organic electrolytes and thus prevent SEI formation. We demonstrate and quantify protection of lithium metal anodes with low ionic conductivity ALD Al₂O₃ coatings to prevent degradation reactions, and probe the surface chemistry and morphology of these anodes. Finally, we demonstrate that protection of Li metal anodes using ALD protection layers can improve the capacity of

Li-S batteries by 60% by preventing anode corrosion by dissolved sulfur species in the electrolyte.

This work has implications beyond the passivation of lithium metal besides its focus and greatest impact on the Li-S battery system, as ALD protection layers could also be applied to other promising metal anode battery systems such as Mg and Na, and other beyond Li-ion technologies such as Li-NMC or Li-Air where similar reactivity issues prevent adoption.

Thin Film

Room: 111 - Session TF-TuA

ALD for Emerging Applications

Moderator: Robert Grubbs, Micron Technology, Erwin Kessels, Eindhoven University of Technology, Netherlands

2:20pm TF-TuA1 **ALD ZnO for Rapid Synthesis of Cu-BTC MOF Thin Films and Patterns**, Junjie Zhao*, W.T. Nunn, P.C. Lemaire, Y. Lin, M.D. Dickey, North Carolina State University, G.W. Peterson, Edgewood Chemical Biological Center, M.D. Losego, Georgia Institute of Technology, G.N. Parsons, North Carolina State University

Metal-organic frameworks (MOFs) are crystalline porous materials that consist of metal ions/clusters and organic linkers. MOFs typically exhibit high surface area, good adsorption capacity and opportunity for post-synthetic modification. However, the insoluble MOF powders typically synthesized through conventional solvothermal methods may not be the ideal configuration for gas filters, chemical sensors and smart membranes etc. Growing MOF thin films onto various functional substrates, especially in a high-throughput process with low energy input, is therefore highly desired for MOF industrial implementation and new applications.

Here we report a rapid room-temperature synthesis route for Cu-BTC (Cu₃(BTC)₂) MOF thin films using ZnO nucleation layers deposited via atomic layer deposition (ALD). We find in just 1 minute of exposure to the Cu-BTC precursor solution, dense Cu-BTC thin films can be integrated onto various ALD ZnO coated substrates including silicon wafers, polymer spheres, and fibrous materials. MOF patterns can also be obtained on pre-patterned ZnO surfaces. The space-time-yield of the Cu-BTC production reaches up to 2.9×10^4 kg·m⁻³·d⁻¹, which is over 10 \times higher than previous reports. We further investigated the surface reactions between ALD ZnO and MOF precursor solutions using high-resolution EDX, XRD and FTIR. The results suggest hydroxyl double salt ((Zn,Cu)(OH)₂NO₃) is an important intermediate to drive the rapid formation of Cu-BTC thin films. Breakthrough tests were performed to demonstrate the high adsorption capacity of these MOF-functionalized materials for toxic industrial chemicals. This rapid room-temperature approach is also promising for new MOF-based composite materials for membrane separation, gas storage, chemical sensing and other applications.

2:40pm TF-TuA2 **Reactions During Atomic Layer Deposition on and in UiO-66-NH₂ Metal Organic Framework Crystals**, Paul Lemaire, J. Zhao, C. Oldham, G.N. Parsons, North Carolina State University

Metal organic frameworks (MOFs) are microporous materials with chemically functionalized high surface areas. MOFs are attractive for multiple applications including filtration, gas storage, and catalysis. Post-synthetic modification (PSM) is a way to impart additional functionality into these materials and most PSM techniques reported are solution based processes. Vapor-phase PSM methods are highly desired due to the advantageous efficiency in reagent and solvent reagent removal.

In this work we report on a fundamental study on the functionalization of the UiO-66-NH₂ MOF through atomic layer deposition (ALD). ALD is a vapor phase self-limiting process that enables the controlled deposition of thin films. The UiO-66-NH₂ MOF is of particular interest for its high thermal and chemical stability and catalytic activity. We investigated how UiO-66-NH₂ interact with ALD precursors, including titanium tetrachloride (TiCl₄), titanium isopropoxide (TTIP), and trimethylaluminum (TMA).

QCM analysis shows that the UiO-66-NH₂ consumes a relatively large amount of precursor in the first exposure, with a ~16% and ~20% for TiCl₄/TTIP and TMA respectively. It is likely that the majority of the MOF pore volume is filled within the first cycle. For the first ALD cycle, purge time ranging 0.5-2.5 hours are necessary to completely remove excess unreacted precursor and byproducts. Following the first cycle, the mass loading per cycle decreases and becomes relatively linear.

* TFD James Harper Award Finalist

In-situ FTIR analysis of the ALD functionalization of UiO-66-NH₂ at 150°C shows that the MOF structure is maintained during the ALD process. Dosing each of the ALD precursors results in a loss of the hydroxyl bands at ~3650, 735, and 675 cm⁻¹, but also a loss of the asymmetric and symmetric carboxylate stretching bands at ~1565 and 1375 cm⁻¹ respectively. Upon water exposure, these bands reappear. These changes in the carboxylate stretching bands was consistent with shifting between the hydroxylated and non-hydroxylated UiO-66-NH₂ structure. Finally, the dehydroxylated UiO-66-NH₂ at 250°C was significantly less reactive towards the ALD precursors, suggesting that hydroxyl sites in UiO-66-NH₂ play a large role in ALD functionalization of the MOF. The ability to deposit metal oxide thin films or nanoparticles within UiO-66-NH₂ pores could help improve the MOF catalytic activity.

3:00pm TF-TuA3 Selective ALD Growth of Pd@Pt Core Shell Nanoparticles and its Application in PROX Reactions. *K. Cao, Q.Q. Zhu, B. Shan*, State Key Laboratory of Material Processing and Die & Mould Technology, China, *Rong Chen*, State Key Laboratory of Digital Manufacturing Equipment and Technology, China

Bimetallic nanoparticles (NPs) have attracted great attention due to their unique properties for catalytic applications. Compared with the physical mixture of monometallic NPs or the alloyed bimetallic NPs, the formation of core shell NPs could further enhance the activity, selectivity and stability. The enhanced properties of core shell structure may originate from the lattice strain, bonding interaction and electron transfer due to the core shell interface. Synthesizing core shell nanoparticles (NPs) with well controlled shell thickness and composition is of great importance in optimizing their reactivity.

Here we report the successful synthesis of core shell NPs using an area-selective ALD technique. The selective ALD approach utilizes pinholes on the unsaturated ODTs SAMs layer to achieve selective core shell structure growth. The size, shell thickness, and composition of the NPs can be precisely controlled by varying the ALD cycles. The catalytic performance of Pd@Pt core shell NPs with different Pt shell thickness have been tested towards preferential oxidation of CO under excess H₂ (PROX) reaction. The results show that the core shell structured NPs exhibit both great selectivity and enhanced activity. Core shell NPs with a completely covered monolayer of Pt shell shows optimized selectivity and activity. Density functional theory simulations have been carried out to explain such behavior of the core shell NPs system towards PROX reactions.

3:20pm TF-TuA4 Thermal and Plasma ALD on Semiconductor Nanowires. *Lachlan Black*, Eindhoven University of Technology, Netherlands, *M.A. Verheijen, A.J. Standing, E.P.A.M. Bakkers*, Eindhoven University of Technology, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Semiconductor nanowires represent a novel class of materials structure with a number of interesting properties that give them potential applications in optoelectronic devices, including light-emitting diodes (LEDs), photoelectrochemical systems, and solar cells. Because of the unusually high surface-to-volume ratio of nanowires, the electrical performance of nanowire devices is especially sensitive to the condition of the semiconductor surface. It is well known that the application of thin-film dielectric and conductive layers to semiconductor surfaces can be an effective means of controlling surface properties. Such layers can provide chemical and electrical passivation, functionalisation, and contacting of semiconductor device surfaces. However, most conventional thin-film deposition techniques face severe challenges when confronted by the high-aspect-ratio features represented by nanowire geometry.

Atomic layer deposition (ALD), on the other hand, is ideally suited to thin film deposition on small-dimensional, high-aspect-ratio structures due to its uniquely self-limiting nature, which results in outstanding uniformity and conformality, and thickness control on the sub-nm level. The application of thin films deposited by ALD to nanowire devices, in order to improve device properties, has previously been reported by a number of authors. However, there has been relatively little effort to systematically study the ALD process on nanowire surfaces in its own right. Nanowires represent an interesting test platform with which to study ALD processes and thin film properties because of the relative ease with which they can be characterised by transmission electron microscopy (TEM).

In this paper we present a fundamental experimental study of ALD on semiconductor nanowires. ALD thin films of various dielectric and conductive materials, including Al₂O₃, TiO₂, ZnO, and HfO₂, are deposited on Si and III-V semiconductor (GaP and InP) nanowire arrays grown by the vapour-liquid-solid (VLS) mechanism, and characterised by high-resolution TEM. Film thickness measured as a function of the number of deposition cycles is used to determine the linearity of the deposition rate and the growth-per-cycle, and these values are compared to those measured on co-deposited planar samples using in-situ and ex-situ ellipsometry. It is shown

that both thermal and plasma-assisted ALD processes are capable of depositing films with excellent conformality and thickness uniformity along the length of the nanowires, although differences are observed for different materials. Moreover, TEM images reveal the presence of clearly defined interfacial layers in some samples.

5:00pm TF-TuA9 Capacitive Deionization for Water Desalination Using Charge Storage in Manganese Oxide Films Grown by Atomic Layer Deposition. *Jasmine Wallas, M.J. Young, C.B. Musgrave, S.M. George*, University of Colorado, Boulder

Capacitive deionization (CDI) is a promising water desalination technique based on the reversible electrosorption of anions (Cl⁻) and cations (Na⁺). Traditional CDI relies on ion storage in the electric double layer (EDL) on the surface of carbon electrodes. Additional ion storage can be achieved through charge storage in thin films of various materials, such as manganese oxide, that are deposited on the electrodes. In this work, we have demonstrated a dramatic improvement in reversible Na⁺ ion storage using MnO₂ films on electrodes prepared using atomic layer deposition (ALD).

The MnO₂ films were prepared by first growing MnO ALD films using bis(ethylcyclopentadienyl) manganese and H₂O on flat Ti electrodes. These MnO films were then electrochemically oxidized to MnO₂. Conversion of MnO to MnO₂ was monitored during electrochemical oxidation with cyclic voltammetry. A large increase in capacitance occurred concurrently with the conversion to MnO₂. The reversible adsorption of Na⁺ under applied potential in NaCl solutions was then confirmed with electrochemical quartz crystal microbalance (E-QCM) analysis. Adsorption of Na⁺ and an elemental composition of Na_{0.25}MnO₂ after Na⁺ adsorption was further verified with x-ray photoelectron spectroscopy (XPS) studies.

MnO₂ films on flat Ti electrodes dramatically increased the ion storage from NaCl solutions. A maximum areal capacitance of 5.6 mF/cm² was observed from MnO₂ films prepared from MnO ALD films with an initial thickness of 447 Å. This areal capacitance is >170 times larger than the areal capacitance of an uncoated Ti electrode. MnO₂ films were also prepared on electrodes composed of high surface area carbon nanotubes (CNTs) using 200 cycles of MnO ALD and electrochemical oxidation. These MnO₂-coated CNT electrodes also displayed a significant increase in areal capacitance compared with uncoated CNT electrodes. These results indicate that MnO₂ coatings on electrodes could substantially enhance the charge storage for CDI and water desalination.

5:20pm TF-TuA10 Magnetoelectric Effect in Multiferroic Nanocomposites of Atomic Layer Deposition Pb(Zr,Ti)O₃ Coupled with Templated Mesoporous CoFe₂O₄. *Diana Chien, A. Buditama, L. Schelhas, S.H. Tolbert, J.P. Chang*, University of California at Los Angeles

Ultra-thin, uniform, and conformal PZT films are needed to engineer nanoscale multiferroic composites with complex architectures. By coupling the piezoelectric PZT film with a magnetostrictive material (e.g. CFO), a magnetization (polarization) can be induced by an applied electric (magnetic) field via the strain-mediated magnetoelectric coupling effect, in which strain is transferred at the interface between the piezoelectric and magnetostrictive layers. Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, an ultra-thin film of PZT can be synthesized with precise control of the film thickness and elemental composition (Zr/Ti = 52/48). ALD provides superior uniformity and conformality over complex surface structures with high aspect ratios.

ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO₂, and TiO₂ layers using Pb(TMHD)₂, Zr(TMHD)₄, and Ti(O-i-Pr)₂(TMHD)₂ as metal precursors and H₂O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. ALD of PZT was studied to obtain (100) oriented Pb(Zr_{0.52}Ti_{0.48})O₃ on Pt (111) oriented silicon substrates. In order to attain a highly oriented PZT thin film, a (100) textured PbTiO₃ seed layer was required because PZT orientation is generally governed by nucleation. The stoichiometry and crystallinity of PZT films were confirmed by XPS and XRD measurements. The conformality was confirmed over high aspect ratio structures.

By controlling the composition, thickness, and conformality of ALD PZT thin films, multiferroic nanocomposites were engineered. Specifically, ALD PZT thin films were shown to uniformly coat the walls of nanoscale templated mesoporous CFO (with neck size of 6 nm in radius) to form a complex 0D-3D nanocomposite. XPS and XRD measurements confirmed the elemental analysis and crystallinity, respectively, of the PZT/CFO nanocomposites. To study the magnetoelectric coupling effect, the nanostructure was electrically poled ex-situ and the resulting magnetic moment was measured via SQUID while sweeping in-plane and out-of-plane magnetic fields. The in-plane results show that there is no change in magnetization as a function of voltage, which is due to the effect of

substrate clamping. The out-of-plane results show that the magnetization changes as a function of voltage. The mesoporous CFO coated with 3 nm thick PZT film shows a greater magnetization change than the 6 nm thick PZT film, suggesting that porosity in the templated mesoporous CFO matrix is needed for a greater magnetoelectric coupling effect.

5:40pm **TF-TuA11 Ultralow Density Metal Oxide Foams by Atomic Layer Deposition on Sacrificial Carbon Nanotube Matrices**, *Jesse Jur, K.L. Stano, P.D. Bradford*, North Carolina State University

Ultralow density materials ($\rho \leq 10 \text{ mg cm}^{-3}$) have recently gained widespread attention, and have been realized in many forms including silica, and carbon-based aerogels, as well as engineered structures such as inorganic micro- and nanolattices. Porous metal oxides, particularly alumina, are desirable due to their semiconducting and dielectric properties as well as thermal, mechanical, and chemical stability. Historically, monolithic alumina aerogels have been fabricated using sol-gel processes. Although this and other self-assembly methods can produce very high surface area aerogels, they have a moderate low density ($\geq 30 \text{ mg cm}^{-3}$), and little to no control over pore size and structure. We present here a method by which aligned CNTFs are used as unique sacrificial templates for the formation of anisotropic, large-scale inorganic nanotube architectures that exhibit the combined characteristics of high surface area, ultralow density, and mechanical robustness. Using ALD, conformal coatings were deposited onto the CNTFs, followed by their removal via calcination in air to leave behind an interconnected network of thin-walled and aligned nanotubes of the ALD metal oxide. Analysis shows that the use of alumina ALD, one can achieve a density as low as 1.2 mg cm^{-3} , 16x lower than previously report alumina foams. Furthermore, both CNT/alumina hybrid foams and pure alumina nanotube foams exhibit unprecedented elastic recovery following 50% compression, and possess values for strength and Young's moduli which exceed those of aerogels with similar densities. The scaling behavior of Young's modulus to foam density for pure alumina foams exhibits a power-law dependence of $n \approx 1.9$, attributed to superb ligament connectivity. As a low thermal conductivity insulation, a foam of 1 cm thickness is demonstrated to reduce a flame temperature of 1000°C to 45°C after 5 min of direct flame contact.

6:00pm **TF-TuA12 The Structure and Optical Properties of ALD W:Al₂O₃ Nanocomposite Films**, *Shaista Babar, A. Mane, Argonne National Laboratory, A. O'Mahony, Incom, Inc., A. Yanguas-Gil, J. W. Elam*, Argonne National Laboratory

A highly robust W:Al₂O₃ nanocomposite material has been reported by ALD method and used in microchannel plates (MCPs) and MEMS devices [1,2]. By adjusting the W cycle percentage during the nanocomposite synthesis, the resistivity can be tuned in the range of $10^{12} - 10^8 \Omega$. Here we report a systematic study of the structure and optical properties of ALD deposited nanocomposite W:Al₂O₃ films using SEM, TEM, XRD, XRR, XPS, ellipsometry and UV-vis-IR spectroscopy. General oscillator and Kramers-Kronig consistent B-spline models were used to extract the optical constants of the films. We studied the impact of the composition and microstructure on the optical properties of W:Al₂O₃ layers as ALD cycle ratio and metal contents. We report a systematic decrease in the bandgap associated with the increase in the W content. We also discuss the high thermal stability and high absorptivity of W:Al₂O₃ and propose it as an ideal candidate for concentrated solar power receivers .

References:

[1] Atomic layer deposition of W:Al₂O₃ nano-composite films with tunable resistivity,

Anil U. Mane, Jeffrey W. Elam, Chemical Vapor Deposition, 19(4-6), (2013) 186

[2] Nanostructured composite thin films with tailored resistivity by atomic layer deposition

Anil U. Mane, Jeffrey W. Elam, SPIE 2013

Wednesday Morning, October 21, 2015

2D Materials Focus Topic

Room: 212C - Session 2D+MN+NS+SP+SS+TF-WeM

Mechanical and Thermal Properties of 2D Materials

Moderator: Oleg Yazev, Ecole Polytechnique Fédérale de Lausanne (EPFL), Petra Reinke, University of Virginia

8:00am **2D+MN+NS+SP+SS+TF-WeM1 Mechanical Properties of Polycrystalline Graphene.** *Joseph Gonzales*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory, *I.I. Oleynik*, University of South Florida

Experimental investigation of mechanical properties indicates that the polycrystalline graphene grown by chemical vapor deposition is as strong as pristine. The microscopic characterization of graphene samples using Atomic Force microscopy (AFM) nano-indentation is limited in the sense that the detailed mechanical characteristics such as stress and strain distributions under the indenter, elastic moduli and breaking strength are not available directly from experiment. Using accurate description of interatomic interactions provided by novel screened environment-dependent bond order, (SED-REBO) potential, we performed large-scale molecular dynamics investigations of mechanical properties of polycrystalline graphene under conditions mimicking nano-indentation AFM experiments. The atomically resolved characterization of the stress and strain distributions under indenter are used to understand detailed mechanisms of graphene strength and failure. The breaking strength, the crack initiation and propagation are investigated as a function of the grain boundary structure and the grain size distribution as well as the position of the indenter – at the center of the grain, at the a single grain boundary and at the junction of three or more grain boundaries.

8:40am **2D+MN+NS+SP+SS+TF-WeM3 Lévy Flights Found in Freestanding Graphene.** *Paul Thibado*, University of Arkansas, *M. Neek-Amal*, *F. Peeters*, University of Antwerp, Belgium

Local, long-time evolution measurements of the height fluctuations of a 2D membrane allows examination of the fundamental foundations of statistical mechanics in soft condensed matter. However, such measurements have proved elusive, thereby forcing critical theoretical assumptions in the best models. We report sub-nanometer, high-bandwidth height measurements of freestanding graphene using constant-current, point-mode scanning tunneling microscopy, as a follow-up to our previous related works [1-2]. By tracking atoms directly, the ability to measure dynamic events is increased by a factor of 1000 over the present state-of-the-art membrane imaging technology. Surprisingly, the membrane velocities follow the Cauchy-Lorentz distribution consistent with a Lévy process, rather than the expected Maxwell-Boltzmann distribution. We introduce a new theoretical approach using fractional-stochastic calculus.

Acknowledgements:

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References:

- [1] P. Xu, M. Neek-Amal, S.D. Barber, J.K. Schoelz, M.L. Ackerman, P.M. Thibado, A. Sadeghi, and F.M. Peeters, *Nature Comm.* **5**, 3720 (2014).
- [2] M. Neek-Amal, P. Xu, J.K. Schoelz, M.L. Ackerman, S.D. Barber, P.M. Thibado, A. Sadeghi, and F.M. Peeters, *Nature Comm.* **5**, 4962 (2014).

9:00am **2D+MN+NS+SP+SS+TF-WeM4 Multilayer Graphene Strength Characterization.** *Joseph Rowley*, *N. Boyer*, *K. Berry*, *R.C. Davis*, Brigham Young University, *R. Creighton*, *J. Abbott*, *S. Cornaby*, *M. Harker*, Moxtek Inc., *R. Vanfleet*, Brigham Young University

Although there are many examples in the literature of multilayer graphene fabrication and electrical characterization, there is a lack of data on the mechanical properties of multilayer graphene, especially many layer. Conversely there is data about the mechanical properties of single layer graphene, and limited information about bilayer and few layer, but little about many layer. Multilayer Graphene was fabricated using chemical vapor deposition on a Nickel catalyst. Different flow rates and cooling rates were investigated to produce many layer films. Due to the high strength in graphene, these films were able to be suspended over millimeter size openings and have a differential pressure applied. This allowed for the characterization of the strength of these membranes using bulge testing.

9:20am **2D+MN+NS+SP+SS+TF-WeM5 Nanoelectromechanical Systems Based on 2D Materials beyond Graphene – Effects from Geometry, Nonlinearity, and Anisotropy.** *Zenghui Wang*, Case Western Reserve University **INVITED**

Investigating and manipulating the mechanical degree of freedom in two-dimensional (2D) nanostructures present unique challenges and opportunities: such effort demands advanced fabrication and measurement schemes, and offers new insight into the physical properties of 2D materials. I will present our explorations and findings in mechanical processes at the nanoscale, through studying resonant nanoelectromechanical systems (NEMS) based on 2D materials beyond graphene (e.g., molybdenum disulfide, black phosphorus, etc.). I will discuss the implications of geometrical irregularities on the nanomechanical responses of 2D-material-based resonators; impacts of device and material parameters on the mechanical nonlinearity and motional noise in 2D resonant transducers; and effects of material anisotropy in nanomechanical resonators based on new types of highly anisotropic 2D materials. These findings open new pathways towards nanomechanical coupling and tuning of the physical properties in 2D nanomaterials, and offer opportunities for building novel devices with new multimode functions.

11:00am **2D+MN+NS+SP+SS+TF-WeM10 Phonon Spectroscopy of Graphene Field Effect Devices with the STM.** *Fabian Natterer*, *Y. Zhao*, *J. Wyrick*, NIST/CNST, *W.Y. Ruan*, *Y.-H.C. Chan*, *M.-Y.C. Chou*, Georgia Institute of Technology, *N.B. Zhitenev*, *J.A. Stroscio*, NIST/CNST

Phonon spectroscopy of graphene by inelastic electron tunneling spectroscopy with the STM has been elusive in previous measurements [1–3]. The difficulty lies within the weak phonon signatures that are buried by other dominant spectral features that inhibit a clear distinction between phonons and miscellaneous excitations. Utilizing a back gated graphene device that permits continuous adjustment of the global charge carrier density, we employ an averaging method where individual tunneling spectra at varying charge carrier density are condensed into one representative spectrum [4]. This method improves the signal for inelastic transitions that appear at constant threshold, while it broadens and thereby suppresses dispersive spectral features. We use this method to demonstrate the mapping of the total graphene phonon density of states, in good agreement with density functional calculations. Using the knowledge about the phonons thusly obtained, we closely examine our gate resolved spectra and observe a surprising and abrupt change in the phonon intensity when the graphene charge carrier type is switched through a variation of the back gate electrode potential. This sudden variation in phonon intensity is asymmetric in carrier type, depending on the sign of the tunneling bias. We invoke a resonance mediated tunneling process that relies on the presence of tip-induced quasi-bound state resonances in graphene, resembling whispering gallery modes for electrons and holes [5]. Our tip-sample system thereby mimics a giant molecular state and shares analogies with resonant enhanced excitations of molecular vibrational or rotational modes [6–9].

- [1] Y. Zhang, V. W. Brar, F. Wang, C. Girit, Y. Yayon, M. Panlasigui, A. Zettl, and M. F. Crommie, *Nature Phys* **4**, 627 (2008).
- [2] V. W. Brar, S. Wickenburg, M. Panlasigui, C.-H. Park, T. O. Wehling, Y. Zhang, R. Decker, Ç. Girit, A. V. Balatsky, S. G. Louie, A. Zettl, and M. F. Crommie, *Phys. Rev. Lett.* **104**, 036805 (2010).
- [3] G. Li, A. Luican, and E. Andrei, *Phys. Rev. Lett.* **102**, 176804 (2009).
- [4] C. E. Malec and D. Davidović, *Journal of Applied Physics* **109**, 064507 (2011).
- [5] Y. Zhao, J. Wyrick, F. D. Natterer, J. F. Rodriguez-Nieva, C. Lewandowski, K. Watanabe, T. Taniguchi, L. S. Levitov, N. B. Zhitenev, and J. A. Stroscio, *Science* **348**, 672 (2015).
- [6] J. Gadzuk, *Phys. Rev. B* **31**, 6789 (1985).
- [7] B. Persson and A. Baratoff, *Phys. Rev. Lett.* **59**, 339 (1987).
- [8] A. Baratoff, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **6**, 331 (1988).
- [9] F. D. Natterer, F. Patthey, and H. Brune, *ACS Nano* **8**, 7099 (2014).

11:20am **2D+MN+NS+SP+SS+TF-WeM11 Edge-state-induced Stabilization of Dopants in Graphene.** *Yuuki Uchida*, *A. Akashi*, *J. Nakamura*, The University of Electro-Communications (UEC-Tokyo) and JST CREST, Japan

Impurity doping is an efficient way to modify electronic properties of graphene. Several groups have reported the stability of dopants in graphene, especially near edges of graphene: Impurity atoms prefer to locate at the zigzag edge of graphene rather than the armchair one[1]. It has also been

reported that the electronic properties are strongly dependent upon the location of dopants, which is derived from the non-equivalence of the two sublattice[2]. It is well-known that the edge-localized state emerges at the zigzag edge[3], which is specific for the so-called bipartite lattice. However, it has not been clarified yet how the edge-state affects the dopant stability depending on the sublattice. In this study, we investigate the role of the sublattice-dependent edge-state on the stabilization of impurities. We evaluate the dependence of the structural stability on the distance of impurity atoms from the zigzag edge using first-principles calculations within the density-functional theory. We have employed two types of graphene nanoribbons (GNRs) with the armchair- (AGNR) or the zigzag- (ZGNR) edge.

For AGNR, the formation energy of dopants does not change neither systematically nor monotonically as a function of the distance from the edge. On the other hand, for ZGNR, the formation energy is lower than that for AGNR and decreases with decreasing distance from the edge. In addition, two types of tendencies are confirmed for odd- and even-numbered sites from the zigzag edge, corresponding to the different sublattices of the bipartite lattice.

Such peculiar behavior as for of the formation energy can be explained as follows : The doped N atom donates its electron to the unoccupied-edge-state just above the Fermi level, resulting in the lowering of the one-electron energy of this state. The smaller the distance of N atoms from the zigzag edge is, the larger the electrostatic attraction between electrons of edge-localized states and positively-charged ion-shell at the N site becomes. Further, N atoms are much more stabilized at the odd-numbered site, because the edge-state has finite amplitude only at the odd-numbered sites.

[1]S. F. Huang et al., Phys. Rev. B, **80**, 235410 (2009)

[2]J. Jiang et al., J. Chem. Phys. **136**, 014702 (2012)

[3]M. Fujita et al., J. Phys. Soc. **65**, 1920 (1996)

11:40am **2D+MN+NS+SP+SS+TF-WeM12 Exploring the Thermal Stability of Two-Dimensional Black Phosphorus, Xiaolong Liu, J.D. Wood, K.-S. Chen, E. Cho, M.C. Hersam**, Northwestern University

Two dimensional (2D) black phosphorus (BP) has attracted significant attention due to its superlative electronic and optical properties. Unlike graphene, its intrinsic and thickness-dependent band gap makes it feasible for direct application in electronic and optoelectronic devices.¹ However, before 2D BP can be effectively employed in such applications, it is necessary to establish the thermal stability of 2D BP since annealing is a key element in most device fabrication processes. Towards this end, we have utilized *in situ* scanning/transmission electron microscopy and spectroscopy methods to characterize the thermal decomposition process of mechanically exfoliated 2D BP.² The decomposition is observed to occur at ~400 °C in the form of sublimation, compared to the 550 °C of bulk BP. This decomposition initiates *via* eye-shaped cracks along the [001] direction and then continues until only a thin, amorphous red phosphorous-like skeleton remains. *In situ* electron energy loss spectroscopy, energy-dispersive X-ray spectroscopy, and energy-loss near-edge structure changes provide further quantitative insight into this chemical transformation process.

(1) Qiao, J.; Kong, X.; Hu, Z.-X.; Yang, F.; Ji, W. *Nature Comm.* **2014**, *5*, 4475.

(2) Liu, X.; Wood, J. D.; Chen, K.-S.; Cho, E.; Hersam M. C. *J. Phys. Chem. Lett.* **2015**, *6*, 773-778.

12:00pm **2D+MN+NS+SP+SS+TF-WeM13 Gas Permeation Through 1 nm Thick Carbon Nanomembranes, A. Beyer, M. Ai, Bielefeld University, Germany, S. Shishatskiy, J. Wind, Helmholtz-Zentrum Geesthacht, Germany, X. Zhang, V. Chinaryan, Y. Yang, Armin Götzhäuser, Bielefeld University, Germany**

The gas permeation characteristics of 1 nm thick carbon nanomembranes (CNMs) from self-assembled monolayers are reported. The assembly of CNMs onto polydimethylsiloxane (PDMS) support membranes allows determination of gas permeation characteristics. Single layer and triple layer CNMs were investigated in respect to permeation of hydrogen, helium, carbon dioxide, oxygen, nitrogen, argon, methane and ethane. In addition, the CNM-PDMS composites were characterized by X-ray photoelectron spectroscopy, helium-ion microscopy as well as atomic force microscopy. A careful analysis about the contribution of the PDMS support membranes to the gas permeation allowed an estimate of the intrinsic CNM permeances. These values indicate a molecular sieve-like property of CNMs which is attributed to molecular-sized channels in CNMs. As an example, hydrogen and carbon dioxide gas molecules display an order of magnitude higher permeance values for single layer CNMs in comparison to oxygen and nitrogen, which possess larger kinetic diameters.

Additive Manufacturing/3D Printing Focus Topic Room: 211B - Session AM+EM+MS+TF-WeM

Materials, Designs, and Applications of Additive Manufacturing

Moderator: Erik B. Svedberg, The National Academies

8:00am **AM+EM+MS+TF-WeM1 An Overview of Additive Manufacturing, Ed Morris, R. Gorham, NCDMM INVITED**

“An Overview of Additive Manufacturing” - Additive manufacturing, also called 3D printing, has captured worldwide attention. Many believe that it is introducing the next industrial revolution because of its impact on product innovation and its unique manufacturing capabilities. America Makes – National Additive Manufacturing Innovation Institute is the first Manufacturing Innovation Institute established as part of a National Network for Manufacturing Innovation. Mr. Ed Morris, Director of America Makes and Vice President, National Center for Defense Manufacturing and Machining, will give an overview of additive manufacturing, and will discuss America Makes’ actions to accelerate the use of additive manufacturing technologies in the United States and increase our nation’s global manufacturing competitiveness.

8:40am **AM+EM+MS+TF-WeM3 Material Considerations and Opportunities for Laser Powder Bed Additive Manufacturing, Michael W. Peretti, D.H. Abbott, General Electric Aviation INVITED**

Additive Manufacturing (AM) has the potential to be a significant supply chain disruptor over traditional means for manufacturing a broad range of components for aerospace and other demanding applications. The ability to unlock complex, high-performance designs while reducing part count and number of manufacturing steps is beginning to revolutionize the way we think about making things. One of the key areas of development to further expansion of opportunities for AM is the production and supply of high-quality raw materials. This presentation discusses the critical issues for AM input raw materials, with particular emphasis on metal powder input stock for laser powder bed AM processes. Some background and experience from GE Aviation’s development of the LEAP fuel nozzle will be shared, along with comments on the direction that the AM industry could take and the role of and potential for AM-specific metal powder alloys.

9:20am **AM+EM+MS+TF-WeM5 High Quality and High Speed EBM 3D Printing by the Integration of High Performance Electron Sources, Colin Ribton, TWI Ltd., UK, S. del Pozo, TWI Ltd. and Brunel University, UK**

Production of high integrity components must use smart manufacturing methods to be efficient in use of scarce materials and other resources, and must ensure its environmental impact is minimized. Advanced manufacturing techniques, such as metal powder bed 3D printing, can be carried out by selective laser melting (SLM) or electron beam melting (EBM). In both cases the component is built layer by layer, with a beam as an intense energy source drawing each layer by melting powder. EBM is significantly faster than SLM and has been used to create metal parts in large quantities over the past 5 years. EBM machines have produced many tens of thousands of orthopedic implants. There are a number of key benefits in employing this manufacturing technology – including ‘complexity for free’, efficient use of material and flexibility of design. Increasingly, the aerospace industry is investigating the use of EBM for the manufacture of aircraft components and aero engine parts. However, the size of many of these components presents challenges to the EBM process in production rate and quality consistency over long build times (i.e. 150 hours).

The aim of this work is to overcome key obstacles concerning future requirements for EBM 3D printing for production of aerospace parts through the integration of two enabling technologies. The work will develop and integrate a novel plasma cathode electron source with an EBM machine focusing on realizing the enhanced capabilities of low maintenance, consistent manufacturing performance and higher productivity. Also, development and integration of an array probe device will provide quantified quality assurance of machine manufacturing readiness. The key research challenges will be the design of the electron source and optics and the development of new build procedures making best use of the new source.

The equipment will enable the wider adoption of EBM leading to efficient use of materials – particularly strategic titanium alloys and nickel based super alloys at first.

9:40am **AM+EM+MS+TF-WeM6 Laser Induced Forward Transfer of High-Viscosity, Polymer-Based VO₂ Inks**, *Eric Breckenfeld, H. Kim, T. Sutto, N. Charipar, A. Piqué*, Naval Research Laboratory

Additive manufacturing direct-write processes such as direct-write assembly, micropen, inkjet, and laser-induced forward transfer (LIFT) have become increasingly popular as interest in printable electronics and maskless patterning has grown. Compared to conventional lithography, these additive manufacturing processes are inexpensive, environmentally friendly, and well suited for rapid prototyping and large-area applications. At the same time, researchers have pursued various chemical solution deposition processes for combining additive manufacturing technology with functional electronic materials. Among a multitude of transition-metal oxides, vanadium dioxide (VO₂) has emerged as a material of particular interest due to its sharp semiconductor-to-metal phase transition near room temperature. A set of distinct optical and electronic properties which arise as a result of this transition have made VO₂ popular for thermochromic coatings, resistive switching, optical storage, light modulators, and other applications. Here, we demonstrate the development of a polymer-based solution for the deposition of VO₂ thin films. By exploring a variety of sintering and annealing conditions as well as exploring different polar solvents, we have optimized the growth of these films on glass and crystalline substrates. We go on to explore printing of VO₂ devices via the LIFT technique, which is notable for its ability to print high-viscosity inks and pastes. Finally, we will discuss our efforts toward the development of low temperature laser sintering in order to realize VO₂ films on substrates incompatible with high furnace temperatures.

11:40am **AM+EM+MS+TF-WeM12 Printing Multi-Functionality using Additive Manufacturing**, *Ryan Wicker*, University of Texas at El Paso

INVITED

Since the commercial introduction of Additive Manufacturing (AM) technologies more than two decades ago, considerable advancements in processing speed, accuracy, resolution and capacity have been achieved and the available AM materials have expanded considerably, enabling customized end-use products to be directly manufactured for a wide range of applications. Many AM technologies have been released that use different processes for fabricating the individual layers from a variety of liquid, solid, and powder-based materials ranging from photoreactive polymers to metals. In 2000, the University of Texas at El Paso identified AM as an emerging technology and invested strategically in establishing the W.M. Keck Center for 3D Innovation (Keck Center). The Keck Center has grown to occupy over 13,000 sq. feet with more than 50 commercial and experimental AM machines, representing 10 system manufacturers, nine distinct layer processing methods, and several custom AM-based patented and patent-pending systems. One particular focus of Keck Center research is on developing the methods and systems required to have automated control over material placement and structure creation, leading to, for example, the realization of complex 3D devices that integrate electronics and thus intelligence within mechanical structures as well as 3D spatially complex bioactive, implantable, tissue engineered constructs. There are myriad issues associated with combining multiple materials to create functional products – from the deposition and processing of different materials to the combined performance of the materials in the resulting product. Despite these issues, the opportunities for AM in aerospace, defense, biomedical, energy and enumerable other applications continue to expand as the achievable length scales in AM decrease, the number of materials available for use in AM increases, the performance of these materials are characterized and controlled in the final product, and new strategies for integrating AM with other manufacturing technologies are successfully demonstrated.

Plasma Science and Technology

Room: 210A - Session PS+SS+TF-WeM

Atomic Layer Etching (ALE) and Low-Damage Processes I

Moderator: Geunyoung Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS+SS+TF-WeM1 Atomic Layer Etching to Escape Process Tradeoffs for 7nm Technology and Beyond**, *Alok Ranjan, M. Wang, S. Sherpa*, TEL Technology Center, America, LLC, *P. Ventzek*, Tokyo Electron America, Inc.

INVITED

With shrinking critical dimensions, dry etch faces more and more challenges. Minimizing each of aspect ratio dependent etching (ARDE), bowing, undercut, selectivity, and within die uniformity across a wafer are met by trading off one requirement against another. The problem of trade-

offs is especially critical for 10nm and beyond technology. At the root of the problem is that roles radical flux, ion flux and ion energy play may be both good and bad. Increasing one parameter helps meeting one requirement but hinders meeting the other. Self-limiting processes like atomic layer etching (ALE) promise a way to escape the problem of balancing trade-offs. ALE [1] was realized in the mid-1990s but the industrial implementation did not occur due to inherent slowness and precision loss from improper balance of self-limiting passivation and its removal processes. In recent years interest in ALE has revived and strides have been made by etch equipment manufacturers primarily through temporal, spatial or combination of these two pulsing approaches. Moderate success has been reported with some of the trade-offs purported to be managed. Difficulty meeting requirements is due to the inability of plasma technologies to control ion energy at low and precise values.

We overcome many of the practical implementation issues associated with ALE by precise passivation process control using plasmas with low electron temperature. Very low plasma potential, high radical flux and high bombardment flux are indispensable for achieving ALE. We demonstrate that ALE can achieve zero ARDE and infinite selectivity. Experimental results will highlight that careful consideration of surface process physics is required to achieve ALE and not simply “slow etching”. Without profile control, ALE is not useful. Profile control will be shown to rely on careful management of the ion energies and angles. For ALE to be realized in production environment, tight control of IAD is a necessary. Experimental results are compared with simulation results generated using MCFPM [2] and theoretical scaling models to provide context to the work.

[1] S. Athavale and D. J. Economou, *J. Vac. Sci. Technol. B*, 14, 3702 (1996).

[2] M. Wang and M. J. Kushner, *J. Appl. Phys.*, 107, 023308 (2010)

8:40am **PS+SS+TF-WeM3 Understanding of new processes for Atomic Layer Etching**, *Florentin Chambettaz, L. Vallier, J. Dubois*, Univ. Grenoble Alpes-CNRS-CEA/Minatex-LTM,38000 Grenoble-France, *O. Joubert*, Univ. Grenoble Alpes-CNRS-CEA, France

In the pace of downscaling in microelectronic, current plasma etching processes show their limits. Actually for critical dimension smaller than 10 nm, atomic precision has to be reached during etching. In this study we are developing an Atomic Layer Etching (ALE) process by focusing on the induced damages related to the chemical and physical interaction(s) with hydrogen (This subject has already been broached in other studies on graphene [1] or carbon nanotubes [2]) and helium plasmas. Hydrogen plasmas have been used for years in the microelectronic industry and studied in the fields of deposition (PECVD, Plasma Enhanced Chemical Vapor Deposition), surface processing (surface passivation, hydrogenation) and plasma etching [3]. However the mechanisms related to these processes are not fully understood yet mainly because hydrogen is an element with peculiar characteristics such its low mass and its electronegativity. Helium plasmas have been also used for many years in the microelectronics industry. Helium is often employed in plasma processes as an additives gas due to its low chemical reactivity and low mass. Consequently ionic species present in the plasma and their effect are well known. To modify the surface of ultrathin layers without damaging the materials, a very low ion bombardment is required (conditions similar to those obtained in a pulsed ICP reactor [4]). At the same time, high energy plasmas are required to obtain satisfying etch rates when several nanometers have to be etched away. In this study we focus on plasma etching of silicon nitride by hydrogen plasma exposure in a commercially available 300 mm reactor, in order to develop an ALE process for spacer etching of future 10nm transistors. Several process conditions are achieved with different ion energies and ion densities, on thin silicon nitride blanket samples. The generated damages in the structure were quantified with an Electron Spin Resonance (ESR) spectroscopy and electrical characterization. The effect of these etching processes on silicon nitride will be discussed.

1. E.Despiau-Pujo, A.Davydova, G.Cunge, L.Delfour, L.Magaud, and D. B.Graves, *Journal of Applied Physics*, **113** (2013)

2. A.Hassanien, M.Tokumoto, P.Umek, D.Vrbancic, M.Mozetic, D.Mihailovic, P.Venturini, and S.Pejovnik, *Nanotechnology*, **16**, 278 (2005)

3. M.Sode, T.Schwarz-Selinger, and W.Jacob, *Journal of Applied Physics*, **113** (2013)

4. C. Petit-Etienne, M. Daron, P. Bodart, M. Fouchier, G. Cunge, E. Pargon, L. Vallier, O. Joubert, and S.Banna, *Journal of Vacuum Science & Technology B*, **31** (2013)

9:00am **PS+SS+TF-WeM4 Self-Limited Ion Implantation for Precise Low-k Spacer Etching**, *Nicolas Posseme*, Cea-Leti, Minatec, France, *M. Garcia-Barros*, *C. Arvet*, ST Microelectronics, *O. Pollet*, Cea-Leti, Minatec, *S. Lagrasta*, *P. Maury*, ST Microelectronics, *F. Leverd*, ST Microelectronics, *C. Richard*, ST Microelectronics, *S. Barnola*, Cea-Leti, Minatec, France

With aggressive device shrinking, parasitic capacitances through the spacer become a greater contributor to the total device capacitance. This issue is exacerbated by the common use of SiN spacers. Since SiN has a relatively large dielectric constant ($k \sim 7.5$), a simple approach to reduce capacitive coupling through the spacer is to supplant it with a low-k material [1]. Therefore, the reduction of spacer k value is a key for the high performance devices. In this context, Low-k films like SiCO, SiOCN or SiBCN have been proposed for the C014 technology node to replace the traditional silicon nitride investigated.

Today, the Low-k spacer etching is considered as one of the most challenging step in the high performance FDSOI devices realization. A trade-off has to be found between silicon germanium (or silicon) recess, foot formation and CD control impacting the device performances. The etch process must also be compatible with epitaxial step.

In a recent study, we proposed a new etch approach [2] for silicon nitride spacer etching. This new etching process is based on a Self-Limited Ion Implantation by plasma. In a first step, the film is modified in volume by a Hydrogen plasma performed in a conventional etch tool (CCP or ICP) followed in a second step by a 1%HF wet cleaning to remove the modified layer selectively to the non-modified material. We demonstrated that the silicon germanium recess was estimated to less than 6Å with no foot formation, while a silicon germanium has grown by epitaxy without defects [2].

In this study, we propose to evaluate the compatibility of this new etch approach with low-k films like SiCO or SiBCN. By playing on plasma operating conditions performed in ICP etch tool, we will demonstrate that the Low-k films can accurately be etched with atomic layer control, stopping on SiGe or Si. The key parameters for such etch precision are identified as H ion energy and H ion dose implanted in the low-k film. The etch mechanisms to remove the modified layer by wet cleaning process will be understood on blanket wafers thanks to XPS and infrared spectroscopy analyses.

Finally the compatibility of this new Low-k spacer etching process with the epitaxial step will also be presented for C014 FDSOI integration.

References

[1] H. Niebojewski, C. Le Royer, Y. Morand, M-A. Jaud, O. Rozeau, E. Dubois, T. Poiroux, "Extra-low Parasitic Gate-to-Contacts Capacitance Architecture for sub-14nm Transistor Nodes", IEEE Euro SOI conference, 2013

[2] N.Posseme, O. Pollet, S.Barnola, "Alternative process for thin layer etching: Application to nitride spacer etching stopping on silicon germanium", Appl. Phys. Lett. 105, 051605 (2014)

9:20am **PS+SS+TF-WeM5 Self-limiting Cyclic Etching of Silicon Nitride using Infrared Irradiation**, *Nobuya Miyoshi*, Hitachi, Japan, *H. Kobayashi*, *K. Shinoda*, Hitachi, *M. Matsui*, Hitachi, Japan, *M. Miyake*, *K. Maeda*, Hitachi, *Y. Kouzuma*, Hitachi High-Technologies, Japan, *Y. Kudo*, *T. Kanekiyo*, *M. Izawa*, Hitachi High-Technologies

Advanced semiconductor device fabrication requires precise control of device dimensions down to the atomic level. Current efforts to achieve atomic level control are focused on cyclic etching that repeatedly forms and removes a reactive layer on a surface. The cyclic etching of SiO₂, for example, has been achieved by repeatedly forming and removing of ammonium hexafluorosilicate ((NH₄)₂SiF₆) [1]. The essential point in realizing atomic level control is achieving a self-limiting process.

Fluorocarbon-based plasma produces a (NH₄)₂SiF₆ layer on silicon nitride surfaces [2]. We have reported the preliminary results of the cyclic etching of silicon nitride using the formation and removal of the (NH₄)₂SiF₆ layer [3]. An analysis using x-ray photoelectron spectroscopy (XPS) revealed that the (NH₄)₂SiF₆ layer formed on silicon nitride after exposure to fluorocarbon-based plasma and was desorbed by annealing the sample.

In this study, the removal of the (NH₄)₂SiF₆ layer using IR irradiation was investigated to achieve high-throughput cyclic etching. The reactive layer of (NH₄)₂SiF₆ was formed on a silicon nitride sample after exposure to radicals in fluorocarbon-based plasma. After formation of the reactive layer, IR light was irradiated to the sample for removal. The sample surface was analyzed by XPS, and the dependence of the etching depth on the radical exposure time was investigated. The temperature of the sample increased over 160°C under IR irradiation for 10 s. A nitrogen 1s peak at 402 eV, which is attributed to (NH₄)₂SiF₆, disappeared after IR irradiation for 10 s. This result shows that IR irradiation is expected to result in fast removal of the reactive layer within 10 s. The etching depth after IR irradiation saturated at

1 nm as the radical exposure time was increased to over 300 s. Therefore, a self-limiting process for silicon nitride was obtained by forming and removing the (NH₄)₂SiF₆ layer. Finally, the cyclic etching was investigated by repeatedly forming and removing the reactive layer. The number of cycles was changed between 1 and 10. The total etching depth increased linearly with the number of cycles, demonstrating the cyclic etching of silicon nitride with high precision.

[1] H. Nishio, et al., J. Appl. Phys. **74**, 1345 (1993).

[2] W. R. Knolle et al., J. Electrochem. Soc. **135**, 2574 (1988).

[3] K. Shinoda et al., AVS Atomic Layer Etching workshop 2015 (2015).

9:40am **PS+SS+TF-WeM6 Prospects for Thermal Atomic Layer Etching: Materials and Selectivity**, *Steven George*, *Y. Lee*, *J.W. DuMont*, University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al₂O₃ and HfO₂ has recently been demonstrated using sequential, self-limiting reactions [1-3]. Al₂O₃ and HfO₂ ALE were performed using Sn(acac)₂ and HF as the reactants [1-3]. Recent work has also shown that Al₂O₃ ALE can be accomplished using Al(CH₃)₃ and HF as the reactants. The ALE reaction mechanism is believed to involve fluorination and ligand-exchange. For Al₂O₃ ALE using Sn(acac)₂ and HF, HF exposures convert Al₂O₃ to AlF₃. Sn(acac)₂ then accepts F from AlF₃ and donates acac to AlF₃ to produce volatile Al(acac)₃ or AlF(acac)₂.

The prospects for thermal ALE are very promising. Thermochemical calculations suggest that many materials should be etched with similar reactions. Metal oxides, metal nitrides, metal phosphides, metal arsenides and elemental metals can all be fluorinated with fluorine reactants such as HF or XeF₂ to form the corresponding metal fluoride. Ligand-exchange reactions can then be conducted with a variety of metal precursors that accept fluorine from the metal fluoride and donate one of their ligands to the metal in the metal fluoride. The metal reaction products then can leave the surface if they are stable and volatile. Preliminary results for GaN etching suggest that metal nitrides are good candidates for thermal ALE.

The metal fluoride reaction products produced by the ligand-exchange process provide pathways for selectivity during thermal ALE. Selectivity can arise depending on the stability of the metal reaction product. For example, Sn(acac)₂ is a metal beta-diketonate that donates acac ligands to the metal in the metal fluoride. Because most metals bind with acac ligands, Sn(acac)₂ may not lead to significant selectivity. In contrast, Al(CH₃)₃ is a metal alkyl that donates CH₃ ligands to the metal in the metal fluoride. Because some metals do not easily form sigma-bonds to bond to CH₃ ligands, more complete selectivity between different materials may be expected for Al(CH₃)₃. The selectivity observed between Al₂O₃ and ZrO₂ etching will illustrate this concept.

1. Younghee Lee and Steven M. George, "Atomic Layer Etching of Al₂O₃ Using Sequential, Self-Limiting Thermal Reactions with Sn(acac)₂ and HF", *ACS Nano* **9**, 2061 (2015).

2. Younghee Lee, Jaime W. DuMont and Steven M. George, "Mechanism of Thermal Al₂O₃ Atomic Layer Etching Using Sequential Reactions with Sn(acac)₂ and HF" *Chem. Mater.* (In Press).

3. Younghee Lee, Jaime W. DuMont and Steven M. George, "Atomic Layer Etching of HfO₂ Using Sequential, Self-Limiting Thermal Reactions with Sn(acac)₂ and HF", *J. Solid State Sci. Technol.* **4**, N5013 (2015).

11:00am **PS+SS+TF-WeM10 Atomic Layer Etching of Al₂O₃ Using Sequential, Self-Limiting Thermal Reactions with Trimethylaluminum and Hydrogen Fluoride**, *Younghee Lee*, *J.W. DuMont*, *S.M. George*, University of Colorado, Boulder

A new approach for the atomic layer etching (ALE) of Al₂O₃ was demonstrated using sequential, self-limiting thermal reactions with trimethylaluminum (TMA) and hydrogen fluoride (HF) as the reactants. Previously, Al₂O₃ thermal ALE was reported using Sn(acac)₂ and HF as the reactants [1,2]. HfO₂ ALE was also demonstrated using Sn(acac)₂ and HF as the reactants [3]. This new approach using TMA expands the variety of ALE reactants and excludes the possibility that Sn could be left on the etched Al₂O₃ film.

Quartz crystal microbalance (QCM) experiments monitored Al₂O₃ ALE at temperatures from 275-325°C. The Al₂O₃ ALE was linear versus number of TMA and HF reaction cycles. The QCM studies showed that the sequential TMA and HF reactions were self-limiting versus reactant exposure. The QCM analysis measured a mass change per cycle (MCPC) of -16 ng/(cm² cycle) at 300°C. This MCPC corresponds to an Al₂O₃ etch rate of 0.53 Å/cycle. X-ray reflectivity analysis confirmed the linear removal of Al₂O₃ and etching rates. Fourier transform infrared spectroscopy measurements also monitored Al₂O₃ ALE by observing the loss of infrared absorbance from Al-O stretching vibrations.

Al₂O₃ ALE is believed to follow the reaction: Al₂O₃ + 4Al(CH₃)₃ + 6HF → 6AlF(CH₃)₂ + 3H₂O. The proposed reaction mechanism involves

fluorination and ligand-exchange. The HF exposure fluorinates Al_2O_3 and forms AlF_3 with H_2O as a reaction product. During ligand-exchange, $\text{Al}(\text{CH}_3)_3$ accepts F from AlF_3 and donates CH_3 to AlF_3 to produce volatile $\text{AlF}(\text{CH}_3)_2$ reaction products. Similar reaction mechanisms based on fluorination and ligand-exchange reactions may extend the range of thermal ALE to a wide variety of additional materials.

1. Younghee Lee and Steven M. George, "Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with $\text{Sn}(\text{acac})_2$ and HF", *ACS Nano* **9**, 2061 (2015).
2. Younghee Lee, Jaime W. DuMont and Steven M. George, "Mechanism of Thermal Al_2O_3 Atomic Layer Etching Using Sequential Reactions with $\text{Sn}(\text{acac})_2$ and HF" *Chem. Mater.* (In Press).
3. Younghee Lee, Jaime W. DuMont and Steven M. George, "Atomic Layer Etching of HfO_2 Using Sequential, Self-Limiting Thermal Reactions with $\text{Sn}(\text{acac})_2$ and HF", *J. Solid State Sci. Technol.* **4**, N5013 (2015).

11:20am **PS+SS+TF-WeM11 Low Damage Etch Chamber for Atomic Layer Etching**, Leonid Dorf, S.R. Dorf, T.G. Monroy, K. Ramaswamy, K.S. Collins, Y. Zhang, Applied Materials

The use of novel, ultra-sensitive materials requires low-damage plasma etching with atomic layer precision, which imposes progressively stringent demands on accurate control over ion energy and radical composition during plasma processing. Using electron sheet beam (e-beam) parallel to the substrate surface to produce plasma in a processing chamber provides an order of magnitude reduction in electron temperature T_e (~ 0.3 eV) and ion energy E_i (< 2 eV without applied bias) compared to conventional plasma technologies, thus making electron beam plasmas an ideal candidate for processing features at 5 nm and below. Furthermore, since dissociation is performed only by high-energy beam and not plasma electrons, and the dissociation cross-section drops off considerably at beam energies of about 1–2 keV, the beam created plasma is typically poor in radicals, which allows an independent control over plasma radical composition. In this presentation, we describe the Low Damage Etch Chamber (LoDEC) for atomic layer etching (ALE). The apparatus consists of (1) an e-beam source for creating radical-poor, low- T_e plasma in the processing chamber, (2) a remote plasma source (RPS) for producing and supplying radicals to the substrate, and (3) a bias generator for creating the voltage drop (with fine control in 0 – 50 V range) between the substrate and the plasma to accelerate ions over etch-threshold energies. Using patterned wafers, we have developed low-bias power (0 – 10 W) processes resulting in very high selectivity (as per high-resolution TEM images) of Si_3N_4 to SiO_2 and poly-Si in fluorocarbon based chemistries. In application to ALE, we note that one existing approach to ALE of Si prescribes injecting Cl atoms to passivate the surface, and then replacing the processing gas with Ar and applying bias to the substrate to initiate the etching. Once the passivation layer is removed, the etch stops, provided Ar^+ ions have energies below sputtering threshold. By repeating passivation and etching steps, this scheme can be used to remove silicon in equally thick portions composed of one to a few atomic layers (few Angstroms), without tight control over the duration of the bias part of the cycle. In LoDEC, this recent pulsed-ALE technique can be performed at ion energies much lower than that in conventional tools, thus minimizing damage to the processed materials. LoDEC also allows implementation of a unique, truly low damage, continuous-ALE technique by using electron beam to create plasma with very low ion energies (with or without an application of low-power bias to accelerate ions) and RPS to create radicals. The results of ALE experiments in LoDEC will be presented.

11:40am **PS+SS+TF-WeM12 Modeling of Electron-Beam Generated Plasmas: Validation and System Design**, Shahid Rauf, A. Agarwal, L. Dorf, K.S. Collins, Applied Materials, Inc., D.R. Boris, S.G. Walton, US Naval Research Laboratory

Plasmas generated using energetic electron beams have unique properties that make them attractive for emerging plasma processing applications. In the work done at the Naval Research Laboratory, [1] it has been demonstrated that electron temperature (T_e) in the electron-beam plasmas generated in molecular gases is typically < 0.6 eV while electron densities are comparable to those obtained in radio-frequency (RF) inductively and capacitively coupled plasmas. In addition, the ions and radicals are primarily produced by highly energetic electrons (few keV) instead of electrons in the tail of a low energy distribution. The plasma chemistry in electron-beam generated plasmas is therefore significantly different than RF plasmas with a much higher ion to neutral radical density ratio in electron beam plasmas. As feature dimensions shrink below 20 nm in microelectronics devices with atomic level precision required during manufacturing, the unique properties of electron-beam generated plasmas (low T_e , low ion energy and unique chemistry) are becoming attractive for plasma processing in the semiconductor industry.

This paper focuses on a multi-dimensional computational model for electron-beam generated plasmas. A fluid model for the bulk plasma is coupled with a Monte Carlo kinetic model for beam electrons. The fluid plasma model uses the drift-diffusion approximation for electrons and negative ions. The momentum equation is solved for positive ions. The model includes the effect of magnetic field on charged species transport. The Monte Carlo model for beam electrons considers electron motion in the ambipolar electric field and externally imposed static magnetic field. Additionally, important collision processes including elastic collisions, ionization, excitation, dissociation and dissociative attachment are considered during the Monte Carlo simulation.

The computational model is validated in Ar, Ar/N_2 and O_2 plasmas using probe measurements over a range of gas pressures and electron beam properties. One factor that has important implications on quantitative accuracy of the model is the influence of magnetic field on electron transport properties. The paper will discuss the classical transport model as well as variations based on semi-empirical approximations. The validated model is applied to the design of electron beam based plasma processing systems.

This work was partially supported by the Naval Research Laboratory Base Program.

[1] S.G. Walton *et al.*, ECS Journal of Solid State Science and Technology, **4** (6) N5033-N5040 (2015)

12:00pm **PS+SS+TF-WeM13 Enhanced Reaction Rate and Precursor Transport in Focused Electron Beam Induced Etching Via Pulsed Laser Assistance**, JooHyon Noh, University of Tennessee, J.D. Fowlkes, Oak Ridge National Laboratory, R. Timilsina, M.G. Stanford, B.B. Lewis, P.D. Rack, University of Tennessee

Focused electron-beam-induced etching (FEBIE) is a versatile, selective or direct write nanomaterials etching technique, and is an alternative to focused ion beam (FIB) etching. FIB etching can cause collateral sub-surface damage due to knock-on collisions and ion implantation. FEBIE in contrast is minimally invasive because of the low electron mass and offers high etch selectivity between different materials. Additionally, the FEBIE process has better spatial resolution due to the smaller beam spot size. However, the low FEBIE etch rate has been a limiting factor for high-throughput applications.

The FEBIE process is governed by an electron-induced reaction with a precursor at the substrate surface, resulting in the volatile etch by-products. This complex process can be rate limited by different mechanisms depending on the electron and precursor parameters, the electron stimulated reaction rates, and the by-product volatility (or residence time). While substrate heating can reduce the by-product residence time, the higher temperature concomitantly decreases the reactant residence time, which can reduce the reactant equilibrium coverage and result in the electron stimulated etching rate. In order to enhance the etch rate, we introduce a laser-assisted focused electron-beam-induced etching (LA-FEBIE) process which emulates an atomic layer etching process. The focused electron beam catalyzes the first half reaction which forms a pseudo-volatile byproduct. The periodic and appropriately synchronized pulsed laser can locally and briefly raise the surface temperature, which can affect the reactant and byproducts and facilitate the reaction kinetics. In this presentation we will overview the laser-assisted electron beam induced etching of Ti with a XeF_2 gas chemistry and will correlate the mechanisms to a selected area atomic layer etching process. We will show results that the Ti electron stimulated etch rate via the XeF_2 precursor can be enhanced up to 6 times with an intermittent pulsed laser assist. The etching evolution is correlated to in situ stage current measurements and scanning electron micrographs as a function of time. Other relevant work on conventional fluorine-based titanium plasma etching suggests the mechanism of Ti-F etching is attributed to the reaction of F radicals with Ti to form TiF_x products; where progressive fluorine incorporation drives x towards the volatile product of TiF_4 . Notably TiF_3 is a stable solid at room temperature. The increased etch rate with laser assistance is attributed to photothermally enhanced Ti-F reaction and TiF_4 desorption and in some regimes enhanced XeF_2 surface diffusion to the reaction zone.

Thin Film

Room: 111 - Session TF+EN-WeM

ALD for Energy

Moderator: Jesse Jur, North Carolina State University,
Angel Yanguas-Gil, Argonne National Lab

8:00am **TF+EN-WeM1 Photovoltage Design for ALD Metal Oxide Protected Solar-Water-Splitting Photoanodes**, *Andrew Scheuermann, J.P. Lawrence, K.W. Kemp, O.L. Hendricks*, Stanford University, *A. Walsh, I. Povey, M.E. Pemble, P.K. Hurley*, Tyndall National Institute, *C.E.D. Chidsey, P.C. McIntyre*, Stanford University

Metal oxide protection layers for photoanodes may enable the development of large-scale solar fuel and chemical synthesis. ALD-TiO₂ is the most widely used material because of its excellent stability under water oxidation conditions and potential for high electrical conductivity both as an ultrathin film and with thicknesses exceeding 100 nm [1-3]. However, the most conductive ALD-TiO₂ films exhibit poor photovoltages of ~ 400 mV and less [3]. Even assuming near-ideal fill factors, these voltages fall far short of the values needed for viable water splitting devices. Photovoltage optimization is especially difficult to achieve in MOS photoanodes because of the presence of a defective metal oxide protection layer and a defective semiconductor/oxide interface in the device structure. Therefore, understanding how to optimize photovoltage and stability is of utmost concern for the advancement of the field.

Here we report a novel observation of photovoltage loss associated with charge transfer in these metal-oxide protected devices, and by eliminating it, achieve photovoltages as high as 630 mV, the maximum reported to date for single-junction water-splitting silicon cells. The loss mechanism is systematically probed in MOS Schottky junction cells compared to buried junction p-n cells, revealing the need to maintain a characteristic hole density at the semiconductor/insulator interface. A capacitor model that predicts this loss is developed, and is related to the dielectric properties of the protective oxide, achieving excellent agreement with the data. From these findings, we extract design principles for simultaneous optimization of charge transfer resistance and interface quality to maximize the photovoltage of metal-oxide protected MOS water splitting devices.

[1] Y.W. Chen, et al. *Nature Mat.* 2011, **10**, 539-544.

[2] A. G. Scheuermann, et al. *Energy Environ. Sci.* 2013, **6**, 2487-2496.

[3] S. Hu, et al. *Science* 2014, **344**, 1005-1009.

Supplemental Figure 1 | Charge transfer in three cell types for water splitting applied to silicon: Shows the Type 0 Semiconductor-Liquid (SL), Type 1 Metal-Insulator-Semiconductor (MIS), and Type 2 p-n junction. The density of states on either side of the oxides and the excitation splitting position with respect to these layers play a crucial role in mediating efficient charge transfer. These effects are so strong that Type 0 protected silicon cells exhibit essentially no photovoltage, Type 1 nSi cells show a linear photovoltage loss with oxide thickness, and Type 2 cells--where the hole concentration on the Si/SiO₂ interface is always high--exhibit record photovoltages at all oxide thicknesses and pH values studied.

8:20am **TF+EN-WeM2 Activity and Thermal Stability Enhanced Platinum catalysts with Nano-scale Oxide Coating via Atomic Layer Deposition**, *Kun Cao, J.M. Cai, B. Shan, R. Chen*, Huazhong University of Science and Technology, Wuhan, China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For most catalytic applications, sintering of Pt NPs is undesired since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs for CO oxidation. The active oxide coated catalysts have additional metal-oxide interfaces which may further improve the catalytic activity besides good sintering resistance. We use cobalt oxide, cerium oxide and nickel oxide as the active oxide encapsulations. Compared with aluminum oxide reference samples, these active oxides have been reported as much better materials with synergetic effect for Pt catalysts. The thickness of the metal oxide film is controlled by varying the number of ALD cycles. CO oxidation measurements were carried out in a micro flow reactor designed for planar model catalysts. Our results indicate that cobalt oxide coated Pt nanoparticles demonstrating the highest activity towards CO oxidation, and the optimal coating thickness is around 1nm. At the same time the coated catalysts have good thermal stability up to 750°C under atmospheric conditions. The enhancement of catalytic activity may originate from the active oxygen at the Pt/cobalt oxide interface, further Co (II) sites show better synergetic effect compared with Co (III) sites.

8:40am **TF+EN-WeM3 Passivation of Highly-doped c-Si Solar Cell Surfaces by Atomic Layer Deposition**, *Bas van de Loo*, Eindhoven University of Technology, Netherlands, *J. Melskens*, Eindhoven University of Technology, *G.J.M. Janssen*, ECN Solar Energy, *K.R.C. Mok, L.K. Nanver*, Delft University of Technology, *A.H.G. Vlooswijk*, Tempres Systems, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) of Al₂O₃ has been successfully implemented in silicon solar cell manufacturing, predominantly to passivate defects at the lowly-doped back surface of *p*-type solar cells. However, also for the passivation of highly-doped *n*⁺ or *p*⁺ type surfaces, present in e.g., high efficiency *n*-type solar cells, ALD films and stacks might become feasible. Yet, for such surfaces, the level of passivation strongly depends on the doping concentration and surface conditions. To allow for an even wider implementation of ALD-based passivation schemes in industrial solar cells, the work presented in this contribution aims to understand the passivation of highly-doped *n*⁺ and *p*⁺ type regions.

First of all, we observed that the passivation of boron-doped (*p*⁺) Si surfaces highly depends on the doping process and the fixed charge density *Q_f* in the passivation layer. For instance, when a boron-rich layer (a B_xSi_y compound) was remained after the doping process, the surface passivation by ALD Al₂O₃ severely deteriorated. The formation of this undesirable layer could be avoided by using an oxidizing ambient during the drive-in of boron, although this results in a significant reduction in boron doping density at the surface. The latter impaired the level of passivation when *Q_f* was virtually zero, such as for ALD SiO₂/ Al₂O₃ stacks. Importantly, the level of surface passivation offered by ALD Al₂O₃ films remained high under these circumstances, due to the strong negative *Q_f*.

Next, for phosphorous doped (*n*⁺) Si surfaces having surface densities of 10¹⁸-10²⁰ cm⁻³, the passivation by dielectrics containing a negative *Q_f* such as ALD Al₂O₃, can be severely compromised, as the negative *Q_f* increases the minority carrier (i.e., hole-) concentration at and near the surface. Moreover, the negative *Q_f* can invert the *n*⁺ Si surface, which triggers (undesirable) increased recombination at low injection levels and parasitic shunting. For those *n*⁺ Si surfaces, it is demonstrated that ALD stacks such as SiO₂/ Al₂O₃ and HfO₂/ Al₂O₃ are promising alternatives to Al₂O₃ single layers, due to the absence of a negative *Q_f*. These stacks are particularly interesting from an industrial point of view, as they can make ALD viable for the passivation *n*⁺ Si surfaces.

Lastly, ALD-based passivation schemes also have the potential to fully replace the heavily-doped *n*⁺ and *p*⁺ Si regions in solar cells. In this new field of 'passivating contacts', the significant recombination losses in the highly-doped regions can be avoided due to accurate band-alignment. Preliminary but promising results on novel electron-selective, passivating stacks of HfO₂ and TiO₂ by ALD will also be presented.

9:00am **TF+EN-WeM4 Low Temperature Plasma-Assisted Atomic Layer Deposition of TiO₂ Blocking Layers for Organo-Metal Halide Perovskite Solar Cells**, *V. Zardetto*, Eindhoven University of Technology, The Netherlands, *F. di Giacomo, G. Lucarelli, T.M. Brown, A. di Carlo, S. Licoccia, A. D'Epifanio*, University of Rome "Tor Vergata", Italy, *W.M.M. Kessels, Mariadriana Creatore*, Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) offers accurate control in terms of film thickness, chemical and opto-electrical properties. This is extremely appealing for the novel class of mesoscopic solar cells (SCs), where the several interfaces between the absorber, charge transport layers and electrical contacts require the control of selected charge transfer and charge recombination processes.

Organo-metal halide perovskite SCs presently catalyze the interest in the PV community due to the remarkable increase in device performance in the last three years. Recently, thermal ALD processes have been applied for the deposition of TiO₂ blocking layers (BLs) in glass-based perovskite SCs[1]. Plasma-assisted ALD allows to extend the process window down to temperatures compatible with conductive plastic substrates. Therefore, in this work we investigate the role of plasma-assisted ALD TiO₂ BLs deposited on ITO/PET substrates for a CH₃NH₃PbI_{3-x}Cl_x perovskite SC. The BLs are required to avoid the charge recombination process at the interface between the transparent conductive oxide layer and the perovskite and/or the hole transport layer. They have been prepared [2] in a remote plasma reactor (FlexAL™) at 150 °C using a heteroleptic alkylamido precursor Ti(Cp^{Me})(NMe₂)₃ exposure step alternated with an O₂ plasma exposure. Very low open circuit voltage (*V_{OC}* = 50mV) and efficiency (η = 0.01%) have been measured in the absence of the blocking layer. In this case, the analysis of dark current-voltage measurements revealed the lack of diode-like behavior and a significant exchange current (7 mA·cm⁻²). The introduction of thin TiO₂ layers brought to an increment in all the photovoltaic parameters (*J_{SC}*, *V_{OC}* and FF), with a saturation in electrical efficiency for a TiO₂ thickness above 5.5 nm. The saturation in the anodic

branch of the JV curve ($V > 0$) for ALD layers thicker than 5.5 nm points out that at this thickness the ALD layer is compact and therefore it suppresses the charge recombination processes. Dark current-voltage measurements have highlighted the decrease of exchange current and dark reverse current ($V < 0$) up to three orders of magnitude with respect to the device without BL. The maximum performance of 9.2% on ITO-PET and 12.9% on ITO-Glass was achieved with 11 nm-thick TiO_2 BL, overcoming the efficiency achieved with conventional sol gel-deposited TiO_2 BLs (respectively, 4% and 8% on the two substrates).

[1] M. Grätzel, *Nature Materials*, 13, 838–842 (2014).

[2] F. Di Giacomo and V. Zardetto et al, *Adv. Energy. Mater.* 1401808 (2015)

9:20am TF+EN-WeM5 Ultra-thin transition Metal Oxide-titania Alloy Coatings for Water Oxidation by Atomic Layer Deposition, Olivia Hendricks, C.E.D. Chidsey, P.C. McIntyre, Stanford University

Synthesizing chemical fuels from solar energy requires a source of electrons. The most obvious choice for generating these electrons is the oxidation of water. The oxygen evolution reaction, however, is kinetically challenging, requiring significant overpotentials even with the best noble metal catalysts. At these positive potentials, preserving catalyst stability becomes a key concern. In industrial chlor-alkali electrolysis, which requires similarly positive potentials, the issue of catalyst durability was solved with the development of the dimensionally stable anode (DSA). Today's DSAs consist of a mixed $\text{TiO}_2/\text{RuO}_2$ coating prepared by thermal decomposition of appropriate precursors on a Ti substrate (Over, H. *Chem. Rev.*, 2012, 112, 3356). The TiO_2 imparts stability by preventing Ru dissolution, while the RuO_2 imparts sufficient activity and conductivity to the electrode. We report on the fabrication of an ultra-thin analogue to the DSA by atomic layer deposition (ALD) of ruthenium and TiO_2 . We hypothesize that a conformal ALD coating of this type on nanostructured electrodes can optimize both the catalytic activity and durability for water oxidation while minimizing the use of transition metal components that have very limited Earth-abundance.

Both TiO_2 and Ru can be deposited simultaneously in our ALD reactor. Thus, by changing the relative number of ALD cycles for each precursor, we can achieve precise control of the catalyst content within the films. Preliminary results suggest that enhanced stability is achieved through the alloying process after annealing. The alloyed films also exhibit overpotentials that are competitive with pure ALD-Ru films deposited on a TiO_2 protective layer, even at relatively low Ru content. By decorating the TiO_2 surface with Ru ions at an optimal areal density, ALD alloying has the potential to achieve efficient catalysis of oxygen evolution from water while minimizing usage of the noble metal catalyst.

9:40am TF+EN-WeM6 Atomic Layer Deposition of Nickel-Iron-Oxide Catalysts for Photoelectrochemical Splitting of Water, Adri Mackus, K.L. Pickrahn, J.G. Baker, S.F. Bent, Stanford University

The splitting of water to form hydrogen using sunlight as the source of energy has been actively researched in recent years to enable the production of green alternatives to fossil fuels. One of the main challenges in this technology is to develop a photoanode that (i) absorbs sunlight, (ii) has the ability to catalyze the oxygen evolution reaction (OER), (iii) is chemically stable in the aqueous electrolyte, and (iv) is made of earth-abundant materials. A strategy to synthesize an improved photoelectrochemical cell is to decouple these functions by conformally coating (e.g. by atomic layer deposition, ALD) a catalytic and protective layer on a nanostructured light-absorbing material.¹

In this work, we investigate ALD of NiO and NiFe_xO_y films and their use as catalysts for the OER. The material NiFe_xO_y was chosen because it is one of the most promising OER catalysts. The NiFe_xO_y films were deposited using an ALD process that combines NiO ALD (NiCp_2 , O_3) with Fe_2O_3 ALD (FeCp_2 , O_3) in a supercycle. Alternatively, NiFe_xO_y films were prepared by soaking ALD-grown NiO films in Fe-containing KOH electrolyte.² Using the latter approach, the best results were obtained when the electrode was preconditioned in Fe-poor KOH, causing the smooth and compact NiO film to partly exfoliate, which increases the number of electrochemically accessible Ni sites. Synchrotron-radiation X-ray diffraction was employed to investigate the phase of the material as a function of the deposition conditions. Moreover, the catalytic activity of the films for the OER was investigated by cyclic voltammetry (CV). It was found that incorporating Fe in the NiO films enhances the activity for OER significantly with a 10-fold increase of the turnover frequency.

1. T.M. Gür, S.F. Bent, and F.B. Prinz, *J. Phys. Chem. C* **118**, 21301 (2014)

2. Y.T. Chong, E.M.Y. Yau, K. Nielsch, and J. Bachmann, *Chem. Mater.* **22**, 6506 (2010)

11:00am TF+EN-WeM10 From Atom to Solid: The Structure of Amorphous ALD Thin Films and Nanolaminates, Angel Yanguas-Gil, Argonne National Laboratory INVITED

Atomic Layer Deposition is currently being used for a wide range of energy applications, such as photovoltaics, artificial photosynthesis, energy storage, and power semiconductor devices. In many cases the films are either very thin, well below 10 nm, or either doped or laminate materials, in which a second constituent is intercalated every few cycles.

Given the low deposition temperatures compared to other thin film processes, one of the key questions is how the microstructure of ALD materials differs from their bulk counterparts. This fundamental question of how atoms transition from isolated clusters or single monolayers to a local coordination environment characteristic of the bulk has important technological implications. Answering this question will allow us to better understand the performance of these materials as well as what makes ALD materials different, and in some cases better, to materials synthesized using other techniques.

In this talk I will discuss the impact that chemistry has on the properties and microstructure of very thin ALD films and nanolaminates of oxide dielectrics, semiconductors, and transparent conductors, comprising ZnO , HfO_2 , and $\text{M:Al}_2\text{O}_3$ nanolaminates. By combining synchrotron X-ray characterization techniques such as X-ray Absorption Fine Structure (XAFS) and Pair Distribution Function (PDF) with in-situ techniques such as QCM and FTIR, my talk will focus on two particular problems: the evolution of coordination environment and the emergence of long-range order from the first monolayer and during the early stages of growth, and the impact that the interaction between dopant and host have in the microstructure of doped and laminate materials.

11:40am TF+EN-WeM12 Inorganic Functionalization of Colloidal Quantum Dot Solar Cells through ALD Infilling, Axel Palmstrom, P. Santra, S.F. Bent, Stanford University

Colloidal quantum dot (CQD) solar cells are of great interest due to the tunable nature of the quantum dot light absorbers through size, composition and interface engineering, together with the potential for low-cost fabrication through solution processing techniques. Lead chalcogenide CQD devices have recently gained traction with rapidly improving efficiencies (>9%). Great strides have been made with organic ligand functionalization of the quantum dot surfaces to enhance CQD transport properties; however, these devices often suffer from poor long-term stability and are still limited by carrier lifetime and mobility. Atomic layer deposition (ALD), a technique that allows for conformal coating of nanostructured surfaces, has been used to improve stability and mobility of CQD solar cells by growing oxides within the quantum dot film. In this work, we explore the inorganic functionalization of CQD solar cells through combinations of ALD materials, including Al_2O_3 , ZnO , NiO and other oxide materials, in thin (~30 nm) devices to ensure infilling throughout the entire device. With the proper choice of ALD oxide, short circuit current density and overall efficiency could be enhanced by 70% and 10% respectively relative to the non-infilled control CQD device. We will discuss the effects of ALD inorganic functionalization on surface passivation and carrier mobility as well as methods to implement ALD infilling on thicker devices in order to ultimately push the limits of CQD solar cell performance.

12:00pm TF+EN-WeM13 Integrating Atomic Layer Deposited Lithium-Containing Thin Films for Lithium-ion Battery Applications, J. Cho, Trevor Seegmiller, J. Lau, L. Smith, J. Hur, B. Dunn, J.P. Chang, University of California at Los Angeles

Lithium-ion (Li-ion) batteries have demonstrated their performance in portable electronics for many years. Li-ion batteries also have the potential to be miniature power sources for microelectromechanical systems (MEMS) through 3-dimensional (3D) battery architectures. In order to fabricate a fully functional 3D Li-ion microbattery, an ultra-thin, highly conformal electrolyte layer is required to fully coat 3D electrodes. Lithium aluminosilicate ($\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$, LASO), a solid oxide Li-ion conductor, synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications due to its adequate ionic conductivity (1×10^{-7} S/cm) in thin film applications as well as improved electrode stability.

The self-limiting nature of ALD allows precise thickness and composition control when applied to complex metal oxides. This results in a highly conformal and pinhole-free coating on complex structures, including high aspect ratio 3D electrodes. Lithium tert-butoxide (LTB), trimethylaluminum (TMA), tris(tert-butoxy)silanol (TTBS), and tetraethylorthosilicate (TEOS) were precursors used to synthesize LASO by ALD. LASO films ranging in thickness from 6 to 12 nm exhibited Li-ion conductivity from 8.2×10^{-8} to 1.4×10^{-9} S/cm. The LASO films were also deposited on anode and cathode materials for evaluating their integration into solid state Li-ion batteries. A Li-ion half-cell consisting of LASO-coated 2D carbon anode showed

reversible electrochemical behavior with coulombic efficiency reaching 98%.

Current research on Li-ion batteries is directed at creating next generation anode materials. Both silicon and germanium have received considerable study due to their high theoretical volumetric capacity (8444 A h L⁻¹ for Li₁₅Si₄ and 7366 A h L⁻¹ for Li₁₅Ge₄ respectively). Upon lithium intercalation, however, these anode materials undergo large volumetric expansion (~300% for Si) which compromises their mechanical integrity. We have started to carry out *in situ* transmission electron microscopy (TEM) studies in which the structural effects of lithium intercalation and deintercalation on silicon/germanium (Si/Ge) alloy nanowires conformally coated with LASO electrolyte are characterized. These *in situ* TEM studies show 40% radial expansion of the Si_{0.4}Ge_{0.6} alloy upon lithium intercalation, and morphological changes upon deintercalation, with the LASO film preserved on the nanowire.

Thin Film

Room: 114 - Session TF+SS-WeM

ALD Surface Reactions and Precursors

Moderator: Sean Jones, National Science Foundation (NSF), Paul Poedt, Solliance/TNO

8:00am **TF+SS-WeM1 High Performance Precursors for Atomic Layer Deposition of Silicon Containing Films.** *Anu Mallikarjunan*, Air Products and Chemicals, Inc. **INVITED**

Conformal and continuous silicon containing films produced by Atomic Layer Deposition (ALD) are enabling novel processing schemes and integrated device structures. The increasing drive towards lower temperature processing requires new precursors with even higher reactivity. A systematic method for identification of high performance precursors is thus very desirable, and needs to incorporate fundamental understanding of precursor chemistry, surface reactions; and relationships between precursor structure and deposited films. The overall approach accordingly relies on integrating molecular and surface reaction modeling, the ability to synthesize stable precursors with reactive groups, in-situ surface studies, and thin film deposition testing. To illustrate this approach, two case-studies will be discussed in this presentation: silicon oxide and silicon nitride ALD. In both cases, a representative monoaminosilane (R¹R²N)SiH₃ called di-sec-butylaminosilane (DSBAS) will be studied. The impact of changing the precursor structure will also be discussed.

8:40am **TF+SS-WeM3 Amorphous In₂O₃ and Sn-doped In₂O₃ Layers by ALD Prepared using Trimethyl Indium and Ozone.** *Anil Mane*, A. Allen, Argonne National Laboratory, *R. Kanjolia*, SAFC Hitech, *J. Elam*, Argonne National Laboratory

Abstract:

Among the transparent conducting oxides (TCOs), Indium oxide (In₂O₃) possesses a wide band gap of 2.9 eV at room temperature yielding high optical transparency and also exhibits good chemical stability. When doped with tin to form Indium tin oxide (ITO), the electrical conductivity increases greatly allowing this material to be used in a wide range of applications including touch screens displays, light-emitting diodes, liquid crystal displays, and sensors. Further amorphous TCOs have several advantages over their crystalline microstructures e.g. lower temperatures deposition which tend to simplify the deposition methods for mainly for plastics for flexible electronics. The lack of grain boundaries in amorphous materials, isotropic nature allows a simpler scheme for uniform etching with lower surface roughness. Unlike crystalline TCOs, the amorphous TCOs electrical and optical are also strongly influenced by the oxygen content of the films. As ALD offers the potential to deposit ITO over large areas at low temperature with high uniformity to address some of these applications, but the viability of this method hinges on developing a robust In₂O₃ ALD process. Trimethyl indium (TMIn) is an attractive economical precursor for In₂O₃ ALD because it offers the advantages of a high vapor pressure and availability in high volume.

In this study we examined the ALD of In₂O₃ using alternating exposures to TMIn and different oxygen sources: O₃ (ozone), O₂, H₂O, and H₂O₂. We first used *in situ* quartz crystal microbalance (QCM) and mass spectrometry measurements to evaluate the effectiveness of the different oxygen sources and found that only ozone yielded sustained growth. These measurements also provided details about the In₂O₃ growth mechanism and enabled us to verify that both the TMIn and the O₃ surface reactions were self-limiting. Next, we prepared ALD In₂O₃ films on a variety of substrates and characterized them using X-ray diffraction, UV-vis. Spectrometry, spectroscopic ellipsometry, X-ray photoelectron spectroscopy, Hall probe

measurements, scanning electron microscopy, and atomic force microscopy. We found that at deposition temperatures of 100-200°C the amorphous growth per cycle was nearly constant at ~0.4 Å/cycle and the films were dense and pure. At higher growth temperatures the In₂O₃ growth rate increased due to thermal decomposition of the TMIn. We succeeded in doping the amorphous In₂O₃ films with tin by substituting tetrakis-(dimethylamino) tin for the TMIn in a fraction of the growth cycles and observed that the electrical conductivity improved substantially in these films.

9:00am **TF+SS-WeM4 Towards Organic Electronics: Atomic Layer Like Deposition of ZnS and ZnO on Organic Thin Films.** *Z. Shi*, *Amy Walker*, University of Texas at Dallas

We discuss our recent studies of atomic layer like deposition (ALLD) of ZnS and ZnO on organic thin films using diethyl zinc (DEZ) as the zinc source. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies. We show that a detailed understanding of the reaction pathways is critical for controlling the properties of ZnO and ZnS films grown by ALD. For both ZnO and ZnS ALLD, the growth rates on -COOH terminated SAMs are approximately 10 % lower than on -OH terminated SAMs. As expected on -OH terminated SAMs, the DEZ reacts with the hydroxyl group. However, on -COOH terminated SAMs DEZ reacts with both the carbonyl and hydroxyl bonds present leading to the formation of a ketone rather than deposition. Further, the composition of the deposited layer and its growth can be affected by the functionality of the surface. For ZnO ALLD, on-COOH terminated SAMs XPS indicates that the initial composition of the layer is similar to Zn(OH)₂. In contrast on -OH terminated SAMs the deposited layer is always composed on ZnO. The growth of the layer also appears to be different. On -COOH terminated SAMs, the layer growth is more two dimensional (layer-by-layer) while on -OH terminated SAMs, the growth appears to proceed via the formation of islands.

9:20am **TF+SS-WeM5 AlF₃ Atomic Layer Deposition or Al₂O₃ Atomic Layer Etching from Sequential Exposures of Trimethylaluminum and HF.** *Jaime DuMont*, *Y. Lee*, *S.M. George*, University of Colorado at Boulder

Sequential exposures of Al(CH₃)₃ [trimethylaluminum (TMA)] and HF can lead to either AlF₃ atomic layer deposition (ALD) or Al₂O₃ atomic layer etching (ALE). The observation of AlF₃ ALD or Al₂O₃ ALE depends on temperature and pressure. AlF₃ ALD occurs at lower temperatures and higher pressures. Al₂O₃ ALE of an initial Al₂O₃ film occurs at higher temperatures and lower pressures. The AlF₃ ALD or Al₂O₃ ALE were investigated using *in situ* Fourier transform infrared (FTIR) spectroscopy and quartz crystal microbalance (QCM) measurements.

The FTIR analysis observed AlF₃ ALD or Al₂O₃ ALE by measuring the absorbance gain of Al-F stretching vibrations in AlF₃ or the absorbance loss of Al-O stretching vibrations in Al₂O₃. At lower temperatures, the HF exposures react with the underlying Al₂O₃ surface to form AlF₃ and HF molecules on the surface. TMA molecules subsequently react with HF on the surface to yield AlF(CH₃)₂ surface species. AlF(CH₃)₂ is then converted to AlF₃ with the next HF exposure producing AlF₃ ALD. At higher temperatures, the HF exposures react with the underlying Al₂O₃ surface to form AlF₃ and fewer HF molecules adsorb on the surface. TMA then accepts fluorine from AlF₃ to form AlF(CH₃)₂ which desorbs from the surface and leads to etching of the initial Al₂O₃ film.

The effect of pressure was also explored by adjusting the N₂ carrier gas flow from 0-150 sccm to vary the background pressure from 30 mTorr to 1.6 Torr. These FTIR experiments revealed that the transition from AlF₃ ALD to Al₂O₃ ALE occurred at higher temperatures for higher background pressures. The higher pressures apparently produce a "cage effect" and increase the lifetime of the AlF(CH₃)₂ surface species that leads to AlF₃ ALD. The QCM experiments measured an AlF₃ ALD growth rate that progressively decreased at higher temperatures and went negative at >250°C when TMA and HF etched the AlF₃ or Al₂O₃ films.

9:40am **TF+SS-WeM6 A Comparison of Water Delivery Methods for Atomic Layer Deposition.** *Tariq Ahmido*, *W.A. Kimes*, *B.A. Sperling*, *J.E. Maslar*, NIST

Water is frequently used as an oxygen source for atomic layer deposition (ALD) of metal oxides. However, water exhibits a relatively high vapor pressure at room temperature and readily adsorbs on reactor surfaces. These characteristics can make it difficult to reproducibly control water delivery during ALD, particularly when small quantities are desired. The focus of this work is characterizing and comparing three different methods of water vapor delivery in an effort to identify techniques for ensuring reproducible delivery of water vapor quantities. For this investigation, three methods of water injection were compared. The first method utilizes a needle valve between the water reservoir and the water injection valve (the valve that

controls the water allowed into the delivery line to the reactor). This method is commonly employed for research grade reactors as the use of an adjustable orifice permits the water flow rate to be varied. However, control of small water quantities can be difficult due to the buildup of water vapor between the needle valve and the water injection valve. The second method overcomes this control limitation by utilizing a pump to vent water vapor from the volume between the needle valve and injection valve prior to injection into the delivery line. This method provides a high degree of control at the cost of added complexity and expense. The third method utilizes a laser-drilled orifice in a VCR gasket as the flow-controlling orifice. This method is simple and inexpensive, however, water flow rates cannot be adjusted without changing the orifice. The performance of these three water injection methods was characterized using an optical water mass flow meter (MFM) that has been developed to rapidly quantify water vapor. This MFM was based upon a wavelength modulation spectroscopic technique utilizing a near-infrared diode laser. This MFM permits quantitative comparison of the performance of these three water injection methods, allowing a potential user to identify method suited to a particular application.

11:00am **TF+SS-WeM10 Stoichiometric Dependence of the Interface of HfO_2 , ZrO_2 , TiO_2 , Ta_2O_5 and La_2O_3 on Si (100) by ALD.** *Pierre Mani*, Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *E. Lopez*, Universidad Autónoma de San Luis Potosí, Mexico, *H. Leos*, Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *H. Hernandez*, Universidad Autónoma de San Luis Potosí, Mexico, *J.A. Hernandez*, *J.R. Farias*, *J.T. Elizalde*, Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *M.A. Melendez*, CINVESTAV, Mexico, *M.A. Vidal*, Universidad Autónoma de San Luis Potosí, Mexico

A systematic analysis was performed to determine the characteristic times of surface coverage of oxidant-agent on silicon substrates (100) by the atomic layer deposition (ALD) method in order to ensure the saturation of the surface substrate for growth. The aperture-times of the precursors have been studied due to stoichiometric impact of the layers and also at the interface. The numbers of cycles were critical for the interface formation at the early stage growth. This work emphasizes in the study and analysis between interface of high k dielectric layer and amount of cycles as function of layers and stoichiometric interface. Previous works complement with results obtained in study the growth of hafnium oxide and titanium oxide by atomic layer deposition (ALD) demonstrating the close relationship between the thickness and composition of the interface layer with the number of cycles performed by the ALD and with the aperture-time of the precursors. This analysis shows a base that will allow create HfO_2 , ZrO_2 , TiO_2 , Ta_2O_5 , La_2O_3 nanofilms with optimal characteristics.

11:20am **TF+SS-WeM11 In-situ Infrared Study of Atomic Layer Deposition of Molybdenum Nitride using Bis(tert-Butylimido)-Bis(dimethylamido) Molybdenum and Hydrazine.** *Abraham Vega*, C.E. Nanayakkara, The University of Texas at Dallas, *G. Liu*, *R. Kanjolia*, SAFC Hitech, *Y.J. Chabal*, The University of Texas at Dallas

Molybdenum nitride films have properties such as high hardness, high melting point, good chemical stability and high conductivity, which makes them suitable for a wide range of technological areas, as diffusion barriers or interconnections in microelectronics and even as catalysts in fuel cells. Molybdenum nitride films have been deposited by variety of techniques, such as chemical vapor deposition, magnetron sputtering, and atomic layer deposition among others.

For atomic layer deposition of molybdenum nitride, molybdenum complexes containing alkylamido and alkylimido ligands are being considered as potential molybdenum precursors. A notable advantage is that they do not produce corrosive byproducts compared to halide based transition metal precursors.¹ A uniform growth has been achieved in the range 260 – 300 °C with bis(tert-butylimido)-bis(dimethylamido)molybdenum when used with NH_3 as a co-reactant.¹

In this study, *in-situ* IR and X-ray photoelectron spectroscopies are used to investigate ALD of bis(tert-butylimido)-bis(dimethylamido)molybdenum and hydrazine an alternative for NH_3 as co-reactant for molybdenum nitride deposition on pre-annealed, oxidized and OH-terminated Si(100) surfaces. While bis(tert-butylimido)-bis(dimethylamido) molybdenum is expected to react with two surface OH groups leaving one amino groups with further reaction with hydrazine leading to a NH_x -terminated surface, the details of the reactions have not been explored, hence the importance of *in-situ* IR spectroscopy.

Bis(tert-butylimido)-bis(dimethylamido) molybdenum reacts with surface Si-OH groups (loss at 3740 cm^{-1}) to form the expected $(\text{O})_2\text{-Mo}=(\text{N-tBu})_2$ structure, as evidenced by broad band from various CH_x stretch bands in the 2900 cm^{-1} region and stretching of CN bonds at 1240 cm^{-1} , respectively. The first hydrazine pulse leads to a loss of tBu vibrational bands [at 2900 and 1240 cm^{-1}]. The steady state ALD process is

characterized by tBu removal by hydrazine and formation of NH_x groups driving the ALD process. A clear ligand exchange is observed at deposition temperatures of 225, 250 and 275 °C for 30 cycles. The ALD window for this process was found to be between 225 and 275 °C, with low carbon content determined by XPS, which is lower than the window when using NH_3 (260-300 °C) instead of hydrazine. No growth is observed above 300 °C, and very poor quality films are obtained at 200°C.

This work confirms the reactivity of bis(tert-butylimido)-bis(dimethylamido) molybdenum with OH-terminated surfaces at low temperatures and illustrates the role of the co-reactant on the thermal window and the quality of the resulting molybdenum nitride films.

1. Chem. Mater., Vol. 19, No. 2, 2007

11:40am **TF+SS-WeM12 Atomic-Layer-Deposited $\text{In}_2\text{O}_3\text{:H}$ Transparent Conductive Oxides: How to Achieve the Best Possible Carrier Mobility.** *Bart Macco**, Eindhoven University of Technology, Netherlands, *H.C.M. Knoops*, Oxford Instruments Plasma Technology, UK, *M.A. Verheijen*, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, we have reported on an atomic layer deposition (ALD) process to prepare H-doped indium oxide ($\text{In}_2\text{O}_3\text{:H}$) transparent conductive oxides (TCOs) with an extremely high carrier mobility (138 cm^2/Vs) and low resistivity (0.27 $\text{m}\Omega\text{cm}$) at low processing temperatures (<200 °C) [1]. This high carrier mobility is especially promising for silicon heterojunction solar cell applications, as it allows for a low resistivity at low carrier density, thereby nullifying parasitic free carrier absorption in the infrared. Here we focus on new insights into the physical mechanisms during the preparation process and explain how such high mobility can be obtained through analysis of the electron scattering and doping mechanisms.

The preparation starts with ALD of $\text{In}_2\text{O}_3\text{:H}$ at 100 °C using InCp , H_2O and O_2 as growth precursors. The films are amorphous, although a low density of very small crystallites is present. Subsequently the films are crystallized by annealing at 150-200 °C. Electron microscopy reveals that crystallization proceeds from grain growth from the pre-existing crystallites without additional nucleation, which makes the final grain size and optoelectronic properties independent of annealing temperature. The resulting crystals extend over the film thickness of 75 nm and have a typical lateral size of a few hundred nm. Analysis of the grain growth by electron microscopy shows a thermally activated behavior, with an activation energy of 1.4 eV.

A combination of temperature-dependent Hall measurements and spectroscopic ellipsometry has been employed to distinguish between the various scattering mechanisms and dopants in crystallized $\text{In}_2\text{O}_3\text{:H}$ films. Key results include the fact that carrier mobility is only limited by ionized impurity and phonon scattering processes and that other extrinsic defect scattering such as neutral impurity and grain boundary scattering can be neglected. Since only unavoidable scattering processes play a role, this means that this TCO has the highest possible mobility at this carrier density. The analysis also excludes a significant contribution from doubly charged donors (i.e. oxygen vacancies), and the source of doping is confirmed to be singly charged H. Furthermore, by comparison of the absolute H-concentration and the carrier density in crystallized films, it is deduced that <4 % of the incorporated H is an active dopant in crystallized films. Therefore, it can be concluded that inactive H atoms do not contribute to defect scattering, which explains why $\text{In}_2\text{O}_3\text{:H}$ films are capable of achieving a much higher carrier mobility than conventional $\text{In}_2\text{O}_3\text{:Sn}$ films.

[1] Macco et al., *P.S.S. - Rapid Res. Lett.*, DOI: 10.1002/psr.201409426

12:00pm **TF+SS-WeM13 Mechanical Property and Corrosion Resistance Evaluation of CrVN and CrSiN Thin Films Grown by a Hybrid High Power Impulse Magnetron Sputtering and Radio Frequency Sputtering Technique.** *Jyh-Wei Lee*, *C.Y. Cheng*, *P.W. Chang*, Ming Chi University of Technology, Taiwan, Taiwan, Republic of China, *B.S. Lou*, Chang Gung University, Taiwan, Taiwan, Republic of China

High power impulse magnetron sputtering (HIPIMS) is a novel coating technology, which is characterized for its high peak power density to achieve unique thin film properties, such as high hardness, good adhesion and tribological performance. The aim of this work was to systematically study the microstructure, mechanical properties and corrosion resistance of CrVN and CrSiN coatings fabricated by a hybrid high power impulse magnetron sputtering and radio frequency sputtering technique. The experimental results showed that the peak power density increased linearly as the duty cycle decreasing from 5% to 2.5%. As compared with the CrVN coating, the higher hardness and better corrosion resistance were obtained for the CrSiN coatings, which can be attributed to their denser microstructures fabricated using the HIPIMS technology under optimal duty cycle and pulse frequency in this work. Effects of Vanadium and Silicon

* TFD James Harper Award Finalist

elements on the microstructure, mechanical and electrochemical properties of CrVN and CrSiN coatings were also discussed.

Wednesday Afternoon, October 21, 2015

Nanometer-scale Science and Technology

Room: 212B - Session NS+EN+MG+SS+TF-WeA

Nanoscale Catalysis and Surface Chemistry

Moderator: Sidney Cohen, Weizmann Institute of Science, Israel

2:20pm NS+EN+MG+SS+TF-WeA1 Effects of γ -Al₂O₃ Support on the Geometry and Electronic Structure of H-covered Pt Nanoparticles, *Sampyo Hong, G. Shafai, T.S. Rahman*, University of Central Florida

We have studied the effects of γ -Al₂O₃(110) support on the geometry and electronic structures of H-covered Pt_x (x=22,44) nanoparticles (NP) using density functional theory (DFT). We find that the unoccupied d-band center of γ -Al₂O₃(110) supported Pt NPs exhibits a blue shift with decreasing Pt size similarly as the measured XANES absorption peak energy of Pt NP samples. In fact, our DFT results reveal that the shift of the unoccupied d-band center of Pt NPs is dependent of surface hydroxylation level on γ -Al₂O₃(110). At higher hydroxylation the calculated unoccupied d-band center can even show red shift. Thus, consideration of hydroxylation level on γ -Al₂O₃(110) is needed to properly interpret support effect from XANES spectra. Overall, the strength of Pt- γ -Al₂O₃(110) binding seems to be a reasonable measure of the shift of unoccupied d-band center as a result of metal-support interaction: the stronger the interaction the more the blue shift. In the light of these results, it is plausible to postulate that the adsorption energy shift of XANES spectra represent the strength of metal-support interaction (support effect). A remarkable example of such hydroxylation tuned metal-support interaction is structural transition of Pt₂₂ from a biplanar to a 3D-like geometry as a function of support hydroxylation.

This work is supported in part by DOE Grant DE-FG02-07ER15842.

3:00pm NS+EN+MG+SS+TF-WeA3 Fabrication and SERS Activity of Metal-loaded TiO₂ Nanometer Scale Particles, *Paolo Reyes, J.C. Hemminger*, University of California Irvine

Our current research focuses on the fabrication and study of metallic loaded titanium dioxide (TiO₂) nanoparticles supported by highly oriented pyrolytic graphite (HOPG). Highly dispersed TiO₂ particles are formed via physical vapor deposition (PVD) under high vacuum settings with an average pseudo-diameter of 11.6 ± 2.65 nm. Metallic loading is completed by an ex-situ photo-deposition method by exposure to precursor metal salt solutions under TiO₂ bandgap UV irradiation. We have attempted to fabricate Pt-, Ag-, Au-, and Pt-Au-TiO₂ particles and observed photocatalytic enhancement with the inclusion of Pt nanoparticles deposited onto TiO₂ surfaces. We believe this enhancement is a result of Pt nanoparticles harboring free excited electrons and preventing electron-hole recombination. We have developed a technique to increase the density of TiO₂ particles by creating site defects on the surface of HOPG through plasma mild oxygen plasma exposure. Highly dispersed TiO₂ nanoparticle distributions allow an increase of metal nanoparticle formation on TiO₂ for surface and intrinsic property observations. Ag nanoparticles have been fabricated in order to observe Surface Enhanced Raman Spectroscopy (SERS) Ag nanoparticles were observed to be an average pseudo-diameter of 2.6 ± 1.4 nm. A probe molecule was used to determine Raman intensity enhancement factor (EF) and we believe that the EF can be affected by the spacing and size of Ag-TiO₂ nanoparticles. We will present our studies of bi-metallic loading of TiO₂.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences through grant number: DE-FG02-96ER45576

4:20pm NS+EN+MG+SS+TF-WeA7 Pyridine Coordination Chemistry for Molecular Assemblies, *Milko Van der Boom*, Weizmann Institute of Science, Israel **INVITED**

Many types of metal-ligand interactions have creatively been used in the chemical sciences since the description of coordination complexes. The rich coordination chemistry of pyridine-type ligands has contributed significantly to the incorporation of metal ions into functional materials on surfaces. We will discuss molecular assemblies formed with a variety of pyridine-based compounds. These assemblies are formed by layer-by-layer deposition from solution that allows for precise fitting of the assembly properties. The degree of intermolecular interactions can be controlled by varying the degree of π -conjugation and the availability of coordination sites. Unlike molecular assemblies that are constructed with organic ligands, assemblies with polypyridyl complexes are active participants in their own

formation and amplify the growth of the incoming molecular layers. Such a self-propagating behavior for molecular systems is rare and the mechanism of their formation will be presented. Incorporating multiple metal complexes into a single assembly give rise to composite materials that exhibit unique electrochemical and electrochromic properties that are dependent on the arrangement of these metal complexes. We will also discuss the coordination chemistry of pyridine-based compounds with nanoparticles, the formation of metal-organic frameworks and their practical applications.

5:00pm NS+EN+MG+SS+TF-WeA9 Atomic Scale Iron Carbide Films on Au(111) and Cu(111) as a Iron Fischer-Tropsch Model Catalyst, *Gilbère Mannie, X. Wen, Y.W. Li*, SynCat@Beijing, China, *J.V. Lauritsen*, Interdisciplinary Nanoscience Center (iNANO), Denmark, *H.J.W. Niemantsverdriet*, SynCat@Beijing, China

Iron-based Fischer-Tropsch synthesis (FTS) is one of the most investigated catalytic systems in the world due to the ability to convert any form of hydrocarbons like coal, natural gas or biomass into diesel, gasoline and chemicals [1]. Although investigated for more than 50+ years, fundamental surface reactions involved in this process are not known or fully understood. Within the FTS community, iron carbide is seen as the active phase in the catalytic process but the atomic-scale surface structure and even the stoichiometry of the bulk phase is a matter of debate [1,2]. In order to fundamentally investigate the active phase, to for example verify molecular modeling studies on iron carbide surfaces (like [3,4]), we successfully synthesized highly-crystalline iron carbide monolayer islands (on Au(111)) and multilayer islands (on Cu(111)). Obtained carbidic films are suitable for analysis with scanning tunneling microscopy (STM) and other surface science techniques. Our atomically-resolved STM results, together with preliminary density functional theory (DFT) results show that we can characterize our iron carbide (Fe_xC_y) islands as iron layer with interstitial carbon atoms, based on the increase of the inter-atomic Fe-Fe distance [5]. During the synthesis of the Fe_xC_y islands we were able to record some STM movies showing the formation of the carbidic phase out of the metallic phase but we could also record movies during dosing experiments of several gasses (H₂, O₂) to the pure iron carbide islands. During the presentation we will explain how we synthesized these crystalline iron carbide films and how these films can act as a model system for fundamental Fischer-Tropsch catalyst research.

[1] E. de Smit, B. M. Weckhuysen, *Chem. Soc. Rev.*, **2008**, *37*, 2758

[2] J. W. Niemantsverdriet, A. M. van der Kraan, W. L. van Dijk, H. S. van der Baan, *J. Phys.*, **1980**, *84*, 3363

[3] J. M. Gracia, F. F. Prinsloo, J. W. Niemantsverdriet, *Catal. Lett.*, **2009**, *133*, 257

[4] M. O. Ozbek, J. W. Niemantsverdriet, *J. Catal.*, **2014**, *317*, 158

[5] G. J. A. Mannie, L. Lammich, Y. W. Li, J. W. Niemantsverdriet, J. V. Lauritsen, *ACS Catal.*, **2014**, *4*, 3255

5:20pm NS+EN+MG+SS+TF-WeA10 Fullerene Interaction with W Surfaces: Synthesis of Nanospheres with Tunable Bandgap, *Ehsan Monazami*, University of Virginia, *J.B. McClimon*, University of Pennsylvania, *P. Reinke*, University of Virginia

The interaction of f C₆₀ molecules with metal surfaces is a topic of considerable interest and discussed in the context of molecular electronics and organic solar cell applications. Our work focuses on the interaction of C₆₀ with W, which is a carbide forming transition metal. It has generally been assumed that the C₆₀ cage breaks up readily on a W surface, but our observations reveal a more complex, temperature induced reaction sequence leading to the formation of nanospheres with variable bandgap, which has been studied with in-situ STM and STS analysis.

The nanospheres are synthesized by initiating the reaction between C₆₀ deposited on a W-thin film surface grown on MgO(001) at about 450 K. In contrast to previous reports, the molecules do not collapse but the spherical shape is retained up to 800 K and the electronic structure changes gradually from wide bandgap C₆₀ to fully metallic nanospheres. The size distribution of the nanospheres is centered at 1.5 nm (600 K) and shifts for higher temperatures to about 2 nm with a concurrent decrease in height resulting in an ellipsoidal shape. These nanospheres present an exceptional resistance to sintering which is a unique feature for metallic nanoparticles. The densely packed C₆₀ and isolated C₆₀ molecules show the same transition in shape and electronic structure which confirms that the transformation is controlled by the reaction with the W substrate.

The transition in the electronic structure progresses gradually from the wide-bandgap molecule (2.3 eV) to a bandgap of ~1eV at 700 K, and a metallic surface at 800 K. We will illustrate this progression with a series of

ST spectra and maps. The bandgap variation offers for the first time a pathway to the formation of nanoscale clusters (nanospheres) with variable bandgap while retaining the surface curvature in narrow range. The detailed structure of the nanospheres is, however, still subject to discussion. We currently favor, based on our experimental results, a substitution model where the W-atoms from the substrate react with the C₆₀ cage which acts as a scaffold. The W atoms are incorporated substitutionally forming a carbide type bonding, whose presence is indicated by XPS analysis. The variation in bandgap is then driven by the degree of substitution and the fullerene molecule acts as a scaffold. We predict that other carbon scaffolds such as nanotubes and carbide forming transition metals can react in the same manner leading to a new class of nanostructures with unique adaptability of the electronic structure. The nanospheres are an excellent testbed for the physics and chemistry of highly curved surfaces.

Supported by NSF-DMR Ceramics DMR-100580.

5:40pm **NS+EN+MG+SS+TF-WeA11 Enantiomeric Separations of Chiral Pharmaceuticals using Chiral Tetrahedral Au Nanoparticles**, *Nisha Shukla, D. Yang, A.J. Gellman*, Carnegie Mellon University

Chiral tetrahedral (24-sided) Au nanoparticles are tested for their use as chiral separators of pharmaceutical drugs in solution phase. Tetrahedral Au nanoparticles were chirally modified with either D- or L-cysteine. They show enantioselective adsorption of pharmaceuticals such as propranolol hydrochloride (used for anxiety and high blood pressure) from a solution of racemic propranolol hydrochloride, thus leaving an enantiomeric excess in the solution phase. This work suggests that chiral nanoparticles can be used for enantiomeric separation of real pharmaceutical drugs. A simple robust model has also been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-propranolol hydrochloride adsorption on the chiral tetrahedral Au nanoparticles. The model obviates the need for experimental determination of the surface area of absorbent Au nanoparticles which is extremely difficult to measure.

6:00pm **NS+EN+MG+SS+TF-WeA12 Electroreduction Catalysis with Defect-Rich Metal Nanoparticles**, *Xiaofeng Feng, M. Kanan*, Stanford University

New design principles for electroreduction catalysts are essential for CO₂ recycling using renewable electricity. Au is one of the most active catalysts for CO₂ reduction to CO, and numerous efforts have been made to optimize Au catalysts by tuning the size, composition, and shape of Au nanostructures. Here we show that grain boundaries (GBs) in Au nanoparticles create highly active surface sites for CO₂ electroreduction (1). Defect-rich Au nanoparticles were synthesized by vapor deposition of Au onto a carbon nanotube thin film, which enables direct TEM characterization without further processing. We compared the CO₂ reduction activity of the as-deposited catalysts to those annealed at different temperatures. While the annealing process has little impact on the distribution of Au surface facets, it reduces the GB density, which is quantified by measuring GB lengths and particle areas from high-resolution TEM images. We found that the surface-area-normalized activity for CO₂ reduction is linearly correlated with GB density in Au nanoparticles in the low overpotential regime. Similarly, GB-density was also found to correlate with catalytic activity for the electroreduction of CO to multi-carbon oxygenates on Cu nanoparticles. Our studies show that grain boundary engineering is a general strategy for improving electrocatalytic activity for carbon fuel synthesis.

References:

(1) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *J. Am. Chem. Soc.* **2015**, *137*, 4606–4609.

Plasma Science and Technology

Room: 210A - Session PS+TF-WeA

Plasma Deposition and Plasma Assisted ALD

Moderator: Sumit Agarwal, Colorado School of Mines

2:20pm **PS+TF-WeA1 Plasma Prize Talk: Plasma Processing of Materials: What makes Plasma Special and Future Outlook?**, *Richard van de Sanden**, DIFFER **INVITED**

Plasma processing of materials is at the heart of present day technologies such as found in the manufacturing of IC's, liquid crystal displays and large scale production of solar cells, to name only a few. For a basic

understanding of the key processes determining the processing quality advanced in situ diagnostics for both the plasma phase as well as diagnostics to characterize the plasma-surface/material interaction are required. This basic understanding will enable control over these processes, such as the control of the ion energy distribution function by tailoring the bias voltage on the materials processed.

The aspects which differentiates plasma processing from other processing technologies such as the presence of charge, short living reactive radicals and nonequilibrium species distribution to name a few, will be discussed. In a future outlook I will argue that the nonequilibrium aspects, especially connected to the vibrational populations in molecular plasmas, are not yet exploited to its full extent. If we succeed in controlling the population of the vibrational states many novel applications in catalysis, gas and surface processing of materials come within reach.

3:00pm **PS+TF-WeA3 Feature Scale Simulation of Atomic Layer Deposition via FPS3D**, *Paul Moroz*, Tokyo Electron US Holdings, *D.J. Moroz*, University of Pennsylvania

Atomic layer deposition (ALD) allows accurate atomic-scale deposition of materials layer-by-layer with almost conformal feature profiles. Together with atomic-layer etching (ALE), it provides the tools necessary for satisfying the ever increasing demands for improved accuracy and miniaturization, and is becoming one of the leading methods among advanced semiconductor technologies. ALD requires cycling processing, with each cycle consisting of at least two timesteps, each timestep having its own parameters corresponding to different fluxes of species and different surface chemistry. Numerical simulation of ALD could be accomplished at the levels of quantum chemistry (QC), molecular dynamics (MD), or feature-scale (FS) calculations. While QC provides an ab-initio approach, MD depends on approximations of interactions with inter-atomic potentials, and FS methods rely on reactions between species. The reactions used in FS simulations could be estimated from experiments or they could be taken from MD or QC calculations. We present here numerical simulations of ALD for the case of deposition of silicon nitride film onto silicon utilizing dichlorosilane gas and ammonia plasma. Our calculations were carried out via the feature-scale simulator FPS3D [1-3], which can efficiently simulate multi-timestep operations and which allowed us to replicate the results of considered ALD experiments. In correspondence with the experiments, the reactions were selected such that the deposition of a single monolayer was produced not in a single cycle, but in two cycles, even when the duration of each timestep was long enough for the processes to saturate. FS simulations run much faster and can operate on a much larger scale than can MD and, especially, QC methods. FS methods can efficiently simulate processing of entire features with complex profiles both in 2D and 3D. We simulate the feature profiles obtained during processing at different conditions and initial settings, and we discuss various effects which could change the roughness of profiles. We also analyze the effects of partial conformity of obtained profiles and the effects of incomplete ALD, during which some reactions may not self-limit due to insufficient processing time.

[1] P. Moroz, IEEE Trans. on Plasma Science, **39**, 2804 (2011).

[2] P. Moroz, D. J. Moroz, ECS Transactions, **50**, 61 (2013).

[3] P. Moroz, D. J. Moroz, Journal of Physics: CS **550**,012030 (2014).

3:20pm **PS+TF-WeA4 Plasma Enhanced Atomic Layer Deposition Applications using an Ion Source**, *F. Papa*, Gencoa USA, *V. Bellido-Gonzalez, H. Li*, Gencoa Ltd, UK, *HD. Ngo*, University of Applied Sciences Berlin, Germany, *K. Kröhnert*, Fraunhofer Institut IZM Berlin, Germany, *O. Ehrmann, K.D. Lang, P. Mackowiak, Piotr*, TU Berlin, Germany, *William Sproul*, Reactive Sputtering, Inc

Atomic Layer Deposition (ALD) has been slowly gaining acceptance in the field of thin film deposition. Although firstly described in the 1960's as molecular layering by researchers in the former USSR, the introduction of the technology to the world came via Tuomo Suntola's group in 1974 (1). The application to ZnS highly ordered films was a real success, and made the electroluminescent displays a reality. Since then the concept has been applied into other technology areas. There are many benefits of ALD, however, in terms of deposition rates, film stress and management of reactive gas species in complex 3D structures there is still a long road ahead.

In order to lower the film stress plasma technology has been applied. Plasma Enhanced ALD (PEALD) has been introduced in order to lower the temperature requirements for the ALD process and also in order to control the properties of the ALD deposited film. The industrialization of such process presents a number of challenges. In PEALD, it is of interest to control the nature and degree of interaction of such plasmas with the surface chemistry. Plasma sources which can control the energy of the ion beam are of special interest. Also, from the industrialisation point of view the sources would need to be able to upscale the process. For those reasons, the authors believe that a Linear Ion Sources (LIS) could help move ALD processes

* PSTD Plasma Prize

into mass production. LIS's have been slowly pushing their way through into vacuum coating technology market for over 15 years. Only last year a small circular ion source, which can replicate the functional properties of large LIS's was introduced (2). This development has enabled rapid transitions from prototyping to manufacturing. The use of such a source is interesting for PEALD as the processes developed in the lab could be easily implemented at an industrial level. As part of the investigation the authors have used the ion source PEALD process on etched silicon wafers in order to produce low temperature conformal depositions. The wafers were etched with different features, like deep aspect ratio trenches, which are of great interest in today's semiconductor devices. Results will be presented.

1.- Riikka L. Puurunen, "A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy" <http://onlinelibrary.wiley.com/doi/10.1002/cvde.201402012/pdf>

2.- F. Papa, D. Monaghan, V. Bellido-Gonzalez, R. Brown, A. Azzopardi, I. Sorzabal-Bellido, "New Circular Ion Sources for Fast Process Development", Proceedings to the 2014 Society of Vacuum Coaters Conference, Chicago, USA, 505/856-7188, pages 187-191.

4:20pm **PS+TF-WeA7 Plasma-Assisted ALD of SiN_x: The Surface Chemistry Studied by Infrared Spectroscopy**, Roger Bosch, L.E. Cornelissen, C.K. Ande, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

Silicon nitride (SiN_x) deposited by ALD is gaining a lot of interest lately, as it allows for conformal films prepared at low temperatures while maintaining a high film quality and uniform thickness. This is challenging for conventional deposition techniques, such as CVD and PECVD. Within the work presented in this contribution, the growth of SiN_x by ALD and the associated surface chemistry have been studied. The chosen plasma-assisted ALD process employs bis(tertiary-butylamino)silane (SiH₂[NHC(CH₃)₃]₂, BTBAS) as precursor and N₂ plasma as co-reactant. Various *in situ* studies have been performed and the experimental work has been complemented with DFT calculations.

More particularly, to study the surface chemistry we developed a versatile setup, which combines ALD with Fourier transform infrared spectroscopy. A sample manipulator was designed that enabled us to study the species present at the surface, with a submonolayer sensitivity, as a function of substrate temperature (100-300°C) and incident angle of the IR beam. The setup also allowed for gas phase measurements.

Gas phase infrared measurements have been performed to identify which species were present in the reactor after the precursor dose and N₂ plasma exposure. The measurements revealed that *tert*-butylamine ((CH₃)₃CNH₂) is the main reaction product after precursor exposure. This indicates that the Si-N bond in the precursor molecule breaks when it interacts with active sites at the surface.

Surface infrared measurements have been conducted at different temperatures to determine which species were present at the surface after one of the ALD half cycles, i.e. after the BTBAS half cycle and after the N₂ plasma half cycle. Amongst others, a pronounced density of Si-H at the surface has been established, and at lower temperatures (~100°C) also a signal from C-H groups was clearly observed after BTBAS dosing. From these infrared measurements, complemented with DFT calculations and additional thin film studies, we propose a mechanism for the growth of SiN_x by ALD using BTBAS and N₂ plasma, which will be discussed during the presentation.

4:40pm **PS+TF-WeA8 Structural Characterization of Surface Dielectric Barrier Discharges (SDBD) for Atmospheric Pressure Plasma Enhanced Spatial ALD (PE-S-ALD)**, Yves Creyghton, J. Emmelkamp, F. Roozeboom, TNO Technical Sciences, Netherlands

Spatial ALD (S-ALD) is an emerging technology with substrates passing a series of spatially separated gas injector zones. This concept enables up to 100x faster deposition rates with respect to conventional ALD. TNO constructed an S-ALD process toolbox for high throughput ALD on wafers, sheets and foils. Recently, SDBDs were selected to extend the toolbox to plasma enhanced ALD. Implementing an SDBD source in an existing rotary wafer reactor, homogeneous PE-S-ALD was shown for the first time. The operating temperature was reduced down to 80°C allowing deposition on polymer foils. Using plasma in N₂, N₂-O₂ and N₂-H₂, new materials were made like TiN, SiO₂, TiO₂, InZnO and Ag, so far inaccessible for atmospheric pressure S-ALD.

Contrary to low-pressure plasma, atmospheric plasma tends to filamentary structures (micro-discharges). The past 2 decades, world-wide efforts have been undertaken to improve plasma homogeneity in DBD systems with the electrodes located at both substrate sides and using He gas, short pulses, high frequencies and gas flows. Single-sided SDBD electrode configurations provide remarkably homogeneous and reproducible plasmas in practical gases. Usually the electrical discharge is a mixture of surface

glow and micro-discharges, the latter being generated with a sufficient density to reach homogeneous deposition. There is a striking analogy between the saturating charge principle of the planar SDBD and the surface limited surface reaction, as characteristic for ALD processes. Merging both technologies yields the best of two worlds.

As a standard condition, SDBD plasma has been generated parallel and close to the rotating substrate. Obviously, when conductive, semiconductor or highly capacitive substrates are used the SDBD plasma may generate filaments towards the substrate and/or electrostatically interact with electric field sensitive structures. Thus we built various alternative remote SDBD sources minimizing electrical-substrate interaction. For the study of the influence of geometry and flow parameters, thin films were deposited by PE-S-ALD using the different sources.

Also static substrate tests were done with both parallel plasma and remote jet treatments using amorphous C-layer etching to visualize the plasma reactivity and homogeneity. The plasma structures visualized by C-layer transmission show the importance of control of flow and plasma homogeneity. The spatial discharge study is complemented by visual light photography and IR thermography. The experimental data have been validated with a CFD model of plasma species transport yielding a deep understanding of the effects of flow, diffusion and temperature of the SDBD source.

5:00pm **PS+TF-WeA9 Plasma Deposited Barrier Coatings on Plastics: Plasma Characterization and Thin Film Analysis**, Peter Awakowicz, F. Mitschker, Ruhr-University Bochum, Germany, A. Nave, INP-Greifswald, Germany, J. Röpcke, INP-Greifswald, G. Grundmeier, Univ. of Paderborn

INVITED

Thin SiO₂ barrier layers are deposited by microwave plasma enhanced CVD (PECVD). The pulsed mw power is fed in with a plasma line system. In addition, the flat or hollow PET substrates are rf-biased in order to increase film quality and minimize defect density.

Plasma diagnostics is performed with quantitative optical emission spectroscopy (Q-OES) based on a collisional radiative model for nitrogen and confirmed with multipole resonance probe measurements. In addition, nine carbon hydride and carbon oxide species are measured by laser absorption IR measurement while plasma diagnostics is performed.

Analysis of the 30 nm thin films are performed by XPS measurements and defect density measurements. Film porosity is measured with proton exchange measurements and cross linking by looking at the fine structure of the Si 2p peak with highly resolved XPS.

Finally it can be shown that good barrier improvement is realized with the applied deposition method on PET foils and a correlation between plasma parameters and film quality is presented.

5:40pm **PS+TF-WeA11 Flexible, Durable, Self-Cleaning Optical Coatings for Optoelectronics**, Thomas Fuerst, C.A. Wolden, Colorado School of Mines

A wide variety of applications such as solar cells, displays, and electrochromics require coatings that manipulate light and provide protective barriers. Silica-titania multilayers have long served as optical components on rigid substrates. Expanding this platform to flexible substrates would allow compatibility with roll-to-roll manufacturing, which would increase manufacturing efficiencies while decreasing costs. Incorporating self-cleaning properties into these coatings would enable longer lifetime, improved efficiency, and reduced maintenance costs for the devices. In this work we describe the design, fabrication, and evaluation of flexible multilayer coating deposited by plasma-enhanced chemical vapor deposition (PECVD) at low temperature. The high and low refractive index materials were TiO₂ and silicone, respectively. PECVD enables the deposition of high quality material at temperatures compatible with polymeric substrates. Silicone is a mechanically robust polymer that imparts flexibility to the coatings and TiO₂ provides UV protection and self-cleaning functionality. The optical stacks were designed using commercial software and validated using UV-Vis-NIR spectrophotometry. The nanoscale control achievable in this process was demonstrated through the fabrication of several Bragg mirrors that were designed to produce blue, green, and red coatings. A five layer broadband anti-reflective (AR) coating was designed and deposited onto a variety of substrates including 1 mm glass, 3 mm FTO-coated glass (TEC-15), flexible polyethylene terephthalate (PET) thin films, and CdTe solar cells built on TEC-15. The absolute transmission of AR-coated glass and PET samples increased by ~5% across the visible spectrum, and solar cells experienced a commensurate boost in efficiency due to improved short circuit density. The multilayer coatings on PET proved to be mechanically robust, as their optical properties remain unchanged after 50,000 cycles of automated bend testing, including both tensile and compressive stress. Lastly, a five layer IR reflector was designed and applied to 1 mm glass and PET. The visible transmittance remained unchanged while the near IR (800-1200 nm)

transmission was reduced from 88% to 27% on PET. Studies are underway to assess the long term durability of these coatings to UV exposure and examine the self-cleaning capability through measurements of contact angle and contaminant removal. These results indicate that these nanolaminates show great promise for use in a variety of flexible optoelectronic applications.

6:00pm PS+TF-WeA12 Microwave Plasma Assisted Chemical Vapor Deposition of High Quality, Single Crystal Diamond Substrates, Shreya Nad, Y. Gu, J. Asmussen, Michigan State University

Single crystal diamond (SCD) substrates have very useful properties like their high thermal conductivity, extreme hardness and chemical inertness and are thus deemed to be novel materials for applications in a varied range of fields like high power electronics and X-ray optics. Microwave Plasma Assisted CVD (MPACVD) is one of the most suitable and efficient methods for the synthesis of diamond substrates. MPACVD is carried out in a microwave cavity plasma reactor (MCPR) which consists of a brass cavity to contain the microwave power, a quartz dome and a water cooled substrate holder.

The reactor is first tuned using the 4 length variables to achieve maximum power coupling efficiency. A mixture of methane and hydrogen gasses flows within the quartz dome. The cavity probe excites the plasma at ~ 5 Torr. The plasma discharge is positioned directly above and adjacent to the seed substrate for the growth process to proceed efficiently. Pressure is then gradually increased and depending upon the growth conditions maintained at a high synthesis pressure of 180 – 240 Torr. The substrate temperature is maintained within 1050 – 1150°C for a smooth, high rate growth of SCD. The stable plasma creates a chemically and thermally suitable environment for SCD deposition. The high pressure and high gas temperatures at the core of the plasma discharge break down the methane and hydrogen gas molecules into the important growth radicals. These growth radicals (like CH₃, C₂H₂ etc.) then diffuse through the boundary layer between the plasma and the seed substrate and then deposit on the substrate surface.

The MPACVD method has been used for the growth of both SCDs and polycrystalline diamond (PCD) substrates at high pressures of 160 – 240 Torr, with high growth rates of 20 – 32 μm/hr and for long growth times of 24 – 72 hours. The diamond substrates are then separated from the underlying seed substrate by laser cutting and then the surfaces are mechanically polished for analyses. These substrates have been characterized using FTIR and UV/Vis spectroscopy, SIMS, optical microscopy and X-ray topography. The SCDs grown are of type IIa quality i.e. they have very low nitrogen concentrations of < 100 ppb. They have high transmission even in the low wavelength range. Etch pit density measurements indicate that the substrates grown have low defect density of ~ 10⁴/cm².

This presentation describes in detail this efficient deposition process for SCDs and the high quality of the diamond substrates hence achieved.

Thin Film

Room: 114 - Session TF+AS+BI-WeA

Thin Films for Biological and Biomedical Applications

Moderator: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, Angel Yanguas-Gil, Argonne National Lab

2:20pm TF+AS+BI-WeA1 On-chip Characterization of Engineered Nanomaterial Surface Properties by Real-time Affinity Monitoring, C. Desmet, A. Valsesia, P. Colpo, European Commission, Joint Research Centre (JRC), Francois Rossi, European Commission, Joint Research Centre (JRC), Italy **INVITED**

The exhaustive characterization of the physico-chemical properties of engineered nanomaterials (ENMs) is essential to understand their mode of action and potential impact on health and environment. The development of characterization methods has been the object of important work in the past years, and has led to a better understanding on the ENM interaction with cellular systems and living organisms. One of the important surface properties of ENMs is the surface energy, for which there is no standard characterization technique established. Here, we demonstrate the feasibility of a characterization method based on a disposable microfluidic chip connected to an optical reader. The detection platform is based on the use of a micropatterned surface with tuned surface properties to bind ENMs selectively by hydrophobic forces and electrostatic interactions. The real-time absorption of ENMs on the differently functionalized micro domains is monitored by a microscope-coupled camera and gives information on the kinetics of adsorption, related to the affinity of the ENMs for the different

surfaces as a function of their sizes and shapes. Interpretation of the results within the extended DLVO theory allows retrieving the surface energy characteristics of the ENMs surfaces. The key advantage of the device is the increase of the characterization throughput thanks to the all-in-one characterization process and the multiplexing that is able to replace the use of different methods and expensive equipment. In this way, the full characterization of ENMs could be expanded in all the areas covering nanomaterial-related applications.

4:20pm TF+AS+BI-WeA7 Titanium-Niobium Thin Films Deposited by Magnetron Sputtering on AISI 316L Stainless Steel Substrate, D. Gonzalez, T.C. Niemeyer, C.R.M. Afonso, Pedro Nascente, Federal University of Sao Carlos, Brazil

Metallurgical biomaterials such as AISI 316L stainless steel (SS), chromium-cobalt alloys, titanium and its alloys are commonly used in medical implants due to their interesting mechanical properties and thermal stability. However, 316L SS and Cr-Co alloys have much higher elastic modulus than bone, causing the loss after some years of implantation [1]. The elastic modulus of Ti-based alloys ranges from 55 to 110 GPa, being significantly lower than those for 316L SS (210 GPa) and Cr-Co alloys (240 GPa), making them more suitable for use in dental and orthopedic applications. Also Ti alloys present high strength, low density, high corrosion resistance, and good biocompatibility [1]. Pure Ti has two allotropic forms: hexagonal closest-packed (hcp), known as α phase, and body centered cubic (bcc), known as β phase, structures. Studies have shown that the addition of alloying β -stabilizing elements such as V, Mo, Nb, Zr, Mo, and Ta causes the decreasing of the modulus of elasticity of the β -Ti alloys without compromising the strength [1]. In this study, thin films of Ti-Nb alloys were deposited on AISI 316L stainless steel substrate by magnetron sputtering, and the structure, morphology, and composition of the films were analyzed by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Thin films of three compositions were produced: Ti₈₅Nb₁₅ (Ti-26wt% Nb), Ti₈₀Nb₂₀ (Ti-33wt% Nb), and Ti₇₀Nb₃₀ (Ti-45wt% Nb). Structural characterization by XRD indicated that only the β phase was present in the thin films. XPS analysis showed a predominance of oxidized Ti and Nb on the film surfaces. TEM analyses were carried out in the following image modes: bright field (BF) images, selected area diffraction (SAD), scanning mode (STEM) BF and in annular dark field (ADF), and X-ray mapping using energy dispersive spectroscopy (EDS). For the Ti₈₀Nb₂₀ alloy film, TEM analysis showed columnar grains (~100 nm width) of α -Ti phase, with a Nb-rich transition layer ranging from finer grains (in contact with SS substrate) to a coarser columnar grains. For the Ti₇₅Nb₂₅ alloy film, TEM analysis showed columnar grains (~50 nm width) of β -Ti phase, with a transition layer away from the SS substrate.

Acknowledgements: A.L. Gobbi, C.A. Silva, S.R. Araujo, and J. Bettini from the Brazilian Nanotechnology National Laboratory, for their assistance in the growth and characterization of the thin films; and CNPq and CNPEM (Brazil), for support.

[1] M. Geetha *et al.*, Prog. Mater. Sci. 54 (2009) 397-425.

4:40pm TF+AS+BI-WeA8 SAM-based Models of Cell Surfaces to Study the Interactions with Lectins and Bacterial Fimbriae, Andreas Terfort, University of Frankfurt, Germany, K. Lindhorst, University of Kiel, Germany

Biologically important events such as cell-cell adhesion or infection typically start by directed and selective interactions with the highly glycosylated layer surrounding most eukaryotic cells. This layer, called the glycocalyx, consists of intricate glycopolymers, which – although in apparent disorder – clearly identify the cells. It is therefore of paramount interest to understand, which structural elements are important for the cell identification.

Self-assembled monolayers (SAM) can be used to simulate the chemical and sterical environment within such a glycocalyx. For this, glycosides are attached to oligoethyleneglycol (OEG) chains, which simulate the hydrogel matrix for the respective receptor. In this talk, we will focus on mannose-derivatives, which can be selectively recognized either by a lectin, concanavalin A, or by the adhesive fimbriae (tiny protein extrusions) of *E. coli* cells.

We would like to present different strategies for the construction of such SAMs [1,2] and discuss the advantages and disadvantages of these approaches. In extension of the mostly static systems, we will also present an approach to dynamically reorient the glycoside at the interface to determine the influence of steric factors on surface recognition [3].

References

[1] Kleinert, M.; Winkler, T.; Terfort, A.; Lindhorst, T.K. *Org. Biomol. Chem.* **6**, 2118-2132 (2008)

[2] Grabosch, C.; Kind, M.; Gies, Y.; Schweighöfer, F.; Terfort, A.; Lindhorst, T. K. *Org. Biomol. Chem.* **11**, 4006-4015 (2013).

[3] Weber, T.; Chandrasekaran, V.; Stamer, I.; Thygesen, M.B.; Terfort, A.; Lindhorst, T.K. *Angew. Chemie Int. Ed.* **53**, 14583-14586 (2014).

5:00pm **TF+AS+BI-WeA9 Improving the Long-Term Stability of Thin-Film Contact and Electrode Metallizations for Implantable Silicon Neural Interfaces**, *Brian Baker, R. Caldwell*, University of Utah, *H. Mandal, Blackrock Microsystems, R. Sharma, P. Tathireddy, L.W. Rieth*, University of Utah

The Utah Electrode Array (UEA) is a penetrating multi-electrode interface designed to be implanted and communicate directly with the brain and peripheral nerves through recording and stimulation. These devices are used for treating neural disorders and controlling prosthetics.

The UEA is micromachined out of single crystal silicon and uses a Pt/Ir/IrOx thin film metallization stack as an electrical interface on the electrode tip and a Pt/Ir/Pt stack on the backside contacts. Delamination of these thin metal layers has been observed during fabrication processes, soak testing, and in vivo operation, and is the critical failure mode examined in this study.

Db-FIB and Cross-sectional STEM analysis were used to identify Kirkendall voids as the root cause of the adhesion failures. This investigation showed that these voids form during the platinum silicide annealing process at the interface between the PtSi and the Ir layers.

Typical thicknesses of the UEA metallization are 200 nm/500 nm/520 nm Pt/Ir/IrOx, and 200 nm/200 nm/325 nm Pt/Ir/Pt. We report the results of replacing the 200 nm base layer with 1) a 25 nm Pt base layer or 2) a 50 nm co-sputtered PtSi base layer. These layers were subjected to typical UEA annealing conditions of 375 °C in forming gas for 45 minutes, followed by a 475 °C, 30 minute oxygen anneal.

Cross-sectional STEM elemental mapping of each film stack showed complete transformation of the platinum layer to PtSi, with a 40 nm layer of iridium silicide formed at the PtSi/Ir interface. In addition, a reduction in the nanogaps caused by Kirkendall voiding was demonstrated by STEM analysis in the two new film stacks.

Both the 25 nm Pt base layer stack and the 50 nm co-sputtered PtSi base layer stack demonstrate low-resistance Ohmic contacts and wire bondability after annealing. Further electrical characterization of these thinner base layer stacks used on tip metal demonstrated impedances of 5-10 kOhms and charge injection capacities of 1-2 mC/cm² for typical electrode tip surface areas. Cross-sectional STEM analysis of the reactively sputtered iridium oxide film reveals a three dimensional morphology whose nanostructures provide a large augmentation of electrode surface area and a corresponding increase in charge injection capacity. In vitro stimulation and accelerated lifetime tests are ongoing and electrical measurements and thin film adhesion stability will be reported.

5:20pm **TF+AS+BI-WeA10 On-Surface Synthesis of Organic Nanostructures on Copper Surfaces**, *Q.T. Fan*, University of Science and Technology of China, *J.M. Gottfried*, Philipps-Universität Marburg, Germany, *Junfa Zhu*, University of Science and Technology of China

The on-surface synthesis of organic nanostructures known as bottom-up approach paves a new way for surface structuring, which plays a vital role in catalysis, sensor systems, or organic electronics. In this presentation, we will report our recent studies on the on-surface synthesis of 2D organic nanostructures on Cu(111) and Cu(110) surfaces using a specially designed bromo-terphenyl precursor, namely 4,4'-dibromo-*meta*-terphenyl (DMTP). The study was performed under ultra-high vacuum conditions using a combination of scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The results indicate that the two different surface structures of Cu drive the precursor molecule to form different nanostructures on the surface. We will show temperature-dependent organic nanostructures formed after DMTP adsorbed on Cu(111) and Cu(110). These organic nanostructures include large-area, defect-free 2D ordered nanostructures of intact DMTP on Cu(111), 1- or 2D polymeric zigzag organometallic intermediates formed on Cu(111) and Cu(110), and the macromolecular nanostructures including hexagonal close-packed arrays of cyclo-octadecaphenylene (hyperbenzene), oligophenylene nanowires formed through Ullmann reaction mechanism. *This work is supported by the National Natural Science Foundation of China (21173200, 21473178) and National Basic Research Program of China (2013CB834605)*

5:40pm **TF+AS+BI-WeA11 Carbon Nanotube-Templated, Porous Films for Thermal Isolation**, *J.M. Lund, D.B. Syme, R. Vanfleet, R.C. Davis, B.D. Jensen, Brian Iverson*, Brigham Young University

Sensor usage has increased dramatically in detection applications due to miniaturization of components through micro and nanofabrication. These

fabrication methods have also greatly increased production rates, as several sensors can be constructed in parallel. Reduction in feature size of sensors has resulted in an increase in sensor component proximity, making thermal diffusion or cross talk detrimental to proper function. This work investigates the use of carbon nanotube-templated manufacturing (CNT-M) to create thin-film, isolation layers for use in thermal sensors. CNT-M is a process wherein carbon nanotubes are used as a scaffold and coated with insulating materials (e.g. SiO₂) to create porous insulating films. Carbon nanotubes are removed in a post-deposition, burn out process rendering a porous matrix of insulating material. Thin-films are characterized using scanning electron microscopy, nanoindentation and the 3-omega method to determine mechanical and thermal properties. Thermal conductivity on the order of air has been observed while still maintaining a rigid structure that is compatible with subsequent MEMS processing.

Thin Film

Room: 111 - Session TF+AS+EM+EN+MN-WeA

CV Infiltration Methods and Energetic and Thermal Properties of Thin Films

Moderator: Richard Vanfleet, Brigham Young University, David Allred, Brigham Young University

2:20pm **TF+AS+EM+EN+MN-WeA1 The Many Avatars of PVD**, *Murali Narasimhan*, Applied Materials, Inc. **INVITED**

Physical Vapor Deposition has been used for many years for depositing thin film coatings for diverse uses ranging from jewelry to industrial cutting tools. PVD has found usage in the manufacture of advanced semiconductor manufacturing for depositing various metals and some specialty dielectrics as well. The majority of high purity metal deposition for semiconductor use has been done using PVD although the use of CVD and ALD has increased over the years because of requirements of conformality and gap fill where conventional planar PVD has not been adequate. However, breakthroughs in PVD technology have been successful in extending the use of PVD to advanced semiconductor manufacturing nodes by changing the geometry of PVD sources and reactors and the nature of the plasma involved. Collimated and long-throw sources developed by the semiconductor equipment industry in the early '90s enabled the deposition of high-purity Ti to lower contact resistance for transistors. Reactive sputtering of TiN enabled a robust barrier for CVD W plugs used at the 0.5um node. Further, use of electromagnetic fields to ionize and then guide the plasma and sputtered ionized atoms has been successful in improving the conformality of PVD Ti films. Ionized Metal Plasma (IMP), Hollow-Cathode Magnetron (HCM) and Self-Ionized Plasma (SIP) were innovations in ionized PVD reactor design that led to widespread adoption of PVD TaN and PVD Cu for Cu interconnect barrier and seed layer production from the 90nm node to the present. The application of thermal energy on the substrate during PVD Al and Cu has been useful in improving the flow of deposited material and subsequent gap-fill of sub-micron features. The use of Radio Frequency (RF) energy to power the target has allowed for more efficient ionization at lower power levels. The application of a capacitive tuner to modulate the ion bombardment on the wafer and tailor the film properties of TiN for hard mask applications has enabled the realization of etched features at the 22nm node. Pulsed DC magnetrons enable sputtering of dielectric materials, thus opening up the controlled deposition of thin films of insulating films for various applications such as improving the brightness of high-efficiency LEDs. Multi-cathode off-axis PVD magnetrons have enabled the deposition of multi-layers of ultra-thin films for magnetic devices such as advanced in-plane and out-of plane MRAM and the manufacture of EUV mask blanks for sub 10nm manufacturing. This talk will present the above listed progression of PVD technology over the years and its use for many applications in semiconductor manufacturing.

3:00pm **TF+AS+EM+EN+MN-WeA3 Reactive Foil Ignition by Laser Irradiation: Experimental and Modeling Results**, *Ryan Murphy, C.D. Yarrington*, Sandia National Laboratories, *R.V. Reeves*, Lawrence Livermore National Laboratory, *D.P. Adams*, Sandia National Laboratories

It has been shown that forced mixing of reactive layers (foils) leads to an exothermic release of energy after initiation by pulsed laser irradiation. In order to understand the ignition of foils initiated by laser irradiation, we study the interaction of laser pulses with Al/Pt multilayer reactive foils prepared by sputter deposition. It will be shown that the single-pulse ignition threshold and dynamics are dependent on the length of the laser pulse as the pulse length is varied from 150 fs to 100 ms. The dependence of the ignition threshold on pulse length is a combination of laser-material interactions such as the size of the heat affected zone and the onset of ablation for ultrafast irradiation. Simulations of single-pulse laser heating

were performed with Aria, the thermal package of the SIERRA finite element computational framework. Three-dimensional geometries were subjected to laser flux boundary conditions equal to those measured from the experimental conditions. Modeling and experimental results are correlated to show the effects of the heat affected zone size and shape on ignition thresholds and onset times.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:20pm TF+AS+EM+EN+MN-WeA4 The Effects of a Heat Sink on Self-Sustained Propagating Reactions in Sputter-Deposited Bimetallic Multilayers, David Adams, R.V. Reeves, M. Hobbs, Sandia National Laboratories

Reactive multilayers grown by sputter deposition have recently attracted interest for applications including material joining (soldering, brazing) and energy sources. For these applications, a metal-metal multilayer is typically designed to have many discrete reactant layers and a composition that corresponds to the peak enthalpy for a given material system. A thickness of reactive multilayers as small as 1.6 microns has recently been demonstrated for microelectronics joining (Brauer et al. ECS Transactions, 2012). However, little is known about the minimal multilayer thickness required for ensuring a self-sustained, high temperature synthesis (SHS) reaction.

With this presentation, we describe the behavior of thin reactive Al/Pt multilayers tested as freestanding foils and as adhered films. For multilayers having a total thickness of 1.6 microns, self-sustained, high temperature reactions readily occur when the multilayer is tested as a freestanding foil. When coupled to a semi-infinite substrate, the likelihood of reaction is reduced depending on the multilayer design.

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5:00pm TF+AS+EM+EN+MN-WeA9 Beyond Deep Silicon Etching – Generating High Aspect Ratio Microstructures by Infiltration of Carbon Nanotube Frameworks, Robert Davis, Brigham Young University INVITED

In addition to being the anchor material for microelectronics, silicon is widely used as the basis of high aspect ratio microfabrication for MEMS with applications ranging from inertial sensors to neural probe arrays. Carbon nanotube templated microfabrication (CNT-M), extends the palette of materials and structures for high aspect ratio microfabrication beyond those achievable with vertically etched bulk silicon. In CNT-M, 3-D forests of patterned vertically-aligned carbon nanotubes are grown as a high aspect ratio framework and then the "forests" are infiltrated with a secondary material by chemical vapor deposition. Precision structures (including nanoporous structures) with very high aspect ratios (greater than 400:1) can be generated with CNT-M. The infiltration materials range from ceramics to metals and include silicon dioxide, silicon nitride, carbon, nickel, and yes silicon. We are using CNT-M to fabricate functional structures for applications including mechanical actuation, chemical separations and detection, and electrochemical energy storage.

5:40pm TF+AS+EM+EN+MN-WeA11 The Influence of Thin Binder Films on Reaction Behavior in Reactive Powder Complexes, Robert Reeves, K.T. Sullivan, A.E. Gash, Lawrence Livermore National Laboratory

With the recently renewed interest in additive manufacturing (AM), there has been a recent upswell in the number of AM processes available. One such process that could be useful for reactive materials utilizes a curable liquid binder to adhere loose powders into coherent solid forms. In this process, tap-density powders are nearly saturated with binder, so the resulting film of binder present on each particle can represent a significant contaminant to the reaction system. In this work, the effect of the binder on reaction behavior in the Ni-Al system is explored. First, the distribution of binder and its elemental constituents are studied by electron microscopy and energy dispersive spectroscopy for powders with varying levels of binder saturation. Then, the effect of binder on the reaction kinetics and overall behavior is investigated. The change in overall heat release and apparent activation energy are quantified through differential scanning calorimetry, and the bulk reaction propagation rate is measured by high speed photography as a function of the weight fraction of binder in the compact. Finally, the reaction products are identified through x-ray diffraction. In all tests, comparisons are made to the neat Ni-Al system.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

6:00pm TF+AS+EM+EN+MN-WeA12 Carbon Nanotube Sheets from Horizontally Aligned Carbon Nanotubes, Nathan Boyer, D.B. Syme, J.T. Rowley, Brigham Young University, M. Harker, R. Creighton, S. Cornaby, Moxtek Inc., R. Vanfleet, B.D. Iverson, Brigham Young University, L. Pei, Johns Hopkins University, R.C. Davis, Brigham Young University

Carbon sheets comprised of horizontally aligned carbon nanotubes (CNT) were prepared by rolling vertically aligned CNTs into a thin-film. A subsequent infiltration step to coat the rolled CNTs with amorphous carbon or polymer has also been performed to improve adhesion of neighboring CNTs. Amorphous carbon infiltration was achieved using chemical vapor deposition and polymer infiltration was performed by dipping the sheet into a solvent-mediated, polymer solution. The typical failure mode of the CNT thin-films is to tear parallel to the alignment of the CNTs. Infiltration of the aligned CNT film with additional materials strengthens the film against tearing and increases burst pressure. Non-infiltrated CNT thin-films have sustained a differential pressure of 1.4 atm over a circular area of 7 mm² on a bulge test apparatus. Both carbon and polymer infiltrated sheets could be used in many applications including micromechanical sensing and actuation.

Thursday Morning, October 22, 2015

2D Materials Focus Topic

Room: 212C - Session

2D+EM+MG+NS+SE+SM+SS+TF-ThM

Emergent 2D Materials

Moderator: Paul Sheehan, Naval Research Laboratory

8:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM1 CVD Growth and Characterization of 2D MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, and MoS₂(1-x)Se_{2x} Alloys**, David Barroso, T. Empante, A. Nguyen, V. Klee, I. Lu, E. Preciado, C. Lee, C. Huang, W. Coley, S. Naghibi, G. von Son, A. Brooks, J. Kim, L. Bartels, University of California, Riverside

Transition Metal Dichalcogenides (TMDs) have been of increasing interest over the past years due to their exciting semiconducting properties. In the bulk, TMDs possess a native indirect bandgap and transition to a direct bandgap as they approach the monolayer limit. The bandgaps range from 1.15 eV to 1.95 eV depending on composition. Using organic liquids and/or inorganic powders as precursors, CVD growth techniques have been realized for MX₂ TMDs (M = Mo, W; X = S, Se, Te) and their alloys at tunable compositions. We achieved consistent synthesis of these TMDs materials. The films can either be made homogeneous in bandgap or exhibiting a linear bandgap gradient. Characterization of the films include Raman and photoluminescence spectroscopy, as well as AFM. Device fabrication allows for transport measurements. Depending on the composition, the materials show n- or p-doping in a consistent fashion.

8:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM2 Investigation of Manganese Dioxide Nanosheets by STM and AFM**, Loranne Vernisse, S. Afsari, S.L. Shumlas, A.C. Thenuwara, D.R. Strongin, E. Borguet, Temple University

Interest in ultrathin two-dimensional nanosheets has grown exponentially thanks to their unique and diverse electronic properties. As they possess atomic or molecular thickness and infinite planar dimension, they are expected to have different properties than the bulk of the material from which they originate. This offers opportunities for the development of devices in various areas, ranging from catalysis to electronics. Using the exfoliation approach, it is possible to investigate 2D nanosheets of different materials in search of new phenomena and applications. Bearing this mind, we focused on manganese dioxide (MnO₂), and more specifically δ-MnO₂ (Birnessite). This mineral has the advantage to present a low surface enthalpy [1], which results in weak water binding. Moreover, the presence of defects, e.g., oxygen vacancies has a dopant effect on water oxidation. These properties make MnO₂ a perfect candidate as a catalytic surface for water splitting and pave the way to the design of clean and renewable energy system. Furthermore, MnO₂ can be easily exfoliated into ultrathin nanosheets owing to the layered structure of the manganese oxide precursors.

Our goal is to investigate the catalytic activity of ultrathin MnO₂ nanosheets using scanning probe microscopy techniques, especially atomic force microscopy (tapping mode) and scanning tunneling microscopy (ambient and electrochemical conditions). In this perspective, we have first improved the deposition processes and find the imaging conditions to observe MnO₂ nanosheets with an average thickness of one or two layers. We have also showed that MnO₂ single layer nanosheets exhibit an expected hexagonal atomic pattern and present some defects. We will now resolve and identify the different defects and investigate the evolution of the conductivity as a function of the defect concentration and the number of layers.

This work was supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575.

[1] M. M. Najafpour, E. Amini, M. Khatamian, R. Carpentier, S. I. Allakhverdiev, Journal of Photochemistry and Photobiology B: Biology (2014), 133, 124.

8:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM3 Two-Dimensional Early Transition Metal Carbides and Carbonitrides "MXenes": Synthesis, Properties and Applications**, Michael Naguib, Oak Ridge National Laboratory

INVITED

Ternary layered carbides and nitrides with formula of M_{n+1}AX_n (M stands for early transition metal, A for group A element, X is carbon or nitrogen, and n=1, 2, or 3), so called MAX phases, are known for their unique combinations properties of ceramics and metals. It was found recently that etching atomically thin layers of aluminum from the MAX phases results in

forming weakly bonded stacks of two-dimensional (2D) layers of early transition, coined as MXenes. The etching was carried out in fluoride contained aqueous systems. Thus MXenes surfaces are terminated with a mixture of groups including OH, O, and F. Sonicating MXenes in water results in delaminating few layers of MXenes from each other. However, to achieve a large-scale delamination, intercalation of a large compound between the layers prior to delamination is needed. MXenes were found to be a very interesting family of 2D materials since they are electrically conductors and hydrophilic. They also showed an excellent performance as electrodes for electrochemical super capacitors and Li-ion batteries. Here the recent progress in MXenes research from the synthesis to properties and applications will be covered, and in more details, large-scale delamination of MXenes will be discussed. Also, light will be shed on the performance of MXenes as electrode materials for electrochemical energy storage systems.

9:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM5 Molecular Beam Epitaxy of Large area HfSe₂(ZrSe₂)/MoSe₂ van der Waals Heterostructures on AlN(0001)/Si substrates**, Athanasios Dimoulas, P. Tsipas, E. Xenogiannopoulou, D. Tsoutsou, K.E. Aretouli, J. Marquez-Velasco, S.A. Giamini, N. Kelaidis, NCSR DEMOKRITOS, Greece

Two dimensional (2D) semiconductor van der Waals heterostructures (HS) made of group IVB (Zr, Hf) and group VIB (Mo, W) metal dichalcogenides are predicted [1] to have type II or type III band alignments mainly because of a large difference in their workfunctions and band gaps, which makes them candidates for novel 2D staggered, or broken gap tunneling field effect transistors (TFET). We use molecular beam epitaxy (MBE) to grow high quality large area HfSe₂ [2,3], ZrSe₂ [4] and MoSe₂ [5] films directly on AlN(0001)/Si(111) substrates. We confirm by RHEED and HRTEM that atomically thin layers (1-6 ML) are grown in single crystal form with a well-defined in-plane orientation on AlN. The films are continuous with smooth surface morphology (0.6 nm RMS roughness) and abrupt interfaces with no detectable reaction as verified by in-situ XPS and HRTEM. Micro Raman mapping for all layers confirms their structural integrity down to one monolayer and reveals very good uniformity on a cm-scale wafer and excellent stability of MoSe₂ over a period of at least two weeks in air. Strong room temperature PL signal of 1 ML MoSe₂ indicate high quality direct gap semiconductor in agreement with valence band structure details imaged by our in-situ ARPES [3, 5]. In a second step, MoSe₂/HfSe₂ [3] and MoSe₂/ZrSe₂ [4] HS were grown. Despite the large lattice mismatch, all layers are grown epitaxially as evidenced by RHEED with no detectable defects at the interfaces as confirmed by HRTEM suggesting good quality vdW epitaxy [6]. Using UPS the workfunctions (WF) were estimated to be 5.2, 5.5 and 5.4 eV for MoSe₂, HfSe₂ and ZrSe₂ respectively [3,4]. The last two differ substantially from theoretical values (~ 6 eV). Based on our STM and DFT calculations [3], we conclude that this difference is due to an ordered Se adlayer which lowers the HfSe₂ and ZrSe₂ WF bridging the WF gap between them and MoSe₂. As a result, small valence band offsets of 0.13 and 0.58 eV were found for the HfSe₂/MoSe₂ and ZrSe₂/MoSe₂ HS, respectively leading to type II band alignments. The availability of low cost wide-gap-AlN/Si wafers in 300 mm wafer sizes defines a manufacturable route for single crystal 2D semiconductor technology.

We acknowledge financial support from ERC Advanced Grant SMARTGATE-291260. We thank IMEC for providing the AlN/Si substrates.

[1] C. Gong et al., *APL*, **103**, 053513 (2013)

[2] R. Yue et al., *ACS Nano*, **9**, 474 (2014)

[3] K. E. Aretouli et al., *APL*, **106**, 143105 (2015)

[4] P. Tsipas et al., *Microelectron. Eng.* (2015), <http://dx.doi.org/10.1016/j.mee.2015.04.113>

[5] E. Xenogiannopoulou et al., *Nanoscale* **7**, 7896 (2015)

[6] F.S. Ohuchi et al., *JAP*, **68**, 2168 (1990)

9:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM6 Surface Investigation of WSe₂ Atomically Thin Film and Bulk Crystal Surfaces**, Rafik Addou, H. Zhu, University of Texas at Dallas, Y.-C. Lin, S.M. Eichfeld, J.A. Robinson, Penn State University, R.M. Wallace, University of Texas at Dallas

Heterogeneous fabrication of semiconducting two-dimensional layered materials presents a promising opportunity to develop highly tunable electronic and optoelectronic materials. (1-2) An example of crystalline monolayer of WSe₂ grown by chemical vapor deposition on epitaxial graphene (EG) grown from silicon carbide had been investigated at nanoscale level. The WSe₂ surface was characterized using atomic force microscopy (AFM) scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS). (3,4) AFM and

large STM images show high-quality WSe₂ monolayers. The sharpness of the W 4f and Se 3d core levels confirms the absence of any measurable reaction at the interface and oxide formation. The photoemission measurements of WSe₂-Graphene interface suggest p-type doping due to charge transfer (EG withdraws electrons from WSe₂) at the interface and formation of Schottky-type contact,(5) suggesting possible applications of such heterostructures as diodes and photodetectors. High-resolution STM images reveal atomic-size imperfections induced by Se vacancies and impurities. Additionally, the investigation of bulk WSe₂(0001) surface shows spatial variation attributed to the presence of two components in W 4f_{7/2} core level attributed to the presence of both n- and p-type behavior. STM images exhibit also various types of defect induced by vacancies and dopants. The STS spectra reveal two main characteristics i) expected p-type conductivity where the Fermi level located at the valence band edge, and ii) zero conductivity at negative bias explained by defect-induced band bending as reported on geological MoS₂ crystal surfaces.(4) In conclusion, the spatial variation (topography and electronic structure) is more noticeable in bulk WSe₂ grown by chemical vapor transport than in CVD thin films.

This work was supported in part by the Southwest Academy on Nanoelectronics sponsored by the Nanoelectronic Research Initiative and NIST and the Center for Low Energy Systems Technology, one of six centers supported by the STARnet phase of the Focus Center Research Program, a Semiconductor Research Corporation program sponsored by MARCO and DARPA.

- (1) Yu-Chuan Lin et al., Nano Lett., **14** (2014) 6936-6941.
- (2) Yu-Chuan Lin et al., Nature Comm. arXiv:1503.05592v1.
- (3) Robert M. Wallace, ECS Trans. **64** (2014) 109-116.
- (4) Rafik Addou, Luigi Colombo, and Robert M. Wallace, ACS Appl. Mater. Interfaces (Accepted, 2015).
- (5) Horacio Coy Diaz, Rafik Addou, and Matthias Batzill, Nanosclae **6** (2014) 1071-1078.

11:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM10 A Kinetic Study on the Adsorption of Polar (Water) and Non-Polar (Benzene) Molecules on CVD Graphene, Nilushni Sivapragasam, U. Burghaus, North Dakota State University**

The adsorption kinetics of water and benzene at ultrahigh vacuum conditions were studied. Two different chemical vapor deposited graphene samples (graphene/SiO₂ and graphene/Cu) were utilized. Different surface analytical techniques (Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy) were used to characterize the surface. Subsequently, a kinetics study - to understand the adsorption of water and benzene- using thermal desorption spectroscopy (TDS) was conducted. The TDS results revealed the hydrophobicity of water on graphene. However, the adsorption kinetics of water on graphene did not mimic the bare substrate, i.e., graphene is non-transparent for water adsorption. In contrast, graphene was transparent for benzene adsorption. Furthermore, the adsorption kinetics of both, water and benzene were substrate dependent.

11:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM11 Epitaxial Ultrathin MoSe₂ Layers Grown by Molecular Beam Epitaxy, Ming-Wei Chen, M.B. Whitwick, O. Lopez-Sanchez, D. Dumcenco, A. Kis, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**

Two-dimensional transition metal dichalcogenides (TMDs) have attracted widespread attention recently, and the focus is specifically on ultrathin layers due to the strong spin-orbit coupling and direct band-gap transition of single-layers. The unique properties of various TMDs also enable the possibilities for future optoelectronic applications. However, the synthesis of TMDs with uniform large-area and high-quality still remains challenging. While chemical vapour deposition has been demonstrated as a promising technique, the complexity of chemical precursors and the lacking of *in-situ* observation technique strongly hinder the progress.

Here, We propose to use ultra-high vacuum molecular beam epitaxy (MBE) to grow MoSe₂ ultrathin layers, down to single-layer in a controllable way. Epitaxial MoSe₂ layers were successfully grown on different crystalline substrates via van der Waals epitaxy mechanism, benefited from the weak interlayer interaction and the lacking of dangling bonds. Reflection high energy electron diffraction (RHEED) was used to *in-situ* monitor the initial growth stage and revealed a clear transition of the streaks, demonstrating the formation of MoSe₂ layer. Sharp streaks were obtained in the growth end, with the streak spacing corresponding to MoSe₂ lattice constant, and no significant strain effect was observed. In order to demonstrate the validity of van der Waals epitaxy, different crystalline substrates with lattice mismatch up to 30 % have been tested. The epitaxial layers showed a smooth and uniform surface in atomic force microscopy, and the quality was further confirmed in Raman spectrum and transmission electron

microscopy. Furthermore, photoluminescence of the single-layer MoSe₂ showing a sharp peak of ~1.58 eV at room temperature demonstrates the direct band-gap feature and indicates the potentials of photovoltaic applications. In the end, the growth of two-dimensional van der Waals heterostructures has also been addressed and the results pave way for heterostructure studies.

In summary, molecular beam epitaxy has been proved to be a reliable route to grow large-area and high-crystalline transition metal chalcogenides, and is promising to facilitate the integration of other two-dimensional materials in the future.

11:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM12 A Two-Dimensional Oxide Quasicrystal, Stefan Förster, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J.I. Flege, Institute of Physics, University of Bremen, Germany, K. Meinel, R. Hammer, M. Trautmann, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J. Falta, Institute of Solid State Physics, University of Bremen, Germany, T. Greber, Physik-Institut, University of Zürich, Switzerland, W. Widdra, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany** **INVITED**

With the recent discovery of the first oxide quasicrystal (QC) aperiodicity is entering the field of two-dimensional materials [1]. Aperiodicity means that the system exhibits long-range order as expressed by sharp diffraction spots but since the ordering follows an aperiodic function the system is lacking translational symmetry. We report here on the complex growth process of the oxide QC involving a high-temperature wetting process and periodic approximant structures.

The QC is derived from BaTiO₃ thin films on a hexagonal Pt(111) substrate and exhibits a sharp twelve-fold diffraction pattern [1]. Based on scanning tunneling microscopy the aperiodic atomic structure had been resolved [1]. It is formed by surface atoms arranged in forms of squares, triangles, and rhombi with a next-neighbour distance of 0.69 nm. In addition to this dodecagonal atomic arrangement, building blocks of squares, triangles, and rhombi are also found on (2+√3) and (2+√3)² larger scales indicating the characteristic self-similarity of an ordered QC [1]. The high-resolution STM measurements allow furthermore to identify atomic flips in the structure indicating lattice excitations in the quasicrystal called phasons. Using low-energy electron microscopy (LEEM) the preparation and the growth of the QC films on top of the hexagonal Pt(111) is monitored in all details from room temperature up to about 1200 K. LEEM shows that upon high-temperature annealing large 3DBaTiO₃ islands are formed with bare Pt(111)-(1x1) in between. At temperatures above 1020 K a wetting layer spreads on the free Pt area. This wetting process can be reversed by annealing in an oxygen atmosphere. In-situ LEEM measurements show that under these conditions the QC decays into small BaTiO₃ islands. The observed interface-driven formation of a 2D QC from a perovskite oxide in contact with a hexagonal substrate is expected to be a general phenomenon.

1. S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Nature* **502**, (2013) 215.

**Additive Manufacturing/3D Printing Focus Topic
Room: 211A - Session AM+EM+MS+TF-ThM**

**Technologies Enabled by Additive
Manufacturing/Future of Additive Manufacturing
Moderator: Vincent Smentkowski, General Electric Global
Research Center**

8:40am **AM+EM+MS+TF-ThM3 Additive Manufacturing Enabling Advanced Technologies, Teresa Clement, Raytheon Company** **INVITED**
The aerospace and defense industry for the last decade has taken note and contributed to significant advances in materials and process capabilities enabled by the field of additive manufacturing (AM) to fabricate beyond state-of-the-art advanced technologies. Conventional and non-conventional industry partners continue to push the boundaries of next-generation materials and multi-materials for additive manufacturing in order to further extend product capabilities. As these material developments continue evolving, our industrial base begins to realize the many benefits of AM: reducing lifecycle costs, engineering resilience and capability surprise by rapidly reconfigurable responses to adaptive adversarial threats, and the enabling of truly agile manufacturing via AM integration with the model based enterprise (aka marrying AM to the 'digital thread'). Some specific examples of advanced technologies are discussed herein, with examples of design iteration cycle-time reduction and use of material/process controls to verify by inspection and full characterization demonstrations of improved or

unprecedented material performance and multi-functionality (electrical, thermal, structural, etc) made possible by additive manufacturing.

9:20am **AM+EM+MS+TF-ThM5 4D Printing: Three Dimensional Printing with Material Composition as the Fourth Dimension**, *Douglas C. Hofmann*, NASA Jet Propulsion Laboratory, California Institute of Technology **INVITED**

Much of the current research in additive manufacturing in the aerospace community is focused on qualifying materials for service, which is a critical requirement for using additive materials. However, additive manufacturing is a powerful tool for creating materials and applications that cannot be replicated using traditional means. In the past, this has meant 3D printing complex geometries that cannot be easily machined. In the current talk, we will discuss what we call 4D printing; 3D printing where the fourth dimension is the material composition. By using multiple materials strategically in additive manufacturing, a whole new frontier of materials science becomes possible. The science behind these alloys and their applications will be discussed.

11:00am **AM+EM+MS+TF-ThM10 The Future of Additive Manufacturing and Multifunctional Parts**, *Phill Dickens*, University of Nottingham, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**

Additive Manufacturing has many advantages for producing complex components and systems and this has already started to be exploited for parts made of a single material. There is now much interest in the possibility of building parts with multiple materials so that electrical circuits and electronic items can be included within the structure. This paper will highlight some of the research that is taking place at the University of Nottingham and some recent examples of simple products that could exploit this technology.

Some of the issues will be covered where the layer manufacturing process provides some limitations.

Thin Film

Room: 111 - Session TF+AS+NS+SA-ThM

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization I

Moderator: Divine Kumah, North Carolina State University

8:00am **TF+AS+NS+SA-ThM1 Oxynitride Thin Films by Reactive Radiofrequency Magnetron Sputtering - Versatile Materials for Optical Applications**, *Angélique Bousquet, A. Farhaoui, F. Zoubian, C. Taviot-Gueho, J. Cellier, E. Tomasella*, Institut de Chimie de Clermont-Ferrand, France **INVITED**

Transition metal oxynitrides are increasingly studied because of their high versatility. Indeed, by tailoring the material composition, their optical, mechanical or electrical properties are tuned. Among thin film deposition processes, reactive sputtering is particularly attractive for this purpose because of its robustness, its wide use in industry and its high versatility. For several years, our research group at ICCF is specialized in control of reactive sputtering process, especially by plasma analysis using Optical Emission Spectroscopy, to deposit thin films for optical applications.

In this presentation, we will show how by tuning the Ar/O₂/N₂ atmosphere during sputtering of elemental target, it is possible to control the film composition in a ternary diagram in metal-rich, oxide, nitride or oxynitride region. The potentiality of this technique will be illustrated by tantalum and silicon oxynitride deposition.

In order to investigate the nature of oxynitride films (Random Bond Model or Random Mixture Model), thin films were characterized by various techniques, such as IR spectroscopy, XPS, XRD/Pair Distribution Function technique and Rutherford Backscattering Spectroscopy. Hence, we obtained an accurate picture of the diversity and the complexity of our material, following the Random Mixture Model, where segregated oxide and nitride phases are randomly distributed at very short scale.

Moreover, the modification of material composition allows controlling their optical properties, characterized by UV-visible spectroscopy and spectroscopic ellipsometry. This latter technique appears as a powerful technique to discriminate metallic, semiconductor and/or insulator contributions into such complex films by using model combining Tauc-Lorentz law and additional Lorentz oscillator. Hence, in a one hand, optical band gap of TaO_xN_y can be changed from 0-4.3 eV. This E_g fine-tuning more particularly in the range of 1.7-2.7 eV is interesting for application in photocatalytic water splitting using visible light. In the other hand, the

refractive index variation in the 1.56-3.7 range (at 1.96 eV) of Si_xO_yN_z films is used to realized antireflective multilayer system from only one target. Finally, oxynitride films present promising properties for applications in material for Energy.

8:40am **TF+AS+NS+SA-ThM3 Surface Science in The Wild: Using Synchrotron Radiation and Lab Grown Thin Films to Understand The Behavior Of SiC in Accident Tolerant Nuclear Fuels**, *Jeffery Terry*, Illinois Institute of Technology **INVITED**

Out in the "real world," systems are typically much less clean and much more complex than what is seen in the laboratory. This is often the case in the extreme environment of the core of a nuclear reactors. However, complexity often makes it very difficult to understand the dynamics that are occurring in the "real world" systems. Often our understanding can be greatly improved by using measurements on the "real world" system in combination with fundamental surface science measurements on likely components. We have applied these combinations to study the behavior of irradiated accident tolerant nuclear fuels. Development of new accident tolerant nuclear fuels is important because the explosions at Fukushima were the direct result of interactions between water and the Zr cladding on the fuel. The high temperature chemistry of those interactions led to the production of hydrogen gas which eventually ignited. Our research group has looked at potential claddings such as ZrC, ZrN, and SiC. Specifically, we are using synchrotron radiation techniques to collect data on reactor irradiated materials. We compare the results of those measurements with well controlled laboratory grown systems. The data is then provided to modelers to evaluate the performance of reactor components in extreme environments (temperature, neutron flux, chemistry). This talk will focus on the carbides and nitrides that may be used in accident tolerant, TRISO fuel pellets for application in both conventional and advanced nuclear reactors.

9:20am **TF+AS+NS+SA-ThM5 iTF Modulus Solution with xProbe Applications for Ultra-thin Film Systems (<=10nm)**, *Anqi Qiu, A. Romano*, Hysitron, Inc.

Reliable measurements of the Elastic Modulus of thin films is particularly challenging due to substrate effect. The prevalent rule of limiting indentation depth to 10% of the coating thickness to avoid the substrate's influence on the mechanical properties is challenging to assure, especially when the film thickness goes below 200nm. The tip radius can be one of the many factors limiting the application of Oliver-Pharr model on the elastic modulus calculation, just as the surface roughness. With the newly developed ultra-low noise xProbe transducer combined with the **Intrinsic Thin Film Property Solution from Hysitron**, quantitative mechanical properties from nanoindentation tests on 10nm thin film systems become possible. Here a MEMS based transducer with a noise floor similar to that of a contact mode Atomic Force Microscope (AFM). The linear actuation allows for direct and fully quantitative measurements without the need of modeling, which leads to more precise mechanical properties estimation and higher analysis throughput. By combining the ultra-low noise xProbe transducer and analytical intrinsic thin film solution (Itf), we quantitatively estimate elastic properties of the ultra-thin film systems of 10nm or below.

9:40am **TF+AS+NS+SA-ThM6 Real-time Study of Plasma Enhanced Atomic Layer Epitaxy of InN Films by Synchrotron X-ray Methods**, *Neeraj Nepal, V. Anderson, S.D. Johnson, B. Downey, D. Meyer*, U.S. Naval Research Laboratory, *A. DeMasi, K.F. Ludwig*, Boston University, *C. Eddy*, U.S. Naval Research Laboratory

Atomic layer epitaxy (ALE) is a layer-by-layer materials growth method. Recently, plasma enhanced ALE (PA-ALE) has been used to grow epitaxial III-nitride films at temperatures ≤500°C [1-2]. At these growth temperatures, the ad-atom mobility is low and the growth process is significantly influenced by the nature of the substrate surface. Thus, the mechanisms of nucleation and growth kinetics is very important to understand to improve material quality for technological applications. Synchrotron x-ray characterization is one of the best methods for this study.

The temporal evolution of high quality InN growth on a-plane sapphire at 200-250°C were probed by synchrotron x-rays. The growth was carried out in a thin film growth facility installed at beamline X21 of the National Synchrotron Light Source at Brookhaven National Laboratory and at Cornell High Energy Synchrotron Source, Cornell University. Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the x-ray incidence angle of 0.8 degrees show that H₂ plasma cleaning roughens the sapphire substrate surface, but this same surface is recovered completely during subsequent N₂ plasma pretreatment. GISAXS also reveals InN growth steps for each PA-ALE cycle at the optimal growth conditions. During the initial cycles the specular peak broadens and the Yoneda Wing (YW) scattering has a correlated length scale (CLS) of 17.4 nm indicating roughening of the surface during homogenous nucleation. At about 1.3 nm of growth the intensity of YW is increased at the CLS of 10.1

nm indicating a decrease in the surface roughening CLS. Despite this scattering, *ex situ* atomic force microscopy-measured roughness is below instrument sensitivity limits, demonstrating the effectiveness of GISAXS compared to more conventional approaches. *In situ* x-ray reflectivity measurements suggest that the InN growth was self-limited with a growth rate of 0.35 nm/cycle between 200-250°C. Hall measurements show electron sheet carrier density and resistance of $3.5 \times 10^{13} \text{ cm}^{-2}$ and 3.59 k Ω /sq, respectively. An electron mobility of 50 cm²/V-s is measured for a 5.6 nm thick InN film on a-plane sapphire, which is higher than the reported value of 30 cm²/V-s for a 1300 nm thick InN grown by MBE directly on sapphire [3]. *In situ* synchrotron x-ray study of the epitaxial growth kinetics of InN films is one of the most powerful methods to understand nucleation and growth mechanisms to improve material quality and broaden material applications.

References:

- [1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).
- [2] Nepal et al., Appl. Phys. Lett. **103**, 082110 (2013).
- [3] Kuo et al., Diamond & Related Materials **20**, 1188 (2011).

11:00am **TF+AS+NS+SA-ThM10 Nucleation and Growth of Few-Layer ALD Films on Various Substrates Studied by Low Energy Ion Scattering (LEIS).** Malcolm Hathaway, Harvard University, T. Grehl, P. Bruener, ION-TOF GmbH, Germany, M. Fartmann, Tascon GmbH, Germany, H. Brongersma, ION-TOF GmbH, Germany

Atomic Layer Deposition has found applications in many semiconductor processes due to its several unique characteristics, including high purity, conformality, pin-hole-free character, and atomic level thickness controllability. It is these last two characteristics which are of particular interest in this present work. The thickness control of ALD films is precise down to the angstrom level, even when depositing layers as thin as a few atomic layers. Ideally, in layers only a few angstroms thick, the ALD process produces material which is completely continuous and free of pin-holes. One of the challenges of characterizing ALD processes is the difficulty of directly measuring such thin films and confirming their continuous nature.

Low Energy Ion Scattering (LEIS) spectroscopy is uniquely suited to exploring these questions, due to its extreme surface sensitivity, easy quantification and its ability to yield additional information about the sub-surface composition. Using LEIS, analytical questions like layer closure, surface composition, diffusion processes, or growth modes can be addressed. In this work, we explore the limits of this technique to characterize few-layer ALD films on a variety of substrates, to confirm the capabilities of LEIS in this arena, and to shed new light on the nature of few-layer ALD films.

In the LEIS process, a noble gas ion beam of (1 -10 keV) is directed at the sample, and the fraction of backscattered ions is measured as a function of kinetic energy. Two main mechanisms determine the spectral response: Firstly, scattering in the first monolayer of atoms creates elemental peaks, allowing quantitative determination of the elemental composition of the outermost atomic layer. The intensity of these peaks is directly proportional to the surface coverage. Secondly, scattering processes below the surface (with the ion penetrating the surface, scattering at deeper layers and returning to the surface before leaving it) provide information about sub-surface layers, sometimes as deep as 10 nm, in a non-destructive way. As the additional energy loss is proportional to penetration depth, these data can be evaluated to determine the layer sequence, layer composition and layer thickness in a single measurement and in addition to the top layer composition.

In this study a number of oxide films (e. g. HfO₂, Al₂O₃) on Si and other substrates like glassy carbon are evaluated. We apply LEIS among other techniques to characterize the films, especially in the early phases of film growth. Using the unique information from LEIS, conclusions on the nucleation behavior and growth are drawn.

11:20am **TF+AS+NS+SA-ThM11 Ni_{1-x}Pt_xSi Film Characterization for sub-32 nm CMOS Fabrication.** Suraj Patil, R. Rai, S. Beasor, L. Zhou, GLOBALFOUNDRIES, NY, USA

Aggressive scaling of CMOS devices demands silicide engineering for high performance in the sub-32nm technology node and beyond. Ni-silicide can satisfy many of the integration challenges but it is limited by morphological stability at elevated temperatures. On the other hand, incorporating Pt into Ni-silicide forms a more robust nickel platinum silicide (Ni_{1-x}Pt_xSi) and improves morphological stability. Advantages of Pt incorporation include extension of the temperature range over which the NiSi exists, delay in the agglomeration of NiSi phase, suppression of the high resistive NiSi₂ phase formation and retardation of the Ni diffusion at the interface and grain boundaries which could lead to encroachment or piping. This work discusses three important aspects of Ni_{1-x}Pt_xSi formation: (1) understanding

NiPt diffusion with two step RTA anneals – formation (RTA1) and transition (RTA2), which is very important for thickness uniformity across structures with varying CDs, encroachment control, device performance and yield; (2) understanding NiSi phase formation for thermal stability, and (3) understanding Pt distribution in the final film with low RTA1 temperatures. For this study Ni_{1-x}Pt_xSi samples were fabricated from a simple n-Si/Ni_{0.85}Pt_{0.15}/TiN stacks, annealed at range of RTA1 temperatures from RTA-20°C to RTA+30°C for 20s followed by a standard RTA2 anneal for 30s. Characterization of final Ni_{1-x}Pt_xSi films obtained at different RTAs based on XRD phase identification and XPS analysis will be presented. Pt distribution in the final silicide films will be discussed.

11:40am **TF+AS+NS+SA-ThM12 Growth of β -Tungsten Films Towards a Giant Spin Hall Effect Logic Device.** Avyaya Narasimham, University at Albany-SUNY, R.J. Matyi, State University of New York, A. Green, University at Albany-SUNY, A.C. Diebold, V. LaBella, State University of New York

Spin-orbit coupling in metastable β -W generates spin transfer torques strong enough to flip magnetic moment of an adjacent magnetic layer. In a MTJ stack these torques can be used to switch between high and low resistive states. This technique can be used in designing efficient magnetic memory and non-volatile spin logic devices. Deposition conditions selective to β -W need to be understood for the large scale fabrication of such devices. The transition from β to α phase of Tungsten is strongly governed by thickness of W layer, base pressure and oxygen availability for example, above 5 nm β film relaxes and forms an α phase. Resistivity measurements as well as x-ray photoelectron spectroscopy and x-ray diffraction and reflectivity analysis are performed to determine the phase and thickness of tungsten films. We show that β phase is influenced by ultrathin thermal oxide of Si layer and the amount of oxygen flow during the growth. These results demonstrate a reliable technique to fabricate β W films up to 20 nm on bare Si and silicon dioxide, while providing insight to growing it anywhere in the device stack.

12:00pm **TF+AS+NS+SA-ThM13 Aluminum Nitride Grown by Atomic Layer Epitaxy Characterized with Real-Time Grazing Incidence Small Angle X-ray Scattering.** Virginia Anderson, N. Nepal, S.D. Johnson, US Naval Research Laboratory, A. DeMasi, Boston University, J.K. Hite, US Naval Research Laboratory, K.F. Ludwig, Boston University, C.R. Eddy, Jr, US Naval Research Laboratory

Aluminum nitride, gallium nitride, and indium nitride have desirable qualities for many semiconductor applications, and have recently been studied intensely.¹ Because of their direct, tunable band gaps and capacity for high current density they are attractive for photovoltaics and high power transistors. The current methods of depositing high-quality III-nitride films, are metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). The temperatures for the depositions make ternaries challenging. Indium nitride, for example, is difficult to mix with aluminum nitride, as typical MOCVD temperatures for AlN and for InN are 1000°C and 450°C respectively. Aluminum nitride deposition with atomic layer epitaxy (ALE) is currently being explored by some groups as a fabrication friendly technique for thin films at lower temperatures.²

Crystalline AlN deposited with plasma assisted ALE (PA-ALE) in a Fiji reactor from Ultratech/Cambridge Nanotech at 500°C currently has lower material purity than the AlN deposited by MBE and MOCVD, and understanding the film deposition mechanism in order to improve quality is the subject of ongoing research.³ There is a need for a better understanding about the film evolution during nucleation. Grazing incidence small angle x-ray scattering (GISAXS) is sensitive to changing surface features and can be conducted at a wide range of pressures, making it useful for real time monitoring of deposition.⁴

AlN deposited by PA-ALE was grown using trimethylaluminum and hydrogen/nitrogen plasma pulses in a custom reactor at the Brookhaven National Synchrotron Light Source and the Cornell High Energy Synchrotron Source. In both instances, GISAXS was used to examine surface changes during the deposition.

GISAXS information collected during AlN growth at nominally 400°C, 450°C, and 500°C suggested that temperature influenced nucleation, with changes in roughening behavior observed. Post-growth examination of the AlN films with x-ray photoelectron spectroscopy and atomic force microscopy gave important information on the final film elemental composition and morphology. The GISAXS data also show that the surface continued to evolve during the cooling after growth completion while still in the reactor. This information only adds to the necessity of *in situ* growth monitoring to fully understand the mechanisms involved in the ALE growth process.

References:

- ¹ M. Mori et al., Appl. Phys. Express **5** 082301 (2012)

Thin Film

Room: 114 - Session TF+EM+NS+PS+SM-ThM

Plasma ALD and Nano-applications

Moderator: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, Richard Vanfleet, Brigham Young University

8:00am TF+EM+NS+PS+SM-ThM1 Atomic Layer Deposition of Silicon Dielectrics: Precursors, Processes, and Plasmas, Dennis Hausmann, Lam Research Corporation INVITED

As the dimensions of modern semiconductor devices continue to shrink below the current 14 nm technology node, novel processes for the deposition of highly conformal, low temperature, silicon based dielectrics will be needed for applications that include sidewall spacers, barriers, and patterning layers. Atomic layer deposition (ALD) is an ideal method for achieving the high conformality and has been used in high volume manufacturing (HVM) to deposit high-k dielectric materials (HfO₂, ZrO₂, etc.) for several technology generations. Plasma assisted ALD is the best known method to meet low temperature (<500°C) requirements and is now being used for depositing conformal silicon dielectrics such as silicon oxide (SiO₂) and silicon nitride (Si₃N₄).

In this presentation, we discuss the current state of the art of precursors, plasmas, and process conditions required to deposit conformal silicon dielectrics by plasma ALD. Theoretical and experimental data will be presented in order to explain the observed reaction characteristics for the plasma ALD of silicon oxide (SiO₂), silicon nitride (Si₃N₄), and the lack (so far) of silicon carbide (SiC). Generic to all ALD processes is the high cost of the precursors relative to traditional chemical vapor deposition (CVD); in the case of silicon dielectric ALD, this is exacerbated by the relative low “reactivity to cost ratio” of available silicon precursors. Although plasmas enable low temperature deposition, they pose challenges for achieving isotropic film properties over the complex topography on today’s semiconductor devices.

8:40am TF+EM+NS+PS+SM-ThM3 ALD Dielectrics for Power Electronics, Veena Misra, NCSU INVITED

Owing to a high critical electric field and high electron mobility, wide band gap materials such as GaN and SiC are being sought for high voltage power electronics applications. In the case of GaN devices, the reliability continues to be a challenge to must be addressed before successful commercialization. In our work, different dielectrics deposited by Atomic Layer Deposition (ALD) have been investigated for improving the threshold voltage stability and dynamic reliability of AlGaN/GaN based MOSFETs. A novel pulsed-IV-based methodology was developed and demonstrated to be applicable for detecting both shallow and deep traps and implemented on evaluating different high-k and low-k ALD dielectrics. Using physics-based simulation models and experimental data, it was demonstrated that the leakage at the surface of the AlGaN, whether through the passivation dielectric bulk or the dielectric/AlGaN interface, must be minimized to restrict the formation of a “virtual gate” and minimize current collapse. It was also found that an optimal passivation dielectric must create a high density of shallow interface donor traps to quicken the de-trapping of electrons from the “virtual gate” and the recovery of the channel underneath. Combining simulation and experimental results, an optimal set of ALD dielectrics for a reliable gate stack and access-region passivation regions, respectively, was determined and will be discussed. In the area of SiC devices, low inversion channel mobility, caused high density of interface states (D_{it}) at SiO₂/SiC interface, limits the wide adoption of SiC MOS devices. Atomic Layer Deposition offers key advantages in the area of gate dielectrics such as good film quality, low substrate damage, superior uniformity, precise thickness control, and low process temperature. Additionally, deposited SiO₂ enables interface engineering to independently control the interface properties. To enhance the channel mobility and maintain good overall gate dielectric properties, a thin layer of a different dielectric material can be inserted to improve interface properties and high quality deposited SiO₂ can be used as the bulk gate dielectric. We have demonstrated a novel interface engineering technique utilizing ultra thin lanthanum silicate (LaSiO_x) at the SiC/dielectric interface and ALD SiO₂ as the bulk gate dielectric. The lanthanum silicate interface

engineering dramatically improves the mobility of 4H-SiC metal oxide semiconductor field effect transistors (MOSFETs) and is attributed to the large driving force of La₂O₃ to react with SiO₂.

9:20am TF+EM+NS+PS+SM-ThM5 Pb(Zr_xTi_{1-x})O₃ Magnetoelectric Tunnel Junctions for Magnetoelectric RAM (MeRAM) Memory Applications, D. Chien, X. Li, K. Wong, P. Khalili, K. Wang, Jane P. Chang, University of California at Los Angeles

As existing memory systems approach fundamental limitations, ultra-thin uniform conformal PZT films are needed for next-generation ultralow-power voltage-controlled non-volatile magnetoelectric RAM (MeRAM) memory devices. By utilizing the magnetoelectric effect, where an electric field or voltage can be used to control the magnetization switching (instead of current), the writing energy can be reduced, resulting in increased memory density (Amiri, P.K. et al., *Journal of Applied Physics*, 2013). Previous research has shown that the voltage-controlled magnetic anisotropy (VCMA) effect increases with the capacitance of the stack (Kita, K. et al., *Journal of Applied Physics*, 2012). Therefore, integrating an ultra-thin PZT film (having a dielectric constant 1-2 orders of magnitudes higher than currently used MgO) into the tunneling oxide layer will enhance the VCMA coefficient, allowing for a lower voltage to switch the magnetization of the free magnetic layer and thus decreasing the write energy.

Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, an ultra-thin film of PZT can be synthesized with precise control of the film thickness and elemental composition (Zr/Ti = 52/48). ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO₂, and TiO₂ layers using Pb(TMHD)₂, Zr(TMHD)₄, and Ti(O-i-Pr)₂(TMHD)₂ as metal precursors and H₂O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. The bottom layers of Ta/CoFeB (free magnetic layer)/MgO were sputtered, the PZT film with thickness of 1.7 nm was deposited by ALD, the top layers of MgO/CoFeB (fixed magnetic layer)/Ta/Pt were sputtered, and the entire stack was annealed at 200°C for 30 minutes in order to fabricate PZT magnetoelectric tunnel junctions (MEJs).

The perpendicular magnetic anisotropy (PMA) of the bottom free magnetic CoFeB layer was verified via superconducting quantum interference device (SQUID) magnetometer, confirming that the ALD PZT deposition process is a viable method for synthesizing PZT MEJs. The tunnel magnetoresistance (TMR) was measured to be 50%, demonstrating a promising read-out process. Due to the integrated ALD PZT layer in the tunneling barrier, the VCMA coefficient of PZT MEJ devices is expected to be double that measured for CoFeB/MgO/CoFeB devices ($\xi = 37$ fJ/Vm) (Zhu, J. et al., *Physical Review Letters*, 2012).

9:40am TF+EM+NS+PS+SM-ThM6 Plasma-Assisted ALD of High-Quality Molybdenum Oxide Films, Martijn Vos, B. Macco, N.F.W. Thissen, A.A. Bol, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

In this contribution we present a novel plasma-assisted atomic layer deposition (ALD) process to deposit high-quality molybdenum oxide films, with a high growth per cycle (GPC) over a wide temperature range of 50 °C to 350 °C. This process complements existing (thermal) ALD MoO_x processes, which are less suited for deposition at low temperature, due to low GPC and contamination. A decent deposition process is of importance as MoO_x films have received great interest due to their remarkable optoelectronic and catalytic properties and find their use in many applications, including solid state lithium batteries, gas sensors, and more recently solar cells.

A variety of deposition techniques exists for the deposition of MoO_x, such as evaporation, sputtering, chemical vapor deposition and ALD. While many of the applications of MoO_x films can benefit from the merits of ALD, i.e. conformality and digital thickness control, only few ALD processes are known from literature [1, 2]. Recently bis(tert-butylimido) bis(dimethylamido) molybdenum ((NtBu)₂(NMe₂)₂Mo) appeared as a promising precursor for ALD of MoO_x films, using O₃ as oxidant [2].

The plasma-assisted ALD process we report on uses (NtBu)₂(NMe₂)₂Mo and O₂ plasma and shows a relatively high GPC between 0.70 Å and 0.93 Å for amorphous films deposited at temperatures up to 250 °C. In comparison, the analogous O₃ process is featured by a low GPC of 0.17 Å at 150 °C. For deposition temperatures above 250 °C polycrystalline growth was observed, accompanied by an increase in GPC to 1.88 Å for 350 °C. From Rutherford backscattering measurements it was determined that the C and N content in the films is below the detection limit (3 at.% and 2 at.% respectively) for all deposition temperatures, which demonstrates the high-quality of the films (while the aforementioned O₃ process resulted in 9.2 at.% N). Furthermore the O/Mo ratio was found to be just below 3, indicative of oxygen vacancies, which are common for MoO_x films and can lead to an increased

conductivity, which is beneficial for many applications. Additional material properties such as band gap, work function and surface morphology will also be discussed and finally an outlook to the application of this ALD process in silicon solar cells will be given.

[1] M. Diskus *et al.*, *J. Mater. Chem.* **21** (2011) 705

[2] A. Bertuch *et al.*, *J. Vac. Sci. Technol.* **32** (2014) 01A119

11:00am **TF+EM+NS+PS+SM-ThM10 Status and Prospects of Plasma-Assisted Atomic Layer Deposition**, *Harm Knoops*, Oxford Instruments Plasma Technology, UK, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

INVITED

Plasma-assisted atomic layer deposition (ALD) or plasma ALD has established itself as a prominent branch in ALD processing and a wide range of plasma ALD processes are currently available. Due to the complexity of plasmas, plasma ALD is different from thermal ALD in various aspects. Even though the main relevant species in plasmas have been identified,¹ the effects of plasma chemistry and plasma-surface interaction need further study. In this contribution an overview on the status of plasma ALD is given and the key prospects for plasma ALD are highlighted.

Regarding the current understanding of plasma ALD, three subjects will be treated. First the basic plasma species (i.e., radicals, electrons, ions, and photons) and their role in plasma ALD will be discussed. For instance, potential damage to the surface from photons, but also cases where plasma species can repair defects (e.g., N₂ plasmas on GaN surfaces).² Second plasma chemistry and potential poisoning or inhibition processes will be treated, which can play a big role in the ALD of nitrides and conductive films. Third, dissociation in the plasma of reaction products can lead to redeposition effects which can have a large influence on for instance SiN_x and TaN_x ALD.

Several topics will be discussed regarding the prospects for plasma ALD. Even though plasma ALD provides additional possibilities, many cases exist where material properties or cycle times are still unsatisfactory and advances in reactor design such as the capability to provide additional energy in the form of a controlled ion bombardment are needed. In addition, advanced processing schemes such as 3-step ABC ALD cycles can be beneficial as shown by ALD of noble metals at low deposition temperatures (e.g., Pt ALD).³ Whether metal films initially grow as continuous films or as nanoparticles (as well as the particle size), will depend on the chemistry, the surface energy, and the growth temperature. Recently, plasma ALD has shown to allow ALD of Ag by spatial ALD at high pressure.⁴ This case shows that more understanding of the plasma is needed because of an unexpected decreased growth at long plasma exposures (presumably caused by NH₃ poisoning). In general, increasing control of the plasma and understanding of the relevant processes at the surface and in the plasma will be key to further develop plasma ALD.

¹ Profijt *et al.*, *JVST A29*, 050801 (2011)

² Chen *et al.*, *Phys. Status Solidi A* (2014) / DOI 10.1002/pssa.201431712

³ Mackus *et al.*, *Chem. Mater.* **25**, 1769 (2013)

⁴ Van den Bruele *et al.*, *JVSTA33*, 01A131 (2015)

11:40am **TF+EM+NS+PS+SM-ThM12 A Novel Plasma-Enhanced ALD Process for HfO₂ using HfCp(NMe₂)₃ and O₂ Plasma**, *Akhil Sharma*, *V. Longo*, *A.A. Bol*, *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

In atomic layer deposition (ALD) the associated precursor chemistry has a large effect on the quality and properties of the deposited thin films. The most commonly used hafnium precursor for ALD of HfO₂ is HfCl₄. This precursor is not ideal for all applications due to possible chlorine contamination and the generation of corrosive by-products during the ALD process. Organometallic precursors such as Hf(NtMe)₄ promise to be a better choice but they typically suffer from a limited thermal stability. In this context, HfCp(NMe₂)₃ might offer a better alternative because of its higher thermal stability. However, while using H₂O as oxygen source in a thermal ALD process it yields a low growth rate¹. This creates an opportunity for studying this precursor in combination with other oxygen sources. In this work, we report on the development of a novel plasma-enhanced ALD (PE-ALD) process using HfCp(NMe₂)₃ in combination with an O₂ plasma to deposit HfO₂ thin films. To our knowledge, to date, the PE-ALD for this precursor has not been reported in the literature.

Our results show that the PE-ALD process offers significant advantages over the reported thermal ALD process such as a high growth rate, reduced deposition temperature, shorter cycle time and good control over composition of the deposited films. In contrast to the thermal ALD process using HfCp(NMe₂)₃ and water¹, the PE-ALD process has resulted into a wide ALD temperature range (150-400°C) with significantly higher growth per cycle values (1.1Å/cycle) and shorter cycle times which ultimately

improves the wafer throughput. The level of impurities were found to decrease with increasing the deposition temperature as concluded from XPS and ERD analyses. The concentrations of residual carbon and hydrogen reduced from 1.0 at% to 0.2 at% and 3.4 at% to 0.8 at%, respectively, by increasing the deposition temperature from 200°C to 400°C. Moreover, RBS studies showed an improvement in stoichiometry of HfO₂ thin films with increase in deposition temperature resulting in a Hf/O ratio of ~0.5 at 400°C. Furthermore, GI-XRD measurements detected a strong transition from amorphous (300°C) to fully crystallized films (400°C), consisting of a mixture of monoclinic, tetragonal and cubic phases. These results therefore have demonstrated that PE-ALD using HfCp(NMe₂)₃ and O₂ plasma is a promising and viable alternative to the thermal ALD process producing high quality HfO₂ thin films over a wider temperature range and with faster cycle times.

1. Consiglio *et al.*, *J. Vac. Sci. Technol.* **A 30**(1), 2012

12:00pm **TF+EM+NS+PS+SM-ThM13 Conductive Hafnium Nitride Layers By Plasma-Assisted Atomic Layer Deposition**, *Saurabh Karwal*, *B.L. Williams*, *W.M.M. Kessels*, *M. Creatore*, Eindhoven University of Technology, The Netherlands

Transition metal nitrides (TMNs) have gained much attention in the semiconductor industry due to their characteristics such as copper and lithium diffusion barriers, metal-like behaviour (i.e. low resistivity) and high hardness, mechanical strength and chemical inertness. Among TMNs, hafnium nitride exhibits a low bulk resistivity of 33 μΩcm and highest negative Gibbs free energy of formation (HfN: -88.2, TiN: -80.4, TaN: -60.3 kcal/mol) and hence could serve as novel material for several applications, such as diffusion barrier and gate electrode in microelectronics, and reflective back contact for CIGS solar cells.

Conductive hafnium nitride thin films were deposited by inductively coupled plasma (ICP)- assisted atomic layer deposition using a heteroleptic metallocene hafnium precursor, tris(dimethylamino)cyclopentadienylnhafnium CpHf(NMe₂)₃ [TDMACpH] and H₂- or N₂- fed plasmas serving as co-reactants. The effects of the substrate temperature, plasma chemistry and plasma exposure time have been investigated in terms of growth-per-cycle (GPC), chemical, electrical and morphological properties of the deposited layer. It has been observed that highly resistive (0.75 Ωcm) Hf₃N₄ thin films are obtained via an A-B type ALD cycle (TDMACpH/N₂ -fed plasma) with a GPC of 0.035 nm/cycle. Furthermore, a limited abstraction of the ligands leads to a residual carbon content in the layer of 7%.

Instead, conductive films (1.8 x 10⁻³ Ωcm) are achieved upon the application of an A-B-C ALD cycle where an intermediate H₂- fed plasma exposure step is included between the TDMACpH exposure and the N₂-fed plasma step, with a GPC of 0.045 nm/cycle. This intermediate step is found to be responsible for a more efficient removal of the precursor ligands and for the reduction of Hf⁴⁺ state to Hf³⁺ state, essential for guaranteeing electron conductivity. This transition of chemical and electrical properties of the deposited thin films is also accompanied by a change in crystallographic properties from amorphous (A-B ALD cycle) to conductive cubic HfN (A-B-C ALD cycle), as revealed by grazing incidence X-ray diffraction.

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Tribology Focus Topic

Room: 230B - Session TR+TF-ThM

Nanolubricants and Coatings

Moderator: Tevis Jacobs, University of Pittsburgh

8:00am **TR+TF-ThM1 Mechanical Mixing and Wear Formation in Metallic Tribocouples**, *Martin Dienwiebel*, *P. Stoyanov*, *T. Feser*, Karlsruhe Institut für Technology (KIT), Germany, *R. Merz*, Insitut für Oberflächen und Schichtanalytik GmbH, Germany, *P. Romero*, Fraunhofer Institute for Mechanics of Materials IWM, Germany, *F.C. Wählich*, INM - Leibniz-Institute for New Materials, Germany, *P. Stemmer*, University of Duisburg-Essen, Germany, *M. Moseler*, Fraunhofer Institute for Mechanics of Materials IWM, Germany, *R. Bennewitz*, INM - Leibniz-Institute for New Materials, Germany, *A. Fischer*, University of Duisburg-Essen, Germany

INVITED

During sliding of metallic surfaces in dry or lubricated conditions the near surfaces undergo significant changes in terms of topography, composition and microstructure [1] and a so-called "third body" or "tribomaterial" [2] develops. The third-body formation strongly influences the frictional and wear behavior of the system.

In this talk we present several experiments on pure metals and alloys that were performed using a novel experimental platform for the on-line correlation of friction, wear and topography under lubricated sliding [3]. Fast topography data is measured in real time by digital holography microscopy (DHM), wear is measured by the Radionuclide wear technique (RNT) and the nanoscale topography is obtained *in-situ* by liquid atomic force microscopy (AFM). The tribological systems that we recently studied include a-brass (CuZn) sliding against steel [4], tungsten and tungsten carbide [5], [6]. The experimental findings were compared to MD simulations. In order to characterize the mechanical behavior, nanoindentation and micropillar compression tests were performed that show that the third body material is softening during the initial running-in [7].

References

- [1] M. Scherge, D. Shakhvorostov, K. Pöhlmann, *Wear*, 255 (2003) 395-400.
- [2] M. Godet, *Wear*, 100 (1984) 437-452.
- [3] S. Korres, M. Dienwiebel, *Rev. Sci. Instr.*, 81 (2010) 063904.
- [4] T. Feser, P. Stoyanov., M. Dienwiebel, *Wear*, 303 (2012) 465-472
- [5] P. Stoyanov et al., *Tribol. Lett.*, 50 (2013) 67-80.
- [6] P. Stoyanov et al., *ACS Appl. Mat. & Int.s*, 5 (2013) 6123-6135.
- [7] P. Stoyanov et al., *ACS Nano* 9 (2015) 1478

8:40am **TR+TF-ThM3 Influence of MoDTC Degradation on Tribological Performances of Steel-Steel Contacts under Boundary Lubrication Conditions**, *Clotilde Minfray, M. De Feo, M.I. De Barros Bouchet*, Ecole Centrale de Lyon - LTDS, France, *B. Thiebaut*, Solaize Research Center, France, *T. Le Mogne, B. Vacher, J.M. Martin*, Ecole Centrale de Lyon - LTDS, France

Nowadays, MoDTC is one of the best-known friction modifier additives used in engine oils for its friction reduction properties. A vast number of papers tackle the subject and converge on the fact that the generation of MoS₂ flake in the contact (in tribofilm) is at the origin of the friction reduction. But it is also known that this positive friction reduction effect is not so durable in time. Therefore, the investigation of MoDTC chemical degradation mechanism and its impact on the tribological properties in steel/steel contacts is of great interest.

It is proposed here to age a lubricant made of mineral base oil blended with 1%w of MoDTC with a thermo-oxidative procedure (open air - 160°C) for different durations. The aged lubricants are then tested under boundary lubrication conditions, with ball-on-flat reciprocating tests running at 100°C. Balls and flats are both in AISI52100 steel.

Concerning the results, clear differences are found in terms of friction behavior as a function of ageing time. A relation between ageing and induction time needed to reach the "low" friction regime is also established. Tribofilms generated on flats were then analyzed by means of XPS surface analysis and FIB-TEM observations for a precise chemical and morphological characterization of each flat sample. The possible presence of two types of molybdenum oxo-sulfide compounds, more or less oxidized, is suggested by XPS results and discussed regarding the friction behavior. Moreover, the TEM observations carried out suggest tribofilms differences in terms of morphology, size and organization. Finally, the effect of MoDTC ageing on friction behavior is discussed considering the composition of tribofilms but also taking into account MoDTC depletion in the bulk of the lubricant, thanks to High Performance Liquid Chromatography (HPLC) experiments.

9:20am **TR+TF-ThM5 General Model for Tribology of Metallic Contacts**, *Michael Chandross*, Sandia National Laboratories, *S. Cheng*, Virginia Tech, *N. Argivay*, Sandia National Laboratories **INVITED**

The tribology community presently relies on phenomenological models to describe the various seemingly disjointed steady-state regimes of metal wear. Pure metals such as gold -- frequently used in electrical contacts -- exhibit high friction and wear. In contrast, nanocrystalline metals, such as hard gold, often show much lower friction and correspondingly low wear. The engineering community has generally used a phenomenological connection between hardness and friction/wear to explain this macroscale response, and thus to guide designs. We present a suite of recent simulations and experiments that demonstrate a general framework for connecting materials properties (i.e. microstructural evolution) to tribological response. We present evidence that the competition between grain refinement (from cold working), grain coarsening (from stress-induced grain growth), and wear (delamination and plowing) can be used to describe transient and steady state tribological behavior of metals, alloys and composites. We will present the results of large-scale molecular dynamics simulations and targeted experiments that explore the seemingly disjointed steady-state wear regimes of metals and alloys, with a goal of

elucidating the structure-property relationships, allowing for the engineering of tribological materials and contacts based on the kinetics of grain boundary motion.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

11:20am **TR+TF-ThM11 Superlubric Sliding of Gold Nanoparticles on Graphite under Ambient Conditions**, *E. Cihan, Mehmet Z. Baykara*, Bilkent University, Turkey

Forming a complete understanding of the physical mechanisms that govern friction on the nanometer and atomic scales is an ongoing endeavor for scientists from various disciplines. While atomic force microscopy (AFM) has proven to be invaluable for the detailed study of nano-scale frictional properties associated with various surfaces, issues related to the precise characterization of the contact formed by the probe tip and the sample surface remain largely unsolved.

In recent years, an alternative approach to nanotribology experiments has involved the lateral manipulation of well-characterized nanoparticles on sample surfaces via AFM and the measurement of associated frictional forces [1]. In line with this idea, we present ambient-condition nano-manipulation experiments involving gold nanoparticles (AuNP) thermally deposited on highly oriented pyrolytic graphite (HOPG), a sample system which has been recently characterized in detail [2]. It is observed that AuNPs experience remarkably low frictional forces during sliding. A detailed study of friction with respect to contact area firmly confirms the occurrence of *superlubric* sliding under ambient conditions for this sample system. The potential reasons behind the observed phenomenon are discussed with support from theoretical considerations.

[1]: D. Dietzel, U.D. Schwarz, A. Schirmeisen, *Friction* 2, 114-139 (2014)

[2]: E. Cihan, A. Özogul, M.Z. Baykara, *Applied Surface Science*, (2015), DOI: 10.1016/j.apsusc.2015.04.099

11:40am **TR+TF-ThM12 Monitoring the Gas-Phase Products of a Shear-Induced Reactions in Ultra-high Vacuum**, *Heather Adams*, University of Wisconsin-Milwaukee, *M.T. Garvey*, Illinois Applied Research Institute, *O. Furlong*, Universidad Nacional de San Luis, Argentina, *W.T. Tysoe*, University of Wisconsin-Milwaukee

Although tribochemical reactions are common in manufacturing, analysis of the mechanism and products is severely limited by the difficulty of probing a solid-solid interface that changes on small time scales. A method to analyze the gas-phase products of a tribochemical reaction in ultra-high vacuum has been developed to allow insight to be obtained into the decomposition pathways of short-chain alkylthiols on copper foils. A UHV-tribometer is used to probe the alkylthiol-covered copper foil by using a mass spectrometer to measure the products evolved from the surface.

Alkylthiols have been chosen due to their thermal stability on a copper surface¹, and their ability to form a tribofilm. Previous studies have found that sulfur moves into the sub-surface layer with rubbing, and the carbon is removed from the surface.²

The shear-induced decomposition of methyl thiolate produces gas-phase methane and measuring the amount of methane produced during each sliding cycle allows the shear-induced reaction rate to be measured. The results are analyzed to give insight into how shear stress lowers the energy barrier for the decomposition reaction.³

1. Furlong, O. J. *et al.* The surface chemistry of dimethyl disulfide on copper. *Langmuir* 26, 16375-16380 (2010).

2. Furlong, O., Miller, B., Kotvis, P., Adams, H. & Tysoe, W. T. Shear and thermal effects in boundary film formation during sliding. *RSC Adv.* 4, 24059 (2014).

3. Adams, H. L. *et al.* Shear-Induced Mechanochemistry: Pushing Molecules Around. *J. Phys. Chem. C* 119, 7115-7123 (2015).

Thursday Afternoon, October 22, 2015

2D Materials Focus Topic

Room: 212C - Session 2D+EM+MG+NS+SS+TF-ThA

Heterostructures of 2D Materials

Moderator: Stefan Förster, Martin-Luther-Universität Halle-Wittenberg, Michael Naguib, Oak Ridge National Laboratory

2:20pm **2D+EM+MG+NS+SS+TF-ThA1 Dielectrics Layer Deposition on 2D Materials by Functionalization with Polar Titanyl Phthalocyanine**, JunHong Park, UC San Diego, S. Fahimpour, University of Notre Dame, I.J. Kwak, UC San Diego, H.C.P. Movva, UT-Austin, S. Vishwanath, H. Xing, Cornell University, S.K. Banerjee, UT-Austin, A.C. Seabaugh, University of Notre Dame, A.C. Kummel, University of California at San Diego

Several novel designs for beyond CMOS devices have emerged using two-dimensional semiconductors. These devices require deposition of thin insulators on 2D semiconductors or between two sheets of 2D semiconductors. However, 2D semiconductors are nearly inert surfaces thereby making uniform nucleation of oxide growth challenging preventing scaling of the insulator thickness. A new technique has been developed to employ a monolayer of ordered metal phthalocyanines (MPc) on 2D semiconductors directly as a nucleation layer for growth of ALD dielectric. TiOPc monolayers were deposited on HOPG surfaces and WSe₂ by organic molecular beam epitaxy. TiOPc forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.6 x 1.6 nm grid on both HOPG and WSe₂. Observation of bright protrusions on each O-TiPc indicates that each O-TiPc in the monolayer is directed outward to vacuum. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H₂O), insulating aluminum oxide was deposited uniformly on TiOPc/HOPG. After formation of AlO_x on TiOPc/HOPG, the band gap of surface increases from 1.7 eV to 3.4 eV, while the conductance decreased. A metal-oxide-TiOPc-graphene capacitor has the lower thickness and the higher capacitance value than any reported graphene MOSCAPs. In the dual gated graphene FET with 40 cycles of AlO_x, TiOPc assisted AlO_x shows very low leakage current. Employing the TiOPc seeding layer also can be expanded to other TMD materials. The bottom gated WSe₂ FET was fabricated. On the bottom gated WSe₂ FET, the TiOPc monolayer was deposited, then 50 cycle of AlO_x was deposited via ALD. In this dual gated WSe₂ FET, the leakage current of the AlO_x is measured as ~0.05 pA/μm² at 0.5 VTG. As a control, 20 cycles of Al₂O₃, and 140 cycles of HfO₂ were deposited on bare WSe₂. The leakage current of the TiOPc assisted 50 cycle Al₂O₃ oxide is 3 orders of magnitude lower than HfO₂/Al₂O₃/WSe₂, consistent with a high nucleation.

2:40pm **2D+EM+MG+NS+SS+TF-ThA2 Direct Probing of the Electronic Structure of Bilayer Homo- and Hetero-Structures and Tracking their Evolution with Interlayer Twist-Angle**, Nader Zaki, P. Yeh, W. Jin, R.M. Osgood, Jr., Columbia University

2D atomic layer materials such as graphene and transition-metal dichalcogenides such as MoS₂ have garnered much interest over the last few years due to their surprising electronic properties. For example, graphene possesses an exceptionally high mobility while monolayer MoS₂ possesses a direct bandgap with an exceptionally high light-matter interaction. One of the directions the 2D materials community is now pursuing is one in which these materials are combined together by way of vertical stacking in order to fabricate custom layered structures with potentially rich physics and unique device properties. Naturally, determining the electronic structure of these custom assembled structures is a necessary task to understanding their electronic behavior. While the electronic structure of the constituent materials have already been studied for monolayer form, the electronic structure of the stacked structures has only recently started to be deciphered. This talk will report on the direct determination of the electronic structure of two bilayer systems: twisted bilayer MoS₂ and twisted graphene/MoS₂. Using LEEM, μLEED, and μARPES, the stack quality, stack orientation, and stack electronic structure are directly probed and resolved with few μm and higher spatial resolution. To be discussed will be the evolution of the electronic structure with twist angle and its implications on the electronic properties of the respective homo- and hetero-structures.

3:00pm **2D+EM+MG+NS+SS+TF-ThA3 In Situ Microscopy on 2D Materials: Heterostructures, Nanostructures, Novel Materials Systems**, Peter Sutter, University of Nebraska - Lincoln **INVITED**

Two-dimensional (2D) materials, such as graphene, hexagonal boron nitride, and a family of metal dichalcogenides have fascinating properties

and show promise for applications. The broad exploration and use of these materials depends on the development of scalable synthesis methods, and of a fundamental understanding of their properties. I will discuss recent advances in understanding the synthesis, processing, and properties of 2D materials derived primarily from in-situ surface imaging.

In-situ microscopy provides the basis for creating complex heterostructures of different 2D materials, such as graphene and hexagonal boron nitride, and for studying atomically precise graphene nanostructures. Real-time imaging yields quantitative information on the growth and processing of new classes of 2D materials, such as metal dichalcogenide semiconductors. Finally, the combination of in-situ microscopy with synchrotron-based spectroscopy represents a unique approach for exploring the electronic band structure of 2D materials.

Our results illustrate that in-situ microscopy can be a powerful tool for realizing and probing the unique characteristics of two-dimensional materials.

4:00pm **2D+EM+MG+NS+SS+TF-ThA6 Direct Growth of Graphene/h-BN(0001) Multilayer Heterostructures for Novel Device Applications**, S. Driver, D. Beatty, B. Olanipekun, S. Reid, Jeffry Kelber, University of North Texas

We report the direct layer-by-layer growth of h-BN(0001) multilayers on Co(0001) by atomic layer epitaxy (ALE), and the direct growth of graphene multilayers on h-BN(0001) by molecular beam epitaxy (MBE). For the first time, this allows the growth of graphene/h-BN heterostructures with graphene and BN thicknesses controlled with atomic precision, and with all graphene and BN layers in azimuthal registry. Such control is a prerequisite for many proposed spintronic and electronic applications that emphasize charge or spin transport perpendicularly through the heterojunction. Further, the growth by direct, scalable methods without physical transfer, is essential for industrial development of such devices. h-BN(0001) multilayers have been deposited on Co(0001)/Al₂O₃(0001), using a BCl₃/NH₃ ALE process at 600 K. X-ray photoelectron spectroscopy (XPS) indicates B:N atomic ratios of 1:1 with negligible Cl contamination or reaction with the metallic substrate. Low energy electron diffraction (LEED) data indicate BN domain sizes of ~300 Å or greater, with the lattice in registry with that of the Co(0001) substrate. LEED data also indicate BN domains larger than those of the Co substrate, suggesting BN overgrowth of Co domain boundaries. The XPS-derived average BN film thickness scales linearly with the number of BCl₃/NH₃ cycles, and the lack of Co oxidation after ambient exposure of a BN bilayer indicates that these films are macroscopically continuous over the 1 cm x 1 cm sample size. Graphene formation on h-BN(0001) was achieved using MBE with a graphite rod source, with deposition carried out at 800 K. LEED data show the expected 6-fold LEED pattern in exact registry with that of the h-BN(0001)/Co(0001) substrate. XPS C 1s spectra indicate a C 1s binding energy near 284.5 eV and with the expected pi-to-pi* transition. A heterojunction consisting of ~3 monolayers (ML) graphene/3 ML h-BN on Co(0001) proved stable in vacuum to at least 1000 K, indicating the adaptability of this growth process to a variety of industrial applications. Other recent results indicate the adaptability of this process to other substrates, such as Ru(0001) or CoSi₂(111). These developments make possible a variety of spin filters, spin valves, and tunneling transistors proposed on the basis of close BN/graphene lattice matching, but not readily achievable with physically transferred films.

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and 2381.003, and by a UNT ROP grant. Peter Dowben and Jian-Ping Wang are acknowledged for stimulating and informative discussions.

4:20pm **2D+EM+MG+NS+SS+TF-ThA7 Al₂O₃ on Black Phosphorus by Atomic Layer Deposition: An in situ Interface Study**, Hui Zhu, S. McDonnell, X. Qin, A. Azcatl, L. Cheng, R. Addou, J. Kim, UT-Dallas, P.D. Ye, Purdue University, R.M. Wallace, UT-Dallas

Black phosphorus ("black-P") is considered to be an appealing 2D material because of its novel properties and potential application in few-layer transistor structures.^{1,2,3} However, a clear challenge in the implementation of black-P is the strong hydrophilic⁴ and oxidation⁵ reactions during device processing and thereafter. Thus, efficient isolation layers are necessary for black-P to preserve its electronic properties. Al₂O₃³ or HfO₂⁶ dielectric layers deposited by atomic layer deposition (ALD) have been used as isolation layers in recent black-P transistors. In this work, three different samples oxidized by ambient air were investigated to understand the interfacial chemistry, and nucleation of atomic layer deposited Al₂O₃ on black-P using *in situ* X-ray photoelectron spectroscopy (XPS). This work suggests that exposing a sample that is initially free of phosphorus oxide to the ALD precursors does not result in detectable oxidation. However, when

the phosphorus oxide is formed on the surface prior to deposition, the black-P can react with both the surface adventitious oxygen contamination and the H₂O precursor at the deposition temperature of 200 °C. As a result, the concentration of the phosphorus oxide increases after both annealing and the atomic layer deposition process. The nucleation rate of Al₂O₃ on black-P is correlated with the amount of oxygen on samples prior to the deposition. The growth of Al₂O₃ follows a “substrate inhibited growth” behavior where an incubation period is required. *Ex situ* atomic force microscopy is also used to investigate the deposited Al₂O₃ morphologies on black-P where the Al₂O₃ tends to form islands on the exfoliated black-P samples.

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Reference:

- 1 L. Li, Y. Yu, G.J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X.H. Chen, and Y. Zhang, *Nat. Nanotech.* 9, 372 (2014).
- 2 H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, and P.D. Ye, *ACS Nano* 8, 4033 (2014).
- 3 F. Xia, H. Wang, and Y. Jia, *Nat. Comm.* 5, 4458 (2014).
- 4 J.D. Wood, S.A. Wells, D. Jariwala, K. Chen, E. Cho, V.K. Sangwan, X. Liu, L.J. Lauhon, T.J. Marks, and M.C. Hersam, *Nano Lett.* 14, 6964 (2014).
- 5 A. Favron, E. Gaufres, F. Fossard, P.L. Lévesque, Anne-Laurence, Phaneuf-L'Heureux, N.Y.-W. Tang, A. Loiseau, R. Leonelli, S. Francoeur, and R. Martel, arXiv:1408.0345 (2014).
- 6 N. Haratipour, M.C. Robbins, and S.J. Koester, arXiv:1409.8395 2 (2014).

4:40pm 2D+EM+MG+NS+SS+TF-ThA8 Topological Winding Number Change and Broken Inversion Symmetry in a Hofstadter's Butterfly, Marc Bockrath, UC Riverside

Recently several research groups have demonstrated accurate placement of graphene on hexagonal BN (hBN) with crystallographic alignment. Due to the resulting superlattice formed in the graphene/hBN heterostructures, an energy gap, secondary Dirac Points, and Hofstadter quantization in a magnetic field have been observed. Using aligned layer transfer we are able to produce graphene/hBN heterostructures with ~1 degree alignment accuracy, and measure the transport properties of the resulting systems. We observe an additional π Berry's phase shift in the magneto-oscillations when tuning the Fermi level past the secondary Dirac points, originating from a change in topological winding number from odd to even when the Fermi-surface electron orbit begins to enclose the secondary Dirac points. At large hole doping inversion symmetry breaking generates a distinct hexagonal pattern in the longitudinal resistivity versus magnetic field and charge density. This results from a systematic pattern of replica Dirac points and gaps, reflecting the fractal spectrum of the Hofstadter butterfly.

5:00pm 2D+EM+MG+NS+SS+TF-ThA9 Compliant Substrate Epitaxy: Au on MoS₂, Yuzhi Zhou, C. Daryl, UC Berkeley

The heteroepitaxial growth of Au on MoS₂, a layered van der Waals bonded dichalcogenide, is analyzed. It is argued that the weak coupling between the layers in the dichalcogenides enables the first substrate layer to deform elastically almost independently from the substrate layers below, and hence enables epitaxial growth for a larger mismatch than might otherwise be expected. Linear, continuum elasticity theory and density functional theory are used to show that a {111} oriented Au film is the preferred over an {001} oriented Au film, despite the fact that the {111} orientation leads to a much higher elastic strain. During the initial stages of growth, the {111} orientation is favored over the {001} orientation due to its lower surface and interfacial energies. As the Au film grows thicker, the elastic relaxation of the first layer of the substrate leads to a reduction in the elastic energy of the growing film. This reduces the elastic energy difference between the {001} and {111} orientations enabling the {111} orientation to remain stable for all film thicknesses. This work is supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

5:20pm 2D+EM+MG+NS+SS+TF-ThA10 Direct Synthesis of 2D van der Waals Heterostructures, Judy Cha, Yale University INVITED

Two-dimensional (2D) chalcogenides have gained renewed interest due to their interesting electrical properties such as topological insulator surface states in Bi₂Se₃ and hydrogen evolution catalytic activities in MoS₂. Our ability to thin them down to a single layer and their anisotropic bonding nature opens up possibilities for novel heterostructures where we can tailor

their electronic properties. I will present one-step, scalable heterostructure synthesis method to synthesize these chalcogenide nanostructures and examine their electronic transport properties. Intercalation into 2D materials will be considered as a novel way to design 2D heterostructures, in which the optical and electrical properties of the host 2D materials can drastically change. I will also discuss ways to control the alignment of molecular layers in these 2D chalcogenides, which exploits stress and strain built in the film during the growth. Electron tomography will be used to reconstruct the 3D structure of vertically oriented molecular layers in MoS₂ thin films. In the second part of the talk, I will present synthesis and electronic properties of SnTe topological crystalline insulator nanoplates. Although SnTe is cubic and not a layered material, large SnTe nanoplates expanding hundreds of microns in lateral dimension with ~100 nm in thickness are possible. I will discuss effects of substrates and growth conditions to promote thin film growth of non-layered materials.

Additive Manufacturing/3D Printing Focus Topic Room: 211A - Session AM+EM+MS+TF-ThA

Additive Fabrication for Electronic Devices and Systems

Moderator: Jim Fitz-Gerald, University of Virginia,
Gregory Whiting, Palo Alto Research Center

2:20pm AM+EM+MS+TF-ThA1 Additive Printing for Flexible Electronic Devices, A.C. Pierre, Ana Claudia Arias, University of California at Berkeley INVITED

The area of printed electronics has been focused on the use of new classes of semiconducting and conducting materials in two main applications, displays and photovoltaics. Both applications require materials long-term stability, long shelf life as well the need for patterning and deposition over large areas. Over the past 10 years significant progress in the performance of printable materials has been reported including highly efficient solar cells, light emitting diodes and thin film transistors with mobilities as high as 10 cm²/Vs. The work is highly motivated by the potential for high through put, high volume, low cost manufacturing. While large area electronics continues to be a good application for printed flexible devices, wearable medical devices, which benefit from new form factors, represent a good shift in direction of research in the field. Wearable medical sensors have the potential to play an essential role in the reduction of health care costs as they encourage healthy living by providing individuals feedback on personal vital signs and enable the facile implementation of both in-hospital and in-home professional health monitoring. In printed flexible electronics however, there are no standards for materials set, device models and fabrication methods. This lack of standards slows down design of new systems and the success of the technology as a whole. In this talk, I will review the state of the art of devices produced by printing and introduce a blade coating method that yields highly homogeneous flexible thin films that are applied to LEDs, photodiodes and TFTs. The application of these devices as building blocks for flexible electronics systems will also be discussed.

3:00pm AM+EM+MS+TF-ThA3 Digital Microassembly for High-performance Printed Electronics, Eugene Chow, J.P. Lu, G.L. Whiting, D.K. Biegelsen, S. Raychaudhuri, A.R. Völkel, J. Veres, P. Maeda, I. Matei, S. Nelaturi, L.S. Crawford, Palo Alto Research Center (PARC) INVITED

Digitally printing micro-scale pre-fabricated building blocks instead of simpler materials enables an alternative route to printed electronics and opens up fundamentally new manufacturing capabilities. However, existing printing technologies do not provide the required accuracy and orientation control to print such micro objects. We will describe a demonstration of the fundamental process steps of such an electronic chip printer based on electrographic manipulation and xerographic concepts.

4:00pm AM+EM+MS+TF-ThA6 3D Printed Bionic Nanomaterials, Michael McAlpine, University of Minnesota INVITED

The ability to three-dimensionally interweave biology with nanomaterials could enable the creation of bionic devices possessing unique geometries, properties, and functionalities. The development of methods for interfacing high performance devices with biology could yield breakthroughs in regenerative medicine, smart prosthetics, and human-machine interfaces. Yet, most high quality inorganic materials: 1) are two dimensional, 2) are hard and brittle, and 3) require high crystallization temperatures for maximally efficient performance. These properties render the corresponding devices incompatible with biology, which is: 1) three dimensional, 2) soft, flexible, and stretchable, and 3) temperature sensitive. These dichotomies are solved by: 1) using 3D scanning and printing for hierarchical, interwoven, multiscale material and device architectures, 2) using

nanotechnology as an enabling route for overcoming mechanical discrepancies while revealing new effects due to size scaling, and 3) separating the materials synthesis and 3D printed assembly steps to enable conformal integration of high quality materials with biology. The coupling of 3D printing, novel nanomaterial properties, and 'living' platforms may enable next-generation nano-bio interfaces and 3D printed bionic nanodevices.

Scanning Probe Microscopy Focus Topic

Room: 212A - Session SP+BI+NS+SS+TF-ThA

Probing Material Growth on the Surface

Moderator: Chuanxu Ma, Oak Ridge National Laboratory

2:20pm **SP+BI+NS+SS+TF-ThA1 Tailoring the Growth of Organic Thin Films via Chemical Reactions at the Molecular Scale, Pengpeng Zhang**, Michigan State University **INVITED**

Control of highly ordered organic molecular thin films with extended π systems is currently of intense interest for integrating molecules into modern electronics due to their tunable nature. Selection of molecules and substrates can lead to desired transport properties such as charge transfer, charge injection, exciton diffusion, etc., at the heterointerface, which is crucial to the development of organic and molecular electronics. However, achieving large-scale molecular ordering remains a significant challenge that requires a thorough understanding of the growth mechanism. I will discuss our recent discovery of the anisotropic crystalline step-flow growth of the prototypical metal phthalocyanine molecules on the deactivated Si(111)-B surface. I will then address the growth mechanism and show that the molecular ordering and molecular orientation can be effectively controlled through selective orbital coupling between the molecule and substrate. Finally, I will illustrate an abnormal temperature dependent growth evolution and discuss the associated mechanism.

This research is funded by the U.S. Department of Energy (DOE) Office of Science Early Career Research Program (DE-SC0006400) through the Office of Basic Energy Sciences.

3:00pm **SP+BI+NS+SS+TF-ThA3 Investigation of Initial Stages of Oxidation of Ni-Cr and Ni-Cr-Mo alloys by Scanning Tunneling Microscopy and Spectroscopy, Gopalakrishnan Ramalingam***, P. Reinke, University of Virginia

Ni-Cr alloys are excellent candidates for use in highly corrosive environments due to the formation of a protective Cr_2O_3 layer. Molybdenum is a common alloying addition as it improves the resistance to localized corrosion and prevents the breakdown of the oxide layer. While the effect of Mo addition on corrosion resistance is well known, the underlying mechanisms at the atomic scale and the role of electronic structure changes due to Mo addition are poorly understood. In the current work, we have used STM/STS to investigate the initial stages of oxidation of Ni, Cr and Ni-Cr (10-25wt.% Cr) alloy thin films and subsequently, the effect of Mo addition (2-10 wt.%) on the oxidation behavior. The alloy thin films are grown on MgO(001) substrates using two recipes that yielded smooth films: (a) deposition at 100 °C and subsequent anneal at 300 °C for 2 hours, and (b) deposition at 400 °C with no post-growth annealing. While recipe (a) yielded smooth Ni films, co-deposition of Ni and Cr resulted in the formation of secondary Ni_2Cr phases. Alloy films grown using recipe (b) did not result in secondary phases and are optimal for oxidation studies of alloy films. STM/STS data of the oxidation (30 L of O_2) of a pure Ni thin film at 200 °C reveal preferential oxidation of some terraces compared to others and indicates a dependence of oxidation rate on the crystallographic orientation of the terrace. dI/dV maps of a Cr surface after 10 L oxidation at 200 °C shows the presence of a bandgap (1.32 eV) throughout the surface and indicates the growth of a uniform oxide layer. In the case of Ni-13wt.%Cr binary alloy, a 25 L exposure (at 1×10^{-8} mbar) at 300 °C results in a complete loss of step structure with a fully formed oxide layer as shown by STS spectra. A bandgap of 1.42 eV is observed throughout the surface and this value is less than the bulk bandgap of all possible oxide species (NiO , Cr_2O_3 or mixed). We will present the results of the initial stages of oxidation (<3 L) of the pure Ni thin films and discuss the differences in the oxidation processes due to the addition of 8-25 wt.% Cr. The progression from chemisorption regime (at low temperatures) to the oxide nucleation regime will be shown for different alloys by performing room temperature O_2 exposures and post-exposure annealing cycles and the effect of alloying additions on this transition will be discussed. Preliminary data on the

changes in the atomic and electronic structure of the thin film and oxidation behavior due to the addition of Mo will be presented.

4:00pm **SP+BI+NS+SS+TF-ThA6 Growth and Properties of Skyrmionic Nanowires and Thin Film, Zheng Gai**, Oak Ridge National Laboratory, J. Yi, S. Tang, University of Tennessee, Oak Ridge National Laboratory, D. Mandrus, University of Tennessee **INVITED**

Magnetic skyrmion lattice, a vortex-like spin texture recently observed in chiral magnets, is of great interest to future spin-electronic data storage and other information technology applications. The combined effect of a large ferromagnetic exchange and a weak DM interaction is to twist the magnetization into a long-period spiral that can be tens to hundreds of nanometers in length. As these spirals are only weakly bound to the underlying lattice in cubic systems, they can be readily manipulated with modest applied fields. The skyrmion lattice in MnSi appears in a small region (known as the A phase) of the H-T phase diagram in bulk samples, but in 2D samples like thin films the skyrmion phase is much more robust. If skyrmion ordering can persist in one-dimensional MnSi nanowires and 2D films, then these systems are very promising for spintronics applications as the magnetic domains and individual skyrmions could be manipulated with small currents. We have systematically explored the synthesis of single crystal MnSi nanowires via controlled oxide-assisted chemical vapor deposition and observed a characteristic signature of skyrmion magnetic ordering in MnSi nanowires. The SiO_2 layer plays a key role for the high yield, correct stoichiometric and crystalline growth of the B20 MnSi nanowires. A growth phase diagram was constructed. For the thin films, an unique growth receipt was developed for the growth of high quality of thin films. The structure and magnetic properties of the films at different thickness were studied.

4:40pm **SP+BI+NS+SS+TF-ThA8 Sulfur-induced Structural Motifs on Cu(111) and Au(111) Surfaces, Holly Walenš**, Iowa State University, D.-J. Liu, Ames Laboratory, J. Oh, H. Lim, RIKEN, Japan, J.W. Evans, Iowa State University, C.M. Aikens, Kansas State University, Y. Kim, RIKEN, Japan, P.A. Thiel, Iowa State University

The interaction of sulfur with copper and gold surfaces plays a fundamental role in important phenomena that include coarsening of surface nanostructures, and self-assembly of alkanethiols. Here, we identify and analyze unique sulfur-induced structural motifs observed on the (111) surfaces of these two metals. We choose very specific conditions: very low temperature (5 K), and very low sulfur coverage (≤ 0.05 monolayers, ML). In this region of temperature-coverage space, which has not been examined previously for these adsorbate-metal systems, the effects of individual interactions between metals and sulfur are most apparent and can be assessed extensively with the aid of theory and modeling. Furthermore, at this temperature diffusion is minimal and relatively-mobile species can be isolated. The primary technique is scanning tunneling microscopy (STM).

On Cu(111), at 0.004 ML S, we find unexpected heart-shaped Cu_2S_3 complexes on the terraces, made up of intersecting linear S-Cu-S units. With supporting density functional theory (DFT) and reaction-diffusion equation analysis, we propose that these hearts are a viable candidate for S-enhanced mass transport of Cu on Cu(111) at higher temperature. As S coverage increases (up to 0.05 ML), a diverse group of Cu-S structures develops which includes concatenated hearts, and eventually the known $(\sqrt{43} \times \sqrt{43})R\pm 7.5^\circ$ reconstruction[1-2]. Analysis of the step edges of Cu(111) indicates that S decorates the step edges preferentially (relative to the terraces) and that the complexes observed on terraces originate at the step edges.

In contrast, no metal-sulfur complexes are observed on Au(111) under similar conditions (0.03 ML). Instead, we observe striking $\sqrt{3}R30^\circ$ rows made up of S adatoms. Using DFT and *ab-initio* Monte Carlo analysis, we construct and test a lattice gas model. This analysis shows that these short rows of S adatoms form because of a complex set of through-metal interactions: a linear three-body attraction, as well as long-range pairwise interactions (up to 5a) between S atoms.

These experimental observations for Cu(111) and Au(111) surfaces—made under essentially-identical conditions—together with extensive DFT analyses, allow comparisons and insights into factors that favor the existence of metal-sulfur complexes, vs. chemisorbed atomic sulfur, on metal terraces.

[1] E. Wahlström, I. Ekvall, H. Olin, S. A. Lindgren, and L. Wallden, Phys. Rev. B **60** 10699 (1999).

[2] E. Wahlström, I. Ekvall, T. Kihlgren, H. Olin, S. A. Lindgren, and L. Wallden, Phys. Rev. B **64** 155406 (2001).

* Morton S. Traum Award Finalist

5:00pm **SP+BI+NS+SS+TF-ThA9 Surface Strain-Modulated Binding of Adsorbates on TiO₂(110)**, *D.V. Potapenko, Richard Osgood, Jr.*, Columbia University

Mechanical elastic strain is commonly present in nanostructured materials and it has been found to change chemical and electronic properties in a broad range of solids. Systematic study of reactivity-strain relationship on surfaces is difficult because of the fact that only very low values of strain (~0.1%) are achievable through mechanical deformation of macroscopic samples. We have developed a method of preparation of nano-scale strain fields on TiO₂ rutile(110) surface by low energy (1keV) Ar ion bombardments combined with specific thermal treatment. Titanium oxide is a brittle material regarded as a prototypical photocatalyst with numerous applications in the areas of solar energy utilization. Subsurface Ar clusters, which are formed through our preparation procedure, cause 5 – 25 nm wide surface deformations with the tensile strain values as high as 4 %. Surface distributions of various molecular and atomic adsorbates on TiO₂(110) have been studied with atomically resolved STM imaging. Our results indicate significant strain-related variations in the surface binding properties. In this presentation we will concentrate on surface hydroxyl groups (OH) as a mobile adsorbate. We derive the O-H binding energy from the statistical analysis of the adsorbate distribution. Then we demonstrate a roughly linear relationship between the values of surface strain and the O-H binding energy.

5:20pm **SP+BI+NS+SS+TF-ThA10 STM/STS Investigation of Organic Charge Transfer Complex TTF-TCNQ on Noble Metal Surfaces at 4.3K**, *Seokmin Jeon, P. Doak, P. Ganesh, B. Sumpter*, Oak Ridge National Laboratory, *J.I. Cerda*, Instituto de Ciencia de Materiales de Madrid, Spain, *P. Maksymovych*, Oak Ridge National Laboratory

TTF-TCNQ (TTF = tetrathiafulvalene; TCNQ = 7,7,8,8-tetracyanoquinodimethane) is a prototypical organic charge-transfer complex providing with a metallic conductivity (up to 900 ohm-1cm-1 at 300K). It also represents a broad class of organic electronic compounds that exhibit strong electron correlations and a rich gamut of phase transitions involving charge ordering, Mott and Peierls metal-insulator transitions and superconductivity, etc. Despite decades of research in this area, quantitative understanding of this compound is still elusive and their low-dimensional form is barely explored. We investigated ultrathin films of TTF-TCNQ on silver surfaces using scanning tunneling microscopy/spectroscopy (STM/STS) at 4.3 K. TTF-TCNQ forms self-assembled molecular lattices on noble metal surfaces with a few different TTF-to-TCNQ ratios depending on evaporation condition. Among them the islands with 1 to 1 stoichiometric ratio are found ubiquitously in less dependent on the evaporation condition. Structures of the monolayer islands are elucidated from sub-molecular resolution STM topography images. Single-point conductivity spectroscopy and conductivity mapping elucidate new electronic states which do not stem from their molecular orbital states are spatially located in the void areas of the TTF-TCNQ molecular lattices. We propose the *sp*-derived metal surface states are confined in the molecular lattices. Due to small periodicity of the lattice, the band minimum of the *sp*-derived metal surface states is shifted by as much as 1eV. This shift is much more significant than the ones normally observed in organic self-assemblies. As a result, we can also infer the height of the potential barrier within a 1D potential well model, which in turn is directly related to strong molecular dipole associated with large charge transfer and bent molecular geometry due to metal-molecule interactions.

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Thin Film

Room: 111 - Session TF+AS+NS+SA-ThA

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization II

Moderator: Jay Hendricks, National Institute of Standards and Technology

2:20pm **TF+AS+NS+SA-ThA1 Dynamic and Structural Stability of Cubic Vanadium Nitride**, *Antonio Mei**, University of Illinois at Urbana-Champaign, *O. Hellman*, California Institute of Technology, *N. Wireklint*, Chalmers University of Technology, Sweden, *C.M. Schlepütz*, Argonne National Laboratory, *D.G. Sangiovanni*, *B. Alling*, Linköping University, Sweden, *A. Rockett*, University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden, *I. Petrov*, *J.E. Greene*, University of Illinois at Urbana-Champaign

Structural phase transitions in epitaxial stoichiometric VN/MgO(011) thin films are investigated using temperature-dependent synchrotron x-ray diffraction (XRD), selected-area electron diffraction (SAED), and resistivity measurements combined with high-resolution cross-sectional transmission electron microscopy (HR-XTEM) and *ab-initio* molecular dynamics (AIMD). At room temperature, VN has the B1 NaCl structure. However, at temperatures below $T_c = 250$ K, XRD and SAED results reveal forbidden (00l) reflections of mixed parity associated with a non-centrosymmetric tetragonal structure. At $T \leq T_c$, forbidden reflections intensify continuously following the scaling behavior $I \propto (T_c - T)^{1/2}$. This suggests a transition of second-order character, but the incompatible symmetries of the parent cubic VN (space group) and product tetragonal VN () phases ultimately requires that the structural transition be first order. Resistivity $\rho(T)$ plots between 300 and 4 K consist of two linear regimes resulting from different electron/phonon coupling strengths in cubic and tetragonal VN.

The VN transport Eliashberg spectral function $\alpha^2_{tr}F(\hbar\omega)$, the product of the phonon density-of-states $F(\hbar\omega)$ and the transport electron/phonon coupling strength $\alpha^2_{tr}(\hbar\omega)$, is determined and used in combination with room-temperature inelastic neutron scattering results to establish that while entropy favors the higher-temperature cubic phase, as T is lowered below T_c , tetragonal VN becomes the thermodynamic ground state due to its lower enthalpy. AIMD renormalized phonon dispersion relations are in agreement, showing that the energy of (00l) X-point phonons in NaCl-structure VN decreases and eventually becomes imaginary at $T \leq 250$ K. We demonstrate that free energy contributions due to vibrational entropy, often-neglected in theoretical modeling, are essential in understanding the room-temperature stability of NaCl-structure VN, and of strongly anharmonic systems in general.

2:40pm **TF+AS+NS+SA-ThA2 Comparison of Solution Based Aluminum Oxide Phosphate Thin Films Deposited via Spin Coating vs. a Novel Mist Deposition System**, *Nishit Murari*, *R.H. Mansergh*, *Y. Huang*, *G. Westerfield*, *D. Keszler*, *J.F. Conley*, Oregon State University

Solution based spin coating techniques are well known for producing high quality organic as well as inorganic metal oxide thin films. However, spin coating is primarily suitable for planar substrates and lacks the ability to form uniform ultrathin films over large surface areas. In recent years, several alternative mist based deposition techniques have been introduced to enable solution based deposition over large areas and non-planar substrates. Mist deposition involves the creation of a precursor mist and its subsequent condensation on the substrate. Mist deposition techniques to date have been limited by disadvantages such as the requirement for highly volatile precursors and the non-homogeneous distribution of the mist, both of which lead to inferior film thickness uniformity. To address these limitations, we employ a new mist deposition system with a novel mist creation technique consisting of an atomizer with two opposing precursor jets. The unique opposing configuration of the atomizer enables the formation of a highly uniform mist even from low volatility precursors. In this work, we address the question of whether this new mist deposition technique can produce film quality comparable to spin coating technique.

Amorphous aluminum phosphate (AlPO) thin films were deposited via mist deposition using a BENEQ ACS 200-101 as well as standard spin coating. All films were deposited at room temperature and pressure using precursors based on aqueous suspensions of aluminum phosphate inorganic clusters. The inorganic ligands decompose at low temperature with minimal volume change presenting a route to high density films at low temperature. Both mist and spin coating achieve thickness uniformity of 5% across a 150 mm Si substrate. Both techniques result in ultra-smooth films with average

* TFD James Harper Award Finalist

surface roughness of less than 1 nm RMS. Variation in film density and roughness as a function of annealing temperature was identical for both techniques. Finally, similar charge transport behavior and dielectric constant were exhibited as a function of anneal temperature.

An aqueous precursor was used in a side by side comparison of spin coating and a novel mist deposition technique. High quality AlPO thin films of similar uniformity, density, roughness, and electrical properties were obtained using both techniques. Based on these results, this novel mist based deposition technique appears to be a promising candidate for the next generation of thin film deposition techniques for large area electronics.

3:00pm TF+AS+NS+SA-ThA3 Electro-Optic Studies of $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ Thin Films Deposited by Chemical Solution Deposition Method, Vaishali Batra, S. Kotru, V.N. Harshan, The University of Alabama, M. Varagas, C.V. Ramana, University of Texas at El Paso

Lanthanum doped lead zirconate titanate (PLZT) of perovskite type crystalline structure is an interesting transparent ferroelectric material due to its large remnant polarization and electro-optic effects, near the morphotropic phase boundary. The excellent optical and electrical properties make it material of choice for applications in MEMS, optical modulators/transducers and smart sensors. Recent studies reveal that this material possesses great potential for use in future photovoltaic (PV) devices which involves combination of optical transparency and ferroelectric properties. The advantage of using this material for PV applications is that the effect can be realized without a need of p-n junction as in semiconductor devices. Additionally the material exhibits bulk PV effect due to internal electric field originating from electric polarization. However, the optimization of processing conditions of deposited films is important to design efficient devices, which require understanding of the structure, its behavior with light, and response to electric field.

Lanthanum-modified lead zirconate titanate (PLZT) thin films with a composition of $(\text{Pb}_{0.95}\text{La}_{0.05})(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$ were deposited on Pt/TiO₂/SiO₂/Si substrates. The films were rapidly annealed in the temperature range of 550 to 750 °C in oxygen ambient to study the effect of crystallization on the electric and optical properties. X-ray diffraction revealed that the post deposition temperature changes the preferential orientation of the films. Optical band gap values determined from UV-visible spectroscopy and spectroscopic ellipsometry for PLZT films were found to be in the range of 3.42-4.00 eV. The optical constants and their dispersion profiles for PLZT films were also determined from SE analyses. PLZT films exhibit an index of refraction ~ 2.5 ($\lambda=630$ nm). The electrical properties were studied using the model for metal-ferroelectric-metal (MFM) heterostructures with Schottky contacts using Au electrodes. High remnant polarization (41.85 $\mu\text{C}/\text{cm}^2$), low coercive voltage (1.19 V) and high free carrier concentration ($\sim 1.1 \times 10^{18} \text{ cm}^{-3}$) were obtained from films annealed at 750 °C. Thus post deposition annealing temperature plays a major role in deciding the electrical and optical properties.

3:20pm TF+AS+NS+SA-ThA4 Electron Scattering at Surfaces of Epitaxial Metal Layers, Pengyuan Zheng, D. Gall, Rensselaer Polytechnic Institute

Epitaxial Cu(001) is grown on MgO(001) with different overlayers to demonstrate that electron surface/interface scattering can be engineered by surface doping, causing a decrease in the resistivity. For instance, the resistivity of 9.3-nm-thick epitaxial and polycrystalline Cu layers is reduced by 11-13% when coated with 0.75 nm Ni. This is due to partially specular surface scattering with specularly parameters $p = 0.3$ and 0.15 for the Ni-coated Cu in vacuum and air, respectively, while scattering is completely diffuse ($p = 0$) for a pure Cu surface in air. This is attributed to the suppression of Cu₂O formation, leading to a lower localized density of states (LDOS) at the surface, and therefore less diffuse electron scattering. The change of surface scattering by controlling the LDOS is further confirmed: the sheet resistance of 9.5-nm-thick epitaxial Cu(001) increases by 4-43% if a 0.1-4 monolayer thick Ti coating is added, but subsequent exposure to 37 Pa of O₂ causes a resistivity reduction of 3-24%. This reduction is due to a recovery of specular interface scattering associated with a reduction of the LDOS during Ti oxidation from 15-27.4 to 2.4-6.5 eV⁻¹nm⁻², as quantified by ab initio calculations. Furthermore the surface scattering effect is found to be orientation dependent. For example, the resistivity of 5-nm-thick epitaxial tungsten layers is two times higher for 001 vs 110 orientated layers. This is due to the anisotropy in the Fermi surface, as indicated by transport simulations based on first-principles band structure calculations, which suggest a 1.5 times smaller size effect for the 110 orientation. These epitaxial films were sputter deposited onto Al₂O₃(11-20) and MgO(001) at 1050 °C and 900 °C, respectively, followed by in situ annealing at 1050 °C for 2 hrs. X-ray diffraction θ -2 θ , ω , and ϕ -scans confirm epitaxy and X-ray reflectivity indicates atomically smooth film-substrate interfaces and smooth film surfaces with a root-mean-square roughness that increases from 0.32 \pm 0.05 to 0.81 \pm 0.05 nm for

W(110) with $t = 5.7$ -39.2 nm, and from 0.21 \pm 0.05 to 0.40 \pm 0.05 nm for W(001) with $t = 4.8$ -50 nm. In summary, we have systematically shown that (1) surface scattering can be altered by carefully controlling the surface LDOS at the Cu surface or interface with the barrier and (2) the crystalline orientation of interconnect wires with non-spherical Fermi surfaces is a major factor when considering alternative metals to replace Cu interconnects.

4:00pm TF+AS+NS+SA-ThA6 Lattice Relaxation in Multilayered Si_xGe_{1-x}/Si (001) Metamorphic Heterostructures, Tedi Kujafsa, J.E. Ayers, University of Connecticut

The inclusion of compositionally-graded metamorphic buffer layers in multilayered heterostructures allows tremendous flexibility designing novel SiGe/Si microelectronic and optical semiconductor devices. For example, advanced CMOS transistors can be fabricated on strain relaxed buffers to obtain enhanced mobility in n-channel and p-channel devices using tensile and compressive strain, respectively. While it is necessary to control the strain in the device layers, it is also desirable to fabricate these structures with low threading dislocation densities and minimum buffer thickness. Thus, understanding lattice relaxation in multilayered and compositionally-graded heterostructures is desirable to provide guidance in designing SiGe/Si devices. This work focuses on the design of the multilayered heterostructures comprising a uniform layer of Si_{1-x}Ge_x (device layer) deposited on a Si (001) substrate with an intermediate compositionally-graded buffer layer of Si_{1-x}Ge_x. The objective of this work is to study the relaxation dynamics and misfit dislocations in the device and buffer layer. We present minimum energy calculations and show that for a given device layer with fixed germanium composition and layer thickness, there exists a combination of the buffer layer thickness and compositional grading to provide tight control of the strain in the device layer. Furthermore, we give a simple model describing the strain in the device layer.

4:40pm TF+AS+NS+SA-ThA8 Growth Stress Evolution in Low Adatom Mobility Fe(Cr) Thin Films, Xuyang Zhou, The University of Alabama, T. Kaub, R.L. Martens, The University of Alabama, G.B. Thompson, The University of Alabama

During the post coalescence portion of thin film deposition, thin film stress is related to the grain size and adatom mobility of the depositing material. This stress state can be regulated by the mobility of atoms into or out of these grain boundaries. Using Fe(Cr) alloy thin films as a case study, the stress evolution during growth was investigated as a function of Cr content up to 8 at.%. During the deposition of the elemental films, each film grew with a tensile stress state on a Si wafer because of their low adatom mobility. Upon alloying 4 at.% Cr to the Fe film, the as-deposited grains grew from ~ 40 nm (pure Fe) to ~ 65 nm (Fe-04Cr), resulting in a stress relaxation from ~ 200 GPa*nm to 50 GPa*nm at a thickness of 300 nm. As the Cr content increased further, the grains refined back towards ~ 50 nm in size resulting in a recovery of the higher tensile stress condition. The reduction of the grain size is contributed to Cr solute segregation to the grain boundaries, clustering, and ultimately precipitation at the boundaries. The real-time stress evolution during growth will be discussed in terms of the inferred microstructural evolution of the film using post-mortem atom probe tomography and transmission electron microscopy characterization. The results of which address how segregating behavior can be used as a means of thin film stress engineering.

5:00pm TF+AS+NS+SA-ThA9 Development of an Analytical Model for Langmuir-Blodgett Silica Microsphere Assembly and Investigation of Ge Back Filling of the Opal Template by Polymer-Assisted Deposition, Sarun Atigyanun, M. Zhou, S.E. Han, S.M. Han, University of New Mexico

Self-assembled photonic crystals find a wide variety of applications, including low-loss waveguides, high-efficiency solar cells, and thermal emission control. Here, we investigate a low-cost scalable fabrication of an opal structure via self-assembly of colloidal silica microspheres and propose a model describing a relationship between assembly parameters. To fabricate an opal structure, silica microspheres with a diameter of ~ 900 nm are first functionalized with allyltrimethoxysilane. Langmuir-Blodgett (LB) method is then used to self-assemble silica microspheres onto Si(100) substrates. By optimally adjusting the pulling speed of the substrate and surface pressure within the trough, a hexagonally closed-packed structure is achieved. By repeating LB coating processes for n number of times, an n -multilayer assembly is formed, creating an opal template structure. Scanning electron microscopy and light diffraction experiment are used to identify assembly parameters that give the largest domain size. An analytical model is also derived from material flux balance and a 2D van der Waals equation of state of silica spheres on water surface to describe the relationship between pulling speed, surface pressure, barrier speed, number of layers, and sphere's diameter for optimal assembly. In this presentation, we will also discuss a facile approach to back-fill opal templates via polymer-assisted deposition of Ge. After forming the template structure, a

solution of polyethylenimine, ethylenediaminetetraacetic acid and germanium dioxide is used to back-fill the voids between microspheres. The sample is then annealed in a forming gas environment, forming Ge films around the microspheres. After the microspheres are removed, the Ge structure is characterized with SEM, XRD, and light transmission.

5:20pm **TF+AS+NS+SA-ThA10 The Determination of Porosity and Pore Size Distribution of The Al_2O_3 Antireflection Coating Deposited By Atomic Layer Deposition**, *Chao Li, M. Goorsky*, University of California at Los Angeles

The porosity and pore size distribution of coatings prepared by atomic layer deposition and by other deposition techniques is important to understand their optical and mechanical properties. Specular X-ray reflectivity (SXRR) is capable of extracting layer thickness with angstrom resolution as well as determining the layer density. This makes it a good candidate for the porosity characterization of the antireflection coatings. On the other hand, advances in the development of X-ray generators and optics have made in-house glancing incidence small angle X-ray scattering (GISAXS) experimentation suitable for the determination of the size and shape of pores (in the scale of sub-nanometer to 100 nm) existing in thin films. It can be realized through the simulation of pore scattering based on distorted wave Born approximation (DWBA). Unfortunately, previous GISAXS studies failed to exclude the scattering from the rough surface and interfaces of thin films from the total scattering that was used for the simulation. In this study, we propose a refined GISAXS method characterizing the pore size distribution with the scattering from the rough surface and interfaces excluded. The scattering from the surface and interfaces was determined by the simulation of X-ray reflectivity (XRR) longitudinal scan with the parameters of the surface roughness σ , the lateral correlation length ξ and the Hurst parameter h extracted from the atomic force microscopy measurement, and layer thicknesses, densities and compositional grading determined by the specular XRR simulation. This refined GISAXS method, together the SXRR technique, was applied to utilize to reveal the effect of deposition techniques on the nanostructures of single-layer Al_2O_3 -based antireflection coatings. They were deposited using atomic layer deposition (ALD) which is a good candidate for multilayer antireflection coatings, due to the self-limiting nature of chemical reactions resulting in the precise control of film thickness and large-area uniformity. Each of them has two amorphous structures on a Si substrate grown with different deposition parameters. It is indicated by the refined GISAXS method that the first Al_2O_3 single layer is porous with a mean pore (spherical shape) radius of 7.2 nm while there are no pores in the second Al_2O_3 single layer. This agrees well with the SXRR showing a lower density of the first Al_2O_3 single layer (2.93 g/cm^3) than that of the second Al_2O_3 single layer (3.04 g/cm^3).

5:40pm **TF+AS+NS+SA-ThA11 Tuning Static and Dynamic Magnetic Properties of FeGa/NiFe Multilayer Composites**, *Colin Rementer, Q. Xu, K. Fitzell, Z. Yao, P. Nordeen, G. Carman, Y. Wang, J.P. Chang*, University of California at Los Angeles

Traditionally, the use of magnetic materials in high frequency applications has been limited to oxides. This is because the materials' high resistivity, which reduces the formation of eddy currents by the incident electromagnetic waves. However, these oxides have limited applications in multiferroics, which are materials that possess more than one ferroic ordering in a single phase or strain-coupled composite systems, due to their low magnetomechanical coupling. Metallic materials are more desirable to this end, but their magnetic hardness and conductive losses have limited their use.

Rare-earth-free iron-gallium (FeGa) is one of the most promising magnetostrictive materials for use in composite multiferroics, due to its high piezomagnetic coefficient (3 ppm/Oe) and high stiffness (70 GPa). It has been integrated into several multiferroic systems, but generally in the MHz range or below¹. This is due to the fact that the material has a large ferromagnetic resonance (FMR) linewidth (>300 Oe) at X band (9.6 GHz), which will result in incident energy being converted to heat. Metalloid dopants have been used to soften magnetic materials and to tune frequency dependent properties, such as permeability and piezomagnetic behavior, but at the cost of saturation magnetization as well as magnetostriction². In this work, multilayer laminates containing alternating hard and soft ferromagnetic layers were fabricated to reduce loss at high frequencies.

FeGa (hard) and NiFe (soft) were sputtered via alloy targets into multilayers on Si [100] and piezoelectric substrates with total thicknesses ranging from 40-500 nm. The compositions of the films were verified via X-ray photoelectron spectroscopy (XPS) and were found to be $\text{Fe}_x\text{Ga}_{1-y}$ ($78 \leq y \leq 85$ at%) and $\text{Ni}_x\text{Fe}_{1-x}$ ($79 \leq x \leq 83$ at%). Static magnetic properties were evaluated via superconducting quantum interference device (SQUID) magnetometry, and it was found that the incorporation of NiFe layers was found to reduce the coercivity by up to 80%, while only reducing the saturation magnetization by 20%. FMR measurements revealed a narrowing of the linewidth by up to 90% at X band. Permeability extracted from the

reflection coefficient (S11) obtained via stripline measurement was found to be affected by layer thickness and number of layers. FeGa showed strong magnetoelastic behavior and the multilayers are expected to exhibit an enhanced piezomagnetic effect due their reduced coercivity.

References:

1.M. Hamashima, C. Saito, M. Nakamura and H. Muro, *Electr Commun Jpn* 95 (5), 1-7 (2012).

2.J. Lou, R. E. Insignares, Z. Cai, K. S. Ziemer, M. Liu and N. X. Sun, *Appl Phys Lett* 91 (18) (2007).

Thin Film

Room: 114 - Session TF+PS-ThA

Thin Film Permeation Barriers and Membranes

Moderator: Mariadriana Creatore, Eindhoven University of Technology, Netherlands

2:20pm **TF+PS-ThA1 Synthesis, Characterisation and Engineering of Moisture Barrier Films Deposited in a Roll-to-Roll High Current Dielectric Barrier Discharge**, *Hindrik de Vries*, FOM institute DIFFER, Netherlands **INVITED**

Atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) is a new and rapidly evolving technology having clear benefits in terms of equipment costs, footprint size and possibilities for in-line processing. The excellent scalability of the dielectric barrier discharge combined with the possibility to generate non-thermal plasma in low-cost helium free gas mixtures, are essential requirements for large scale processing of functional films on web-rolled substrates.

In this work a cylindrical drum shaped DBD reactor configuration was implemented to facilitate roll-to-roll processing. We performed a systematic study of the discharge physics investigated by fast ICCD camera and voltage-current waveforms and we comprehensively analyzed the silica-like films deposited under barrier deposition conditions using AFM, XPS, SE and FTIR.

The time evolution of the atmospheric discharge was studied in 2 orthogonal directions of the cylindrical electrode geometry showing a glow-like discharge character. Detailed AFM morphology study and surface statistical analysis of the silica growth dynamics was carried out. The microstructure of the silica layers was studied using polarized ATR-FTIR and linked to the water vapor transmission rate (WVTR). The remarkable power law scaling between WVTR and film thickness was tentatively explained by the percolating nature of the moisture transport through the films. Based on this hypothesis, different approaches were investigated towards (bi-)layer architectures using AP-PECVD as well as other deposition techniques. Such a bi-layer architecture typically consists of a first porous silica layers that is subsequently covered by a dense silica capping layer.

In this contribution we will focus on the processing of silica bi-layers synthesized in different deposition regimes. The process conditions of the layers will be discussed in the frame of different scaling parameters like the energy spent per precursor molecule and the local deposition rate. Gas permeation properties were characterized by Technolox Deltaperm and calcium test. It was shown that AP-PECVD grown silica thin films of less than 30 nm deposited on a porous silica layer can yield excellent overall moisture barrier values (WVTR) typically $\sim 6 \cdot 10^{-4} \text{ g/m}^2 \text{ day}$ at 40°C, 90%RH accelerated ageing conditions.

3:00pm **TF+PS-ThA3 Investigation on Nano-Porosity in Moisture Permeation Barrier Layers by Electrochemical Impedance Spectroscopy**, *Alberto Perrotta*, Eindhoven University of Technology, Netherlands, *S.J. Garcia Espallargas*, Delft University of Technology, Netherlands, *J.J. Michels*, Max Planck Institute for Polymer Research, Germany, *M. Creatore*, Eindhoven University of Technology, Netherlands

High-tech devices relying on organic semiconductors require device encapsulation against moisture and oxygen permeation, which would otherwise negatively affect the device opto-electrical performance.

The water permeation in inorganic moisture barriers has been shown to occur through macro-scale defects/pinholes (ranging from tens of nms to several μms) and nano-pores, down to sizes approaching the water kinetic diameter (0.27 nm). Both permeation paths can be identified by the calcium test, which allows discerning between the effective water vapor transmission rate (WVTR) and the intrinsic WVTR, the latter solely attributed to the permeation through the nano-porosity characterizing the bulk of the barrier layer. Recently [1], we have shown that ellipsometric porosimetry (EP) is a valid method to classify and quantify the nano-

porosity content of inorganic barriers and a correlation has been found between their relative pore content and intrinsic WVTR values [1]. However, no information can be retrieved on the macro-scale defects nor on the kinetics of water permeation through the barrier, both essential elements in assessing the quality of the barrier layer.

In this study, electrochemical impedance spectroscopy (EIS) is demonstrated as a sensitive method to obtain quantitative information on both nano-porosity and macro-scale defects, complementing the barrier property characterization obtained by means of EP and calcium test.

EIS analysis is carried out on thin SiO₂ barrier layers deposited by plasma enhanced-CVD. The layer capacitance has been determined by modelling the impedance data with the proper equivalent circuit and the change of the capacitance upon water permeation has been followed. The Brasher-Kingsbury equation has been successfully applied and water uptake in the range of 0.8-4% have been found, in agreement with the nano-porosity content inferred by EP. A good linear correlation between the nano-porosity and the values of the electrical components used in the fitting procedure of the EIS data has been obtained, suggesting the direct calculation of open nano-porosity from an EIS fit. Furthermore, the kinetics of water permeation can be followed by EIS: the water diffusivity for the SiO₂ layers has been determined and found in agreement with literature values. Moreover, differently from ellipsometry-based techniques, EIS data are shown to be sensitive to the presence of local macro-defects, inferring its possible use for the prediction of the barrier performance with the calcium test.

[1] A. Perrotta *et al.*, Microporous Mesoporous Mat., 188 (2014) 163-171

4:00pm **TF+PS-ThA6 Thin-film Dielectrics for Chronic Nonhermetic Encapsulation of Electrically Active Neural Implants, Stuart Cogan, The University of Texas at Dallas** **INVITED**

The needs of emerging clinical applications of neural stimulation and recording in the treatment of many diseases and disorders are driving a reduction in the size of implanted devices and the development of strategies to manage the large number of electrical interconnects between implanted electrodes and control electronics. The requirements for large numbers of electrodes, exceeding many hundreds for vision prostheses, and the ability to interface with nerves that may be as small as 100 microns in diameter, precludes the use of conventional packaging with hermetically sealed metal or ceramic cans. One of the few practical alternatives to hermetically sealed enclosures is the use of thin-film dielectrics, possibly combined with polymer over-layers. Besides the need for these thin-film coatings to provide effective passivation against corrosion, they also serve a multifunctional role providing adhesion between polymer and metal layers in flexible devices, providing a biocompatible interface to neural tissue and in some devices, providing a surface for functionalization with bioactive molecules. Conventional passivation materials such as silicon dioxide and silicon nitride are prone to corrosion *in vivo* and recent experience with polymer encapsulation such as Parylene-C suggests that this otherwise excellent barrier layer may fail after chronic implantation for more than about one year. The implanted electronics on these devices operates typically at 3 V or higher and neural stimulation involves pulsatile currents that may also induce unexpected failures at interfaces. In this context, other thin-film materials such as amorphous silicon carbide (a-SiC), ultra-nanocrystalline diamond (UNCD), and atomic-layer-deposition (ALD) Al₂O₃ are being investigated as alternative passivation materials that can provide chronic protection of active implants. A discussion of the physical and chemical requirements for these materials and results reported to date is presented. Emphasis is placed on understanding the constraints of the application including processing compatibility with temperature-sensitive substrates, the need for conformal coatings, and appropriate test methodologies to validate predictions of chronic *in vivo* lifetimes. Early results are promising with some combinations of thin-film and polymer encapsulation exhibiting excellent stability and biocompatibility. Of particular interest, are the relative roles and importance of interfacial properties and bulk barrier properties in achieve long-term chronic passivation of implanted active devices.

4:40pm **TF+PS-ThA8 Atmospheric Pressure Roll-to-Roll Plasma Enhanced CVD of High Quality Silica-like Bi-layer Moisture Barrier Films: The Influence of Input Energy, Fiona Elam, FUJIFILM Manufacturing Europe B.V., Netherlands, A. Meshkova, S.A. Starostin, DIFFER, Netherlands, J.B. Bouwstra, FUJIFILM Manufacturing Europe B.V., Netherlands, M.C.M. van de Sanden, H.W. de Vries, DIFFER, Netherlands**

Atmospheric Pressure-Plasma Enhanced Chemical Vapour Deposition (AP-PECVD) is a new enabling technology that can be easily integrated into many existing manufacturing systems to facilitate the mass production of functional films. To date, roll-to-roll AP-PECVD has been successfully used to produce ultra-smooth, dense, 100 nm single layer silica-like thin

films that demonstrate good water vapour barrier performance, therefore showing particular promise as a technique in the field of protective layer synthesis for flexible organic solar cells. However, this technology is only viable for moisture barrier production if high quality films can be manufactured at high throughput and at low cost. The generation of bi-layer silica-like thin films comprising a 'dense layer' synthesised using very low precursor gas flows deposited on top of a 'porous layer' synthesised at a high deposition rate, could provide one potential solution to this scientific challenge.

A glow-like AP dielectric barrier discharge in a roll-to-roll set-up was used to deposit a series of ~90 nm bi-layer silica-like thin films composed of a ~60 nm 'porous layer' and ~30 nm 'dense layer' onto a polyethylene 2,6 naphthalate substrate by means of AP-PECVD. Tetraethyl orthosilicate (TEOS) was used as the precursor gas, together with a mixture of nitrogen, oxygen and argon. In each case, the deposition conditions for the 'porous layer' were kept constant, while the conditions for the synthesis of the 'dense layer' were varied in order to study the effect of increased input energy per precursor gas molecule (~6 – 70 keV/TEOS molecule) on the chemical composition and porosity of the 'dense layer' and hence, the influence of this 30 nm layer on the moisture barrier performance of the overall film.

Each film was characterised in terms of its water vapour transmission rate, its chemical composition (*s*-, *p*- and *un*-polarised Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy and X-ray Photoelectron Spectroscopy) and its morphology (Atomic Force Microscopy) as a function of the input energy per precursor gas molecule during the 'dense layer' deposition. The analysis provided valuable information concerning the structure of the silica network within each 'dense layer', and hence the influence of input energy per precursor gas molecule on the ultimate film quality.

The ~90 nm bi-layer silica-like thin films were seen to exhibit water vapour transmission rates of at least 6.2×10^{-4} g m⁻² day⁻¹ (at 40°C, 90% RH), illustrating that it is possible to produce exceptionally high quality moisture barrier films using the presented bi-layer approach in a roll-to-roll AP-PECVD set-up.

5:00pm **TF+PS-ThA9 Use of Aluminum Oxide as a Permeation Barrier for Producing Thin Films on Aluminum Substrates, James Provo, Consultant, J. L. Provo Consulting**

Aluminum has desirable thermal properties (i.e. conductivity, diffusivity and specific heat), electrical and optical properties of resistivity and reflectivity, and the characteristic of being non-magnetic and having a low atomic weight (26.98 g-atoms), but because of its low melting point (660°C) and ability as a reactive metal to alloy with most metals, it has been ignored as a substrate for use in processing thin films. The author, proposed a simple solution to this problem, by putting a permeation barrier of (Al₂O₃) onto the surface of Al substrates, by using a standard oxidation process of the surface (i.e., anodization), before additional film deposition of reactive metals at temperatures up to 500°C for 1 hour, without the formation of alloys or inter-metallic compounds that would affect the properties of the Al substrates. The chromic acid anodization used (MIL-A-8625) produced a film barrier of ~10k Å of alumina. The fact that refractory Al₂O₃ can inhibit the reaction of metals with Al at temperatures below 500°C suggests that Al is a satisfactory substrate if properly oxidized prior to film deposition. To prove this concept, thin film samples of Cr, Mo, Er, Sc, Ti, and Zr were prepared on anodized Al substrates and studied by Auger/ argon sputter surface analysis to determine any film substrate interactions. In addition, a thin film of (ErD₂) on an anodized aluminum substrate was studied with and without the alumina permeation barrier. Films for study were prepared on 1.27 cm O.D. high purity Al substrates with ~5k Å of the metals studied after anodization. Substrates were weighed, cleaned, and vacuum fired at 500°C prior to use. The aluminum substrates were deposited with the metals studied, using standard electron beam evaporation techniques, and after film deposition the erbium film was hydride with D₂ gas using a standard air-exposure hydriding technique. All processing was conducted in an all metal ion pumped high vacuum system. Results showed that e-beam deposition of all films studied onto Al substrates could be successfully performed, if a permeation barrier of Al₂O₃ from (5-10)k Å was made prior to thin film deposition up to temperatures of 500°C for 1 hour. Dihydrides, can also be successfully produced with full gas/metal atomic ratios of ~ 2.0 as evidenced by the (ErD₂) thin films produced. Thus the use of a simple permeation barrier of Al₂O₃ on Al substrates prior to additional metal film deposition, was proven to be a successful method of producing both thin metal and hydride films of various types for many applications without the formation of alloys or inter-metallic compounds that would affect substrate properties.

Thin Film

Room: Hall 3 - Session TF-ThP

Thin Films Poster Session

TF-ThP2 The Nano-power Generator Fabricated with Thin Atomic Layer Deposited Films, *Giovanna Scarel*, James Madison University

The energy of low power infrared (IR) radiation can be transferred to a power generator (PG) device and transformed into usable power [1, 2]. This process, called IR power generation, is demonstrated with commercially available PG devices [1, 2]. However, active media, such as Nb-doped TiO₂ films, can be fabricated in the form of thin films [3]. Voltage production through IR power generation was recently realized using atomic layer deposited (ALD) films [4], but not optimized. This poster outlines the strategies in terms of film architecture and fabrication method that can be employed to increase the efficiency of nano-PG devices fabricated via ALD.

[1] R. J. Parise and G. F. Jones, Collection of Technical papers – 2nd International Energy Conversion Engineering Conference, 1172–1181 (2004).

[2] Y. Schwab, H. S. Mann, B. N. Lang, J. L. Lancaster, R. J. Parise, A. J. Vincent-Johnson, and G. Scarel, *Complexity* **19**, 44-55 (2013).

[3] J. Niemelä, H. Yamauchi, and M. Karppinen, *Thin Solid Films* **551**, 19-22 (2014).

[4] H.S. Mann, B.N. Lang, Y. Schwab, J.-P. Niemelä, M. Karppinen, and G. Scarel, *J. Vac. Sci. Technol. A* **33**, 01A124 (2015).

TF-ThP3 Influence of Deposition Time on the Microstructure of Electrodeposited ZnO Films and p-Si/n-ZnO Heterojunction Diode Fabrication, *Salih İlican, Y. Caglar, S.A. Aksoy, M. Caglar*, Anadolu University, Turkey

ZnO is one of the widely studied materials for its number of exciting properties. It is a wide band gap semiconductor material with $E_g \sim 3.3$ eV. Electrodeposition is well known for depositing metals and metallic alloys at the industrial level, with a wide range of applications from large area surface treatments to most advanced electronic industries. Electrodeposition of semiconducting materials thus represents a new challenge, not only from the academic point of view, but also from the economic point of view, since this method presents interesting characteristics for large area, low cost and generally low temperature and soft processing of materials. ZnO nanorod array films were grown by electrochemical deposition onto p-Si substrates from an aqueous route. Aqueous solution of Zn(NO₃)₂·6H₂O and hexamethylenetetramine (HMT) was prepared using triple distilled water. The bath temperature is maintained at 90 °C during the electrodeposition of the ZnO films. The effect of deposition time on the crystallinity and nanorod arrays were investigated. The crystalline structure and orientation of the ZnO films were investigated using XRD method. The lattice parameters and texture coefficient values of the films were determined. Microstructure was analyzed by a field emission scanning electron microscope (FESEM), and the effects of the deposition time in the microstructure of the films were investigated. The film was determined the most appropriate structural properties and the p-n heterojunction diode was fabricated by using this film. The diode parameters were determined from the analysis of the measured dark I-V curves. Rectifying behavior was observed from I-V characteristics of these heterojunction diodes.

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TF-ThP7 The Effect of Nickel Content on Structural and Optical Properties of ZnO Films by Sol Gel Process, *Seval Aksoy, Y. Caglar, M. Caglar, S. İlican*, Anadolu University, Turkey

Semiconductor materials have received much attention because of their novel properties. Zinc oxide (ZnO) has been attracting attention because of the commercial demand. It is well known that the addition of impurities into a wide band gap semiconductor. A selective doping element into ZnO has become an important route for enhancing and controlling its structural, morphological, electrical, and magnetic performance. The magnetic property in III–V semiconductors do not attract much attention for device fabrication. Ni is an important dopant in the magnetic materials. Additionally, Ni²⁺ (0.69 Å) has the same valence compared to Zn²⁺ and its radius is close to Zn²⁺ (0.74 Å), so it is possible for Ni²⁺ to replace Zn²⁺ in ZnO lattice.

In this work, undoped ZnO and Ni doped ZnO (ZnO:Ni) films have been deposited by sol-gel method using spin coating technique. As a starting

material, zinc acetate dihydrate was used. 2-methoxyethanol and monoethanolamine were used as a solvent and stabilizer, respectively. The dopant source of Ni was nickel (II) acetate tetrahydrate. The effects of Ni concentration on the crystal structure and orientation of the ZnO films have been investigated using X-ray diffraction (XRD) study. The crystal structure and orientation of the ZnO film were determined to be a hexagonal wurtzite structure and a preferred orientation of (002). The average crystallite size, texture coefficient, dislocation density and lattice constants of the ZnO:Ni films were calculated. The average crystallite size values for the films was found to be in the range of 33–42 nm. The highest grain size value was obtained for the undoped ZnO film. Surface morphology of the films has been also studied by a field emission scanning electron microscope (SEM). The transmittance spectra of the films were measured to investigate their optical properties. All the films are highly transparent with average transmission (>81%) in the visible range. The optical constants of these films were determined using transmittance and reflectance spectra.

Acknowledgement: This work was supported by Anadolu University Commission of Scientific Research Project under Grant No. 1404F245

TF-ThP8 Effect of Applied Voltage on the Structural and Morphological Properties of Electrodeposited ZnO Films, *Pinar Bilgic Ozden, Y. Caglar*, Anadolu University, Turkey

ZnO is a widely used and produced n-type semiconductor material which can be obtained by several deposition techniques. Among them electrochemical deposition technique is one of the most promising technique for depositing ZnO because of the simplicity of the experiments and lower cost. It is possible to obtain high quality films by changing deposition parameters.

In this study, ZnO films were electrodeposited onto 100nm thick tin doped indium oxide (ITO) coated glass substrate via electrochemical deposition technique. Hexamethylenetetramine (C₆H₁₂N₄) and zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O salts were used as precursors in a 90°C aqueous solution. In our experimental setup, potassium chloride saturated silver/silver chloride (Ag/AgCl) electrode, a platinum (Pt) wire and ITO substrate were used as reference, counter and working electrodes, respectively. Experiments were carried out at -0.8, -0.9, -1.0, -1.1 and -1.2V for 90min of deposition time. After the depositions process, Structural and morphological properties of the ZnO films were investigated using Bruker D8 Advance XRD and Zeiss Ultra Plus FESEM.

From FESEM images, it is observed that as the applied voltage increase, the amount of the deposited film increase as well, but lower voltage values lead to insufficient coatings. XRD patterns reveal that films which deposited up to -1.0V applied voltage were grown along (002) orientation. Higher applied voltage values caused films to lost some part of their layers, it is probably the main reason of the weak diffraction peaks. As a result -1.0V applied voltage is found to be the best voltage value for this technique with using the parameters and materials mentioned above.

Acknowledgement: This work was supported by Anadolu University Commission of Scientific Research Project under Grant No. 1501F031

TF-ThP10 Self-Assembled ZnO Nanoparticles Embedded in a Silicon Oxide Matrix Produced by Reactive RF Sputtering*, *A. Lara-Sanchez, Facultad de Ingenieria, Universidad Autonoma de Chihuahua, Mexico, A. Hernandez-Hernandez, Escuela Superior de Apan, Universidad Autonoma del Estado de Hidalgo, Mexico, A. Garcia-Sotelo, E. Campos, S. Gallardo-Hernandez, Departamento de Fisica-Cinvestav-IPN, Mexico, M. Zapata-Torres, J.L. Fernandez-Muñoz, CICATA-IPN, Legaria, E. Valaguez-Velazquez, UPIITA-IPN, MiguelAngel Melendez-Lira, Departamento de Fisica-Cinvestav-IPN, Mexico*

Self-assembled silicon and germanium nanoparticles embedded within a SiO₂ matrix taking advantage of surface roughness have been successfully produced taking advantage of the roughness associated with the sputtering deposition process[1,2]. The aforementioned approach has been employed to explore the possibility to produce ZnO nanoparticle les embedded within a silicon oxide matrix on soda-lime glass and p-silicon substrates. Silicon dioxide and metallic Zn films were deposited employing silicon and zinc targets. Oxygen content of the working plasma was modulated through argon partial pressure. X-ray diffraction characterization do not shown the presence of metallic zinc. Secondary ion mass spectroscopy shown an interdiffusion of zinc throughout the SiO₂ matrix. TEM micrographs indicated the presence of nanoparticles. XPS shown ZnO formation under specific growth parameters. Photoluminescence emission at room temperature for samples grown on silicon substrates was not observed. Transport properties were studied measuring the IvsV characteristics of the films. For samples grown on silicon rectifying behavior and spectral response are observed . The observed results of photoluminescence and

transport properties are discussed in terms of the crystalline structure of the ZnO nanoparticles and its interaction with SiO₂ matrix.

*: Partially funded by CONACyT-Mexico

[1]. Mota-Pineda, E., et al. Journal of Applied Physics 108.9 (2010): 094323.

[2] Hernández-Hernández, A., et al. Journal of Applied Physics 111.4 (2012): 044327.

TF-ThP11 Development of Dispersed C₆₀/TiAlN Nano-Composite Thin Films with Superior Mechanical Properties, Yuki Ishiyama, A. Matsumuro, Aichi Institute of Technology, Japan

We have succeeded in the development of innovative dispersed C₆₀ molecule nano-composite Al and TiN thin films with great high hardness and excellent tribological properties. Fabrication method of their composite films has been used by our original unique vacuum evaporation method with both RF magnetron sputtering source and heat evaporator source. Nano-indentation hardness of 1.0 wt.%C₆₀/Al nano-composite thin film showed increased up to 3 times larger than that of Al film. And 2.0 wt.%C₆₀/TiN nano-composite thin film, both nano-indentation hardness and tribological properties increased up to 30 % larger than those of a conventional TiN thin film. These results clearly indicated that dispersion of C₆₀ molecules in the conventional films contributed improvement in mechanical properties.

In our study, we challenged to apply the established techniques to fabricate nano-composite materials using C₆₀ to TiAlN, which is harder than TiN. Development of the synthesis method of C₆₀/TiAlN nano-composite thin films with the excellent mechanical properties more than those of TiN nano-composite must give effective industrial contributions. C₆₀/TiAlN nano-composite thin films with constant thickness 200 nm were deposited on Si(100) water-cooled substrates using by the same method with both Ti and Al sputtering targets for 30 minutes. The concentrations C₆₀ molecule powder were changed in the range from 0.5 to 40 wt.%, and the evaporation temperature was controlled in the range of 523-723 K. The structure analyses of all nano-composite thin films showed that XRD patterns indicated only TiAlN crystalline structure and absorption peaks estimated by FT-IR also corresponded to those of C₆₀ molecule. From these results, the microstructures of C₆₀/TiAlN nano-composite thin films were confirmed to consist of both C₆₀ molecule and TiAlN crystalline metallic compound. Nano-indentation hardness made clear that the hardness of the composite films of 2.0 wt.%C₆₀/TiAlN showed the maximum hardness of 20 GPa and this value was increased up to 20 % larger than that of TiAlN thin film. Furthermore, tribological properties were also increased up to 20 % larger than that of TiAlN.

On the basis of remarkable results of the previous researches and the present results, it clearly indicates that C₆₀ nano-composite is extremely effective in great mechanical properties improvement to dispersed C₆₀ uniformly in matrix conventional thin films. Therefore, this study let us know one of bright future view of development of the innovative great hard composite thin films using by C₆₀ molecules.

TF-ThP12 Interface of Mo/Si Multilayer formed by Magnetron Sputtering for Extreme Ultraviolet Lithography, Chao-Te Lee, D. Chiang, P.-K. Chiu, H.P. Chen, C.N. Hsiao, National Applied Research Laboratories, Taiwan, Republic of China, H.-B. Zhang, C.-C. Jaing, Minghsin University of Science and Technology, Taiwan, Republic of China

The periodic Mo/Si bilayers with Ru capping layer were deposited on Si (100) substrate by RF magnetron sputtering with Mo, Si, and Ru targets. The multilayers were designed for reflectivity at the wavelength of 13.5 nm. The effects of Ru capping layer on the microstructure, surface roughness and reflectance of multilayers were investigated by atomic force microscopy (AFM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and a spectrometer. The surface roughness of Ru thin film was decreased from 0.35 nm to 0.15 nm when the RF power was increased from 50 W to 200 W. The AFM measurements showed the uniform morphology with a very low surface roughness value under 0.15 nm with 50V dc-bias assisting. It was found that the Mo-on-Si, Si-on-Mo, and Ru/Si interface layers were discriminated by HRTEM, and XPS. The Mo-on-Si interface layer was 0.45 nm. However, the Si-on-Mo interface layer was increased with thickness increased from 0.9 nm to 1.35 nm. The cause of Mo/Si and Ru/Si interfaces form was attributed to the substrate temperature was increased during sputtering. In this work, the reflectivity of the multilayers was 60 ~ 65 % which was attributed to form the Mo/Si and Si/Ru interfaces.

TF-ThP13 Influence of Cu Doping on the Electrical Transport Properties of Transparent ZnO Nanocrystalline Films Prepared by Sol-Gel Spin Coating Process, Chung-Yuan Kung, Department of Electrical Engineering, National Chung Hsing University, Taichung, Taiwan, Taiwan, Republic of China, S.L. Young, H.H. Lin, Department of Electronic Engineering, Hsiuping University of Science and Technology, Taichung, Taiwan, Taiwan, Republic of China

ZnO and Zn_{0.98}Cu_{0.02}O nanocrystalline films were separately deposited on the glass substrates by sol-gel spin-coating technique for the exploration of Cu doping effect. X-ray diffraction patterns of the films show the same wurtzite hexagonal structure and preferential orientation along the *c*-axis. The grain size of ZnO and Zn_{0.98}Cu_{0.02}O films are 52.3 and 126.4 nm calculated by Scherrer Formula, respectively. The increase of grain size induced by Cu doping result can be also observed by SEM images. Hall mobility and carrier concentration of the *p*-type Zn_{0.98}Cu_{0.02}O films decrease and resistivity increase as Cu doping due to the increase of defects examined by photoluminescence spectra. Temperature dependence resistivity reveals a semiconductor transport behavior for both nanocrystalline films. Exponent relationship $\sigma(T) = \sigma_{00} \exp[-(T_0/T)^{1/4}]$ at low temperature region and Arrhenius equation $\sigma(T) = \sigma_0 \exp[-(E_a/KT)]$ at high temperature region are both fitted well, which separately reveals Mott variable range hopping behavior and thermal activation conduction. Activation energy *E_a* increases from 46 meV for ZnO to 124 meV for Zn_{0.98}Cu_{0.02}O calculated by Arrhenius equation, respectively. The results demonstrate that the crystallization and the corresponding carrier transport behavior of the Zn_{0.98}Cu_{0.02}O films are affected by Cu doping.

TF-ThP14 Design and Fabrication of MgF₂ Protected Aluminum Mirrors for the DUV Spectral Range, Hung-Pin Chen, W.H. Cho, C.N. Hsiao, National Applied Research Laboratories, Taiwan, Republic of China, C.C. Lee, National Central University, Taiwan

Protected or enhanced aluminum is widely used for the preparation of highly reflective coatings in the DUV spectral range. The obvious choice for a coating with high reflectance above DUV Spectral Range is Al protected with MgF₂. This article presents our preliminary experimental studies on processes to produce MgF₂ protected aluminum mirror, the focus is placed on high reflective coatings for the DUV wavelength range above 125nm to 325nm. Aluminum layers protected with fluoride coatings have been deposited by ion beam-assisted deposition, all the samples were deposited on fine polished fused silica substrate. The optical parameters of optical interference coatings were optimized using admittance loci analysis by the Essential MacLeod software. The corresponding properties of the films were investigated by in situ optical monitoring, surface quality of the layers has been judged by means scanning electron microscopy, and atomic force microscopy scanning. The reflectance results were measured at the BL04B Beamline of National Synchrotron Radiation Research Center (Taiwan) in DUV spectral region. The highest average reflectance of the DUV reflector (with protect coating) is about 80%. Interference coatings were added to the basic protected Al design to enhance the reflectance.

TF-ThP15 Reliability Analysis of Zinc Tin Oxide Thin Film Transistor under Mechanical Stress and NBIS (Negative Biased Illuminated Stress) Condition, Sungmin Kim, H.J. Kim, Seoul National University, South Korea

Amorphous zinc tin oxide (ZTO) attracts attention as a new channel material of switching thin film transistor (TFT). It has remarkable properties like high field effect mobility (>10 cm²/Vs) as well as high uniformity and low processing temperature. In this study, electrical properties like threshold voltage (*V_{th}*), mobility, and subthreshold swing of ZTO TFTs with/without mechanical stress were investigated to find the effects of the photo-bias instability of ZTO TFTs on their mechanical stress.

The fabricated ZTO TFTs have a bottom gate and top contact configuration. Thinned Si wafers of 50μm thickness were used as substrates to allow ZTO TFTs to be flexible. To measure the effects of mechanical stress to electrical properties and photo-bias instability, the negative biased illuminated stress (NBIS) tests were performed in three illumination conditions with the photo-wavelengths of 400, 450 and 500 nm as well as in two mechanical bending directions, parallel and perpendicular to a channel width of TFTs, with a bending curvature of 40mm.

Under a mechanical strain, a mobility and a subthreshold swing of ZTO TFTs remained unchanged, but a *V_{th}* showed noticeable changes. Tensile strain under the bending parallel to a channel width caused more severe photo-instability with more *V_{th}* shift. *V_{th}* of ZTO TFTs remained unchanged under the 500nm NBIS condition, while for 400 and 450 nm NBIS conditions *V_{th}* shifted with a mechanical strain. Particularly, parallel bending of ZTO TFTs under the 400nm NBIS condition showed severe instability, a large and negative *V_{th}* shift of -11.6V compared to -7.2V of a non-bended sample. And for the 450 nm NBIS condition, relatively small *V_{th}* shift of -6.1V and -4.4 V for bended and non-bended samples,

respectively, was observed, showing similar tendency to the 400nm case. But in case of the bending perpendicular to a channel width showed less V_{th} shift from non-bending condition; -15.8 V to -15.2 V and -5.5 V to -4.0 V for the 400nm and 450 nm NBIS conditions, respectively.

The exact mechanism of this phenomenon is not clear at this point, but the strain in film might change the distance between metal atoms, causing the variation of an orbital overlap in the bandgap and an activation energy for V_{th} shift. G. Zhang et al. reported that a strain in a channel layer makes difference of ZnO band structure like midgap states from the first principle simulation. The tensile strain can cause more midgap levels in bandgap, and vice versa. It is in a good agreement well with our result. The more reasonable mechanisms of strain to affect the band structure is under investigation.

TF-ThP17 Laser Surface Modification of AZ31B-H24 for Improved Corrosion Resistance, Michael Melia, University of Virginia, *N. Birbilis,* Monash University, Australia, *J.R. Scully, J.M. Fitz-Gerald,* University of Virginia

The development of Mg alloys has been accelerated over the last decade due to the need for significant weight reduction of structural components. One long-standing obstacle regarding the use of Mg alloys for widespread field application is their intrinsically poor corrosion resistance and lack of surface films or oxides. Micro-galvanic induced "self-corrosion" due to alloy heterogeneity is a key concern. Therefore, chemical and structural homogenization is of long standing and great interest. Furthermore, there is a need to exploit possible benefits of low fluence LSM, local composition variations and LSM processing gas environments on corrosion behavior. Here we report on the effect of laser surface modification (LSM) on the corrosion resistance of an Mg alloy (AZ31B-H24).

Samples were processed with a pulsed excimer laser operating at 248 nm and a fluence = 1.5 J/cm². Microstructure and composition were characterized with scanning electron microscopy (SEM), grazing incidence X-ray diffraction (GIXRD), and energy dispersive spectroscopy (EDS). Corrosion analysis was performed in a standard three electrode corrosion cell in quiescent 0.6 M NaCl solution. Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization measurements were used to determine corrosion resistance, anodic/cathodic behavior, pitting potential and open circuit potential (OCP). Corrosion experiments were imaged by optical video microscopy during testing to draw conclusions regarding the breakdown of the irradiated surface.

Layered structures of nanoscale MgO, Mg₃N₂, and AlN constituents formed in the irradiated region as a function of process gas and proximity to the Al₃Mn₅ intermetallic particles (IMPs). Partial homogenization of IMPs was observed, reducing the initial particle size by 40-60% and creating large areas of Al/Mn enrichment, irrespective of process gas used (Ar, N₂). The results show that a reduction in the H₂ evolution reaction rate was achieved correlated with an order of magnitude decrease in the cathodic current density, as well as a 100 mV to 200 mV reduction in the open circuit potential over short immersion times of up to 4 hours, irrespective of processing gas. In addition, Impedance results support these findings with a 4 and 25 fold increase in the polarization resistance after processing in both N₂ and Ar atmospheres respectively. The behavior in full immersion has not been extrapolated to long term field testing.

Acknowledgements

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TF-ThP18 Enhanced Mechanical Properties of Boron Doped Amorphous Carbon Films by UV Laser Annealing, ChulMin Yoon, T. Choi, Sejong University, Republic of Korea, *J.Y. Yang,* TES Co. Ltd., Republic of Korea, *K.P. Park, G.H. Hur,* TES Co., Ltd., Republic of Korea. The hard forms of amorphous carbon (a-C, diamond like carbon) include hydrogenated amorphous carbon (a-C:H) and tetrahedral amorphous carbon have raised interest as coating materials. Recently, boron doped amorphous carbon films have been studied as hard mask materials of 3D vertical NAND flash memory. Hard mask was demanded to enhance critical dimension (CD) uniformity, anti-etching and lifting while decreasing thickness. Boron has been widely known efficient dopant for passivating the oxidation of various carbon materials. We have prepared boron doped amorphous carbon film deposited with the fixed B₂H₆ flow rate as a function of the process temperature using plasma enhanced chemical vapor deposition (PECVD). We investigated the physical and optical properties of film with the refractive index, hardness and chemical bonding configuration. Especially, the effect of ultraviolet (UV) laser annealing on the hardness was studied. UV annealing caused a change of chemical bonding configuration, i.e., sp²/sp³ bonding ratio and C-H bonds, through analysis of the Fourier transform-infrared (FT-IR) and RAMAN spectrum. It is found that a significant enhancement of hardness could be attributed to

surface confined graphitization and increase of the sizes of sp² and sp³ clusters, which occur without any damage of surface and delamination of films. In addition, the influence of laser annealing on the stress relief behavior and electronic properties of boron doped amorphous carbon layers will be discussed. Our approach can offer easy control of surface properties of amorphous carbon materials.

TF-ThP19 Influence of Zn(O,S) Buffer Layers on the Performance of Cu₂ZnSn(S,Se)₄ Earth-abundant Thin Film Solar Cells, H. Hong, Jaeyeong Heo, Chonnam National University, Republic of Korea

A solar cell is an electrical device that converts light energy into electricity. One of the crucial parts of realizing high-performance thin-film-based solar cells is an *n*-type buffer layer. Instead of the widely used, but toxic CdS buffer layer, we investigated the possibility of using Zn(O,S) as an alternative material grown by atomic layer deposition (ALD). First of all, structural, electrical, chemical, and optical properties of Zn(O,S) thin films were studied. In addition, this new buffer layer was applied for earth-abundant Cu₂ZnSn(S,Se)₄ solar cells and the highest power-conversion efficiency (PCE) of ~2.7% was achieved by optimizing oxygen-to-sulfur (O/S) ratio. Detailed device analysis which includes current-voltage (J-V), external quantum efficiency (EQE), dark current-voltage, transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX) will be presented.

TF-ThP22 Low-Temperature Atomic Layer Deposition of Platinum Using (Methylcyclopentadienyl)trimethylplatinum and Ozone, Huazhi Li, N. Sullivan, P. Chinoy, Arradiance

Because of the excellent electric and catalytic properties of Pt, ALD of Pt has attracted considerable attention for applications in nanoelectronics, electrochemistry, catalysis, and sensing. The most commonly applied ALD process for Pt uses (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe₃) and O₂ as precursors. It was found that the optimum process window of this process is 250 - 300 °C. Below 250 °C, very low growth rates and poor Pt nucleation on some substrates such as Si or SiO₂, are observed. These limitations rule out applications on heat sensitive polymer substrates.

To address the need for low temperature ALD Pt, processes based on ozone² and oxygen plasma with a subsequent reduction by H₂³ have been reported. O₃ is being used in a growing number of atomic layer deposition (ALD) processes because O₃ is a powerful oxidizer and is easier to purge than H₂O, particularly at lower growth temperatures (≤ 100 °C). The development low temperature ALD processes using O₃ process⁴ and low temperature plasma processes will be reported. In this work, growth kinetics, crystalline structure, resistivity, and purity of Pt thin films grown using O₃ as reactant gas in combination with the MeCpPtMe₃ precursor are studied. Additionally, the conformality of the MeCpPtMe₃/O₃ process and its nucleation behavior on a SiO₂ surface will be discussed. The results reported describe a process that is highly suited for Pt deposition on thermally fragile substrates.

Literature:

1. T. Aaltone, M. Ritala, T. Sajavaara, J. Keinonen, M. Leskela; "Atomic Layer Deposition of Platinum Thin Films"; Chem. Mater. 2003, 15, 1924-1928.
2. J. Hamalainen, F. Munnik, M. Ritala, M. Leskela; "Atomic Layer Deposition of Platinum Oxide and Metallic Platinum Thin Films from Pt(acac)₂ and Ozone"; Chem. Mater. 2008, 20, 6840-6846.
3. H. C. M. Knoops, A. J. M. Mackus, M. E. Donders, M. C. M. van de Sanden, P. H. L. Notten, W. M. M. Kessels; "Remote Plasma ALD of Platinum and Platinum Oxide Films" Electrochem. Solid-State Lett. 2009, 12, G34-G36
4. H. Li, J. Narayanamoorthy, N. Sullivan, D. Gorelikov; "Low Temperature (LT) Thermal ALD Silicon Dioxide Using Ozone Process"; ALD 2014, Kyoto, Japan.

TF-ThP25 Flash Networking Poster: Surface Characterization and Luminescent Properties of Pulsed Laser Deposited Dysprosium-Doped Rare-Earth Oxyorthosilicates Thin Films, Martin Nwaeeborwa, S.N. Ogugua, H.C. Swart, University of the Free State, South Africa

Luminescent materials or phosphors have a wide range of technological applications in electronic information displays, solid state lighting, solar cells, advertising, medical imaging, etc. Although phosphors are usually used as powders, thin films have more advantages in many practical applications. We report luminescent properties and surface states of dysprosium (Dy³⁺)-doped lanthanum gadolinium oxyorthosilicate (La_{2-x}Gd_xSiO₅:Dy³⁺; where x = 0, 0.5, 1.0, 1.5, 2) that were ablation deposited onto Si (111) substrates using the pulsed laser deposition (PLD) technique. Several deposition parameters were varied, including vacuum versus partial

pressure of gas (O_2 or Ar), and substrate temperature using the 266 nm Nd:YAG excimer laser. The ablated targets were prepared from powders which were synthesized by combustion method. The films exhibited tunable and white photoluminescence emission when excited by either a monochromatized xenon lamp or a 325 nm HeCd laser in air at room temperature. The PL emission colour and the peak intensity were dependent on the ratio of La to Gd, concentration of Dy^{3+} , and deposition conditions. Data from scanning electron microscopy (SEM) and atomic force microscopy (AFM) show that the major influence of the deposition conditions on the PL peak intensity was through changes in the morphology and topography of the films, which affects light scattering and out-coupling. The time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was used to study the distribution of atomic and molecular ionic species on the surface of the films, while X-ray photoelectron spectroscopy (XPS) was used to analyse the chemical composition and electronic states of our samples.

TF-ThP28 Effect of a Substrate Temperature on the Properties of the RF-sputtered Indium Selenide Thin Films as a Buffer Layer for CIGS Photovoltaics, MyoungHan Yoo, N.H. Kim, Chosun University, Republic of Korea

CIGS, which has suitable optical absorption, tunable band gap, good electrothermal stability, and no toxic/hazardous pollutant, has been used in thin film solar cells with the conventional structure of glass/Mo/CIGS/buffer layer/TCO. Instead of the very noxious and polluting CdS buffer layer, Cd-free materials have been attracted great interest in the buffer layer for CIGS photovoltaic applications. The Cd-free buffer layers require some qualifications, such as a band gap energy between CIGS and TCO (typically zinc oxide, $E_g \sim 3.4$ eV), an optical transmittance $\geq 80\%$, and a resistivity $\leq 10^4 \Omega\text{-cm}$ [1] to replace the conventional CdS buffer layer. Indium selenides are III-VI semiconducting compounds with the wide deviation from stoichiometry, which were proposed for the Cd-free buffer layer in CIGS photovoltaics with several advantages including better heterointerface of the same elemental effusion with CIGS absorber layer. In the prior studies, indium selenides were prepared by using RF-magnetron sputtering method with $InSe_2$ target and rapid thermal annealing. The variations in film thickness, stoichiometry, annealing duration, and annealing temperature did not affect the crystallization of indium selenide precursors in amorphous nature. Subsequently, the substrate temperature, which induces significant changes in the properties of indium selenide, was varied in the RF sputtering process. Rapid thermal annealing process was performed to transform the 50-nm-thickness indium selenide into the γ -phase In_2Se_3 at 700°C for 1 min. Some analyses were examined in the structural, optical and electrical properties of the RF-sputtered indium selenide thin films with the different substrate temperatures for the optimal buffer layer in CIGS photovoltaics. [1] J. H. Yoon, W. M. Kim, J. K. Park, Y. J. Baik, T. Y. Seong and J. Jeong, Prog. Photovolt: Res. Appl. 22, 69 (2014).

TF-ThP33 Stress-curvature Relationship for Configurations with Thin and Anisotropic Substrates undergoing Large Deformations, SaiSharan Injeti, R. Annabattula, Indian Institute of Technology Madras, India

In a thin film configuration, the film is often stressed to conform to the surface of the substrate, commonly due to epitaxial effects, difference in thermal expansion coefficients between the film and the substrate materials, or phase transformations accompanied with volume changes. This stress causes the film-substrate system to assume a curvature. The relation that relates this curvature to the stress in the film is referred to as the Stoney equation. One of the major assumptions of the Stoney equation is that the substrate is orders of magnitude thicker than the film, leading to small and purely elastic deformation of the substrate. Moreover, the well known equation also assumes that the substrate material is isotropic in nature.

At the moment, the traditional Stoney equation is being used to relate the film stress to the system curvature. However, in majority of the cases where the film stress is measured from the system curvature, Si wafers are used as substrates. Si wafers are anisotropic in nature as they are obtained by slicing single crystals. In this paper, a more generalized version of the Stoney equation is presented.

This form of the equation is derived by first relaxing the constraints that the film is very thin compared to the substrate and that the deformations are small. Next, this formula is modified specifically for the cases of Si(001) and Si(111) wafers. Ultimately, a modified version of the Stoney equation is presented which can be used for configurations with anisotropic substrates where the thicknesses of the film and substrate are comparable, and the deformations are large. Extension of this expression to systems assuming asymmetric elliptical configurations rather than symmetric spherical deformations, is also discussed.

Keywords: Thin film, Large deformation, Stoney, Silicon, Wafer curvature

TF-ThP34 Doping of High-aspect Ratio Silicon Structures using Thin Film Dopant Sources Grown by Plasma-assisted Atomic Layer Deposition, Bodo Kalkofen, Otto von Guericke University Magdeburg, Germany, A.A. Amusan, Otto von Guericke University, Magdeburg, Germany, M. Lisker, IHP, Frankfurt (Oder), Germany, Y.S. Kim, Lam Research Corporation, E.P. Bulte, Otto von Guericke University, Magdeburg, Germany

Plasma-assisted atomic layer deposition (PALD) was carried out for growing thin oxide films of silicon dopants onto flat and high-aspect ratio silicon substrates. The applicability of these films as dopant sources for shallow doping of silicon using various rapid thermal annealing methods, such as RTP, flash lamp anneal, and laser anneal, was investigated. Remote CCP and ICP sources were applied for generating oxygen radicals in the PALD processes. Tris(dimethylamido)borane was used as boron containing precursor for p type silicon doping, source layers for n type doping were grown using triethylphosphite and triethylantimony as phosphorus and antimony containing oxides, respectively.

The as-deposited films of boron oxide were highly unstable in ambient air and could be protected by capping with in-situ PALD grown antimony oxide films. Phosphorus containing films were stabilized by incorporating them into a silicon dioxide matrix by carrying out ALD processes with supercycles of phosphorus and silicon precursor reactions with oxygen radicals. Also capping of the phosphorus containing films was applied. Antimony oxide films were stable at ambient air conditions. Conformal growth of such films could be obtained on silicon trench structures of 6:1 to 10:1 aspect ratio with pitch below 50 nm.

Boron and phosphorus doping of silicon could be obtained using the respective oxide films as dopant sources. This was confirmed by SIMS and sheet resistance measurements. Diffusion of antimony into silicon from antimony oxide needs to be further improved by optimizing the annealing conditions. The influence of source layer thickness and different annealing conditions during rapid thermal annealing processes on the doping results was investigated. Controlled doping of 3-D nanostructured devices by pre-deposition with ALD source layers should be feasible by this method.

TF-ThP36 Kurt J. Lesker- TORUS "Mag Keeper" Sputtering Sources- "Enabling Thin Film Coating Technology for a Better World", Jason Hrebik, Kurt J. Lesker Company

The thin film coating industry, particularly in magnetron sputtering, is a critical means for our current and future advancements in technology. There are a wide range of applications, which have many critical performance requirements to make them successful. The main component driving these applications is the magnetron sputtering cathode or "magnetron".

In many cases, it is difficult to find an ideal "magnetron" that can meet all of the process requirements. In addition, there are a broad range of "magnetron" providers in the industry that all have advantages and disadvantages to their technology. This can make choosing the best option very difficult.

One of the most critical performance requirements in any magnetron design is target cooling. Good thermal conductivity between the target and the cathode is essential for maximum power density and sputtering rate. The new Mag Keeper sputtering source utilizes an enhanced target cooling design in which the cooling water flows through a brazed copper channel that is in direct contact with the backside of the sputtering target. This along with a magnetically enhanced clamping force provides an uncompromised cooling advantage.

In addition, the Mag Keeper design has only a single metal seal, contains no O-rings, and utilizes all ceramic insulators, making it both HV and UHV compatible.

Over the course of extensive performance testing campaign, the design showed several key advantages. Using a variety of target materials, it was found that the Mag Keeper's cooling efficiency is comparable to that of a direct-cooled magnetron providing the ability to run at power densities over 200 watts/in² with thermally conductive materials such as copper and aluminum. A key advantage to the magnetic profile was the ability to operate a 0.375" thick non-magnetic target at 0.5mTorr pressure. In terms of target erosion, the Mag Keeper design has a very broad profile maximizing both utilization and uniformity. In addition, with the High Strength magnet configuration, a 3" source was able to sputter up to 3mm thick Fe.

From a mechanical standpoint, the Mag Keeper source does not use a target clamp or anode shield assembly resulting in a very quick target change averaging less than 5 minutes due to only having to loosen (2) bolts in order to access the target.

In conclusion, the Mag Keeper magnetron design offers the industry a design that is capable of meeting a very broad range of application

requirements with the conveniences needed for meeting production efficiencies!

TF-ThP39 Femtosecond X-Ray Magnetic Circular Dichroism Spectroscopy at an X-Ray Free Electron Laser, Daniel Higley, K. Hirsch, E. Yuan, E. Jal, G.L. Dakovski, A.A. Lutman, J. MacArthur, A.H. Reid, T. Liu, SLAC National Accelerator Laboratory, J. Joseph, Lawrence Berkeley National Laboratory, A. Tsukamoto, Nihon University, H.A. Durr, W.F. Schlotter, SLAC National Accelerator Laboratory

In the last twenty years, the field of ultrafast magnetization dynamics has seen tremendous growth and development. Ferromagnetic transition metals have been seen to demagnetize on a sub-picosecond time-scale when excited by ultrafast laser pulses, much faster than expected from dynamics close to equilibrium. The mechanism of this ultrafast magnetization quenching, almost twenty years after its discovery, is still a matter of active debate. Other materials exhibit ultrafast switching of the magnetization when excited similarly. The switching mechanism, however, is also still debated. To unravel the mysteries of these processes requires probes which can sensitively and reliably probe the transfer of angular momentum and energy between the electronic, electronic spin, and lattice systems.

X-ray magnetic circular dichroism spectroscopy (XMCD) directly and element-specifically probes the spin and orbital magnetic moments of electrons in matter and has proven invaluable in studies of static magnetism. This information is extracted from the difference in absorption of right- and left-circularly polarized x-rays at spin-orbit split resonances where core-level electrons are excited into unoccupied valence states.

XMCD with femtosecond time resolution is an ideal tool to investigate ultrafast magnetization dynamics. Femtoslicing beamlines at synchrotrons have been used to perform such measurements and make seminal contributions to the field of ultrafast magnetization dynamics. The low photon throughput of these sources, however, necessitates long integration times for measurements and restricts the possibility of systematic studies as well as measurement of small signals. X-Ray Free Electron Lasers (XFELs), which provide femtosecond pulses with a much increased flux compared to femtoslicing sources, give an important path to extending these results.

Here, we report on ultrafast XMCD spectroscopy measurements in the soft x-ray range at an XFEL utilizing a recently installed variable polarization undulator at the XFEL LCLS at the SLAC National Accelerator Laboratory. We are able to record static XMCD spectra of GdFeCo samples over the iron L-edges and gadolinium M5 edge which match those observed at synchrotrons. In addition, by monitoring the time-resolved XMCD at these edges we reproduce the classic observation of a transient ferromagnetic alignment of antiferromagnetically coupled spins in amorphous GdFeCo during ultrafast, laser-induced, switching. With the high-flux and intrinsically ultrafast pulses of XFELs, we are able to record this measurement in less than an hour, a fraction of the time required for the original measurement.

Friday Morning, October 23, 2015

Plasma Science and Technology

Room: 210B - Session PS+SS+TF-FrM

Atomic Layer Etching (ALE) and Low-Damage Processes II

Moderator: Toshihisa Nozawa, Tokyo Electron Ltd.

8:20am **PS+SS+TF-FrM1 Atomic Layer Etching of Silicon Dioxide to Enable Self-aligned Contact Integration**, *B. Finch, H. Singh, Eric Hudson*, Lam Research Corporation **INVITED**

CMOS devices have continued to scale dimensionally following the implementation of FinFET transistors. Self-alignment of the source and drain contact to the gate has been presented as an integration solution starting at the 22nm technology node¹. This self-aligned contact (SAC) integration creates additional challenges and constraints on the etch process for the 10 nm node and beyond. Due to smaller feature dimensions, lithography overlay, and full contact wrap-around of the transistor fins, unprecedented etch precision is now required.

A novel approach for SAC oxide etching has been developed which addresses the many tradeoffs of this application using a directional atomic layer etch process (ALE) as reported by Hudson et al². Key trade-offs to enable contact etching capability of CDs as small as 10 nm include SAC spacer loss, lack of profile control, and contact not-opens. This cyclic SiO₂ ALE process repeats discrete unit process steps of fluorocarbon deposition and ion bombardment to achieve high selectivity of SiO₂ to Si₃N₄ while simultaneously addressing these tradeoffs. Oxide removal rates can be precisely controlled with minimal removal of Si₃N₄ films, enabling a highly selective etch process. Anisotropic, directional etch behavior superior to traditional SiO₂ etch is enabled, creating vertical oxide profiles. This capability is highly desirable for SAC etch applications as it maintains the integrity of the gate electrode spacer during etch. Experimental results showing the ability of this oxide ALE process to eliminate tradeoffs is presented

[1] C. Auth, et al, "A 22 nm high performance and low-power CMOS technology featuring fully-depleted tri-gate transistors, self-aligned contacts and high density MIM capacitors," accepted in VLSI Symp. Tech. Dig., Jun. 2012.

[2] E. Hudson, et al, "Highly Selective Atomic Layer Etching of Silicon Dioxide Using Fluorocarbons," accepted in AVS 61st International Symp. & Exhibition, Nov. 2014.

9:00am **PS+SS+TF-FrM3 High Performance Self Align Contact Etching with Newly developed Quasi-ALE**, *Akihiro Tsuji*, Tokyo Electron Miyagi Limited, Japan, *M. Tabata, H. Watanabe, T. Katsunuma*, Tokyo Electron Miyagi Limited, *M. Honda*, Tokyo Electron Miyagi Limited, Japan

The Self-Aligned Contact (SAC) process has been widely adopted to achieve aligned narrow contacts between electrodes as the pitch shrinkage has progressed with the miniaturization of devices in high-scale integration. In SAC fabrication, it is important to achieve high selectivity of the interlayer insulator (SiO₂) over an etch stop film (SiN) to improve insulation tolerance between the contact plug and the wiring. Such high-selective etch processes have been realized by depositing fluorocarbon (FC) film selectively on the SiN film by using the composition difference between SiO₂ and SiN with fluorocarbon plasma, which protects SiN surface during SiO₂ etch. In order to minimize SiN loss, a balance of FC film thickness and the penetration depth of the ion energy on SiN become significant [1,2]. When trying to achieve improved SiN loss reduction, reducing ion energy is one effective solution, but a balance of ion energy flux and FC radical flux ($E_i \Gamma_i / \Gamma_{CF}$) breaks down, resulting in an excess amount of deposition, causing etch stop to occur. This is caused by the limited control margin of the ion energy flux over the FC radical flux ratio using conventional processes.

Atomic Layer Etching (ALE) concept has attracted great attention in recent years for its precise fabrication potential at the atomic level and its ability to solve this issue [3,4]. ALE method enables clear separation of ion energy flux and FC radical flux supply by controlling $E_i \Gamma_i / \Gamma_{CF}$ dynamically using a new parameter of flux ratio respective to step time. Furthermore, specific control of the surface condition at each cycle is expected to be effective for precise fabrication. This report discusses the application of the ALE concept in the SAC process as a Quasi-ALE scheme with consideration for implementation to volume production. This scheme realized a dramatic improvement of SiO₂ etch performance with substantial reduction of SiN loss. Further analysis of the surface condition by XPS,

SIMS, HR-RBS helped determine the mechanism of selectivity enhancement. Quasi-ALE technology is a promising weapon, corresponding to leading-edge processes of various fabrication requirements along with the miniaturization of devices, towards 10nm and beyond.

Reference

- [1] T. Tatsumi, M. Sekine et al. JVST B 18(4), 2000
- [2] M. Matsui, M. Sekine et al. JVST A 19(4), 2001
- [3] D. Metzler, G.S. Oehrlein et al. JVST A 32(2), 2014
- [4] M. Honda, AVS 61th Int. Symp. & Exhibit. (2014)

9:20am **PS+SS+TF-FrM4 Fluorocarbon Based Atomic Layer Etching of Si₃N₄ and Selectivity of SiO₂ over Si₃N₄**, *Chen Li, D. Metzler, G.S. Oehrlein*, University of Maryland, College Park, *C.S. Lai, M. Danek, E.A. Hudson, A. Dulkan*, Lam Research Corporation

Angstrom-level plasma etching precision is required by semiconductor manufacturing for the sub-14 nm technology node. Atomic layer etching (ALE), achieved by a series of self-limiting cycles, can precisely control the amount of reactant available and resulting etching depths. Recently, controlled etching of SiO₂ at the Angstrom-level based on steady-state Ar plasma, periodic injection of a defined number of fluorocarbon (FC) molecules, and synchronized plasma-based Ar⁺ ion bombardment has been demonstrated [1,2]. This novel ALE approach is achieved by deposition of a thin (several Angstroms) reactive FC layer on the material surface using pulsed FC flow. Subsequent low energy Ar⁺ ion bombardment removes the FC layer along with SiO₂ from the surface. The ion energies were selected to allow only chemical enhanced etching to take place without any physical sputtering, which enables a self-limited SiO₂ removal. We report on controlled etching of Si₃N₄ and SiO₂ layers of the order of one to several Angstroms using this cyclic ALE approach. The work was performed in an inductively coupled plasma reactor. Using SiO₂-Si₃N₄-SiO₂ multi-layer stacks on a Si substrate enabled precise evaluation of selectivity, self-limitation, and modification by *in situ* real time ellipsometry. Si₃N₄ etching and etch selectivity of SiO₂ over Si₃N₄ were studied and evaluated with regard to the dependence on FC surface coverage, precursor selection, ion energy, and etch step length. Surface chemistries of SiO₂ and Si₃N₄ were investigated by vacuum transferred x-ray photoemission spectroscopy (XPS) at each stage of the ALE process. The choice of precursor can have a significant impact on the surface chemistry and therefore the chemically enhanced etching characteristics.

The authors gratefully acknowledge financial support of this work from National Science Foundation (CBET-1134273) and Lam Research Corporation.

References:

- [1] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, "Fluorocarbon assisted atomic layer etching of SiO₂ using cyclic Ar/C₄F₈ plasma", J Vac Sci Technol A 32, 020603 (2014)
- [2] E. Hudson, V. Vidyarthi, R. Bhowmick, R. Bise, H.J. Shin, G. Delgado, B. Jariwala, D. Lambert, S. Deshmukh, "Highly selective etching of Silicon Dioxide Using Fluorocarbons"; AVS 61st International Symposium & Exhibition (2014);

9:40am **PS+SS+TF-FrM5 Chamber Wall Effect for Fluorocarbon Assisted Atomic Layer Etching of SiO₂ Using Cyclic Ar/C₄F₈ Plasma**, *Masatoshi Kawakami*, Hitachi High-Technologies, Japan, *D. Metzler, C. Li, G.S. Oehrlein*, University of Maryland, College Park

The requirement for atomic scale etching is becoming more important with increasing miniaturization of semiconductor devices. A novel approach for oxide etching has been developed by Metzler et al [1]. Controlled etching of SiO₂ at the angstrom-level is based on steady-state Ar plasma and deposition of a thin reactive fluorocarbon layer enabled by precise, periodic C₄F₈ injection. High process stability is necessary for the success of this method and its use in mass production. Chamber wall interactions are crucial to the stability of this process. In this research, we studied the influence of chamber wall temperature and chamber wall chemical state on ALE process performance. The experiments were conducted in an inductively coupled plasma system excited at 13.56 MHz. The temperature of the quartz coupling window was measured with an infrared temperature sensor. *In situ* real time ellipsometry allows for film thickness measurements during the process. Plasma gas-phase chemistry was characterized by optical emission spectroscopy. We conducted the cyclic Ar/C₄F₈ SiO₂ ALE process using different initial chamber temperature, and chamber wall polymer coverage condition. It was found that although the polymer film thickness deposited in each cycle is constant, the etching behavior changed, likely related to a change in depositing species. Chamber

wall temperature shows a clear effect on the CO and SiF emission and their relative ratio. When the surface of the quartz coupling window started to be covered by a fluorocarbon film, the overall CO and SiF intensity decreased while the CO/SiF emission peak ratio did not change. The relationship to observed etching behavior will be discussed.

The authors gratefully acknowledge financial support of this work from National Science Foundation (CBET-1134273) and US Department of Energy (DE-SC0001939).

References:

[1] D. Metzler, R. Bruce, S. Engelmann, E.A. Joseph, and G.S. Oehrlein, *J Vac Sci Technol A* **32**, 020603 (2014)

10:00am **PS+SS+TF-FrM6 Potential Solutions for Atomic Precision Etching**, *Olivier Joubert*, LTM-CNRS, France, *E. Despiau-Pujo*, LTM, France, *G. Cunge*, LTM - CEA/LETI, France, *L. Vallier*, *J. Dubois*, *A. Tavernier*, Univ. Grenoble Alpes-CNRS-CEA/Minatoc-LTM, France, *O. Luere*, *S. Banna*, *Y. Zhang*, Applied Materials **INVITED**

The continuous downscaling of device dimensions and introduction of new transistor architectures such as FDSOI or FINFETs transistors is bringing up new challenges for plasma etching technologies. For the gate transistor for example, future technological nodes require patterning capabilities in a range of dimension going below 10 nm. Extremely thin layers (less than 1nm) of materials are now involved in the stacks of materials to pattern requiring in some cases an etch precision better than 1 nm. In other words, the etch selectivity and physical/ chemical damage induced by the plasma must be controlled in a way such as the plasma can stop in a layer of materials as thin as 1nm without damaging the underlayers or the substrate material. Such a precision in processes becomes difficult to reach with the state of the art plasma technologies.

In this presentation, we will describe two plasma technologies that could potentially reach that goal.

A new Technology is the so-called "Thin Layer Etching" technology. In the first step of the TLE technology, H₂ or He ions produced by a capacitive plasma induce modification of silicon based materials while in a second step the modified material is removed in an all dry NF₃/NH₃ remote plasma that form volatile products with the modified silicon based materials. Performance achieved by TLE for nitride spacer etching will be shown and compared to conventional ICP results.

Fast gas pulsing technology could also be a promising way to form ultra-thin reactive layer during plasma processing, allowing atomic precision etching to be achieved. This concept will be explained and discussed based on preliminary result of silicon etching in chlorine plasmas using atomistic simulation.

10:40am **PS+SS+TF-FrM8 Molecular Dynamics Simulations of Atomic Layer Etching by Low Energy Ions**, *Jun-Chieh Wang*, *S. Rauf*, *J.A. Kenney*, *L. Dorf*, *K.S. Collins*, Applied Materials Inc.

In the semiconductor industry, the use of atomic layer etching (ALE) makes it feasible to accurately control the critical dimensions to nanometer level or smaller. In ALE, the target substrate is first exposed to a reactive gas that passivates the surface, which is then followed by ion bombardment with energy below the sputtering threshold. It is critical to precisely control the ion energy and flux during the etching process to remove the topmost layer of the passivated surface without damaging the underlying substrate. Once the passivation layer is removed, the etch process stops. The passivation and etching steps are repeated until one has etched to the desired thickness. In contrast to conventional plasma etch processes, microfabrication using ALE promises high selectivity and low damage to the substrate.

In this presentation, we discuss the properties of ALE using results from molecular dynamics (MD) simulations. The simulation procedure is conceptually similar to those described in previous publications [1,2]. In this study, a crystalline Si(100)-(2x1) or amorphous surface (made by low energy Ar⁺ ion bombardment) was generated and equilibrated at room temperature. The bottom layers were fixed in space, and the periodic boundary conditions were applied laterally to remove the boundary effect. The ions are modeled as energetic neutrals. The surface was passivated by repeated bombardment with low energy Cl atoms at normal incident, which was followed by Ar⁺ or Cl⁻ ion bombardment to remove the passivation topmost layers. The Berendsen scheme is used between ion/neutral impacts to remove the energy from the surface region and cool the surface layer to room temperature. The Stillinger Weber (SW) type potentials are used for Si-Si, Si-Cl and Cl-Cl interactions. The Ar-Si and Ar-Cl interactions were modeled using Molire potentials. The leap-frog form of Verlet algorithm was used to numerically integrate the Newton's equation of motion. The MD is applied to study several variants of the ALE process. The fundamental properties of Si etching are also investigated for both bare and Cl-passivated Si surfaces with several ions including Ar⁺, Cl⁻ and Cl₂⁺.

These fundamental studies are used to interpret our layer-by-layer ALE experiments in our laboratory.

Reference

[1] N. A. Kubota, D. J. Economou and S. J. Plimpton, *J. Appl. Phys.* **83**, 4055 (1998).

[2] B. A. Helmer and D. B. Graves, *J. Vac. Sci. Technol. A.* **16**, 3502 (1998).

11:00am **PS+SS+TF-FrM9 Atomic Layer Etching of InGaAs using Cl₂/Ar Ion Beam**, *Jinwoo Park*, *D.H. Yun*, *H.S. Kim*, *G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Atomic layer etching can be one of next-generation etching techniques that can be applied to various materials including III-V compounds semiconducting materials such as indium-gallium arsenide (InGaAs) which is a great potential material due to the high carrier mobility for nano-scale devices. In this study, the atomic layer etching characteristics of InGaAs has been investigated using chlorine as adsorption gas and low energy Ar ion for desorption during the etch cycle to control the etch depth precisely and to minimize the surface damage of the material. For the chlorine adsorption, chlorine radical was adsorbed on the InGaAs surface and, during the desorption, the chlorine adsorbed InGaAs was removed by the Ar ion with the energy of about 20eV. By using the atomic layer etching technique, the controlled InGaAs etch depth per cycle and very high etch selectivity of InGaAs over dielectric materials such as silicon dioxide and hafnium dioxide could be obtained. The surface roughness of etched InGaAs characterized by atomic force microscopy was similar to that of un-etched InGaAs at the atomic layer etching condition.

11:20am **PS+SS+TF-FrM10 InGaN Quantum Nanodisks Fabrication by Bio-Template and Neutral Beam Etching**, *Yi-Chun Lai*, National Chiao Tung University, Taiwan, Republic of China, *A. Higo*, *C. Thomas*, *C.Y. Lee*, *T. Tanikawa*, *K. Shojiki*, *S. Kuboya*, *R. Katayama*, Tohoku University, Japan, *T. Kiba*, Hokkaido University, Japan, *I. Yamashita*, Nara Institute of Science and Technology, Japan, *A. Murayama*, Hokkaido University, Japan, *P.Yu. Yu*, National Chiao Tung University, Taiwan, Republic of China, *S. Samukawa*, Tohoku University

III-N quantum dots (QDs) gain media have generated great interest because of their desirable properties such as low threshold and temperature independence due to the discrete nature of the density of states. A uniform and high-density two-dimensional (2D) array of an isolated QD structure is required when considering applications in visible wavelength such as white LED. In general, size distribution, uniformity, and high-density are trade-offs when using a conventional self-assembly method; therefore, we have developed a technique that integrates a bio-template with neutral beam etching (NBE) process.

In this work, quantum nanodisks (QNDs) were fabricated from InGa_{0.1}N/GaN single quantum well (SQW) by using a bio-template and NBE. We developed a damage-less, top-down fabrication process for achieving high density of QNDs such as 2 x 10¹¹ cm⁻² embedded in 10 nm in diameter and 20 nm high nanopillars. The fabricated QNDs have great potential for fabricating quantum optoelectronic devices because of controllable diameter and thickness.

The InGa_{0.1}N/GaN SQW wafer was grown on a 2-inch c-plane sapphire substrate by metal-organic vapor phase epitaxy (MOVPE). The structure consisted of a 1μm-thick GaN buffer layer, 3nm-thick In_{0.1}GaN and a 10nm-thick GaN capping layer. We used ferritins modified with polyethylene glycol (PEG ferritins) that include a metal oxide core for the etching mask. Oxygen annealing in vacuum was used to remove the ferritin protein shell at 350°C, at chamber pressure of 32 Pa. Therefore the 7 nm diameter iron core was remained on the surface. Then hydrogen radial treatment, hydrogen passivation and NBE etching process were performed. At first, hydrogen radical treatment was realized to remove the surface oxide at chamber pressure of 32 Pa at 350°C. Subsequently, hydrogen passivation was done to avoid any re-oxidation during the process. Finally, SQW was etched completely to form nanopillars using 40 sccm Cl₂ at a chamber pressure of 0.1 Pa, with a substrate temperature of 100°C, ICP power of 800 W and bottom electrode bias power of 10W. As a result, InGa_{0.1}N/GaN 10 nm in diameter and 20 nm high nanopillars could be fabricated. The etching profile was confirmed by Transmission electron microscopy (TEM).

After etching, we measured the photoluminescence (PL) and time-resolved PL (TRPL) to observe the quantum confinement energy levels. According to the PL measurements, we found an energy shift of 1.25 eV, from 2.9eV for SQWs to 2.75eV for QNDs. Although these measurements are still on-going now, we will clearly analyze and discuss the phenomena related to this shift in energy in the near future.

11:40am **PS+SS+TF-FrM11 Towards a Nanoscale Plasma Etching Precision: Molecular Dynamics Simulations of Si-Cl Interactions.** *Paulin Brichon*, Univ. Grenoble Alpes-CNRS-CEA/Minattec-LTM,38000 Grenoble-France, *E. Despiau-Pujo*, LTM, France, *O. Mourey*, Univ. Grenoble Alpes-CNRS-CEA/Minattec-LTM,38000 Grenoble-France, *G. Cunge*, LTM - CEA/LETI, France, *O. Joubert*, Univ. Grenoble Alpes-CNRS-CEA, France

Due to high ion bombardment energies and significant fragmentation rates, conventional CW plasma processes are not able to selectively etch ultrathin films without damaging the active layers of advanced nanoelectronic devices (FDSOI, FinFET). In order to achieve uniform and damage-free etching of sub-nm-thick materials, one alternative is to lower the electron temperature (T_e) of the plasma. This can be achieved temporally by pulsing the plasma (i.e. switching on and off the RF source power), which introduces two additional parameters to tune an etching process, the pulsation frequency and the duty cycle (DC). Pulsed-plasma discharges exhibit lower average ion energies ($E_i \sim 5-10\text{eV}$); their chemical reactivity (or dissociation rate) can also be controlled by varying the DC. Another alternative is to lower T_e spatially, by segregating the electron heating region far from the wafer. These low- T_e plasmas are characterized by very low E_i ($E_i < 5\text{eV}$) and high radical densities.

With lower E_i and controllable reactivity, these plasmas are promising to etch sub-nm-thick stacked materials. However, the interactions between reactive plasmas and surfaces are so complex that the efficient development of new processes can require numerical simulations. Therefore, we develop Molecular Dynamics (MD) simulations to understand the impact of various plasma technologies on the interactions between ultrathin Si films and Cl_2 plasmas under a wide range of plasma conditions. They help to understand the precise role of E_i in plasma-surface interactions, the relationship between the flux/energy of reactive species bombarding the surface and its structural/chemical modifications.

In this study, MD simulations - coupled with experiments - are performed to quantify modifications (plasma-induced damage, etch rate) of Si films after exposition to various Cl_2 plasma conditions, simulated by bombarding the substrate with both ion and neutral species. All simulations show the formation of a stable SiCl_x reactive layer and a constant etch yield (EY) at steady state. The key plasma parameter to control the etching of ultrathin Si layers is E_i , which lowers both the damaged layer thickness and EY when it is decreased. The neutral-to-ion flux ratio (Γ) is the 2nd key parameter: its increase reduces the damaged layer thickness while the etch rate grows. While maintaining Γ constant, the neutral dissociation rate and the ion composition do not influence significantly the etching process. Etching simulations of a simple Si pattern are then compared to the etching of blanket silicon, focusing on phenomena such as ion channeling, passivation/damage of pattern sidewalls and top pattern erosion.

Thin Film

Room: 111 - Session TF+MI-FrM

Thin Films for Light Trapping, Plasmonic, and Magnetic Applications

Moderator: Angel Yanguas

8:20am **TF+MI-FrM1 Designing and Deposition of Multilayer Selective Surface for Tuning Absorption and Reflection of Solar Spectra.** *Z. Ren, Feng Cao*, University of Houston **INVITED**

Spectrally-selective solar absorbers are widely used in solar hot water and concentrating solar power (CSP) systems. However, the performance at high temperatures ($>500\text{ }^\circ\text{C}$) can be further improved. Recent progress on cermet-based solar absorbers has shown promising high temperature thermal stability and wavelength selectivity. Here we explore W-Ni- Al_2O_3 , W-Ni-YSZ (yttria-stabilized-zirconia), and W-Ni- SiO_2 cermet based spectrally selective surfaces for high-temperature solar absorber applications. The developed multilayer selective surfaces are deposited by magnetron sputtering on different substrates depending on applications. The absorber consists of two solar absorbing cermet layers with different W-Ni volume fraction inside the dielectric matrix, one or two anti-reflection coatings (ARCs), and one tungsten IR reflection layer for reduced IR emittance and improved thermal stability. All these absorbers show an absorbance of $> 90\%$ for temperature up to $500\text{ }^\circ\text{C}$ and emittance of $\sim 5\%$ at about room temperature and 10-15% at $500\text{ }^\circ\text{C}$.

Recently we are developing a new kind of absorber that reflects a certain range of wavelength and absorbs the rest of the whole solar spectra. The absorbed part is used for electrical power generation by steam engine and the reflected part is used for solar photovoltaic conversion. The thermal

energy can be easily stored for later conversion to provide electrical power around the clock without worrying the Sun's night time.

9:00am **TF+MI-FrM3 Femtomagnetism in FePt Nanoparticles for Heat Assisted Magnetic Recording.** *J.-Y. Bigot, J. Kim, M. Vomir*, Institut de Physique et Chimie des Matériaux de Strasbourg: Université de Strasbourg and CNRS, France, *O. Mosendz, S. Jain, Dieter Weller*, HGST a Western Digital company **INVITED**

Implementing larger and faster recording capacities, like in Heat Assisted Magnetic Recording (HAMR) devices, requires investigating the magnetization dynamics of nanostructures at the sub-picosecond time scale. The case of $L1_0$ FePt "nanocrystals" is of particular interest as HAMR media can be designed with grain diameter below today's $D \sim 8\text{ nm}$. The magnetic anisotropy is sufficiently high and results in coercive fields larger than 5 Tesla at room temperature [1, 2].

Femtosecond magneto-optics allows investigating the dynamical properties of such films [3] and nanoparticles [4] with a temporal resolution well adapted to the actual needs of performant materials that can be addressed in the time scale of a few picoseconds or faster. In the case of materials for HAMR, the pre-heating with femtosecond laser pulses allows reaching very high electron temperatures beyond the Curie point without over heating the lattice. It is therefore a relevant approach to use femtosecond pulses as it allows improving the conditions for obtaining an efficient switching due to the laser pre-heating. In that context, the variation of the coercive field H_c and magnetization at saturation M_s are important quantities to be characterized. We have investigated such dynamics in $L1_0$ FePt nanoparticles and accurately characterized the nonlinear variation of M_s and H_c upon varying the laser density of energy. We demonstrate that the Curie temperature can be reached during a few hundreds of femtoseconds, showing that the speed for addressing bits of information can be further improved in ultrafast HAMR applications.

[1] O. Mosendz, et al., J. Appl. Phys. 111, 07B729 (2012)

[2] D. Weller et al., Phys. Stat. Solidi A 210, 1245 (2013)

[3] S. Wicht et al., J. Appl. Phys. 114, 063906 (2013) & J. Appl. Phys. 117, 013907 (2015)

[4] E. Beaupaire, J.-C. Merle, A. Daunois, J.-Y. Bigot, Phys. Rev. Lett. 76, 4250 (1996)

[5] J.-Y. Bigot, M. Vomir, Annalen der Physik 525, 2–30 (2013)

10:00am **TF+MI-FrM6 Application of High Refractive Index Layers to Perfect Absorbers for Solar and Thermal Radiations.** *Motofumi Suzuki, K. Nishiura, S. Masunaka, K. Namura*, Kyoto University, Japan

In this presentation, we demonstrate that high refractive index materials such as $\beta\text{-FeSi}_2$ are key to achieve anti-reflective interference coatings on an opaque substrate. $\beta\text{-FeSi}_2$ is known as an eco-friendly semiconductor and its bulk refractive (n) and extinction (k) indices are higher than 5 and zero, respectively, in infrared (IR) region ($\lambda > 1.55\text{ }\mu\text{m}$). We have reported that the high refractive index of $\beta\text{-FeSi}_2$ is quite useful to reduce the reflectance of metal substrates and that $\beta\text{-FeSi}_2$ thin films/stainless steel substrate systems show nice spectrally selective absorption properties in IR region. For sputtered polycrystalline $\beta\text{-FeSi}_2$ thin films, we recently found that $k \approx 0.3$ in IR region, which is different from the bulk value. Thus, we redesigned antireflective-layered structures on an opaque substrate and prepared them. As the results, a system of $\beta\text{-FeSi}_2/\text{W}$ shows perfect absorption properties, where absorbance reaches higher than 99% at desired wavelength regions, while that in other regions is lower than a few %. On the other hand, another interesting optical property of $\beta\text{-FeSi}_2$ is that both n and k are considerably high in visible to NIR region ($\lambda < 1.55\text{ }\mu\text{m}$). This enables us to design multilayered broadband absorbers for VIS to $\lambda < 2.0\text{ }\mu\text{m}$. The designed multilayers consist of $\text{SiO}_2/\beta\text{-FeSi}_2/\text{SiO}_2/\beta\text{-FeSi}_2/\text{W}$, where the upper $\beta\text{-FeSi}_2$ layer absorbs VIS and NIR ($\lambda < 1.0\text{ }\mu\text{m}$) and the bottom $\beta\text{-FeSi}_2$ layer/W absorbs IR ($1.0\text{ }\mu\text{m} < \lambda < 2.0\text{ }\mu\text{m}$). The optimized multilayers absorb more than 95% of solar energy and the emittance at $450\text{ }^\circ\text{C}$ is lower than 6%. No significant change in absorptive properties in both single and multilayered absorbers has been recognized after they are annealed in air at least up to $500\text{ }^\circ\text{C}$. The perfect absorbers with high refractive index layers are useful for applications to solar selective absorbers for solar thermal power generation and spectrally selective thermal emitters for thermophotovoltaic power generation, IR heaters, radiation cooling.

10:20am **TF+MI-FrM7 Antireflection Coatings for Tandem Solar Cells.** *Bo Yuan*, University of Delaware, *B. Thibeault*, University of California at Santa Barbara, *K. Dobson*, University of Delaware, *A. Barnett*, University of New South Wales, Australia, *R.L. Opila*, University of Delaware

Because of the ability to exploit multiple absorption bands, Multi-junction Solar Cells (MJSCs) are the most efficient solar cells ever developed. As on single junction solar cells, Antireflection Coatings (ARCs) are utilized to

achieve broadband absorption. Due to the fact that the total current of MJSCs is limited by the subcell that has the lowest generated current, ARCs on MJSCs must have the ability to minimize light loss at the range of limiting cell, but optimally all across the visible spectrum.

Unlike conventional Double Layer Antireflection Coatings (DLARCs) that can only reduce light reflection at certain wavelengths, moth eye structures are able to mitigate light loss over broadband wavelength due to their smooth change of refractive index. We report the fabrication of such a Subwavelength Structure (SWS) by using wet etching and dry etching of dielectric materials. Silicon wafers are used here as the substrate to test the quality of ARCs. ZnO has been chosen as one dielectric material because of its excellent transmittance and durability. It also has a close index match to the underlying GaInP window layer in this tandem cell. Wet etching using oxalic acid has been utilized here to texture the ZnO surface because it is a simple and cost-effective method. A low reflection (less than 10%) over a broad range of wavelength (400-970nm) has been achieved. However, it turns out that wet etching is not very controllable and cannot fabricate the high aspect ratio periodic structure necessary for optimal absorption. A $\text{Zn}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ bulk phase was found on the ZnO surface.

Thus, lithography and plasma etching have been employed because of their better process control capability and less dependence on the crystalline orientation of the material. We then switched to using Ta_2O_5 since it has similar optical properties to ZnO and also a broad bandgap to ensure its transparency. Dry etching of Ta_2O_5 gives us nanocones with aspect ratio (height over base diameter) of 1.26. At an angle of 8 degree from normal incidence, textured Ta_2O_5 achieved the averaged reflection as low as 6% over 320-900nm and it outperforms DLARCs and textured ZnO over a wide range of wavelength. Future work will focus on fabricating this moth eye structure on III-V/SiGe tandem cells and simulating the reflectance spectra using Finite Difference Time Domain methods.

10:40am **TF+MI-FrM8 Preparation and X-ray Characterization of Highly Oriented Magnetic and Magnetoelectric Thin Films**, *Radomir Kuzel*, Charles University in Prague, Czech Republic, *J. Bursik, M. Soroka, K. Knizek*, Academy of Sciences of the Czech Republic

Different kind of thin films with remarkable magnetic and magnetoelectric properties require strong preferred orientation in order to utilize strong anisotropy of their properties.

The main aim of the work is to prepare the films of hexagonal ferrites showing magnetoelectric effects. There are several types of these materials marked as e.g. M-type $[(\text{Ba},\text{Sr})\text{Fe}_{12}\text{O}_{19}]$, space group $\text{P6}_3/\text{mmc}$, Y-type $[(\text{Ba},\text{Sr})_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}]$, s. g. R-3m , Z-type $[(\text{Ba},\text{Sr})_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}]$, s. g. $\text{P6}_3/\text{mmc}$, and others. Our attention was focussed mainly to Y-type where the best properties are expected. All these lattices are long along *c*-axis and this should be oriented perpendicular to the surface. The films were prepared through the chemical solution method either on SrTiO_3 (111) or sapphire Al_2O_3 (0001) substrates, respectively. We are looking not only for suitable substrates but also we have succeeded in using seed template interlayers, for example M hexaferrite $\text{SrFe}_{12}\text{O}_{19}$. A detailed inspection revealed that growth of seed layers starts through the break-up of initially continuous film into isolated grains with expressive shape anisotropy and hexagonal habit. Promising type of such seed layers seem also to be $\text{SrAl}_{12}\text{O}_{19}$ films where two kinds of preparation were investigated – deposition of $\text{SrAl}_{12}\text{O}_{19}$ onto sapphire substrate and reaction $\text{SrO} + \text{Al}_2\text{O}_3$.

Other type of magnetic films studied were magnetic spinels Co_3O_4 prepared by decomposition of films of layered cobaltates Na_xCoO_2 deposited by chemical solution deposition method and grown on sapphire substrates.

The films were characterized mainly by AFM and by several XRD techniques. Phase transitions and thermal stability were studied in symmetric Bragg-Brentano geometry, degree of preferred orientation by rocking curves (omega scans) and phi scans of asymmetric reflections, pole figures and also by reciprocal space maps. Residual stresses were also tested but they were usually zero or negligible. All the films were strongly oriented with the planes parallel to the surface but different kind of in-plane orientations was observed often structures with with several domains.

11:00am **TF+MI-FrM9 Size Effects on the Order-Disorder Phase Transition Temperature in FeNiPt Nanoparticles**, *G. Sutherland, D. Wood*, Brigham Young University, *A. Warren, K. Coffey*, University of Central Florida, *Richard Vanfleet*, Brigham Young University

Chemically ordering metal alloys such as FePt are hard magnets and good candidates for magnetic data storage in their ordered phase but not in the disordered state. The order-disorder phase transition temperature is impacted by the size of the particle with surface energies becoming significant for nanometer sized particles. Theoretical and computational approaches have predicted lowering of phase transition temperatures as the particle size decreases. Experimental evidence is more limited. Observation of ordering in nanoparticles is a complex interplay between thermodynamic and kinetic factors. Using Fe-Ni pseudo binary alloys with Pt allows

isolation of thermodynamic variables. We see a size dependent reduction of order-disorder temperature in this system with particles in the 5 – 12 nm range. At 6 nm the reduction is ~15%

11:20am **TF+MI-FrM10 A Comparison of Heptane Solvent Annealing versus Thermal Annealing Block Copolymers for Bit Patterned Advanced Media**, *Allen Owen, A. Montgomery, H. Su, S. Gupta*, University of Alabama

Hard disk drive storage media is trending towards both smaller physical size and greater storage capacity by increasing the areal density of the magnetic storage media. Bit patterning shows potential as a method for increasing this areal density. A block copolymer template can be used to provide an etch mask for bit patterning a magnetic thin film. Statistical designs of experiments were carried out comparing the effect of nanopatterning via ion milling Co/Pd multilayers using two different annealing methods for PS-PFS block copolymers. The design of experiments for each annealing method varied the etch angle, etch time and etch power during ion milling. Wafers that were sputter-deposited with Co/Pd multilayered thin films were spin-coated with PFS block copolymer and solvent annealed under heptane vapor in an oil bath at 35 °C for 6 hours. Identical wafers were thermally annealed in atmosphere at 140 °C for 48 hours. After annealing, the films were ashed in oxygen to remove the PS, leaving the PFS spheres as masks for the subsequent ion milling. The results from each annealing study showed that nanopillars with a nominal size of ~ 30 nm have been fabricated. The thermally annealed Co/Pd multilayers yielded a 407% increase in coercivity to ~6.6 kOe, while the heptane annealed thin film resulted in a 223% increase to ~4.2 kOe. A statistical design of experiments comparing two different etch techniques: (i) inductively coupled plasma reactive ion etching (ICP-RIE) and (ii) ion milling was carried out for these two annealing methods. The results indicate that process optimization can be achieved with a combination of the correct annealing and etching techniques.

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- Harshan, V.N.: TF+AS+NS+SA-ThA3, **48**
- Hatayama, T.: TF+AS+SS-MoM9, **6**
- Hathaway, M.: TF+AS+NS+SA-ThM10, **40**
- Hausmann, D.M.: TF+EM+NS+PS+SM-ThM1, **41**
- Hearn, G.: 2D+EM+NS+SS+TF-TuM11, **13**
- Hehn, I.: TF+AS+SS-MoM1, **5**
- Hellman, O.: TF+AS+NS+SA-ThA1, **47**
- Hemminger, J.C.: NS+EN+MG+SS+TF-WeA3, **31**
- Henderson, W.A.: EN+EM+NS+SE+SS+TF-TuA4, **17**
- Hendricks, O.L.: TF+EN-WeM1, **26**;
TF+EN-WeM5, **27**
- Heo, J.: TF-ThP19, **53**
- Heo, S.: EN+AS+EM+NS+SE+SS+TF-MoM6, **3**
- Hernandez, H.: TF+SS-WeM10, **29**
- Hernandez, J.A.: TF+SS-WeM10, **29**
- Hernández, S.C.:
2D+EM+NS+PS+SP+SS+TF-MoM1, **1**
- Hernandez-Hernandez, A.: TF-ThP10, **51**
- Hersam, M.C.: 2D+MN+NS+SP+SS+TF-WeM12, **22**
- Hight Walker, A.:
2D+EM+NS+PS+SP+SS+TF-MoM8, **2**
- Higley, D.J.: TF-ThP39, **55**
- Higo, A.: PS+SS+TF-FrM10, **57**
- Hirsch, K.: TF-ThP39, **55**
- Hite, J.K.: 2D+EM+NS+PS+SP+SS+TF-MoM1, **1**; 2D+EM+NS+PS+SP+SS+TF-MoM3, **1**; TF+2D+MG+NS-MoA5, **10**;
TF+AS+NS+SA-ThM13, **40**
- Hobbs, M.: TF+AS+EM+EN+MN-WeA4, **36**
- Hodges, D.R.:
EN+AS+EM+NS+SE+SS+TF-MoM5, **3**
- Hofmann, D.C.: AM+EM+MS+TF-ThM5, **39**
- Holleitner, A.W.: 2D+EM+NS+SS+TF-TuM11, **13**
- Holzwarth III, C.W.:
EN+EM+NS+SE+SS+TF-TuA9, **17**
- Homola, T.: TF+EM+MI+MS-TuM4, **14**
- Honda, M.: PS+SS+TF-FrM3, **56**
- Hong, H.: TF-ThP19, **53**
- Hong, S.: NS+EN+MG+SS+TF-WeA1, **31**
- Hrebik, J.H.: TF-ThP36, **54**
- Hsiao, C.N.: TF-ThP12, **52**; TF-ThP14, **52**
- Huang, C.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **37**
- Huang, Y.: TF+AS+NS+SA-ThA2, **47**
- Hudson, E.A.: PS+SS+TF-FrM1, **56**;
PS+SS+TF-FrM4, **56**
- Hultman, L.: TF+AS+NS+SA-ThA1, **47**
- Hur, G.H.: TF-ThP18, **53**
- Hur, J.: TF+EN-WeM13, **27**
- Hurley, P.K.: TF+EN-WeM1, **26**
- **I** —
- Ikeda, N.: TF+EM+MI+MS-TuM6, **14**
- Ilican, S.: TF-ThP3, **51**; TF-ThP7, **51**
- Illiberi, A.: EN+AS+EM+NS+SE+SS+TF-MoM8, **3**
- Injeti, S.: TF-ThP33, **54**
- Ishiyama, Y.: TF-ThP11, **52**
- Iverson, B.D.: TF+AS+BI-WeA11, **35**;
TF+AS+EM+EN+MN-WeA12, **36**
- Izawa, M.: PS+SS+TF-WeM5, **24**
- **J** —
- Jain, S.: TF+MI-FrM3, **58**
- Jaing, C.-C.: TF-ThP12, **52**
- Jal, E.: TF-ThP39, **55**
- Janakiraman, S.:
EN+AS+EM+NS+SE+SS+TF-MoA6, **8**
- Janssen, G.J.M.: TF+EN-WeM3, **26**
- Jasiuk, I.: MG+2D+MI+NS+TF-MoA5, **9**
- Jena, D.: 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
- Jensen, B.D.: TF+AS+BI-WeA11, **35**
- Jeon, S.: SP+BI+NS+SS+TF-ThA10, **47**
- Jin, W.: 2D+EM+MG+NS+SS+TF-ThA2, **44**; EN+EM+NS+SE+SS+TF-TuA9, **17**
- Johansson, P.: TF+EM+MI+MS-TuM4, **14**
- Johnson, E.V.: TF+2D+MG+NS-MoA10, **11**
- Johnson, N.: EN+AS+EM+NS+SE+SS+TF-MoM9, **4**
- Johnson, S.D.: TF+AS+NS+SA-ThM13, **40**;
TF+AS+NS+SA-ThM6, **39**
- Joseph, J.: TF-ThP39, **55**
- Joubert, O.: PS+SS+TF-FrM11, **58**;
PS+SS+TF-FrM6, **57**; PS+SS+TF-WeM3, **23**
- Ju, H.X.: EN+AS+EM+NS+SE+SS+TF-MoA7, **8**
- Jur, J.S.: TF+2D+MG+NS-MoA1, **10**; TF-TuA11, **20**
- **K** —
- Kakalios, J.: EN+AS+EM+NS+SE+SS+TF-MoA9, **9**
- Kalanyan, B.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
- Kalkofen, B.: TF-ThP34, **54**
- Kaminski, P.M.:
EN+AS+EM+NS+SE+SS+TF-MoM11, **4**
- Kanan, M.: NS+EN+MG+SS+TF-WeA12, **32**
- Kanekiyo, T.: PS+SS+TF-WeM5, **24**
- Kang, H.J.: EN+AS+EM+NS+SE+SS+TF-MoM6, **3**
- Kanjolia, R.: TF+SS-WeM11, **29**; TF+SS-WeM3, **28**
- Karim, A.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA7, **16**
- Karwal, S.: TF+EM+NS+PS+SM-ThM13, **42**
- Katayama, R.: PS+SS+TF-FrM10, **57**
- Katsunuma, T.: PS+SS+TF-FrM3, **56**
- Kaub, T.: TF+AS+NS+SA-ThA8, **48**
- Kava, D.: EN+AS+EM+NS+SE+SS+TF-MoM5, **3**
- Kawakami, M.: PS+SS+TF-FrM5, **56**
- Kawamura, M.: TF+AS+SS-MoM8, **6**
- Kelaidis, N.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, **37**
- Kelber, A.: 2D+EM+MG+NS+SS+TF-ThA6, **44**
- Kemp, K.W.: TF+EN-WeM1, **26**
- Kenney, J.A.: PS+SS+TF-FrM8, **57**
- Kessels, W.M.M.: PS+TF-WeA7, **33**;
TF+EM+NS+PS+SM-ThM10, **42**;
- TF+EM+NS+PS+SM-ThM12, **42**;
TF+EM+NS+PS+SM-ThM13, **42**;
TF+EM+NS+PS+SM-ThM6, **41**;
TF+EN-WeM3, **26**; TF+EN-WeM4, **26**;
TF+SS-WeM12, **29**; TF-TuA4, **19**
- Keszler, D.: TF+AS+NS+SA-ThA2, **47**
- Khalili, P.: TF+EM+NS+PS+SM-ThM5, **41**
- Kiba, T.: PS+SS+TF-FrM10, **57**;
TF+AS+SS-MoM8, **6**
- Kim, H.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA11, **16**; AM+EM+MS+TF-WeM6, **23**
- kim, H.J.: TF-ThP15, **52**
- Kim, H.S.: PS+SS+TF-FrM9, **57**
- Kim, J.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **37**; 2D+EM+MG+NS+SS+TF-ThA7, **44**; TF+MI-FrM3, **58**
- Kim, K.H.: TF+AS+SS-MoM8, **6**
- Kim, N.H.: TF-ThP28, **54**
- Kim, S.: TF-ThP15, **52**
- Kim, Y.: SP+BI+NS+SS+TF-ThA8, **46**
- Kim, Y.S.: TF-ThP34, **54**
- Kimes, W.A.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**; TF+SS-WeM6, **28**
- Kind, M.: TF+AS+SS-MoM1, **5**;
TF+AS+SS-MoM11, **7**
- Kis, A.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM11, **38**
- Kitano, M.: TF+EM+MI+MS-TuM6, **14**
- Klee, V.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **37**
- Knizek, K.: TF+MI-FrM8, **59**
- Knoops, H.C.M.: TF+EM+NS+PS+SM-ThM10, **42**; TF+SS-WeM12, **29**
- Kobayashi, H.: PS+SS+TF-WeM5, **24**
- Koehler, A.D.: TF+2D+MG+NS-MoA5, **10**
- Kolmakov, A.:
2D+EM+NS+PS+SP+SS+TF-MoM8, **2**
- Kotru, S.: TF+AS+NS+SA-ThA3, **48**
- Kouzuma, Y.: PS+SS+TF-WeM5, **24**
- Kozen, A.C.: EN+EM+NS+SE+SS+TF-TuA11, **18**
- Kröhnert, K.: PS+TF-WeA4, **32**
- Kuboya, S.: PS+SS+TF-FrM10, **57**
- Kudo, C.: TF+AS+SS-MoM8, **6**
- Kudo, Y.: PS+SS+TF-WeM5, **24**
- Kujofsa, T.: TF+AS+NS+SA-ThA6, **48**
- Kummel, A.C.: 2D+EM+MG+NS+SS+TF-ThA1, **44**;
EN+AS+EM+NS+SE+SS+TF-MoM1, **3**;
EN+AS+EM+NS+SE+SS+TF-MoM2, **3**
- Kung, C.Y.: TF-ThP13, **52**
- Kuusipalo, J.: TF+EM+MI+MS-TuM4, **14**
- Kuzel, R.: TF+MI-FrM8, **59**
- Kwak, I.J.: 2D+EM+MG+NS+SS+TF-ThA1, **44**
- **L** —
- LaBella, V.: TF+AS+NS+SA-ThM12, **40**
- Lagasta, S.: PS+SS+TF-WeM4, **24**
- Lahav, M.: TF+AS+SS-MoM3, **6**
- Lai, C.S.: PS+SS+TF-FrM4, **56**
- Lai, Y.-C.: PS+SS+TF-FrM10, **57**
- Lang, K.D.: PS+TF-WeA4, **32**
- Lanigan, D.: EN+AS+EM+NS+SE+SS+TF-MoA10, **9**
- Lara-Sanchez, A.: TF-ThP10, **51**
- Lasne, J.: TF+AS+SS-MoM2, **5**
- Lau, J.: TF+EN-WeM13, **27**
- Lau, K.K.S.: EN+AS+EM+NS+SE+SS+TF-MoA6, **8**
- Lauritsen, J.V.: NS+EN+MG+SS+TF-WeA9, **31**
- Lawrence, J.P.: TF+EN-WeM1, **26**
- Le Mogne, T.: TR+TF-ThM3, **43**
- Lee, C.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **37**
- Lee, C.C.: TF-ThP14, **52**
- Lee, C.-T.: TF-ThP12, **52**

- Lee, C.Y.: PS+SS+TF-FrM10, 57
- Lee, D.H.: EN+AS+EM+NS+SE+SS+TF-MoM6, 3
- Lee, H.I.: EN+AS+EM+NS+SE+SS+TF-MoM6, 3
- Lee, J.W.: TF+SS-WeM13, 29
- Lee, S.I.: TF+EM+MI+MS-TuM1, 13
- Lee, W.K.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 16
- Lee, Y.: PS+SS+TF-WeM10, 24;
PS+SS+TF-WeM6, 24; TF+SS-WeM5, 28
- Leighton, C.: EN+AS+EM+NS+SE+SS+TF-MoA9, 9
- Leijtens, T.: EN+AS+EM+NS+SE+SS+TF-MoA3, 8
- Leite, M.: 2D+EM+NS+PS+SP+SS+TF-MoM8, 2
- Lemaire, P.C.: TF-TuA1, 18; TF-TuA2, 18
- Leos, H.: TF+SS-WeM10, 29
- Leverd, F.: PS+SS+TF-WeM4, 24
- Lewis, B.B.: PS+SS+TF-WeM13, 25
- Li, C.: PS+SS+TF-FrM4, 56; PS+SS+TF-FrM5, 56; TF+AS+NS+SA-ThA10, 49
- Li, H.: PS+TF-WeA4, 32; TF-ThP22, 53
- Li, J.: EN+AS+EM+NS+SE+SS+TF-MoM10, 4
- Li, M.: EN+AS+EM+NS+SE+SS+TF-MoA9, 9
- Li, S.: EN+AS+EM+NS+SE+SS+TF-MoA5, 8
- Li, X.: TF+EM+NS+PS+SM-ThM5, 41
- Li, Y.W.: NS+EN+MG+SS+TF-WeA9, 31
- Liccoccia, S.: TF+EN-WeM4, 26
- Lim, H.: SP+BI+NS+SS+TF-ThA8, 46
- Lim, J.S.: MG+BI+MS+NS+TF-MoM8, 5
- Lin, F.: EN+EM+NS+SE+SS+TF-TuA1, 17
- Lin, H.H.: TF-ThP13, 52
- Lin, Y.: TF-TuA1, 18
- Lin, Y.-C.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 37; 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Lindhorst, K.: TF+AS+BI-WeA8, 34
- Linford, M.R.: MG+2D+MI+NS+TF-MoA6, 10
- Lisker, M.: TF-ThP34, 54
- Liu, D.-J.: SP+BI+NS+SS+TF-ThA8, 46
- Liu, G.: TF+SS-WeM11, 29
- Liu, L.-H.: EN+AS+EM+NS+SE+SS+TF-MoA1, 8
- Liu, Q.: EN+EM+NS+SE+SS+TF-TuA10, 18
- Liu, T.: TF-ThP39, 55
- Liu, X.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2; 2D+MN+NS+SP+SS+TF-WeM12, 22
- Liu, Y.: EN+EM+NS+SE+SS+TF-TuA9, 17
- Long, J.W.: EN+EM+NS+SE+SS+TF-TuA7, 17
- Longo, V.: TF+EM+NS+PS+SM-ThM12, 42
- Lopez, E.: TF+SS-WeM10, 29
- Lopez-Sanchez, O.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM11, 38
- Losego, M.D.: TF-TuA1, 18
- Lou, B.S.: TF+SS-WeM13, 29
- Lu, D.: EN+EM+NS+SE+SS+TF-TuA4, 17
- Lu, I.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 37
- Lu, J.P.: AM+EM+MS+TF-ThA3, 45
- Lucarelli, G.: TF+EN-WeM4, 26
- Ludwig, K.F.: TF+AS+NS+SA-ThM13, 40; TF+AS+NS+SA-ThM6, 39
- Luere, O.: PS+SS+TF-FrM6, 57
- Luna-López, J.A.: TF+2D+MG+NS-MoA7, 11
- Lund, J.M.: TF+AS+BI-WeA11, 35
- Lutman, A.A.: TF-ThP39, 55
- M —
- MacArthur, J.: TF-ThP39, 55
- Macco, B.: TF+EM+NS+PS+SM-ThM6, 41; TF+SS-WeM12, 29
- Mackowiak, Piotr, P.: PS+TF-WeA4, 32
- Mackus, A.J.: TF+EN-WeM6, 27
- Maeda, K.: PS+SS+TF-WeM5, 24
- Maeda, P.: AM+EM+MS+TF-ThA3, 45
- Maksymovych, P.: SP+BI+NS+SS+TF-ThA10, 47
- Malko, A.V.: EN+AS+EM+NS+SE+SS+TF-MoA1, 8
- Mallikarjunan, A.: TF+SS-WeM1, 28
- Mandal, H.: TF+AS+BI-WeA9, 35
- Mandrus, D.: SP+BI+NS+SS+TF-ThA6, 46
- Mane, A.: TF+SS-WeM3, 28; TF-TuA12, 20
- Mani, P.G.: TF+SS-WeM10, 29
- Mannie, G.J.A.: NS+EN+MG+SS+TF-WeA9, 31
- Manno, M.: EN+AS+EM+NS+SE+SS+TF-MoA9, 9
- Mansergh, R.H.: TF+AS+NS+SA-ThA2, 47
- Markus, I.: EN+EM+NS+SE+SS+TF-TuA1, 17
- Marquez-Velasco, J.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 37
- Martens, R.L.: TF+AS+NS+SA-ThA8, 48
- Martin, J.M.: TR+TF-ThM3, 43
- Martinez, J.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA4, 16
- Martirez, J.M.: MG+BI+MS+NS+TF-MoM8, 5
- Maslar, J.E.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1; TF+SS-WeM6, 28
- Mastro, M.A.: TF+2D+MG+NS-MoA5, 10
- Masunaka, S.: TF+MI-FrM6, 58
- Matei, I.: AM+EM+MS+TF-ThA3, 45
- Matsui, M.: PS+SS+TF-WeM5, 24
- Matsumuro, A.: TF-ThP11, 52
- Matyi, R.J.: TF+AS+NS+SA-ThM12, 40
- Maurice, J.L.: TF+2D+MG+NS-MoA10, 11
- Maury, P.: PS+SS+TF-WeM4, 24
- Maydannik, P.S.: TF+EM+MI+MS-TuM4, 14
- McAlpine, M.: AM+EM+MS+TF-ThA6, 45
- McClimon, J.B.: NS+EN+MG+SS+TF-WeA10, 31
- McCoustra, M.R.S.: TF+AS+SS-MoM2, 5
- McDonnell, S.: 2D+EM+MG+NS+SS+TF-ThA7, 44
- McGehee, M.D.:
EN+AS+EM+NS+SE+SS+TF-MoA3, 8
- McIntyre, P.C.: TF+EM+MI+MS-TuM6, 14; TF+EN-WeM1, 26; TF+EN-WeM5, 27
- Mei, A.B.: TF+AS+NS+SA-ThA1, 47
- Meinel, K.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 38
- Melendez, M.A.: TF+SS-WeM10, 29
- Melendez-Lira, M.: TF-ThP10, 51
- Melia, M.A.: TF-ThP17, 53
- Melskens, J.: TF+EN-WeM3, 26
- Mende, P.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Merz, R.: TR+TF-ThM1, 42
- Meshkova, A.: TF+PS-ThA8, 50
- Metzler, D.: PS+SS+TF-FrM4, 56; PS+SS+TF-FrM5, 56
- Meyer, D.: TF+AS+NS+SA-ThM6, 39
- Meysing, D.M.:
EN+AS+EM+NS+SE+SS+TF-MoM10, 4
- Michels, J.J.: TF+PS-ThA3, 49
- Miller, B.: 2D+EM+NS+SS+TF-TuM11, 13
- Minfray, C.: TR+TF-ThM3, 43
- Misra, V.: TF+EM+NS+PS+SM-ThM3, 41
- Mitschker, F.: PS+TF-WeA9, 33
- Mitzi, D.B.: EN+AS+EM+NS+SE+SS+TF-MoM1, 3
- Miyake, M.: PS+SS+TF-WeM5, 24
- Miyoshi, N.: PS+SS+TF-WeM5, 24
- Mok, K.R.C.: TF+EN-WeM3, 26
- Monazami, E.: NS+EN+MG+SS+TF-WeA10, 31
- Monfil-Leyva, K.: TF+2D+MG+NS-MoA7, 11
- Monroy, T.G.: PS+SS+TF-WeM11, 25
- Montgomery, A.: TF+MI-FrM10, 59
- Moon, B.K.: EN+EM+NS+SE+SS+TF-TuA9, 17
- Mork, F.: EN+AS+EM+NS+SE+SS+TF-MoA9, 9
- Moroz, D.J.: PS+TF-WeA3, 32
- Moroz, P.: PS+TF-WeA3, 32
- Morris, E.: AM+EM+MS+TF-WeM1, 22
- Moseler, M.: TR+TF-ThM1, 42
- Mosendz, O.: TF+MI-FrM3, 58
- Mourey, O.: PS+SS+TF-FrM11, 58
- Movva, H.C.P.: 2D+EM+MG+NS+SS+TF-ThA1, 44
- Mowll, T.R.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- Mueller, T.: 2D+EM+NS+SS+TF-TuM3, 12
- Muñoz-Zurita, A.L.: TF+2D+MG+NS-MoA7, 11
- Murari, N.: TF+AS+NS+SA-ThA2, 47
- Murayama, A.: PS+SS+TF-FrM10, 57
- Murphy, N.R.:
EN+AS+EM+NS+SE+SS+TF-MoA8, 9
- Murphy, R.D.: TF+AS+EM+EN+MN-WeA3, 35
- Murray, C.B.:
EN+AS+EM+NS+SE+SS+TF-MoA5, 8
- Musgrave, C.B.: TF-TuA9, 19
- Myers-Ward, R.L.: 2D+EM+NS+SS+TF-TuM10, 13; TF+2D+MG+NS-MoA5, 10
- N —
- Nad, S.: PS+TF-WeA12, 34
- Nagase, M.: TF+EM+MI+MS-TuM6, 14
- Naghbi, S.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 37
- Naguib, M.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM3, 37
- Nakamura, J.: 2D+MN+NS+SP+SS+TF-WeM11, 21; TF+AS+SS-MoM9, 6
- Nam, J.G.: EN+AS+EM+NS+SE+SS+TF-MoM6, 3
- Namura, K.: TF+MI-FrM6, 58
- Nanayakkara, C.E.: TF+SS-WeM11, 29
- Nandasiri, M.I.: EN+EM+NS+SE+SS+TF-TuA4, 17
- Nanver, L.K.: TF+EN-WeM3, 26
- Narasimham, A.J.: TF+AS+NS+SA-ThM12, 40
- Narasimhan, M.: TF+AS+EM+EN+MN-WeA1, 35
- Nascence, P.A.P.: TF+AS+BI-WeA7, 34
- Nath, A.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1; TF+2D+MG+NS-MoA5, 10
- Natterer, F.D.: 2D+MN+NS+SP+SS+TF-WeM10, 21
- Nave, A.: PS+TF-WeA9, 33
- Neek-Amal, M.: 2D+MN+NS+SP+SS+TF-WeM3, 21
- Nelaturi, S.: AM+EM+MS+TF-ThA3, 45
- Nepal, N.: TF+2D+MG+NS-MoA5, 10; TF+AS+NS+SA-ThM13, 40; TF+AS+NS+SA-ThM6, 39
- Nesladek, M.: 2D+EM+NS+SS+TF-TuM2, 12
- Ngo, HD.: PS+TF-WeA4, 32

- Nguyen, A.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 37
- Niemantsverdriet, H.J.W.: NS+EN+MG+SS+TF-WeA9, 31
- Niemeyer, T.C.: TF+AS+BI-WeA7, 34
- Nishiura, K.: TF+MI-FrM6, 58
- Noh, J.H.: PS+SS+TF-WeM13, 25
- Nordeen, P.: TF+AS+NS+SA-ThA11, 49
- Ntwaeaborwa, O.M.: TF-ThP25, 53
- Nunn, W.T.: TF-TuA1, 18
- Nyakiti, L.O.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
- O —
- O'Brien, L.: EN+AS+EM+NS+SE+SS+TF-MoA9, 9
- Oehrlein, G.S.: PS+SS+TF-FrM4, 56; PS+SS+TF-FrM5, 56
- Ogugua, S.N.: TF-ThP25, 53
- Oh, J.: SP+BI+NS+SS+TF-ThA8, 46
- Ojeda-Durán, E.: TF+2D+MG+NS-MoA7, 11
- Olanipekun, B.: 2D+EM+MG+NS+SS+TF-ThA6, 44
- Oldham, C.: TF-TuA2, 18
- Oleynik, I.I.: 2D+MN+NS+SP+SS+TF-WeM1, 21
- O'Mahony, A.: TF-TuA12, 20
- Ong, E.W.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- Opila, R.L.: TF+MI-FrM7, 58
- Orzali, T.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Osgood, Jr., R.M.: 2D+EM+MG+NS+SS+TF-ThA2, 44; SP+BI+NS+SS+TF-ThA9, 47
- Owen, A.: TF+MI-FrM10, 59
- P —
- Pala, I.R.: EN+EM+NS+SE+SS+TF-TuA7, 17
- Palmstrom, A.: TF+EN-WeM12, 27
- Papa, F.: PS+TF-WeA4, 32
- Park, G.S.: EN+AS+EM+NS+SE+SS+TF-MoM6, 3
- Park, J.B.: EN+AS+EM+NS+SE+SS+TF-MoM6, 3
- Park, J.H.: 2D+EM+MG+NS+SS+TF-ThA1, 44
- Park, J.W.: PS+SS+TF-FrM9, 57
- Park, K.P.: TF-ThP18, 53
- Parker, J.F.: EN+EM+NS+SE+SS+TF-TuA7, 17
- Parsons, G.N.: TF-TuA1, 18; TF-TuA2, 18
- Partes, C.: TF+AS+SS-MoM11, 7
- Parzinger, E.: 2D+EM+NS+SS+TF-TuM11, 13
- Patil, S.K.: TF+AS+NS+SA-ThM11, 40
- Peeters, F.: 2D+MN+NS+SP+SS+TF-WeM3, 21
- Pei, L.: TF+AS+EM+EN+MN-WeA12, 36
- Pemble, M.E.: TF+EN-WeM1, 26
- Pena-Hueso, A.: EN+EM+NS+SE+SS+TF-TuA3, 17
- Peng, W.N.: EN+AS+EM+NS+SE+SS+TF-MoA1, 8
- Peretti, M.W.: AM+EM+MS+TF-WeM3, 22
- Perriot, R.: 2D+MN+NS+SP+SS+TF-WeM1, 21
- Perrotta, A.: TF+PS-ThA3, 49
- Peterson, G.W.: TF-TuA1, 18
- Petrov, I.: TF+AS+NS+SA-ThA1, 47
- Pham, C.: TF+2D+MG+NS-MoA9, 27
- Pickrahn, K.L.: TF+EN-WeM6, 27
- Pierre, A.C.: AM+EM+MS+TF-ThA1, 45
- Pintauro, P.: TF+2D+MG+NS-MoA5, 10
- Piqué, A.: AM+EM+MS+TF-WeM6, 23
- Pollet, O.: PS+SS+TF-WeM4, 24
- Poodt, P.: EN+AS+EM+NS+SE+SS+TF-MoM8, 3; TF+EM+MI+MS-TuM3, 13
- Posseme, N.: PS+SS+TF-WeM4, 24
- Potapenko, D.V.: SP+BI+NS+SS+TF-ThA9, 47
- Povey, I.: TF+EN-WeM1, 26
- Preciado, E.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 37
- Provo, J.L.: TF+PS-ThA9, 50
- Pujari, S.P.: TF+AS+SS-MoM10, 7
- Q —
- Qin, X.: 2D+EM+MG+NS+SS+TF-ThA7, 44
- Qiu, A.: TF+AS+NS+SA-ThM5, 39
- R —
- Rack, P.D.: PS+SS+TF-WeM13, 25
- Rahman, T.S.: 2D+EM+NS+SS+TF-TuM5, 12; NS+EN+MG+SS+TF-WeA1, 31
- Rai, R.: TF+AS+NS+SA-ThM11, 40
- Rajagopalan, R.: TF+EM+MI+MS-TuM10, 14
- Ramalingam, G.: SP+BI+NS+SS+TF-ThA3, 46
- Ramana, C.V.: TF+AS+NS+SA-ThA3, 48
- Ramaswamy, K.: PS+SS+TF-WeM11, 25
- Ramprasad, R.: MG+2D+MI+NS+TF-MoA3, 9
- Randall, C.: TF+EM+MI+MS-TuM10, 14
- Ranjan, A.: PS+SS+TF-WeM1, 23
- Rappe, A.M.: MG+BI+MS+NS+TF-MoM8, 5
- Rauf, S.: PS+SS+TF-FrM8, 57; PS+SS+TF-WeM12, 25
- Raychaudhuri, S.: AM+EM+MS+TF-ThA3, 45
- Reese, M.O.: EN+AS+EM+NS+SE+SS+TF-MoM10, 4
- Reeves, R.V.: TF+AS+EM+EN+MN-WeA11, 36; TF+AS+EM+EN+MN-WeA3, 35; TF+AS+EM+EN+MN-WeA4, 36
- Reid, A.H.: TF-ThP39, 55
- Reid, S.: 2D+EM+MG+NS+SS+TF-ThA6, 44
- Reinke, P.: NS+EN+MG+SS+TF-WeA10, 31; SP+BI+NS+SS+TF-ThA3, 46
- Rementer, C.: TF+AS+NS+SA-ThA11, 49
- Ren, Z.: TF+MI-FrM1, 58
- Renault, O.J.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA11, 16
- Reyes, P.: NS+EN+MG+SS+TF-WeA3, 31
- Ribton, C.N.: AM+EM+MS+TF-WeM5, 22
- Richard, C.: PS+SS+TF-WeM4, 24
- Rieth, L.W.: TF+AS+BI-WeA9, 35
- Robinson, J.A.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 37; 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Robinson, J.T.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 16
- Robinson, Z.R.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1; 2D+EM+NS+PS+SP+SS+TF-MoM2, 1; TF+2D+MG+NS-MoA5, 10
- Rockett, A.: EN+AS+EM+NS+SE+SS+TF-MoM9, 4; TF+AS+NS+SA-ThA1, 47
- Rolison, D.R.: EN+EM+NS+SE+SS+TF-TuA7, 17
- Romano, A.: TF+AS+NS+SA-ThM5, 39
- Romero, P.: TR+TF-ThM1, 42
- Roozeboom, F.: PS+TF-WeA8, 33
- Röpcke, J.: PS+TF-WeA9, 33
- Rossi, F.J.: TF+AS+BI-WeA1, 34
- Rosuvinsen, A.: TF+AS+SS-MoM2, 5
- Routkevitch, D.: TF+EM+MI+MS-TuM5, 14
- Rowley, J.T.: 2D+MN+NS+SP+SS+TF-WeM4, 21; TF+AS+EM+EN+MN-WeA12, 36
- Ruan, W.Y.: 2D+MN+NS+SP+SS+TF-WeM10, 21
- Rubloff, G.W.: EN+EM+NS+SE+SS+TF-TuA11, 18
- Ruzic, D.N.: MG+2D+MI+NS+TF-MoA5, 9
- S —
- Saidi, W.A.: MG+BI+MS+NS+TF-MoM8, 5
- Saldana-Greco, D.: MG+BI+MS+NS+TF-MoM8, 5
- Sampat, S.C.: EN+AS+EM+NS+SE+SS+TF-MoA1, 8
- Samukawa, S.: PS+SS+TF-FrM10, 57
- Sana, C.O.: EN+AS+EM+NS+SE+SS+TF-MoM5, 3
- Sangiovanni, D.G.: TF+AS+NS+SA-ThA1, 47
- Santra, P.: TF+EN-WeM12, 27
- Sardashti, K.: EN+AS+EM+NS+SE+SS+TF-MoM1, 3; EN+AS+EM+NS+SE+SS+TF-MoM2, 3
- Sasaki, T.: TF+AS+SS-MoM8, 6
- Satpathy, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Sauter, A.J.: EN+AS+EM+NS+SE+SS+TF-MoA6, 8
- Scarel, G.: TF-ThP2, 51
- Schelhas, L.: TF-TuA10, 19
- Scheuermann, A.G.: TF+EN-WeM1, 26
- Schleppütz, C.M.: TF+AS+NS+SA-ThA1, 47
- Schlotter, W.F.: TF-ThP39, 55
- Schuster, S.: TF+AS+SS-MoM1, 5; TF+AS+SS-MoM11, 7
- Schwarz, A.: EN+EM+NS+SE+SS+TF-TuA4, 17
- Scully, J.R.: TF-ThP17, 53
- Seabaugh, A.C.: 2D+EM+MG+NS+SS+TF-ThA1, 44
- Seegmiller, T.: TF+EN-WeM13, 27
- Self, E.: TF+2D+MG+NS-MoA5, 10
- Shafai, G.: NS+EN+MG+SS+TF-WeA1, 31
- Shahriar, S.: EN+AS+EM+NS+SE+SS+TF-MoM5, 3
- Shan, B.: TF+EN-WeM2, 26; TF-TuA3, 19
- Sharma, A.: TF+EM+NS+PS+SM-ThM12, 42
- Sharma, K.: TF+EM+MI+MS-TuM5, 14
- Sharma, R.: TF+AS+BI-WeA9, 35
- Shchelkanov, I.A.: MG+2D+MI+NS+TF-MoA5, 9
- Sheehan, P.E.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 16
- Sherpa, S.: PS+SS+TF-WeM1, 23
- Shi, Z.: TF+SS-WeM4, 28
- Shinoda, K.: PS+SS+TF-WeM5, 24
- Shishatskiy, S.: 2D+MN+NS+SP+SS+TF-WeM13, 22
- Shojiki, K.: PS+SS+TF-FrM10, 57
- Shukla, N.: NS+EN+MG+SS+TF-WeA11, 32
- Shumlas, S.L.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 37
- Simmons, J.G.: TF+2D+MG+NS-MoA1, 10
- Simsek, E.: 2D+EM+NS+SS+TF-TuM1, 12
- Singam, S.K.R.: 2D+EM+NS+SS+TF-TuM2, 12
- Singh, B.: MG+2D+MI+NS+TF-MoA6, 10
- Singh, H.: PS+SS+TF-FrM1, 56
- Sivapragasam, N.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM10, 38
- Smith, L.: TF+EN-WeM13, 27
- Smolin, Y.Y.: EN+AS+EM+NS+SE+SS+TF-MoA6, 8
- Smulders, M.M.J.: TF+AS+SS-MoM10, 7

- Soroka, M.: TF+MI-FrM8, 59
- Soroush, M.: EN+AS+EM+NS+SE+SS+TF-MoA6, 8
- Sperling, B.A.:
2D+EM+NS+PS+SP+SS+TF-MoM4, 1;
TF+SS-WeM6, 28
- Sproul, W.D.: PS+TF-WeA4, 32
- Sridhara, K.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1
- Sridhara, K.S.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
- Standing, A.J.: TF-TuA4, 19
- Stanford, M.G.: PS+SS+TF-WeM13, 25
- Stano, K.L.: TF-TuA11, 20
- Starostin, S.A.: TF+PS-ThA8, 50
- Stemmer, P.: TR+TF-ThM1, 42
- Stiff-Roberts, A.D.: TF+2D+MG+NS-MoA2, 10
- Stoyanov, P.: TR+TF-ThM1, 42
- Stranick, S.J.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Strongin, D.R.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 37
- Stroschio, J.A.: 2D+MN+NS+SP+SS+TF-WeM10, 21
- Su, H.: TF+MI-FrM10, 59
- Sullivan, K.T.: TF+AS+EM+EN+MN-WeA11, 36
- Sullivan, N.: TF-ThP22, 53
- Sumpter, B.: SP+BI+NS+SS+TF-ThA10, 47
- Sutherland, G.: TF+MI-FrM9, 59
- Sutter, P.W.: 2D+EM+MG+NS+SS+TF-ThA3, 44
- Sutto, T.: AM+EM+MS+TF-WeM6, 23
- Suzer, S.: EN+AS+EM+NS+SE+SS+TF-MoM9, 4
- Suzuki, M.: TF+MI-FrM6, 58
- Swart, H.C.: TF-ThP25, 53
- Syme, D.B.: TF+AS+BI-WeA11, 35;
TF+AS+EM+EN+MN-WeA12, 36
- **T** —
- Tabata, M.: PS+SS+TF-FrM3, 56
- Tang, S.: SP+BI+NS+SS+TF-ThA6, 46
- Tanikawa, T.: PS+SS+TF-FrM10, 57
- Tathireddy, P.: TF+AS+BI-WeA9, 35
- Tavernier, A.: PS+SS+TF-FrM6, 57
- Taviot-Gueho, C.: TF+AS+NS+SA-ThM1, 39
- Terfort, A.: TF+AS+BI-WeA8, 34;
TF+AS+SS-MoM1, 5; TF+AS+SS-MoM11, 7
- Terry, J.: TF+AS+NS+SA-ThM3, 39
- Thenuwara, A.C.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 37
- Thibado, P.: 2D+MN+NS+SP+SS+TF-WeM3, 21
- Thibeault, B.: TF+MI-FrM7, 58
- Thiebaut, B.: TR+TF-ThM3, 43
- Thiel, P.A.: SP+BI+NS+SS+TF-ThA8, 46
- Thiesen, P.H.: 2D+EM+NS+SS+TF-TuM11, 13; 2D+EM+NS+SS+TF-TuM6, 12
- Thimsen, E.: EN+AS+EM+NS+SE+SS+TF-MoA10, 9
- Thissen, N.F.W.: TF+EM+NS+PS+SM-ThM6, 41
- Thomas, C.: PS+SS+TF-FrM10, 57
- Thompson, G.B.: TF+AS+NS+SA-ThA8, 48
- Tieckelmann, R.:
2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Timilsina, R.: PS+SS+TF-WeM13, 25
- Tolbert, S.H.: TF-TuA10, 19
- Tomalia, D.A.: EN+EM+NS+SE+SS+TF-TuA4, 17
- Tomasella, E.: TF+AS+NS+SA-ThM1, 39
- Trautmann, M.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 38
- Tseng, F.: 2D+EM+NS+SS+TF-TuM1, 12
- Tsipas, P.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 37
- Tsoutsou, D.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 37
- Tsuji, A.: PS+SS+TF-FrM3, 56
- Tsukamoto, A.: TF-ThP39, 55
- Turkowski, V.: 2D+EM+NS+SS+TF-TuM5, 12
- Tyagi, P.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- Tysoe, W.T.: TR+TF-ThM12, 43
- **U** —
- Uchida, Y.: 2D+MN+NS+SP+SS+TF-WeM11, 21
- Usrey, M.: EN+EM+NS+SE+SS+TF-TuA3, 17
- **V** —
- Vacher, B.: TR+TF-ThM3, 43
- Valaguez-Velazquez, E.: TF-ThP10, 51
- Valentin, M.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA4, 16
- Vallier, L.: PS+SS+TF-FrM6, 57;
PS+SS+TF-WeM3, 23
- Valesia, A.: TF+AS+BI-WeA1, 34
- van de Loo, B.W.H.: TF+EN-WeM3, 26
- van de Sanden, M.C.M.: PS+TF-WeA1, 32;
TF+PS-ThA8, 50
- van den Bruele, F.: TF+EM+MI+MS-TuM3, 13
- Van der Boom, M.E.: NS+EN+MG+SS+TF-WeA7, 31
- van der Zande, A.M.:
2D+EM+NS+PS+SP+SS+TF-MoM5, 2
- Vanfleet, R.: 2D+MN+NS+SP+SS+TF-WeM4, 21; TF+AS+BI-WeA11, 35;
TF+AS+EM+EN+MN-WeA12, 36;
TF+MI-FrM9, 59
- Varagas, M.: TF+AS+NS+SA-ThA3, 48
- Varaksa, N.: TF+EM+MI+MS-TuM5, 14
- Vargas, M.: EN+AS+EM+NS+SE+SS+TF-MoA8, 9
- Vega, A.: TF+SS-WeM11, 29
- Ventrice, Jr., C.A.:
2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- Ventzek, P.: PS+SS+TF-WeM1, 23
- Veres, J.: AM+EM+MS+TF-ThA3, 45
- Verheijen, M.A.: TF+SS-WeM12, 29; TF-TuA4, 19
- Vernisse, L.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 37
- Vidal, M.A.: TF+SS-WeM10, 29
- Vishwanath, S.: 2D+EM+MG+NS+SS+TF-ThA1, 44; 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Vlooswijk, A.H.G.: TF+EN-WeM3, 26
- Voiry, D.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA11, 16
- Völkel, A.R.: AM+EM+MS+TF-ThA3, 45
- Vomir, M.: TF+MI-FrM3, 58
- von Son, G.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 37
- Vos, M.F.J.: TF+EM+NS+PS+SM-ThM6, 41
- **W** —
- W. Elam, J.: TF-TuA12, 20
- Wächter, T.: TF+AS+SS-MoM11, 7
- Wählisch, F.C.: TR+TF-ThM1, 42
- Walen, H.: SP+BI+NS+SS+TF-ThA8, 46
- Walker, A.V.: TF+SS-WeM4, 28
- Wallace, R.M.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 37; 2D+EM+MG+NS+SE+SS+TF-ThA7, 44
- Wallas, J.M.: TF-TuA9, 19
- Walls, J.M.: EN+AS+EM+NS+SE+SS+TF-MoM10, 4;
EN+AS+EM+NS+SE+SS+TF-MoM11, 4
- Walsh, A.: TF+EN-WeM1, 26
- Walter, J.: EN+AS+EM+NS+SE+SS+TF-MoA9, 9
- Walton, S.G.: PS+SS+TF-WeM12, 25
- Wang, C.P.: EN+EM+NS+SE+SS+TF-TuA9, 17
- Wang, F.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA9, 16
- Wang, J.: PS+SS+TF-FrM8, 57
- Wang, J.K.: TF+2D+MG+NS-MoA10, 11
- Wang, K.: TF+EM+NS+PS+SM-ThM5, 41
- Wang, M.: PS+SS+TF-WeM1, 23
- Wang, Y.: TF+AS+NS+SA-ThA11, 49
- Wang, Z.: 2D+MN+NS+SP+SS+TF-WeM5, 21; TF+AS+SS-MoM10, 7
- Warren, A.: TF+MI-FrM9, 59
- Watanabe, H.: PS+SS+TF-FrM3, 56
- Wattendorf, M.D.:
EN+EM+NS+SE+SS+TF-TuA7, 17
- Weller, D.: TF+MI-FrM3, 58
- Wen, X.: NS+EN+MG+SS+TF-WeA9, 31
- Westerfield, G.: TF+AS+NS+SA-ThA2, 47
- Wheeler, V.D.:
2D+EM+NS+PS+SP+SS+TF-MoM1, 1;
TF+2D+MG+NS-MoA5, 10
- Whitener, K.E.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 16
- Whiting, G.L.: AM+EM+MS+TF-ThA3, 45
- Whitwick, M.B.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM11, 38
- Wicker, R.B.: AM+EM+MS+TF-WeM12, 23
- Widdra, W.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 38
- Williams, B.L.: TF+EM+NS+PS+SM-ThM13, 42
- Wind, J.: 2D+MN+NS+SP+SS+TF-WeM13, 22
- Wireklint, N.: TF+AS+NS+SA-ThA1, 47
- Wolden, C.A.:
EN+AS+EM+NS+SE+SS+TF-MoM10, 4; PS+TF-WeA11, 33
- Womack, G.: EN+AS+EM+NS+SE+SS+TF-MoM11, 4
- Wong, K.: TF+EM+NS+PS+SM-ThM5, 41
- Wood, D.: TF+MI-FrM9, 59
- Wood, J.D.: 2D+MN+NS+SP+SS+TF-WeM12, 22
- Wu, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Wurstbauer, U.: 2D+EM+NS+SS+TF-TuM11, 13
- Wyrick, J.: 2D+MN+NS+SP+SS+TF-WeM10, 21
- **X** —
- Xenogiannopoulou, E.:
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 37
- Xiao, J.: EN+EM+NS+SE+SS+TF-TuA4, 17
- Xing, H.: 2D+EM+MG+NS+SS+TF-ThA1, 44; 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Xu, Q.: TF+AS+NS+SA-ThA11, 49
- Xu, X.D.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- **Y** —
- Yamashita, I.: PS+SS+TF-FrM10, 57

- Yang, D.: NS+EN+MG+SS+TF-WeA11, 32
 Yang, J.Y.: TF-ThP18, 53
 Yang, Y.: 2D+MN+NS+SP+SS+TF-WeM13, 22
 Yanguas-Gil, A.: TF+EN-WeM10, 27; TF-TuA12, 20
 Yao, Z.: TF+AS+NS+SA-ThA11, 49
 Yarrington, C.D.: TF+AS+EM+EN+MN-WeA3, 35
 Ye, P.D.: 2D+EM+MG+NS+SS+TF-ThA7, 44
 Yeh, P.: 2D+EM+MG+NS+SS+TF-ThA2, 44
 Yeom, G.Y.: PS+SS+TF-FrM9, 57
 Yi, J.: SP+BI+NS+SS+TF-ThA6, 46
 Yin, X.: 2D+EM+NS+SS+TF-TuM12, 13
 Yoo, M.H.: TF-ThP28, 54
 Youn, C.M.: TF-ThP18, 53
 Young, A.F.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA1, 16
 Young, M.J.: TF-TuA9, 19
 Young, S.L.: TF-ThP13, 52
- Yu, P.Yu.: PS+SS+TF-FrM10, 57
 Yu, Y.: EN+EM+NS+SE+SS+TF-TuA10, 18
 Yuan, B.: TF+MI-FrM7, 58
 Yuan, E.: TF-ThP39, 55
 Yulaev, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, 2
 Yun, D.H.: PS+SS+TF-FrM9, 57
- **Z** —
- Zaki, N.: 2D+EM+MG+NS+SS+TF-ThA2, 44
 Zapata-Torres, M.: TF-ThP10, 51
 Zardetto, V.: TF+EN-WeM4, 26
 Zhang, H.-B.: TF-ThP12, 52
 Zhang, P.P.: SP+BI+NS+SS+TF-ThA1, 46
 Zhang, X.: 2D+MN+NS+SP+SS+TF-WeM13, 22;
 EN+AS+EM+NS+SE+SS+TF-MoA9, 9
 Zhang, Y.: PS+SS+TF-FrM6, 57;
 PS+SS+TF-WeM11, 25
 Zhao, J.: TF-TuA1, 18; TF-TuA2, 18
 Zhao, Y.: 2D+MN+NS+SP+SS+TF-WeM10, 21
- Zharnikov, M.: TF+AS+SS-MoM1, 5;
 TF+AS+SS-MoM11, 7; TF+AS+SS-MoM4, 6
 Zheng, P.Y.: TF+AS+NS+SA-ThA4, 48
 Zhitenev, N.B.: 2D+MN+NS+SP+SS+TF-WeM10, 21
 Zhou, L.: TF+AS+NS+SA-ThM11, 40
 Zhou, M.: TF+AS+NS+SA-ThA9, 48
 Zhou, X.: TF+AS+NS+SA-ThA8, 48
 Zhou, Y.: 2D+EM+MG+NS+SS+TF-ThA9, 45
 Zhu, H.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 37; 2D+EM+MG+NS+SS+TF-ThA7, 44
 Zhu, J.F.: EN+AS+EM+NS+SE+SS+TF-MoA7, 8; TF+AS+BI-WeA10, 35
 Zhu, Q.Q.: TF-TuA3, 19
 Zojer, E.: TF+AS+SS-MoM1, 5
 Zoubian, F.: TF+AS+NS+SA-ThM1, 39
 Zuilhof, H.: TF+AS+SS-MoM10, 7
 Zurek, E.: MG+BI+MS+NS+TF-MoM10, 5