Electronic Materials and Processing Division
Room: 210 - Session EM-MoM

Dielectrics for Novel Devices and Process Integration
Moderator: S. King, Intel Corporation

8:20am **EM-MoM1 Surface Cleaning and Monolayer Seeding for ALD of High-k Studied by In Situ STM, STS, and XPS**, ***W. Melitz***, *T. Kent, J. Shen, A.C. Kummel*, University of California San Diego

Air exposed III-V surfaces nearly always defects which prevent full modulation of the Fermi level thereby impeding their use in practical semiconductor devices such as MOSFETs. For a high speed device, the air induced defects need to be removed to reduce trap states while maintaining an atomically flat surface to minimize interface scattering thereby maintaining a high carrier mobility. For silicon, the only commercial atomic layer deposition (ALD) high-k fabrication process is a replacement gate process to avoid processing induced damage. Surface channel III-V MOS devices can be fabricated with ALD high-K gate-first processes; while ALD is known to greatly reduce surface contaminants, contamination removal is not complete and the order of the surface after ALD cleanup is unknown. Using in-situ scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) the surface morphology of a multistep process was explored for gate-last unpinning of air exposed InGaAs and InP surface via cleaning with atomic H and ALD nucleating/passivating with trimethyl aluminum (TMA). STM of atomic H cleaned surfaces shows the dosing temperature and a post deposition anneal are critical to forming surfaces that resemble the decapped InGaAs or a highly ordered InP surfaces. For InGaAs(100), 300K H dosing can produce large multilayer etch features which cannot be annealed out; however by dosing at elevated temperatures these features can be avoided. After H cleaning at 380°C, the surface contains dark features consistent with monolayer etch pits, and these features are reduced by a factor ~50 with a post deposition anneal. The H cleaned and annealed surface can be unpinned by a half cycle dose of TMA followed by annealing because it generates an ordered dimethyl aluminum layer providing monolayer nucleation density, and an atomicly flat surface, critical for aggressive EOT scaling. For InP, a low dose of H at similar temperatures and post deposition anneal generates a mixed surface reconstruction; however, with a higher dosing temperature around 440°C and post deposition anneal around 470°C, a single surface reconstruction is observed. A similar atomic H cleaning and TMA dosing procedure has been demonstrated to produced an ordered passivation layer on air exposed InP(100). It has been shown that for InGaAs and InP an oxide free surface can be achieved with atomic H dosing and annealing, however there is a dependence of surface roughness and defect densities on dosing and annealing conditions. The combination of atomic H cleaning and TMA dosing provides a flat ordered surface ideal as a template for ALD of high-k gate dielectrics.

8:40am **EM-MoM2 Selective Area Regrowth of Self-Aligned, Low-Resistance Ohmic Contacts on InGaAs**, ***J.J.M. Law***, *A.D. Carter, G.B. Burek, B. Thibeault, M.J.W. Rodwell, A.C. Gossard*, University of California, Santa Barbara

As electronic device areas scale with each generation by 1:4, resistances must remain constant, so contact resistivities must scale by 1:4. The high dopant concentrations achievable by molecular beam epitaxy (MBE) provide a method for creating low-resistance ohmic contacts; however, line-of-sight deposition and low desorption of atomic species may hinder the self-alignment of such regrowth. Careful control over growth conditions makes MBE a suitable technique for creating self-aligned, low resistance ohmic contacts to InGaAs.

Samples were grown by solid source MBE lattice matched to semi-insulating InP with layer structure as follows from the substrate: 400 nm InAlAs, 3 nm of Si-doped 2 and 3×10^{19} cm^{-3} InAlAs, and 25 and 15 nm of InGaAs, respectively. 300 nm of SiO_2 and 20 nm of Cr were deposited by PECVD and e-beam evaporation. A combination of electron beam and photolithography followed by ICP dry etching was used to define dummy spacer pillars. Oxidation and oxide removal of exposed InGaAs was done with UV o-zone and a dilute 10 H_2O:1 HCL dip. Samples were heated to 420 °C and treated with thermally cracked hydrogen ($\approx1\times10^{-6}$ Torr) for 40 minutes prior to regrowth. 70 nm of 5×10^{19} Si-doped InAs was grown on the exposed InGaAs regions with quasi-migration enhance epitaxy (MEE) at 500 °C with V:III beam equivalent pressures of 4.0, 5.6, and 8.0. After regrowth, shorts over the dummy pillar were removed, and samples were metalized with lifted-off e-beam evaporated Ti/Pd/Au and mesa isolated. Contact resistances were extracted by transmission line measurements (TLM).

RHEED images during regrowth showed 4x2 surface reconstructions for regrowths with V:III ratios of 4.0 and 5.6 indicating a group In-rich surface reconstruction. SEM of regrowths at V:III ratios of 4.0 and 5.6 showed no faceting and fill-in to the dummy pillar edge. AFM showed roughened surfaces possibly due to high Si incorporation and lattice mismatch between InGaAs and InAs. Regardless of the V:III ratio during growth, 25 nm thick InGaAs channels showed contact resistances of 190 Ω µm while 15 nm thick InGaAs showed contact resistances of 105 Ω µm. Metal-semiconductor contact resistances were 2.1 Ω µm. Local electrode atom probe shows that the regrowth carries some of the Ga along with it creating a varying InGaAs alloy concentration throughout the regrowth.

9:00am **EM-MoM3 Boron Nitride Development and New Applications for sub-20nm Device Fabrication**, ***M. Balseanu***, *L.Q. Xia, V. Nguyen, M. Naik, D. Cui, K. Zhou, J. Pender, B. Mebarki*, Applied Materials, Inc. **INVITED**

The continuous need for films with lower dielectric constant, higher strength, and greater etch resistance drives the need to explore new materials. In this paper we present a study of boron nitride and other boron-based materials for multiple applications in semiconductor devices discussing the benefits and integration challenges.

As critical dimensions shrink and RC delay increases, the dielectric constant of the interconnect is a continuous area of focus. The current silicon carbo-nitride (SiCN) Cu barrier film has a dielectric constant greater than 5.0 and relatively poor step coverage. Significant advances have been made in recent years to develop a low k, conformal and manufacturable BN thin film for Cu barrier applications. The BN film was shown to have improved leakage, mechanical properties and insensitivity to UV cure relative to SiCN.

Back-end of line patterning has increased in complexity with the introduction of ultra-low k (ULK) dielectric materials. Dual hardmask (HM) patterning scheme eliminates the ULK damage caused by photoresist strip process. The TiN HM has faced challenges in extending below 20nm due to post etch residue and high stress leading to line bending. A boron-based HM material was developed to address those integration challenges. The new material has a low and tunable stress eliminating the line bending concerns. Boron content was optimized for the best selectivity to ULK without impacting the film stress. Significant defectivity and queue time improvement was observed with the boron-based HM due to volatility of the etch byproducts. 9% RC reduction relative to the conventional tri-layer patterning scheme was measured using 45nm 2-metal level electrical test structures.

Double or quadruple patterning technique is required for critical dimensions reduction due to the lack of manufacturable EUV lithography. Spacer-based double patterning (SADP) is one of the most adopted process flows to generate one-dimension regular array structures. Its implementation is impacted by the poor step coverage of the conventional PECVD SiN spacer leading to metal line cuts after final polishing step. A low temperature BN film with superior step coverage, minimum pattern loading, good uniformity and low cost was developed for 20nm node and beyond. Its benefit for SADP was verified using a 20nm half pitch logic structure where a 200mm long serpentine yield was improved by 80%.

Evaluation of the boron-based thin films for Cu barrier and patterning applications has shown their potential to replace the conventional materials used today in the logic and memory process flow and thus enabling scaling below 20nm.

9:40am **EM-MoM5 Novel Organosilicate Polymers for Ultralow-Dielectric Films with High Modulus, Low CTE, and Closed-Pore Morphology**, ***D.Y. Yoon***, *J.H. Sim*, Seoul National University, Korea, *M. Liu*, University of Michigan, *H.W. Ro, C.L. Soles*, National Institute of Standards and Technology, *D.W. Gidley*, University of Michigan **INVITED**

Novel organosilicate polymers are prepared using porogen bridged comonomers for ultralow-dielectric constant insulator applications. We synthesize silsesquioxane based terpolymers with methyltrimethoxysilane, ethylene bridged silane (1,2-bis(triethoxysilyl)ethane) and a porogen bridged silane comonomer via sol-gel reaction. The conventional route to generate nanoporous organosilicate films is to blend in a low molecular mass porogen that phase separates from the organosilicate network into isolated nanoscale domains that template the pores. However, using this approach it is difficult to achieve isolated nanopores with diameters below 2 nm when the total porosity becomes greater than 20 % by volume, which is essential for obtaining ultralow-k (k<2.2) films. Our novel approach here is to covalently tether the both terminal ends of linear organic porogen to

the trialkoxysilane monomers. This helps minimize the phase separation of the porogen during the thermal curing process of organosilicate polymers and keeps the resultant pores both smaller and less interconnected. For comparison we also prepare an analogous grafted version of this terpolymer series where only one end of the linear porogen is tethered to a trialkoxysilane monomer. The pore structures and porosities of this series of bridged and grafted porogen films are fully characterized with positron annihilation lifetime spectroscopy (PALS) and X-ray porosimetry (XRP). The resulting nanoporous films from the porogen bridged organosilicate polymers show much smaller pore sizes (1 nm to 2 nm), reduced interconnectivity of the pore structure, and superior mechanical properties in comparison with their analogs using the porogen grafting approach, especially at the high porosities (ca. 30 %) that are relevant for ultralow-k (2.0 to 2.2) insulators for advanced microprocessor applications.

10:40am **EM-MoM8 Interface Traps and Low Subthreshold Swing in III-V Tunnel FETs**, ***A. Seabaugh***, *S.-D. Chae, P. Fay, W.-S. Hwang, T. Kosel, R. Li, Q. Liu, Y. Lu, T. Vasen, M. Wistey, H. Xing, G. Zhou, Q. Zhang,* University of Notre Dame, *R.M. Wallace*, University of Texas at Dallas **INVITED**

Tunnel field-effect transistor (TFETs) are metal-oxide semiconductor (MOS) devices that use the gate electrode to control the band-overlap of a Zener tunnel junction. In TFETs, the subthreshold swing can be less than the thermal limit of 60 mV/decade in MOSFETs, allowing lower supply voltages for the same on/off current ratio, and lower power dissipation. Traps, however, at the high-k-dielectric/semiconductor interface act to terminate the gate field without contributing charge carriers to the channel and thereby degrade the subthreshold swing. This presentation will examine the relationship between interface traps and subthreshold swing and show, through impedance and transport measurements on InAs/AlGaSb TFETs, our current understanding of the interface, physics, charge control, and channel transport.

11:20am **EM-MoM10 Impact of Vertical Structured Devices for Future Nano LSI**, ***T. Endoh***, Tohoku University, Japan **INVITED**

For the past thirty years, the device downscaling has been the guiding principle in Si-LSI. The planar MOSFET has supported the expansion of the semiconductor industry; however, recently, the limit of planar MOSFETs is becoming apparent. As the feature size of planar MOSFETs approach the nano generation, it is becoming more difficult to improve its performance by SCE etc. Moreover, the process cost becomes expensive. In order to extend the scalability of CMOS technology to the nano generation; a new device structure is necessary. From above viewpoint, many new structured MOSFETs are proposed. The key points of next generation MOSFET are multi-gate structure, floating body structure and 3D structure. Therefore, proposed Vertical MOSFET [1-2] is emerging as one of the candidate to replace the conventional MOSFET.

In this paper, I will show the excellent performance of Vertical MOSFETs in comparison with others structured MOSFETs from viewpoints of high packing density and large driving current and good gate controllability etc. Moreover, I will show the impact of Vertical MOSFET for high density Memory [3].Next, I will discuss that by using both proposed Vertical MOSFETs[4] and Spin device, Silicon ULSI can be evolved even if becoming in nano generation in forces to Logic. Logic demands new scheme technology for realizing lower power operation and managing the total power consumption. On the other hands, Memory, especially non-volatile memory demands new cell technology for shrinking cell size and realizing high speed programming, low voltage operation and good reliability including endurance. From above viewpoint, we will show the excellent performance of both Logic-in-Memory Architecture [5-7] using MTJ, and MTJ based Vertical structured cell, as follows. First, it is shown that by Logic-in-Memory Architecture using MTJ, a compact LSI with a standby-power-free and immediate-power-up capability can be realized. Next, it is shown that by Vertical structured cell using MTJ, ultra high density non-volatile memory can be realized with utilizing both a capability of Vertical structure MOSFET such as large drive current, excellent gate controllability and compact footprint, and a capability of MTJ such as unlimited endurance and manufacturability integrated in backend metal line of Silicon CMOS technology. Finally, we discuss the impact of spintronic devices for future Nano Si-LSI.

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[2] T.Endoh,etal. AWAD, 2008

[3] T.Endoh,etal. IEEE IEDM, 2001

[4] T.Endoh,etal. IECE Trans.EL. E92-C, 2009

[5] A.Mochizuki, etal. IEICE Trans.EL E88-A, 2005

[6] S.Matsunaga, etal. APEX 1, no.9, 2008

[7] M.Kamiyanagi,etal. AWAD, 2009

Electron Transport in Low Dimensional Materials Focus Topic
Room: 209 - Session ET+EM+SS-MoM

Quantum Transport: From 0- to 2-Dimensions
Moderator: A.-P. Li, Oak Ridge National Laboratory, K. Varga, Vanderbilt University

8:20am **ET+EM+SS-MoM1 Charge and Spin Transports at Surfaces of Strong Spin-Orbit-Coupling Materials**, ***S. Hasegawa***, *T. Hirahara*, University of Tokyo, Japan **INVITED**

Transports of charge as well as spin at crystal surfaces are now intensively studied by various kinds of experiments. Surface electronic states are generally decoupled from the bulk states and therefore intrinsically low-dimensional. Furthermore, space-inversion symmetry is broken down at crystal surfaces; one side of the surface is empty vacuum while other side is full of electrons in the crystal. These effects provide rich physics of transport, especially on surfaces of strong spin-orbit-coupling (SOC) materials. The surface-state bands are known to be spin-split of such strong SOC crystals such as Bi and Bi alloys, which is called by Rashba effect [1-4]. Similar effect is observed on a special kind of materials called topological insulators such as BiSb, BiSe, and BiTe alloys. Some of them have spin-split Dirac-cone type surface-state bands. This implies that spin-polarized current will flow at the surfaces of such materials.

In my presentation, by using samples of pure Bi [1-4], BiSb [5], BiSe [6,7], and BiTe, I will show that the surface-state bands are really spin-split and the Dirac-cone conductivity is directly measured by microscopic four-point probe method. An on-going project to detect the spin-polarization of surface current by using magnetic tips in a four-tip STM will be also introduced.

[1] T. Hirahara, et al., Phys. Rev. Lett. 97, 146803 (2006).

[2] T. Hirahara, et al., Phys. Rev. B 76,153305 (2007).

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[7] T. Hirahara, et al., Phys. Rev. B82, 155309 (2010).

9:00am **ET+EM+SS-MoM3 Electron Transport in Ferroelectric Domains and Walls**, ***A. Baddorf***, Oak Ridge National Laboratory **INVITED**

Ferroelectric tunneling, where electron transport is controlled by the polarization state, has recently been realized in a number of experiments. Polarization-controlled transport effects have been detected in tunnel junctions, thin films, single crystals and at domain walls. Yet, little analysis of data has undertaken to determine the transport mechanisms and their interaction with ferroelectric fields and domain boundaries involved in switching. We present seminal experimental observations of transport in thin films of $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) and $BiFeO_3$ (BFO). Earlier we have shown that both materials exhibit pronounced polarization-controlled electroresistance [1]. Temperature and voltage dependence of currents are not well fit by any one standard model. Instead a transition between surface and bulk limiting effects is observed. Upon close inspection, I-V curves exhibit a reproducible region of negative differential conductance associated with ferroelectric switching. Although this anomaly may originate from extrinsic processes, e.g. due to oxygen vacancies or charge injection, we have carried out a series of control experiments on PZT films that unequivocally connect variation of conductance with the size of the polarization domain in the plane of the surface. The I-V anomaly therefore originates from significant conductivity of the domain wall and a relatively slow expansion of the domain following polarization switching. However, our results do not imply simply that transport is through domain walls, but further that nanoscale domains formed by switching have fundamentally different conduction behavior [2]. We suggest that domains formed by tip-applied bias have curved walls and are consequently charged, modifying adjacent material much as charge accumulation modifies a semiconductor. Engineering the ferroelectric domain size produces a tunable conductance reminiscent of analogue memristors, providing a quasi-continuous spectrum of non-volatile resistive states, even though the PZT polarization itself is bistable. Ferroic memristive behavior, which based on our measurements is likely to be universal to ferroic semiconductors, is a striking departure from the conventional picture of discrete electron transport states in ferroelectrics.

Research was conducted at the Center for Nanophase Materials Sciences and sponsored by the Division of Scientific User Facilities, U.S. Department of Energy.

[1] P. Maksymovych et al., Science 324 (1421) 2009.

[2] P. Maksymovych et al., submitted.

9:40am **ET+EM+SS-MoM5 Electronic Instabilities, Fluctuations, and Transport in Epitaxial Nanowires**, ***H.H. Weitering***, University of Tennessee and Oak Ridge National Laboratory **INVITED**

Quantum transport is at the heart of nanoscience and marries a fundamental law of nature — quantum mechanics — with applied electrical engineering and emerging materials technologies. Ultimately, nanoscale electronic devices will contain networks of wires whose cross sections will be so small as to represent one-dimensional conductors with novel transport properties. We have fabricated exceptionally long and uniform YSi_2 nanowires via self-assembly of yttrium atoms on Si(001). The wire widths are quantized in odd multiples of the Si substrate lattice constant. The thinnest wires represent one of the closest realizations of the isolated Peierls chain, exhibiting van Hove type singularities in the one-dimensional density of states and charge order fluctuations below 150 K. Conduction through individual nanowires follows an inverse Arrhenius behavior, indicative of thermally-assisted tunneling of small polarons between defect centers. Quantitative analysis of individual wire resistances, probe resistances, and negative differential resistances of nanowire networks indicates significant electronic interwire coupling below 150 K. The long-range coupling mechanism involves the dielectric polarization of the substrate, which induces current blockades in neighboring conduction channels.

This work is sponsored by the NIH/NHGRI and was partially conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy

10:40am **ET+EM+SS-MoM8 Grain Boundary Resistivity in Copper Nanowires**, ***T.H. Kim***, POSTECH, South Korea **INVITED**

The reliable choice of the interconnect materials in current integrated circuits is copper because of its higher electrical conductivity and improved stability against electromigration among all possible candidates. However, as the width of interconnects is approaching a mean free path of the electrons, the resistivity of copper interconnects is known to increase dramatically. Typically, this increase in the resistivity of the narrow interconnect is attributed to enhanced sequential scattering of electrons from defect planes such as either grain boundaries (GB) or other surfaces/interfaces. But, it is very challenging to distinguish which scattering factor is dominant over others in such a small scale.

To answer such a fundamental question, theorists developed semi-empirical methods and the relative contribution of various electron scattering mechanisms has been understood largely by relying on the semi-empirical methods based on the theories of Fuchs-Sondheimer and Mayadas-Shatzkes. The direct measurements of the resistance of individual GBs have been surprisingly lacking mainly due to technical difficulty to access single GBs in a nanowire that could not be realized by conventional fabrication methods using a fixed electrical contacts. Recently, Y. Kitaoka *et al.* have observed a resistance change along a damascene Cu interconnect wire with four-probe scanning microscope. They successfully separated the GB scattering effect from other scattering sources; however, the direct correlation between the GB structure and the specific GB resistivity remained unclear.

Here we present the direct measurement of individual GB resistances and the critical role of GB structure in the increased resistivity in copper nanowires with a four-probe scanning tunneling microscope. The resistances of high symmetry coincidence GBs are then calculated using a first-principle method, which confirms that the coincidence GBs have orders of magnitude smaller resistance than those measured at the high-angle random GBs. As well, to explain high resistivity of random GBs, we used free-electron-with-random-point-scatterer (FERPS) model. In the FERPS model, we derived that the specific GB resistivity of random GB is independent of the specific structures of random GB such as orientation and is determined entirely by the Fermi wavelength of the bulk.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

11:20am **ET+EM+SS-MoM10 Tunable Coulomb Blockade and Giant Coulomb Blockade Magnetoresistance in a Double Quantum Dot System**, ***X.-G. Zhang***, Oak Ridge National Laboratory, *T. Xiang*, Chinese Academy of Sciences

We propose a Hubbard model to describe the tunneling effect of electrons in a double quantum dot system connected in the parallel circuit configuration to electrodes. The change in the interdot coupling is shown to dramatically influence the Coulomb blockade properties. For magnetic double dots, the interdot coupling can be tuned by the external magnetic field, leading to a giant Coulomb blockade magnetoresistance. Possible detection of this effect in organic systems is discussed.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

11:40am **ET+EM+SS-MoM11 Quantum Transport in Crossbar Devices**, ***B. Cook***, *P. Dignard, K. Varga*, Vanderbilt University

Electronic devices with crossbar geometries have recently been fabricated with nanoscale features (Zhong. et al, Science Vol. 302). Consisting of a two dimensional grid, devices have been formed with a variety of components including carbon nanotubes and semiconductor nanowires. These devices are assumed to operate classically, but as the dimensions of the device shrink consideration of quantum effects becomes necessary. We consider a single junction between two wires up to a four by four grid of wires. Through a series of calculations with atomistic first-principles, tight-binding and analytic models of multi-terminal devices we demonstrate the presence of unique behavior, such as interference effects, not present in classical models. It is expected that exploitation of these effects will useful in the creation of circuit components.

Nanometer-scale Science and Technology Division
Room: 203 - Session NS+EM-MoM

Nanowires and Nanoparticles I: Assembly and Devices
Moderator: M. Hines, Cornell University

8:20am **NS+EM-MoM1 ZnO Nanowire Logic Inverter with the Difference of Two Gate Electrode**, *J.K. Kim,* ***Y.T. Lee****, R. Ha, H.J. Choi, S.I. Im*, Yonsei University, Republic of Korea

Recently, zinc oxide nanowires (ZnO NWs) have attracted much attention for high mobility and sensing properties. These advantageous give us strong possibility to use nanostructures as nanoelectronic device application; such as field effect transistors (FETs), diodes, and logic circuit devices.[1] In this work, we fabricated the logic circuit inverter using difference of gate electrodes which have the different work function.[2]

In order to fabricate the inverter devices, grown ZnO NWs were dispersed to the SiO_2/Si substrate by using a drop-and-dry method. The Ni/Ti source and drain electrodes were deposited by e-beam evaporator with a combination of photo-lithography and lift-off process. To make 30nm-thick Al_2O_3 gate insulator layer, we used Atomic Layer Deposition (ALD) system. And then, Pd and Ni/Ti top gate electrodes were deposited and these two devices were connected by wire bonding technique.

The threshold voltage of the Pd top gate ZnO NWs FET shows more positive value (~ 0 V) than that of the other FET (~ -1 V) with Ni/Ti top gate, and these transistors are able to be used as a driver and a load, respectively. The linear mobility of the driver shows about 119 cm^2/Vs at V_D = 0.6 V and the inverter device has high gain value of ~15 at V_{DD} = 5 V. Furthermore, the dynamic property of the logic inverter was measured under the 5 V square input voltages.

More details will be discussed in the meeting.

References

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2. K.M. Lee, J.H. Kim and S.I. Im, *Appl. Phys. Lett*. **88**, 023504 (2006)

8:40am **NS+EM-MoM2 Control of Growth Kinetics for Three-Dimensional III-nitride Nano-Heterostructures Towards Nanowire Devices**, ***S.D. Carnevale****, P.J. Phillips, T.F. Kent, J. Yang, M.J. Mills, R.C. Myers*, Ohio State University

The geometry of semiconductor nanowires (NWs) allows for both vertical and coaxial heterostructures, while only vertical heterostructures can be formed using planar structures. This is especially important for III-nitride NWs because crystallographic directions in which heterostructures are formed largely determine the magnitude of internal electric fields due to polarization. Here we describe a method to control the relative vertical and coaxial growth rates in catalyst-free GaN/AlN NW heterostructures grown on Si(111) substrates by plasma-assisted molecular beam epitaxy*.

A growth phase diagram is established relating NW density to substrate temperature and III/V ratio. This diagram reveals a reduction in effective growth rate and an increase in nucleation time caused by GaN decomposition. Using this information, a two-step method is developed to independently control NW density from NW deposition time. To begin we

nucleate NWs until a small but appreciable density is reached. If deposition continues under these conditions, density will increase over time until reaching a saturation point. To suppress this increase, substrate temperature is increased upon completion of the initial nucleation time. NWs already nucleated continue to grow, but there is no new nucleation, thus controlling density. Additionally, the change in conditions alters growth kinetics, leading to purely vertical NW growth, which allows for the formation of NWs with arbitrarily large aspect ratios and small diameters (~20 nm). Kinetics that favor coaxial growth are also achieved. A low density, high aspect ratio NW array is prepared using the method described above then material is deposited at a lower substrate temperature. The relative coaxial growth rate increases due to lower Ga ad-atom mobility at the lower substrate temperature. Using this dynamic method, we demonstrate multiple period GaN/AlN (2 nm / 2 nm) superlattices along either the vertical or coaxial NW axis, which exhibit atomically sharp compositional profiles. A coaxial, AlN/GaN resonant tunneling diode structure is presented. Large areas of nanowires are processed for electrical measurements without removing them from the Si(111) substrate. Preliminary electrical measurements are provided for both room temperature and low temperature conditions. This work is supported by the ONR under grant N00014-09-1-1153.

* S.D. Carnevale, J. Yang, P.J. Phillips, M.J. Mills,and R.C. Myers. “Three-Dimensional GaN/AlN Nanowire Heterostructures by Separating Nucleation and Growth Processes”. *Nano Letters* 11, 2, pp. 866-871, Jan. 2011.

9:00am **NS+EM-MoM3 III-V Nanowire MOSFETs**, ***L.-E. Wernersson***, Lund University, Sweden **INVITED**

III-V Nanowire transistors are cosidered possible candidates to extend the transistor scaling roadmap. The improved electrostatic control in the cylindrical geometry provides benefits for scaling and the advantageous transport properties of the III-V materials may be used to increase the drive current. Besides heterostructure design may be used to tailor the properties in the transistor channel.

In this talk, we will review some of the efforts made in Lund to realize high-perfromance III-V nanowire transistors using vertical nanowires grown by MOVPE. We will show how bottom-up technologies can be combined with top-down processing to realize nanowire-based RF-devices on Si 2" wafers. We use CV techniques to characterize the properties of the high-k material in vertical nanowire capacitors and compare the data to the 1/f-noise characteristics of scaled transistors to evaluate the influence of the high-k material on the transistor performance. We also show that the transistor channel may be reduced down to a diameter of 15 nm without degradation of the transport properties. Finally, we explore the use of novel materials in the transistor structures as we developed GaSb/InAs heterostructures with excellent Esaki diode characteristics to be used for TFET implementations.

9:40am **NS+EM-MoM5 Optimizing Quantum Efficiency in Quantum Dot Display**, ***S.J. Lim***, *J. Kwon, Y. Oh,* Seoul National University, Republic of Korea, *B.L. Choi, K. Cho,* Samsung Advanced Institute of Technology, Republic of Korea, *Y. Kuk*, Seoul National University, Republic of Korea

In our previous study, we were able to fabricate full-color, 4-inch display made of colloidal quantum dot (QD). Despite such a demonstration of QD light emitting device which is one of candidates for next-generation display, understanding the interface characteristics between QD layer and electron (or hole) accumulation layer is still lacking and further study for improvement of quantum efficiency is essential. Here, we report on a study of scanning tunneling microscopy (STM), spectroscopy (STS) and cathode luminescence induced by tunneling current, performed on individually manipulated QD. We control the distance between two QDs using STM to reveal the mechanism of interaction between QDs. STS measurement showed shift of energy levels as manipulating the distance between two QDs. This result suggests that there exists the optimal distance between QDs for efficient light emission. Besides by making contacts between separated QDs and organic molecules, we simulated contacts between QD layer and electron (or hole) accumulation layer. From these experiments, we could understand excitonic behavior and carrier hopping from QD to QD or surrounding materials. Our findings thus suggest optimal configuration for QD application in display.

10:00am **NS+EM-MoM6 Polarization Engineered 1-Dimensional Electron Gas**, ***D.N. Nath***, *P.S. Park, M. Esposto,* Ohio State University, *D. Brown, S. Keller, U.K. Mishra,* University of California Santa Barbara, *S. Rajan*, Ohio State University

One-dimensional electron gas (nanowire) based devices are of great interest due to their promise in high-performance electronics and other future device applications. However, synthesis and patterning of arrays of nanowires is a challenge in all material systems since both bottom-up and top-down approaches have their own merits and demerits.

Here we report on the demonstration of pure 1-dimensional arrays of electrons with current density up to 130 mA/mm and carrier confinement greater than 100 meV using lateral polarization engineering in N-polar vicinal AlGaN/GaN heterostructures. The width of the atomic terraces characteristic of vicinal surfaces defines the dimensions of the nanowires which are found to exhibit sharp and clear signatures of 1-dimensionality at room temperature making them promising for novel device applications.

We report on devices fabricated on MOCVD grown N-polar AlGaN/GaN HEMT structures on vicinal sapphire substrate (4^0 miscut towards a-plane) with anisotropy in current and channel pinch-off voltages. Channels parallel to the miscut direction pinched off at higher negative gate biases than those perpendicular to the steps and carried more charge as measured by direction-dependent C-V profiling. An electrostatic model which predicts a saw-tooth energy band profile in the lateral direction has been proposed to explain the charge anisotropy. Each atomic terrace characteristic of the surface morphology of vicinal GaN with its corresponding saw-tooth energy profile is proposed to exhibit quasi-1D confinement. We will discuss the heterostructure/polarization design of structures demonstrating pure 1-D transport in direction parallel to steps.

Gated structures were fabricated to investigate the physics of the system as the Fermi occupation function is varied by varying gate bias. To confirm that the carriers are indeed 1-dimensional, we used direction-dependent small-signal capacitance voltage measurements to probe the density of state function and hence dimensionality of electrons as a function of gate bias. We developed a 2-band model consisting of one 1-D and one 2-D subband to describe the behavior of these wires at room temperatures. The variation of capacitance as well as charge density for a pure 1-D and a pure 2-D system as a function of applied gate bias as predicted by our 2-band model based on density of states matches very well with the data measured experimentally for 1-D and 2DEG respectively. This confirms that the channels created are indeed 1-dimensional in nature. Since 1-D channels are atomic terrace defined, they are promising for eliminating the disadvantages of both bottom-up and top-down approaches.

10:40am **NS+EM-MoM8 Adding New Capabilities to Silicon CMOS via Deterministic Nanowire Assembly**, ***T.S. Mayer***, *M. Li, T. Morrow, J. Kim, B. Won, K. Sun, X. Zhong, K. Liddell, J.S. Mayer, C.D. Keating*, Penn State University **INVITED**

Integrating functionalized nanowires directly onto Si CMOS chips has the potential to combine highly selective and sensitive chemical and/or biological sensing capabilities with electronic signal processing in a single ultra compact, low power platform. Conventional integrated circuit manufacturing methods place considerable limits on the range of and number of different materials and molecules that can be incorporated onto Si chips, making it difficult to realize this goal. This talk provide an overview a new deterministic assembly approach that uses electric field forces to direct many different types of bioprobe-coated nanowires to specific regions of the chip and to provide accurate registration between each individual nanowire and a specific transistor on the chip. This is achieved by synchronizing sequential injections of nanowires carrying different bioprobe molecules with a programmed spatially-confined electric field profile that directs nanowire assembly. Subsequent back-end lithographic and metal deposition processes are then used to electrically and mechanically connect all of the nanowire devices to the Si chip at the same time. Using this technique, individual nanowire device integration yields exceeding 90% have been demonstrated with a less than 1% mismatch across three populations of DNA-coated nanowires for arrays with densities of 106 cm-2. The nanowire-bound DNA retained its ability to selectively bind complementary target strands following assembly and device fabrication showing that this process is compatible with these back-end manufacturing steps. The uniformity in the electrical properties of nanowire device arrays that were fabricated using this hybrid integration strategy will also be discussed.

11:20am **NS+EM-MoM10 Solid-State Dewetting of Direct Nanoimprinted Metallic Thin Films**, ***R. Clearfield***, North Carolina State University, *J.D. Fowlkes,* Oak Ridge National Laboratory, *P.D. Rack,* University of Tennessee Knoxville, *N. Samatova,* Oak Ridge National Laboratory, *A.V. Melechko*, North Carolina State University

Heat applied to thin films below a critical thickness will generally cause transformation of the film into isolated particles. This process is known as dewetting. Solid state dewetting occurs below the melting temperature of the film and is governed by diffusive mass transport. Currently two mechanisms of dewetting are distinguished: hole nucleation and growth, and spinodal dewetting. Spinodal dewetting proceeds via film surface undulations that have characteristic wavelengths related to the thickness of

the film. Lithographic patterning of thin films has been utilized to direct the dewetting instability development toward designed nanostructured geometry of nanoparticle arrays. Tailoring the geometry of thin film edge have been shown to affect both heterogeneous nucleation and spinodal dewetting regimes. Nanoimprint lithography, conventionally used for definition of the edges of thin films, is a fabrication method where a stamp is pressed into a thin normally monomer or polymer film at elevated temperatures. Nanoimprinting can also be conducted in direct mode where the stamp is pressed into a metallic film. Surface undulations characteristic for spinodal dewetting will be used to direct the stamp design. Such imprinting allows setting initial conditions, programming instability, in the thin metallic film that is linked to the spinodal surface instability. In this work we are presenting the results of the investigation into behavior of thin films in which a 3D structure has been imprinted. We present observations on the effect of direct nanoimprint lithography on nanoscale Au and Ni films using periodic arrays of cylinders. Our focus is on the spatial distribution of the particles produced from dewetting of the nanoimprinted films. Particles in patterned regions are characterized in terms of their spacing, periodicity and size, and shape. The geometry of the dewetted patterns is compared to that of the 3D features created after direct nanoimprinting of the films. Analysis of spatial correlation of the final dewetted patterns to stamp patterns is presented.

Electronic Materials and Processing Division
Room: 209 - Session EM1-MoA

Group III-Nitrides and Hybrid Devices
Moderator: K. Kavanagh, Simon Fraser University, L. Porter, Carnegie Mellon University

2:00pm **EM1-MoA1 Electrically-Monitored Gate-Recess for Normally-Off AlGaN/GaN High-Electron Mobility Transistors**, ***H. Kim***, *M. Schuette, W. Lu*, The Ohio State University

GaN-based power devices have been intensively investigated for high power switching applications as well as high power microwave applications. Particularly, high breakdown voltage and high saturation velocity of GaN-based heterostructures facilitate reduction in on-state loss and switching loss compared to currently dominant Si-based power devices. Moreover, normally-off GaN-based power field-effect transistors (FETs) offer their inherent safety, reduced power consumption, and diverse circuit functionality with normally-on ones. Recently, we developed a zero-bias Cl-based dry etching process to thin AlGaN barrier with a minimal damage for enhancement-mode AlGaN/GaN FETs. However, it has been difficult to control gate-recess process for normally-off GaN-based FETs due to strong polarization effects. Namely, 1 nm under- or over-etchings near the critical AlGaN barrier thickness where the channel is pinch-off result in a negative threshold voltage (V_T) or a degraded transconductance (G_m), respectively. In this work, we report a methodology to control our Cl-based gate-recess for both positive V_T and high $G_{m,MAX}$ by relating electrical properties of the gate-recessed area before gate metallization to V_T and G_m in AlGaN/GaN FETs.

Gate-recessed AlGaN/GaN FETs were fabricated through fast etching with BCl_3 and slow etching with Cl_2/N_2/10%-O_2 to thin AlGaN barrier. The slow etching runs under inductively-coupled plasma mode only to minimize the damage. For monitoring purpose, resistance at 0 V (R_{0V}) and drain-to-source current ($I_{D,SAT}$) at 10 V between source and drain contacts were measured before gate metallization to correlate with V_T and G_m after gate metal deposition.

I_D-V_{GS}, G_m-V_{GS}, and capacitance-voltage characteristics of gate-recessed FETs with different AlGaN thicknesses by doing Cl_2/N_2/10%-O_2 etching for different times were measured and V_T values were extracted by linear extrapolation at $G_{m,MAX}$. V_T and $G_{m,MAX}$ were correlated with the monitoring parameters of R_{0V} or $I_{D,SAT}$. V_T and $G_{m,MAX}$ distributions with R_{0V} or $I_{D,SAT}$ guide us for monitoring as well as design of gate-recess process. For example, a recessed FET showing R_{0V} = 1700 W with 7 nm AlGaN barrier exhibits V_T of 0.56 V and $G_{m,MAX}$ of 300 mS/mm. In addition, our recess process offers sufficiently long monitoring time (at least 4 minutes) to tune the gate recess for target V_T together with high $G_{m,MAX}$. Based on the distribution, the necessity of tuning process is determined and its progress is monitored by R_{0V} or $I_{D,SAT}$ before gate metallization until target R_{0V} or $I_{D,SAT}$ is met. Our electrically monitoring method allows gate recess process to be well-controlled for target V_T and $G_{m,MAX}$.

2:20pm **EM1-MoA2 Atom Probe Tomography Studies on Green Light Emitting InGaN/GaN Multi Quantum Wells Grown on GaN Substrates**, ***F. Liu***, *L. Huang*, Carnegie Mellon University, *S.V.N.T. Kuchibhatla, D.K. Schreiber*, Pacific Northwest National Laboratory, *M. Zhang*, University of Michigan, *E.A. Preble, T. Paskova, K.R. Evans*, Kyma Technologies, Inc., *L. Porter, R.F. Davis*, Carnegie Mellon University

Carrier *delocalization* in InGaN/GaN multi-quantum wells (MQW) contained within green light-emitting diodes (LEDs) has been proposed as a contributor to LED efficiency droop. By contrast, interface roughness and fluctuations in composition within the MQWs may act to localize and confine carriers[1]. In this study, InGaN/GaN MQWs were grown on both (0001)GaN layers and on $In_xGa_{1-x}N$ buffer layer with graded In mole frations from 0 to 10%. Both heterostructures were grown on chemomechanically polished (0001)GaN substrates. Calculations using temperature-dependent photoluminescence spectra revealed a four-fold increase in the internal quantum efficiency (IQE) in the latter structure. A LEAP 4000X HR^{TM} pulsed UV laser (355 nm at 200 kHz) atom probe tomograph was used to investigate the elemental and spatial characteristics of the interface of the $In_xGa_{1-x}N$/GaN MQWs. To establish consistent atom probe operation parameters for reliable comparison among different samples, a systematic study was conducted to optimize the evaporation rate and laser energy. The concentration profile of $In_xGa_{1-x}N$/GaN MQW showed slightly varied In fraction among different QWs, ranging from x=0.21 to x=0.27, while the XRD results showed an average In fraction in all QWs of x=0.25. Furthermore, based on isoconcentration surface analysis and proximity histograms the upper surfaces of InGaN QWs appear to be more diffuse than the lower surfaces. These results indicate surface roughening of the InGaN layer. A detailed comparison of the two structures will be presented and the ability of 3-D atom probe tomography for such an analysis and the impact of the results on next generation LED technologies will be discussed.

1. J. Hader, J. V. Moloney and S. W. Koch, Appl. Phys. Lett. **96** (22), 221106 (2010).

2:40pm **EM1-MoA3 Local Surface Electrical Characterization of Polar GaN Surfaces**, ***J.D. Ferguson***, *M.A. Reshchikov, A.A. Baski*, Virginia Commonwealth University

While GaN is a widely-used material in optoelectronic devices, localized surface-related electrical properties are not well-understood. These properties affect the operational performance and lifetimes of GaN-based devices. Here, several atomic force microscopy (AFM) techniques were used to characterize the Ga-polar, +c [0001], and N-polar, -c [0001bar], surfaces of free-standing bulk GaN. Samples were prepared by either a chemical-mechanical polish (CMP) or mechanical polish (MP) of HVPE-grown GaN. AFM data showed that the Ga-polar surfaces (MP and CMP) were uniformly flat with rms roughness of less than 1 nm over a 5x5 micron image. In contrast, the N-polar surfaces were significantly rougher (~5 nm rms) with scratch-like features (100 nm wide, microns long), where the CMP treatment resulted in the presence of surface protrusions (~100 nm dia.) in proximity of the scratches. We then examined the local electrical properties using conducting AFM (C-AFM) to map surface conductivity and to obtain I-V spectra. C-AFM images at forward-bias (<6V) showed small contrast variations for all samples except the N-polar CMP surface. In that case, we observed less conducting behavior on the protrusions as compared to the surrounding surface. Local I-V data also revealed a higher forward-bias, turn-on voltage for the N-polar vs. Ga-polar samples. To investigate the local surface charging behavior, we used a two-step technique. First, a metallized AFM tip was used to locally charge the surface by applying a DC voltage, and then the resulting change in surface potential was monitored as a function of time with scanning Kelvin probe microscopy (SKPM). These surface charging data showed a smaller change in surface potential for the N- vs. Ga-polar samples, which appears to be consistent with the lower onset of conduction for the N-polar orientation. Finally, we measureed the photo-induced changes in surface potential under UV light exposure (100W Hg lamp), otherwise known as the surface photovoltage effect (SPV). The N-polar samples had a smaller SPV compared to Ga-polar, which indicates a smaller amount of band bending at the surface. Additionally, N-polar GaN restored to dark-state conditions at a much faster rate, regardless of CMP or MP treatment. In summary, we observed differences in morphology and electrical behavior for the two polar, c-plane GaN surfaces, as well as differences in behavior due to CMP and MP treatments. These data suggest a less pronounced surface charging behavior on N-polar vs. Ga-polar GaN.

3:00pm **EM1-MoA4 The Effect of Ammonia - TMI Pulse Separation on the Structural Properties of InN Epilayers**, ***R. Atalay***, Georgia State University, *M. Buegler*, Technische Universität Berlin, Germany, *S. Gamage, I. Senevirathna, A.G.U. Perera*, Georgia State University, *J.S. Tweedie, R. Collazo*, North Carolina State University, *N. Dietz*, Georgia State University

Over the last decade, significant research efforts have been devoted to understand and improve the properties of InN epilayers. However, even today, there is a significant lack of on understanding of the InN surface and growth chemistry and its affect on the physical bulk properties. Crucial challenges in the growth of InN epilayers are the vast different partial pressures between indium and nitrogen and associated fragments of the utilized precursors trimethylindium (TMI) and ammonia (NH3).

In this work, high-pressure chemical vapor deposition (HPCVD) is employed and explored in order to control and suppress the disassociation of InN alloys at higher growth temperatures. In order to reduce gas phase reactions and to control the surface chemistry, a pulsed precursor injection approach has been implemented, which provides additional process control parameters for the optimization of the physical epilayers properties.

In the pulsed precursor injection approach, the precursor separation times between the metal organic (MO) sources (TMI and TMG) and ammonia (S1), and ammonia and MO (S2) are two critical process parameters.

This contribution will present results on how the precursor separation times between the TMI and ammonia (S1) and ammonia and TMI (S2) affect the structural and optical properties of InN epilayers grown on GaN/sapphire

templates and/or sapphire substrates. In this study, the separation times S1 and S2 have been varied from 1000 to 2500 ms and 250 to 500 ms, respectively. The results show that a longer S1 separation of around 1700 ms and short S2 separation of around 360 ms provide the best structural properties of InN epilayers.

The InN epilayers have been analyzed by Raman scattering, X-ray diffraction, IR reflection, and transmission spectroscopy. The Raman studies showed that the lowest FWHM of E2(high) vibrational mode with about 8 cm-1 for a S2 separation time of 358 ms. XRD 2Θ-ω scans on these InN epilayers and the analysis of the InN (0002) Bragg reflex confirm the improved structural properties for the optimized S2 separation.

3:40pm **EM1-MoA6 Neutron Scattering Provides a New Model for Optimal Morphologies in Organic Photovoltaics: Rivers and Streams**, ***M. Dadmun**, W. Yin,* University of Tennessee*, J. Ankner, K. Xiao*, Oak Ridge National Laboratory

Organic Photovoltaics (OPVs) have attracted increasing interest as a lightweight, low-cost and easy to process replacement for inorganic solar cells. Moreover, the morphology of the OPV active layer is crucial to its performance, where a bicontinuous, interconnected, phase-separated morphology of pure electron donor and acceptor phases is currently believed to be optimal. In this work, we use neutron scattering to investigate the morphology of a model OPV conjugated polymer bulk heterojunction, poly[3-hexylthiophene] (P3HT) and surface-functionalized fullerene 1-(3-methyloxycarbonyl) propy(1-phenyl [6,6]) C_{61} (PCBM). These results show that P3HT and PCBM form a homogeneous structure containing crystalline P3HT and an amorphous P3HT/PCBM matrix, up to *ca.* 20 vol% PCBM. At 50 vol% PCBM, the samples exhibit a complex structure containing at least P3HT crystals, PCBM crystals, and a homogeneous mixture of the two. The 20 vol% PCBM samples exhibit behavior consistent with the onset of phase separation after 6 hours of thermal annealing at 150 °C, but appears to be miscible at shorter annealing times. This suggests that the miscibility limit of PCBM in P3HT is near 20%. Moreover, for the 50 vol% PCBM sample, the interface roughens under thermal annealing possibly owing to the growth of PCBM crystals. These observations suggest a different morphology than is commonly presented in the literature for optimal bulk heterojunctions. We propose a novel 'rivers and streams' morphology to describe this system, which is consistent with these scattering results and previously reported photovoltaic functionality of P3HT/PCBM bulk heterojunctions.

4:20pm **EM1-MoA8 Novel Boron Carbide-Based Semiconducting Polymers for Enhanced Electronic Properties**, ***F. Pasquale**, J. Kelber*, University of North Texas

We report the controlled modification of valence band electronic structure of semiconducting boron carbides with sharply narrowed band gap, by combination of 1,4 diaminobenzene (DAB) with orthocarboranes to form a novel boron-carbide based semiconducting film. Semiconducting boron carbide films ($B_{10}C_2H_x$) and related materials formed from crosslinking of carborane icosahedra are of rapidly increasing interest in neutron detection, nanoelectronics, spintronics, and even conventional CMOS ULSI applications. The ability to modify the material's electronic structure in a controlled manner is of obvious interest in all these areas. We report x-ray and ultraviolet photoelectron spectra (XPS, UPS), demonstrating that electron-induced cross-linking of carborane and DAB results in a novel semiconductor with a significantly enhanced valence band density of states near the Fermi level, resulting in a shift, as determined by UPS, in the valence band maximum from ~ 4.3 eV to ~ 1.7 eV below the Fermi level. Importantly, this effect is relatively insensitive to total film thickness and for DAB/orthocarborane atomic ratios (determined by XPS) ranging from 1:4 to 1:1. Films were formed by condensation and cross-linking of alternating layers of orthocarborane and DAB precursors under ultrahigh vacuum (UHV) conditions, allowing precise control of relative DAB and carborane concentrations. This procedure also yielded films of systematically varied DAB/carborane concentration and film thicknesses between 20 Å and 100 Å average thickness, as determined by attenuation of $Cu(2p_{3/2})$ photoemission intensity from the substrate. The films exhibited shifts in the valence band spectra of ~ 0.2 eV to lower binding energies upon cross-linking, indicating a surface photovoltage effect, and the formation of a true *p*-type semiconducting film. The results demonstrate formation of a new semiconducting material based on carborane icosahedra but modified by the addition of an organic species. These data further indicate the potential for the development of a broad range of novel boron carbide-based polymers using carboranes and other organic additives, with film formation by a variety of methods, including photon or electron bombardment, or plasma-enhanced chemical vapor deposition.

4:40pm **EM1-MoA9 Analysis and Application of Hybrid Electronic Structures Formed by Nanoscale Conductive Coatings on Textiles**, ***J.S. Jur**, W. Sweet, C.J. Oldham, G.N. Parsons*, North Carolina State University

Electronic functionalization of complex fibrous systems is of interest for developing new hybrid electronic systems geared toward integrating biological detection and energy harvesting devices in textile materials. Reliable methods to evaluate the electrical properties of these textiles are necessary for future device design and performance improvement. This work investigates conformal, nanoscale coatings of zinc oxide and tungsten produced by atomic layer deposition (ALD) on natural and synthetic fibers structures, resulting in novel hybrid-based electronic structures. A modified 4-probe test method is introduced to evaluate the effective conductivity of these coatings. An applied normal force orthogonal to the current and field direction improves the fiber/fiber contact, resulting in consistent evaluation of the effective conductivity of the coatings across fiber systems and is a unique method of evaluating the mechanical behavior of these coated fiber structures. Optimization of the coatings has resulted in conductivity values as high as 40 S cm^{-1} for zinc oxide coatings (~75 nm) on polypropylene and cotton fiber, as well as 1150 S cm^{-1} for ALD tungsten (~50 nm) on quartz fiber matrices. Device application of these coated fiber matrices are benefited by their "all-fiber" structure, with characteristic high porosity and surface area. For example, a textile-based flow-through metal-insulator-metal capacitors fabricated from tungsten-coated quartz fibers is shown as an application in liquid chemical sensing. The mechanisms related to electron transport in a surface-coated textile fabric and implications on device fabrication and improvement will be discussed.

5:00pm **EM1-MoA10 Quantum Dot Transfer using Patterned Self-Assembled Monolayers**, ***S. Miller**, A.J. Muscat*, University of Arizona

Nano particles such as light emitting quantum dots offer many exiting new possibilities for device manufacturing. Along with the potential for low cost manufacturing, the ability to make quantum dot based solar cells and LEDs, has lead to the potential to make arrays of light detectors and nanometer scale patterned LEDs. Using two such devices together results in an optical switch, which may be employed in computer processing as a fast memory readout device. In addition ROM memories can be created using direct patterning of light emitting quantum dots on a disk. Because quantum dots of different size emit different wavelengths it is possible to code data in several wavelengths allowing the data from each wavelength to be written in the size limited area of focused light, dramatically increasing data storage. Many of the potential devices which can be made using nano particles require precise control over nano particle placement and layer thickness. We have found that it is possible to control quantum dot placement using a patterned self-assembled monolayer (SAM). Due to the hydrophobic properties of octadecyltrichlorosilane (OTS) it is possible to form an OTS SAM on which quantum dots will not deposit. This SAM layer can then be patterned using one of several methods. One approach is to use direct UV light exposure in air through a shadow mask, this will remove the OTS SAM in the open areas of the mask, allowing for quantum dot deposition to occur only in the open areas. OTS SAMs can also be formed on pre-made chemical patterns. Ultra high resolution patterns can be formed using nano-lithography including conductive atomic force microscopy, STM, and EBL. Arrays of conductive atomic force microscope tips can be used to pattern repeated patterns such as those required for detectors. Quantum dots or an alternate SAM can then be deposited directly into the open pattern areas. However, because of the time required for nano-lithography, it is desirable to use the patterned OTS SAM as a nano particle master stamp, where the quantum dots are transferred from the patterned OTS surface to a surface which chemically binds them. A self-assembled monolayer such as APTMS can be used to bind the quantum dots and remove them from the master patterned stamp, allowing the patterned OTS SAM to be repeatedly filled with quantum dots and stamped. This has been demonstrated using CdTe quantum dots with TGA ligands; however, there are a variety of nano particles with which this technique will work. Therefore by creating a patterned SAM and utilizing selective deposition and appropriate transfer chemistry it is possible to open a new realm of potential device manufacturing.

5:20pm **EM1-MoA11 Solution Processed Quantum Dots for Infrared Imaging**, ***J. Lewis**, E.J.D. Klem, C. Gregory, G. Cunningham, D. Temple*, RTI International

While InGaAs-based focal plane arrays (FPAs) provide excellent detectivity and low noise for short wave infrared (SWIR) imaging applications, wider scale adoption of systems capable of working in this spectral range are limited by high costs, limited spectral response, and costly integration with Si readout circuits (ROICs). RTI has demonstrated a novel photodiode technology based on a heterojunction between IR-absorbing, solution-processed PbS colloidal quantum dots (CQD) and C_{60} fullerenes that can overcome these limitations of InGaAs FPAs. We have fabricated devices with quantum efficiencies exceeding 50%, and detectivities greater than

10^{12} Jones, that are competitive with the performance of InGaAs photodiodes. Dark currents of ~2 nA/cm^2 were measured at temperatures compatible with solid state cooling. Additionally, by processing these devices entirely at room temperature we find them to be compatible with monolithic integration onto ROICs, thereby removing any limitation on device size. We will show early efforts towards demonstrating a direct integration of this sensor technology onto a Si ROIC IC and describe a path towards fabricating sensors sensitive from the visible to 1700 nm at a cost comparable to that of CMOS based devices. This combination of high performance, dramatic cost reduction, and multispectral sensitivity is ideally suited to expand the use of SWIR imaging in current applications, as well as to address applications which require a multispectral sensitivity not met by existing technologies.

Electronic Materials and Processing Division
Room: 210 - Session EM2-MoA

Dielectrics for Ultra Dense Memory Devices
Moderator: A.C. Kummel, University of California San Diego

2:00pm **EM2-MoA1 Oxides for Spintronics**, ***K.L. Wang***, *P. Khalili, F. Xiu*, University of California Los Angeles **INVITED**

Mainstream CMOS technology in today's electronics continues to scale down in its feature size. However, power dissipation per unit area and variability post two major issues and challenges for the continuing scaling. Spintronics, as an emerging technology that exploits the intrinsic spin of the carriers, could potentially offer power savings, low variability and improved scalability. In the talk, we will address the importance of functional oxides such as MgO in field controlled spin FET devices and magnetic tunnel junctions.

Toward the realization of spin logic devices, electric-field manipulation of ferromagnetism offers a potential for achieving low power dissipation. The control of collection of spins is critical in accomplishing room - temperature s pin field effect transistors for dilute magnetic semiconductors such as MnxGe1-x. We found that by using high-quality MgO as gate oxide, the ferromagnetism of the quantum dots can be modulated up to 300 K, which opens the possibility to build room-temperature spin FETs.In addition, MgO was also shown to be effective for unpinning Schottky barrier height and improving the spin injection. U sing an epitaxially grown Fe/MgO/n-Ge tunnel junction, we have obtained single crystalline and atomically smooth Fe/MgO on Ge. This high quality Fe/MgO/Ge junction not only passivates the Ge surface states to favor electronic transport, but also leads to an enhanced spin injection efficiency due to the symmetry induced spin filtering property of the MgO. By using this junction, we show electrical spin injection to bulk Ge.

We also studied the effect of MgO tunnel barrier thickness on the spin-transfer torque-induced switching of CoFeB-MgO-CoFeB magnetic tunnel junction (MTJ) devices used for nonvolatile memory. We studied the effect of MgO thickness on the resistance-area product (RA) and tunneling magnetoresistance (TMR) of the structures using both film-level current-in-plane tunneling (CIPT) and device-level electrical transport measurements. The TMR showed a large distribution for RA values lower than 4 Ω-µm2 (corresponding to an MgO thickness ~0.85 nm), while it increased to ~150% for larger RA > 6 Ω-µm2. The results allow for optimization of RA and MgO thickness for low write energy and high-density of magnetoresistive random access memory (MRAM) switched by spin-transfer torque (STT). We obtained switching times < 1 ns and write energies < 0.3 pJ for CoFeB-MgO-CoFeB MTJ devices. We also studied the effect of CoFeB free layer composition and thickness on device performance.

2:40pm **EM2-MoA3 Charge Trap Memories and 3D Approaches**, ***G. Molas***, CEA Leti Minatec Campus, France **INVITED**

Charge Trap Memories and 3D Approaches

The standard planar Floating gate Flash memory has been scaled down over 20 years. However, many critical limitations are appearing (charge loss through the top or bottom dielectrics, cell to cell coupling interference, Random Telegraph Noise, reduction of the number of stored electrons, process induced variability…), making difficult further scaling of the memory device.

In this context, charge-trapping memories, based on the TANOS (TaN-Al_2O_3-Si_3N_4-SiO_2-Si) gate stack, are foreseen as the backbone of future NAND technologies, allowing to reach the 20nm era with planar device structures and to overcome the 1X node when coupled to novel 3D vertical memory architectures. Nevertheless, to face this challenging Flash memory evolution, several process innovations are still required, and an in-depth physical understanding of the gate stack material properties, is needed.

This paper discusses the potentialities and limitations of charge trap memories, and proposes some paths of improvements to fulfil the stringent requirements of future memory generations.

First the engineering of the memory gate stack is investigated. In particular, engineered tunnel dielectrics, alternative charge trapping layers and improved control dielectric stacks are proposed, and their impact on the memory performances and reliability is debated. Experimental results are analyzed by means of models and simulations.

Then in a second part, the integration of charge trap memories in 3D architectures is studied. The various approaches investigated in the literatures are reported, and an original method to process stacked 6nm crystalline nanowires with gate all around SONOS configuration is proposed.

3:40pm **EM2-MoA6 A Survey of Cross Point Phase Change Memory Technologies**, ***D. Kau***, Intel Corporation **INVITED**

This survey reviews the current advances in phase change memory and the integrated selector. Based on memory cell configuration in array, there are 3 basic array types, including 2-termanl cross point array [1-6], 3-terminal NOR array [7, 8], NAND string [9]. Among all the configurations, stackable thin-film cross point memory delivers the densest array, therefore the most compact die size. Combining its attributes in cost, performance and reliability, cross point phase change technologies stimulate potential opportunities in computing memory hierarchy.

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[7] Y.N. Hwang, et.al., Symposium on VLSI Circuits, p173 (2003)

[8] Fabio Pellizzer, *et.al.*, *Symposium on VLSI Technology*, p122, (2006)

[9] Y. Sasago, *et.al.*, *Symposium on VLSI Tech.*, T5B-2 (2011)

4:40pm **EM2-MoA9 Resistive Switching in HfO_2 Metal-Insulator-Metal Devices (RRAM)**, ***M. Bonvalot***, Laboratoire des Technologies de la Microélectronique (LTM), France, *C. Mannequin, P. Gonon, C. Vallee*, LTM-CNRS, France, *V. Jousseaume, H. Grampeix*, Minatec, France

HfO_2 is attracting interest as a high-k dielectric for several applications in microelectronics, including transistor and Flash memory gate stacks, as well as Metal-Insulator-Metal (MIM) capacitors for DRAMs and rf circuits. As such, the assessment of HfO_2 reliability is of special importance.

In this work we investigate resistive switching of HfO_2-based devices. The HfO_2 thin films (10 and 20 nm thick) are deposited by the Atomic Layer Deposition (ALD) technique on TiN/Si or Pt/Si wafers (bottom electrode) and top Au electrodes. The MIM devices are subjected to a constant dc voltage stress (CVS) and the current is monitored as a function of time. During these experiments we observe transient leakage currents, followed by a progressive increase of conductivity. Phenomena are related to oxygen vacancy defects. Upon bias application oxygen vacancies drift (space charge limited transient currents) to form conducting filaments (leakage increase) through the HfO_2 thickness. Influence of the electrode is discussed since we found oxygen vacancies in MIM devices to be strongly correlated to the metal oxygen affinity [1]. Identical results have been recently found for TiO_2 RRAM devices [2].

We also proposed to modify the oxygen vacancies and study their effects on the RRAM electrical properties by applying post deposition plasma treatment. Different hydrogen-based (NH_3 and H_2) plasma annealing treatments of the HfO_2 dielectric are carried out in order to study the influence of the oxygen vacancies or defects on the subsequent switching behaviour before the deposition of the top electrode. The RRAM devices are then electrically and physically characterized. I(V) curves are then recorded and switching parameters such the SET voltage are compared for devices with and without plasma treatment. The modifications of switching properties are correlated to chemical analysis results, mainly Angle-resolved X-ray Photoelectron Spectroscopy, Attenuated Total Reflexion (ATR) and Spectroscopic Ellipsometry (SE) up to 8 eV, with special attention devoted to metal/oxide interface investigations.

[1] C. Vallée *et al*, Appl. Phys. Lett. **96** (2010) 233504

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Energy Frontiers Focus Topic
Room: 103 - Session EN+EM+NS-MoA

Nanostructured Materials for Third Generation Solar Cells
Moderator: W.A. Tisdale, Massachusetts Institute of Technology

2:00pm **EN+EM+NS-MoA1 Fabrication of Two-dimensional Array of Sub-10nm GaAs Nanodisk using Bio-template Neutral Beam Etching Process**, ***S.-H. Lin**, X.-Y. Wang, C.-H. Huang, Y. Ohno, M. Iagarashi,* Tohoku University, Japan*, A. Murayama,* Hokkaido University, Japan*, S. Samukawa*, Tohoku University, Japan

Recently, 3-dimensional (3D) or 2-dimensional (2D) quantum dot superlattice are widely investigated to develop the new generation devices, such as quantum dot solar cell. Quantum dot superlattice consists of quantum dots with lower band gap energy in the matrix with higher band gap energy. For the device application, the structure requires high QD density, periodic QD array and uniform dot size and inter-dot spacing. Molecular beam epitaxy (MBE) and Metal-organic chemical vapor deposition (MOCVD) are two attractive methods among various bottom-up fabrication methods to fabricate quantum dots. However, there is limitation of bottom-up process to control the size, spacing and density of quantum dots. To brealkthrough these peoblems, we have proposed the ultimate top-down process by combination of bio-template and damage-free neutral beam etching (NBE) for fabricating defect-free 2D array of quantum dots.

In this study, we developed a series of novel process for fabricating uniform size and high density 2D array of GaAs nanodisk with unform inter-dot-spacing. Firstly, the hydrogen-radical treatment was used to remove the native oxide on GaAs surface. To utilize two-dimensional array of ferritin (protein including 7-nm-diameter iron core) as an etching mask, the formation of a hydrophilic 1-nm thick GaAs neutral beam oxidation film is key point. It is found that protein shell can be removed with oxygen-radical treatment at a low temperature of 280oC without thermal damage to GaAs. After protein shell removal, the iron oxide cores inside the ferritins remained on the surface. Then, using the iron core as an etching mask, neutral beam could etch the defect-free nanodisc structure of GaAs. Finally, we developed that iron oxide core was removed by wet etching with diluted hydrogen chloride and completed a fabrication process without inflicting any damage to GaAs. The result shows the quantum dot superlattice structure with a two-dimensional array of GaAs quantum dots with a diameter of ~7-nm, a height of ~10-nm, and a quantum dot density of more than $7\times10^{11}cm^{-2}$ was successfully demonstrated without any damage to GaAs.

This work is supported by the Core Research of Evolutional Science and Technology (CREST) of Japan Science and Technology Agency (JST).

2:40pm **EN+EM+NS-MoA3 Solution Processed Quantum Dots for Low Cost Photovoltaics**, ***E.J.D. Klem**, J. Lewis, C. Gregory, G. Cunningham, D. Temple*, RTI International **INVITED**

For solar energy to be a significant component of our energy supply new technologies are needed that enable the fabrication of low cost, high efficiency solar cells. Research into solar energy devices which incorporate carbon fullerenes and semiconducting polymers represent one such technology. One factor limiting their further advance is their lack of absorption in the infrared (IR). As half the sun's energy lies beyond 700 nm and one third beyond 1000 nm, low-cost device technologies are needed which capture this lost infrared potential. An additional factor limiting the further advance of these devices is the relatively poor electrical transport properties of most semiconducting polymers.

The use of solution processed quantum dots provides a potential route towards overcoming both of these limitations. Solution processed quantum dots can be tuned to absorb light well into the infrared, and quantum dot composite thin films have been shown to have charge carrier mobilities approaching that of amorphous silicon.

In this presentation we will present a brief overview of colloidal quantum dots and the field of quantum dot photovoltaics. We will discuss a range of device architectures and material systems that have been explored experimentally. This includes quantum dot-metal Schottky junctions, quantum dot heterojunctions, and quantum dot-metal oxide junctions.

We will also present a device architecture which is based on the heterojunction formed between infrared-sensitive PbS quantum dots and C_{60} fullerenes. In this device pre- and post-deposition treatments to are used passivate carrier traps and increase the conductivity of the quantum dot films. A device stack is presented that is designed to steer photo-excited charge carriers to the charge-separating interface, reducing recombination pathways and improving carrier extraction efficiency. Under simulated solar illumination the devices exhibit short circuit current densities greater than 20 mA/cm^2, power conversion efficiencies greater than 5%, and spectral sensitivity out to 1500 nm. This represents a significant step towards demonstrating the commercial viability of solution processed quantum dot technology

3:40pm **EN+EM+NS-MoA6 Role of Quantized and Mid-Gap States in "Dark" Charge Transport and Photoconductivity in Semiconductor Nanocrystal Films**, ***P. Nagpal***, Los Alamos National Laboratory

Colloidal semiconductor nanocrystals (NCs) have attracted significant interest for applications in solution-processable devices such as light-emitting diodes and solar cells. However, poor understanding of charge transport in NC assemblies, specifically the relation between electrical conductance in dark and under light illumination, hinders their technological applicability. Here, we simultaneously address the issues of "dark" transport and photoconductivity in films of PbS NCs by incorporating them into optical field-effect transistors (OFETs), in which the channel conductance is controlled by both gate voltage and incident radiation. Spectrally resolved photoresponses of OFETs reveal a weakly conductive mid-gap band (MGB) which is responsible for charge transport in dark. The mechanism for conductance, however, changes under illumination when it becomes dominated by band-edge quantized states. In this case, the MGB still plays an important role as its occupancy (tuned by the gate voltage) controls the dynamics of band-edge charges. Our study has broad implications for NC-based electronics and optoelectronics, and specifically, suggests that design guidelines for NC devices might be different depending on whether they are intended for operation in dark (diodes and transistors) or under illumination (photodetectors and solar cells).

4:00pm **EN+EM+NS-MoA7 Using Surface Chemistry to Modulate the Bandgap of Ge Nanowires**, ***S. Sivaram**, M.A. Filler*, Georgia Institute of Technology

Small-diameter semiconductor nanowires are highly attractive building blocks for next generation photovoltaic devices because they exhibit highly tunable optoelectronic properties as a result of quantum confinement. Bottom up approaches, such as the vapor-liquid-solid (VLS) growth mechanism, are controllable down to ~20 nanometers but significant challenges exist at smaller length scales where property tuning is maximized. Furthermore, it is expected that the optoelectronic properties of quantum-confined nanowires will be heavily dependent on surface chemistry, yet there are no experimental studies that fundamentally probe this relationship. Germanium is an ideal system to study because of its large Bohr exciton radius, low rate of oxidation, and chemical similarity to silicon. In this work we controllably synthesize germanium nanowires with diameters from 5 to 20 nanometers using gold catalyst particles with a narrow size distribution. To obtain epitaxial Ge nanowires with uniform diameters and lengths, a two-step growth process is employed that includes a brief, high-temperature nucleation (390°C) above the Au-Ge eutectic point, followed by elongation at various process conditions, generally below the eutectic point (280 – 340°C, $1x10^{-7}$ – $1x10^{-4}$ Torr). To limit catalyst diffusion and formation of the $\sqrt{3}$ x $\sqrt{3}$ Au/Si reconstruction on the Si(111) surface, a key problem for controllable sub-20 nm growth, the substrate is passivated with -CH_3 groups prior to nanowire synthesis by introducing small quantities of methylgermane. Nanowire surface chemistry is probed with *in-situ* transmission infrared (IR) spectroscopy both during and after growth. We introduced different adsorbates (-H and -CH_3) and monitored their influence on the band gap as a function of surface coverage. We show that the band gap of Ge nanowires blue shifts with H passivation and red shifts with CH_3 termination.

4:20pm **EN+EM+NS-MoA8 Production of Multi-milligram Yields of Ternary II-VI Semiconductor Nanocrystals Under Non-coordinating Amine Activated Synthesis**, ***M. Plaisant**, P.H. Holloway*, University of Florida

Thermolysis of Zn and Cd precursors under a non-coordinating one-pot wet-chemical synthesis has successfully produced a heterogeneous ternary $Cd_xZn_{1-x}Se$ alloy with an extensive spectral red shift of 200nm in the visible range. Large yields of twenty milligram of the $Cd_xZn_{1-x}Se$ alloy are minimally required for inclusion of the material in the active layer of an inorganic/organic photovoltaic device. The facile synthesis of such large yields of ternary semiconductor nanocrystal alloys has not commonly been reported in the literature. Herein we discuss first the thermolytic synthesis of the material beginning from the ZnSe core through the inclusion of the Cd-precursor. We then discuss the production of the ternary II-VI semiconductor $Cd_xZn_{1-x}Se$ material through a process of non-coordinating

synthesis with amine-activation to produce the high multi-milligram yields required for device inclusion.

4:40pm **EN+EM+NS-MoA9 Type-II ZnTe/ZnSe Quantum Dots for Intermediate Band Solar Energy Conversion**, ***C. Chen***, *B. Juang, J. Hwang, S. Kim, X. Pan, J. Phillips*, University of Michigan

Intermediate band solar cells and impurity photovoltaics have been proposed to achieve high efficiency solar energy conversion by introducing electronic states within the bandgap of the host material. The intermediate electronic states provide enhanced photocurrent through the addition of sub-bandgap optical transitions while maintaining a voltage that follows the host material. Approaches to realize these solar cells include the incorporation of dopants/impurities, dilute alloys, and nanostructures such as quantum dots. Self-assembled quantum dots such as InAs/GaAs possess excellent optical properties and have been applied to numerous optoelectronic devices including demonstration of the intermediate band solar cell concept. The highly radiative transitions in these type-I materials result in short radiative carrier lifetimes – a feature that is desirable for light emitters, but can be problematic for photodetectors and solar cells. Semiconductor nanostructures with type-II band alignment result in spatially separated electron and hole wavefunctions, resulting in reduced oscillator strength and corresponding reduction in optical absorption, spontaneous radiative recombination rate, and increased radiative carrier lifetime. The tradeoff between carrier lifetime and optical absorption may be effectively used to provide a closer match to the generation-recombination rates desired for intermediate band solar energy conversion. In this work, ZnTe/ZnSe type-II quantum dots are proposed for intermediate band solar energy conversion. The theory of intermediate band solar energy conversion in this material system will be presented along with initial experimental results on the epitaxial growth, structural properties, and optoelectronic response of the materials. The ZnTe/ZnSe quantum dots were grown by molecular beam epitaxy, where three-dimensional island formation is observed via strained layer growth in the Stranski-Krastanow growth mode. Low temperature photoluminescence spectra reveal optical transitions from ZnSe (2.8eV), Te_{Se} isoelectronic centers (2.6eV), and broad emission in the range of 2.0-2.4eV attributed to type-II quantum dots.

Electronic Materials and Processing Division
Room: 210 - Session EM+TF-TuM

High-k Dielectrics for MOSFETs Part 1
Moderator: R.M. Wallace, University of Texas at Dallas

8:20am **EM+TF-TuM2 *In Situ* TMA Pre-Treatment Study of GaAs and $In_{0.53}Ga_{0.47}As$ Surfaces**, ***B. Brennan***, *D.M. Zhernokletov, H. Dong, R.V. Galatage, J. Kim, E.M. Vogel, R.M. Wallace*, University of Texas at Dallas

One of the major issues preventing the integration of high mobility III-V semiconductors into next generation CMOS devices is the formation of high levels of interfacial defects at the high-k/III-V interface. These can have the effect of pinning the Fermi level and preventing optimal operation of the devices. Engineering the interface between these materials therefore becomes of critical importance to try and reduce the defect density. Identification of the individual defects however is not a trivial matter with correlation between electrical data and physical measurement techniques rarely seen. This study aims to investigate the effect of *in-situ* chemical treatments prior to Al2O3 deposition on (NH4)2S treated GaAs and InGaAs surfaces, in terms of both physical characterization by X-ray photoelectron spectroscopy (XPS) and electrical measurements from MOS capacitors.

The reduction of interfacial oxides through a "clean up" effect by a ligand exchange mechanism with the tri-methyl aluminum (TMA) precursor for atomic layer deposition (ALD) of Al2O3 is well known, [1,2] however little work has been carried out to optimize this process and determine whether variations in the effect are seen as a result of changes in the number of TMA cycles or pulse time prior to oxide deposition. Variations in the presence of arsenic surface features, (i.e. As-As bonding or surface dimers) come under particular focus.The effect of post deposition annealing is also investigated specifically in terms of the potential role hydrogen could play in passivating defects at the interface. [3]

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[2] B. Brennan, M. Milojevic, H.C. Kim H.C, P.K. Hurley, J. Kim, G. Hughes, R.M. Wallace, Electrochem. Solid-State Lett., 12, 6, (2009)

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8:40am **EM+TF-TuM3 Half-cycle Atomic Layer Deposition Studies of HfO_2 on the GaSb(001) Surface**, ***D.M. Zhernokletov***, *H. Dong, B. Brennan, J. Kim, R.M. Wallace*, University of Texas at Dallas

Since GaSb(001) is a candidate surface channel material for p-MOSFET and an interfacial passivation layer for buried channel quantum well and tunneling FETs (GaSb static dielectric constant of ~ 16), it is necessary to understand its interface with high-κ dielectric materials which would act as gate dielectrics in these devices[1]. An *in-situ* half-cycle atomic layer deposition/X-ray photoelectron spectroscopy (ALD/XPS) study is conducted in order to investigate the evolution of the HfO_2 dielectric interface with the GaSb(001) surface after sulfur passivation procedures and HCl etching designed to removed the native oxides. Monochromatic XPS is used to examine the surfaces following the various surface treatments and then without breaking vacuum, after each individual ALD pulse of tetrakis-dimethyl-amino-hafnium (TDMA-Hf) and deionized water (DIW) precursors (i.e. single TDMA-Hf pulse/XPS scan; single DIW/XPS scan; etc.) for two full cycles and finally after 1 nm of HfO_2 deposition to determine whether there is any "clean up" effect of the native oxides due to the ALD process. The various surface preparation techniques are compared to determine which is more effective at minimizing native oxides. The behavior of the sulfides and the effect of HCl surface cleaning procedure upon HfO_2 deposition are discussed as well as a comparison to previous results from half cycle Al_2O_3 deposition on GaSb [2]. This work is supported by the Semiconductor Research Corporation FCRP MSD Focus Center, the Nanoelectronics Research Initiative and the National Institute of Standards and Technology through the Midwest Institute for Nanoelectronics Discovery (MIND). and the NSF (ECCS-0925844).

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[2] S. McDonnell, D. M. Zhernokletov, A. P. Kirk, J. Kim, and R. M. Wallace. Applied Surface Science Letters, submitted (2011).

9:00am **EM+TF-TuM4 Remote Phonon and Surface Roughness Limited Universal Electron Mobility of $In_{0.53}Ga_{0.47}As$ Surface Channel MOSFETs**, ***E.M. Vogel***, *A.M. Sonnet, R.V. Galatage*, University of Texas at Dallas, *P.K. Hurley, E. Pelucchi, K. Thomas, A. Gocalinska*, Tyndall National Institute, *J. Huang, N. Goel, G. Bersuker*, SEMATECH, *W.P. Kirk, C.L. Hinkle*, University of Texas at Dallas **INVITED**

The inversion layer electron mobility in n-channel In0.53Ga0.47As MOSFET's with HfO2 gate dielectric with several substrate impurity concentrations (~1×1016 cm-3 to ~1×1018 cm-3) and various surface preparations (HF surface clean, (NH4)2S surface clean and PECVD a-Si interlayer with a HfO2 gate dielectric) have been studied. The peak electron mobility is observed to be strongly dependent on the surface preparation, but the high field mobility is observed to be almost independent of the surface preparation. A detailed analysis of the effective mobility as a function of electric field, substrate doping, and temperature was used to determine the various mobility components (surface roughness, phonon, and coulombic scattering limited mobility components). For the substrates with high doping concentration, the electron mobility at low vertical electric field is dominated by Coulomb scattering from the substrate dopants, whereas, for lower substrate doping the Coulombic scattering is dominated by the disorder induced gap states. Low temperature measurements were used to determine the surface roughness scattering and phonon components. The results show that room temperature mobility of In0.53Ga0.47As surface channel MOSFETs with HfO2 gate dielectric at high electric field is limited primarily by remote phonons whereas the Al2O3 gate dielectric is limited by surface roughness scattering.

9:40am **EM+TF-TuM6 Structural Characterization of Ultra-thin High-*k* Gate Oxide Films through a Multi-technique Approach**, ***E.J. Bersch***, *J.D. LaRose, I.B. Wells*, University at Albany, *S.P. Consiglio, R.D. Clark, K.N. Tapily, G.J. Leusink*, TEL Technology Center, America, LLC, *A.C. Diebold*, University at Albany

High-*k* HfO_2-based gate oxides have recently been put into production in CMOS-based integrated circuits, and their future use in this capacity depends on how well they can continue to be downscaled. To this end, efforts to increase the dielectric constant (*k*) of HfO_2-based gate oxides are ongoing. Recent work has shown that by tailoring annealing procedures, *k* values for HfO_2 films of greater than 30 have been obtained.[1] These higher *k* values for HfO_2 occur for the metastable tetragonal and cubic crystalline phases, while the thermodynamically preferred monoclinic phase has a lower *k* value (~20). To evaluate the crystalline structure of ultra-thin (< 100 Å) HfO_2 films which have undergone various annealing treatments, we used several techniques, including grazing incidence in-plnae X-ray diffraction (GIIXRD), X-ray and UV photoemission spectroscopy (XPS and UPS, respectively) and spectroscopic ellipsometry (SE). GIIXRD measurements showed that ~60 Å HfO_2 films grown with a sequence of depositions and anneals (so-called DADA process[2]) were monoclinic, while those which were post deposition annealed (PDA) were in a mixture of monoclinic and either tetragonal or orthorhombic phases. Pole figure measurements of these films showed that the DADA film had a monoclinic (-111) fiber texture, while the PDA film was randomly oriented. For HfO_2 films with thicknesses of ~25 Å, GIIXRD measurements showed that DADA films were tetragonal or orthorhombic, while PDA films were also tetragonal or orthorhombic, but also possibly with a monoclinic component. XPS and UPS measurements of the valence bands of HfO_2 films were found to be useful in distinguishing between crystalline and non-crystalline films, but were not useful in distinguishing between crystalline phases.[3] SE has been shown to be useful in indentifying crystallinity in HfO_2 through a feature that appears in the HfO_2 extinction coefficient curve at the absorption edge. We have observed this absorption edge feature for films that were crystalline and strongly monoclinic, but not for films that were only weakly crystalline or mostly non-monoclinic, in keeping with previous work.[4]

References:

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10:40am **EM+TF-TuM9 Research Advances on III-V and Ge MOS/MOSFETs Beyond Si CMOS**, *T.D. Lin, M.L. Huang, Y.C. Chang, W.C. Lee,* National Tsing Hua University, Taiwan, Republic of China*, T.W. Pi,* National Synchrotron Radiation Research Center, Taiwan, Republic of China*, J. Kwo,* National Tsing Hua Univ. and National Taiwan Univ., Taiwan, Republic of China*, **M. Hong***, National Tsing Hua University, Taiwan, Republic of China **INVITED**

Metal-oxide-semiconductor (MOS) and MOS field-effect-transistors (MOSFETs) of high k dielectrics on high carrier mobility channels of InGaAs and Ge have been feverishly studied, as they are now strongly considered for technologies beyond Si complementary MOS (CMOS) integrated circuits (ICs). The post Si CMOS research is now facing unprecedented challenges in materials and physics, as key material/electrical/processing issues have to be met/solved in order to realize the new advanced devices; these include equivalent oxide thickness (EOT) < 1 nm, interfacial density of state (Dit) ≤ 1011 eV-1cm-2, high-temperature thermal stability for self-aligned process, low parasitic, and integration with Si. Using *in-situ* ultra high vacuum (UHV) and *in-situ/ex-situ* atomic layer deposited (ALD) high k's of Ga2O3(Gd2O3), Al2O3, and HfO2 on InGaAs and Ge, this research group has made advances in achieving an EOT of 0.5 nm, Dit of low 1011 eV-1cm-2(with a flat distribution versus energy within the semiconductor bandgap), and high-temperature stability of the MOS structures (rapid thermal annealing to 800-900°C and 500-600°C for the high k's/InGaAs and /Ge, respectively). Atomic manipulation to perfecting the high k's/InGaAs and /Ge interfaces is the key for the above achievements. Probing of the interfaces and gaining insightful understanding of the electronic properties was made possible using our uniquely designed experiments of *in-situ* synchrotron radiation photoemission. High-performance self-aligned inversion-channel high k's/InGaAs MOSFETs in achieving record-high drain currents and transconductances, and record-low sub-threshold swings, and high k's/Ge MOSFETs without employing interfacial passivation layers will also be discussed.

11:20am **EM+TF-TuM11 SiO_2 Interlayer Thickness Dependence of the Density and Polarity of Charges in $Si/SiO_2/Al_2O_3$ stacks**, ***N.M. Terlinden***, *G. Dingemans, M.M. Mandoc, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

In this contribution, we investigate the influence of the SiO_2 thickness on the *density* and *polarity* of built-in charges in SiO_2/Al_2O_3 stacks deposited on Si(100). Such charges lead to the development of a space-charge region (SCR) in the Si at the dielectric interface, having consequences such as flat band voltage shifts in MOS devices and electric-field induced passivation in optoelectronic devices like solar cells. We have employed the nonlinear optical technique of second-harmonic generation (SHG) to probe the Si(100) SCR electric field through the effect of electric-field-induced SHG (EFISH). Using this non-intrusive and contactless technique we found previously that the built-in charge density at the SiO_2/Al_2O_3 interface is independent of the Al_2O_3 thickness down to ~2 nm.[1] Here we report on the influence of the interfacial SiO_x layer, present between the Si(100) substrate and the atomic layer deposited (ALD) Al_2O_3 film, addressing the origin, density, and polarity of the charges. For this reason, we have synthesized SiO_2/Al_2O_3 stacks with intentionally grown SiO_2 interlayers having a thickness in the range ~1.4-150 nm using various deposition methods (e.g. thermal oxidation, PECVD, ALD). Spectroscopic SHG measurements were carried out with a femtosecond pulsed Ti:sapphire laser tunable in the 1.33-1.75 eV photon energy range. From the obtained spectra we found that the charge density is highly influenced when increasing the SiO_2 thickness, dropping from 10^{13} to 10^{11} cm^{-2}, with the polarity switching from negative to positive. These measurements were confirmed by *C-V* measurements and surface voltage measurements employing corona charging of the stacks. On the basis of the observations the mechanism and consequences of charge trapping in $Si/SiO_2/Al_2O_3$ stacks will be addressed.

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11:40am **EM+TF-TuM12 Study of the Interface Barrier of Atomic Layer Deposited (ALD) Al_2O_3 on GaN**, *M. Esposto, S. Krishnamoorthy, D.N. Nath, S. Bajaj, S. Rajan,* ***T.-H. Hung***, Ohio State University

We report on the deposition and energy band diagram analysis of high-quality low-leakage Al_2O_3/GaN using atomic layer deposition. As GaN-based transistors are scaled to achieve higher frequency operation, atomic layer deposition techniques offer a promising way to achieve low leakage while scaling gate-to-channel distance. In addition, applications of GaN in power switching systems require ultra-low leakage that can be achieved using metal-insulator-semiconductor (MISHEMT) structures. In this work, we have made quantitative estimates of conduction band offsets and interface charge density.

MIS structures with varying oxide thickness were fabricated on an n+/n-GaN sample grown by RF plasma MBE on low dislocation density Lumilog GaN templates. Three Al_2O_3 layers of nominal 6 nm, 12 nm, and 18 nm were deposited by atomic layer deposition at 300˚C, using trimethylaluminum (TMA) and H_2O as precursors. The pre-deposition treatment of the surface consisted in a 10:1 HF-dip for 15s. All three samples were then annealed at 600˚C in forming gas for 1min. A new ALD deposition procedure was also developed to achieve low leakage in these structures.

A quantitative analysis of the interface barrier of Ni/Al_2O_3/GaN capacitors was carried out to determine conduction band discontinuity, interface fixed charge and pinning effects. The I-V measurements show extremely low current density for thin dielectric films. A quantitative energy band diagram was estimated from capacitance voltage (C-V) measurements by extracting the apparent charge profiles of the MIS capacitors taking into account the spontaneous polarization in GaN and doping. The extracted flat-band voltages were -0.36 V, -1.55 V and -2.73 V for the 6 nm, 12 nm and 18 nm-thick oxide respectively. The hysteresis in the C-V profile for the 6nm-thick capacitor pointed out a D_{it} charge density of approximately $5x10^{11}$ cm^{-2} and higher for the thicker capacitors. This was because the deposition and post deposition annealing conditions were optimized for very thin oxide layers (~ 5-6 nm). A linear relationship between the flat-band voltage and the oxide thickness was experimentally observed, indicating absence of Fermi-level pinning at the Al_2O_3/GaN interface. The conduction band offset at the Al_2O_3/GaN interface was calculated to be 2.66 eV. In addition, we estimate that a non-zero field of approximately 2 MV/cm exists in the oxide under flat band conditions in the semiconductor. This non-zero field is attributed to a fixed charge density at the Al_2O_3/GaN interface of $2.79x10^{13}$ cm^{-2}.

Electron Transport in Low Dimensional Materials Focus Topic
Room: 209 - Session ET+EM+NS+GR-TuM

Electron Behaviors in Nanoelectronics, Interconnect, and Carbon-based Materials
Moderator: J. Wendelken, Oak Ridge National Laboratory, A. Swan, Boston University

8:00am **ET+EM+NS+GR-TuM1 Electron Transport Study of Graphene on SiC Using Scanning Tunneling Potentiometry**, ***K. Clark***, *S. Qin,* Oak Ridge National Laboratory*, G. He,* Carnegie Mellon University*, G. Gu,* The University of Tennessee*, R.M. Feenstra,* Carnegie Mellon University*, A.-P. Li*, Oak Ridge National Laboratory

The unique electronic and transport properties of graphene have helped this material emerge as a perspective graphene based electronic system. Single layers of graphene formed on SiC look to be a promising system for the realization of graphene electronics. To utilize the full potential of graphene on SiC a complete understanding of the physical and electronic properties of this system is needed. This study uses Scanning Tunneling Microscope (STM) images along with scanning tunneling spectroscopy to characterize the sample surface. STM images clearly show the distinction between 1 monolayer (ML) and 2ML regions. The 1ML to 2ML transition is further confirmed by point spectroscopy measurements and spectroscopic mapping across the boundary. Defects, grain boundaries, step edges and other potential scattering centers are thought to play a major role in the electronic properties, especially in transport, along the graphene sheets. Using a low temperature four-probe scanning tunneling microscope, potentiometry measurements are performed on epitaxial graphene grown on 4H-SiC. Potentiometry maps spanning the transition from 1ML to 2ML graphene layers show a contrast change indicating a potential change at this interface. Preliminary results of the transport along this potentially revolutionary new electronic system will be presented. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

8:20am **ET+EM+NS+GR-TuM2 Engineering the Electronic States of CVD Grown Few Layer Graphene by Twisting and Lattice Distortion**, ***M.H. Pan***, Oak Ridge National Laboratory*, X.T. Jia, S. Bhaviripudi,* Massachusetts Institute of Technology*, V. Meunier,* Rensselaer Polytechnic Institute*, M.S. Dresselhaus, J. Kong*, Massachusetts Institute of Technology

Few layer graphene (FLG) can have advantages over single layer graphene because it has a larger current-carrying capacity and the electronic properties are sensitive to more engineerable system parameters. In particular, Hass et al. have demonstrated that orientational disorder is normally present in carbon-face SiC epitaxial FLG samples.[1] Recently both theoretical and experimental studies suggest that strain can be used to engineer graphene electronic states through the creation of a pseudo–

magnetic field. [2] Here we present both scanning tunneling microscopic/spectroscopic (STM/S) studies of chemical vapor deposition grown few layer graphene samples. There indeed exists a twisting between the stacked graphene layers, confirmed by both high-resolution STM images and low temperature spectroscopic measurements. Our results show that, by stretching graphene along three symmetry directions, a strain-induced pseudo magnetic field can lead to the formation of different Charge Density Wave (CDW) states at the top layer of graphene.

[i] Hass, J., Varchon, F., *Phys. Rev. Lett.* **100,** 125504(2008)

[ii] Levy, N. et al., *Science* **329**, 544 (2010).

8:40am **ET+EM+NS+GR-TuM3 Unique One- and Two-Dimensional Phenomena Observed in Carbon Nanotubes and Graphene***,* ***S. Cronin***, University of Southern California **INVITED**

Our ability to fabricate nearly defect-free, suspended carbon nanotubes (CNTs) has enabled us to observe several phenomena never seen before in CNTs, including breakdown of the Born-Oppenheimer approximation[1], mode selective electron-phonon coupling[2], leading to negative differential resistance (NDR) and non-equilibrium phonon populations, and a Mott insulator transition[3]. In this work, Raman spectroscopy is used to measure individual, suspended CNTs under applied gate and bias potentials. Raman spectroscopy of periodic ripple formation in suspended graphene will also be reported. As will be shown, preparing clean, defect-free devices is an essential prerequisite for studying the rich low-dimensional physics of CNTs and graphene.

1. Bushmaker, A.W., Deshpande, V.V., Hsieh, S., Bockrath, M.W., and Cronin, S.B., "Direct Observation of Born-Oppenheimer Approximation Breakdown in Carbon Nanotubes." Nano Letters, 9, 607 (2009).

2. Bushmaker, A.W., Deshpande, V.V., Bockrath, M.W., and Cronin, S.B., "Direct Observation of Mode Selective Electron-Phonon Coupling in Suspended Carbon Nanotubes." Nano Letters, 7, 3618 (2007).

3. Bushmaker, A.W., Deshpande, V.V., Hsieh, S., Bockrath, M.W., and Cronin, S.B., "Large Modulations in the Intensity of Raman-Scattered Light from Pristine Carbon Nanotubes." Physical Review Letters, 103, 067401 (2009).

9:20am **ET+EM+NS+GR-TuM5 Probing Surface Band Conduction through Back-Gated Conductance Measurements on Si Nanomembranes***,* ***W.N. Peng*********, J. Endres, S. Scott, Z. Aksamija, D.E. Savage, I. Knezevic, M.G. Lagally, M. Eriksson*, University of Wisconsin Madison

Silicon-on-insulator substrates provide large-area Si nanomembranes (SiNMs) mechanically supported by bulk handle wafers. Because of the intervening oxides, SiNMs are also electrically isolated from the substrates. The typical membrane thickness is less than a few hundred nanometers. Because they are so thin, SiNMs display interesting transport phenomena influenced by surface effects. Here, we demonstrate a novel method to probe surface transport via conductance measurements on SiNMs. When contacts are placed on the front surface, a current flows between the source and the drain via the membrane body as well as its surface. By utilizing an underlying back gate (the Si handle substrate), the conductance through the membrane can be continuously tuned and made smaller than the surface contribution, enabling experimental determination of the surface conductance. We measure the membrane conductance as a function of both the membrane thickness and the backgate voltage in ultra-high vacuum. In contrast to H-terminated Si surfaces, clean reconstructed Si(001)(2×1) surfaces show a constant-conductance regime when the backgate voltage is varied, and the conductance in this regime does not depend on membranes thickness. We demonstrate that the constant conductance (on the order of 10^{-9} Siemens) stems from an additional conduction channel through the dimer-reconstructed surface π* band. By comparing the experimental results to numerical simulations, the surface band mobility is determined to be in the range 10-50 cm^2/Vs.

Research supported by NSF [UW MRSEC, award DMR-0520527, as well as awards 0937060 (subaward CIF-146) and ECCS-0547415] and DOE

* NSTD Student Award Finalist

9:40am **ET+EM+NS+GR-TuM6 Ferroelectric Field-Effect Transistor Behavior in CdS Nanotetrapods***,* ***S. Qin****,* Oak Ridge National Laboratory*, W. Fu, L. Liu,* Chinese Academy of Sciences*, T.H. Kim,* Oak Ridge National Laboratory*, S.L. Hellstrom,* Stanford University*, W. Wang, W. Liang, X. Bai, E. Wang,* Chinese Academy of Sciences*, A.-P. Li*, Oak Ridge National Laboratory

Complex nanostructures such as branched semiconductor nanotetrapods are promising building blocks for next-generation nanoelectronics. Here we report on the electrical transport properties of individual CdS tetrapods in a field-effect transistor (FET) configuration with a ferroelectric $Ba_{0.7}Sr_{0.3}TiO_3$ film as high-κ, switchable gate dielectric. A cryogenic four-probe scanning tunneling microscopy is used to probe the electrical transport through individual nanotetrapods at different temperatures. A *p*-type field effect is observed at room temperature, owing to the enhanced gate capacitance coupling. And the reversible remnant polarization of the ferroelectric gate dielectric leads to a well-defined nonvolatile memory effect. The field effect is shown to originate from the channel tuning in the arm/core/arm junctions of nanotetrapods. At low temperature (8.5 K), the nanotetrapod devices exhibit a ferroelectric-modulated single-electron transistor behavior. The results illustrate how the characteristics of a ferroelectric such as switchable polarization and high dielectric constant can be exploited to control the functionality of individual 3-dimensional nano-architectures. *Acknowledgement:* The research at the Center for Nanophase Materials Sciences is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy. The research in Beijing is supported by MOST and CAS of China.

10:40am **ET+EM+NS+GR-TuM9 Probing Electron-Electron Correlations in Quantum Dots Using Transport: Quantum Monte Carlo Studies***,* ***H.U. Baranger***, Duke University **INVITED**

Strong electron-electron correlations occur in nanoscale systems in a variety of contexts – when electrons form a crystal at low density, for example, or in correlations between quantum dots. Nanoscale systems introduce in addition an unprecedented level of control over the physical parameters determining such correlations. As electron transport is one of the primary probes of nanosystems, the effect of e-e correlations on transport is a key issue. I shall discuss an example in which we used quantum Monte Carlo (QMC) techniques to calculate the conductance:

Consider a system of four quantum dots designed to study the competition between three types of interactions: Heisenberg, Kondo, and Ising. We find that the competition produces a rich phase diagram containing two sharp features: a quantum phase transition (QPT) between charge-ordered and charge-liquid phases, and a dramatic resonance in the charge liquid visible in the conductance. The conductance is calculated using a world-line QMC method: extrapolation of the imaginary time QMC data to zero frequency yields the linear conductance, which is then compared to numerical renormalization group results in order to assess its accuracy. The QPT is of the Kosterlitz-Thouless type with a discontinuous jump in the conductance at the transition. We connect the sharp resonance phenomenon with the degeneracy of three levels in the isolated quadruple dot and argue that this leads to an emergent symmetry. I shall end by discussing the sensitivity to parameter variation and possible experimental realizations in laterally gated quantum dots as well as carbon nanotubes.

This work was done in collaboration with Dong E. Liu and Shailesh Chandrasekharan (Duke University).

11:20am **ET+EM+NS+GR-TuM11 Resistivity Increase due to Electron Scattering at Surfaces and Grain Boundaries in Metal Thin Films and Nanowires***, J.S. Chawla,* ***D. Gall***, Rensselaer Poltechnic Institute

The effect of surface and grain boundary scattering on the resistivity of Cu thin films and nanowires is quantified using (i) *in situ* transport measurements on single-crystal, atomically smooth Cu(001) layers, (ii) textured Cu(111) layers and patterned Cu wires with independently varying grain size, thickness and line width, and (iii) *in situ* grown interfaces including Cu-Ta, Cu-MgO, Cu-SiO2 and Cu-oxygen. In addition, the electron surface scattering is also measured *in situ* for single-crystal Ag(001) and TiN(001) layers. These findings are important for the development of future generation narrow low-resistivity Cu interconnects and TiN metal gates.

Cu(001), Ag(001), and TiN(001) layers with a minimum continuous thickness of 4, 5 and 1.8 nm, respectively, are grown by ultra-high vacuum magnetron sputter deposition on MgO(001) substrates and are found to be atomically smooth single crystals by a combination of x-ray diffraction θ-2θ scans, ω-rocking curves, pole figures, reciprocal space mapping, Rutherford backscattering, x-ray reflectometry, transmission electron microscopy, and *in-situ* scanning tunneling microscopy. Polycrystalline Cu layers with a 111-texture are deposited on thermally grown SiO2, with and without Ta barrier layer. Subsequent *in-situ* annealing at 350oC followed by sputter

etching in Ar plasma yields Cu layers with independently variable thickness and grain size. Cu nanowires, 50 to 150 mm long, 70 to 350 nm wide, and 45 nm thick, are patterned using electron beam lithography and sputter etching.

In-situ electron transport measurements at room temperature in vacuum and at 77 K in liquid nitrogen for single-crystal Cu and Ag layers is consistent with the Fuchs-Sondheimer (FS) model and indicates specular scattering at the metal-vacuum boundary with an average specularity parameter p = 0.6 and 0.4, respectively. In contrast, layers measured *ex-situ* show completely diffuse surface scattering due to sub-monolayer oxidation. Electron transport measurements for polycrystalline Cu/Ta layers and wires show a ~10% and ~11% decrease in resistivity, respectively, when increasing the average lateral grain size by factor 2. *In-situ* deposition of 0.3 to 8 nm thick Ta barrier layers on Cu(001) leads to a resistance increase that indicates a transition from p = 0.8 to p = 0, independent of the Ta thickness. *In-situ* exposure of Cu(001) layers to O2between 10-3 and 105 Pa-s results in a sequential increase, decrease and increase of electrical resistance which is attributed to specular surface scattering for clean Cu(001) and for surfaces with a complete adsorbed monolayer, but diffuse scattering at partial coverage and after chemical oxidation.

11:40am **ET+EM+NS+GR-TuM12 Control of Contact Formation via Electrodeposition on GaAs Nanowires***, **C. Liu**, O. Einabad, S. Watkins, K.L. Kavanagh*, Simon Fraser University, Canada

Copper (Cu) electrical contacts to as-grown gallium arsenide (GaAs) nanowires have been fabricated via electrodeposition. The nanowires are zincblende (111) oriented grown epitaxially on n-type Si-doped GaAs(111)B

substrates by gold-catalyzed Vapor Liquid Solid (VLS) growth in a metal organic vapour phase epitaxy (MOVPE) reactor. The epitaxial electrodeposition process, based on previous work with bulk GaAs substrates, consists of a substrate oxide pre-etch in dilute ammonium hydroxide carried out prior to galvanostatic electrodeposition in a pure Cu or Fe sulphate aqueous electrolyte at 20C. The conductivity of wires was controlled via the addition of carbon tetrabromide (CBr4) during growth. For nominally undoped GaAs nanowires, we find that Cu or Fe has a preference for growth on the gold catalyst avoiding the sidewalls. After etching the gold, both metals still preferred to grow only on the tops of the nanowire, consistent with the location of the largest electric field. Core-shell GaAs nanowires with highly conductive carbon-doped shells were fabricated via changing the Ga precursors form triethylgallium to trimethylgallium for radial growth. Increasing the conductivity of the nanowires in this way, not surprisingly; meant that Cu nucleation and growth began to occur on the sidewalls as well as on the gold catalyst. Finite element simulations will be compared to our electrodeposition results towards the calibration of nanowire conductivity.

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+EM-TuM

Graphene: Optical Properties, Optoelectonics and Photonics
Moderator: P.E. Sheehan, U.S. Naval Research Laboratory

8:00am **GR+EM-TuM1 Graphene Optoelectronics: From Ultrafast Lasers to Flexible Displays***, **A.C. Ferrari***, University of Cambridge, UK **INVITED**

The richness of optical and electronic properties of graphene attracts enormous interest. So far, the main focus has been on fundamental physics and electronic devices. However, we believe its true potential to be in photonics, plasmonics and optoelectronics, where the combination of its unique optical and electronic properties can be fully exploited, the absence of a bandgap can be beneficial, and the linear dispersion of the Dirac electrons enables ultra-wide-band tenability [1]. The rise of graphene in photonics and optoelectronics is shown by several recent results, ranging from solar cells and light emitting devices, to touch screens, photodetectors and ultrafast lasers. Despite being a single atom thick, graphene can be optically visualized [2]. Its transmittance can be expressed in terms of the fine structure constant [3]. The linear dispersion of the Dirac electrons enables broadband applications. Saturable absorption is observed as a consequence of Pauli blocking [4,5]. Chemical and physical treatments enable luminescence [1,6]. Graphene-polymer composites prepared using wet chemistry [4-6] can be integrated in a fiber laser cavity, to generate ultrafast pulses, down to 100fs with up to 1 W average power, and enable broadband tunability [4,5]. Graphene-based mode-locked laser are a near term application for this extraordinary material, and can provide simple, low-cost, and convenient light sources for metrology, sensing, medicine and micromachining. Graphene is an ideal transparent flexible conductor. A flexible electrically switchable smart window will be reported, with over 230 contrast ratio, as well as an electro-tactile screen for mobile phone applications. The optoelectronic properties of graphene can be enhanced by combination with plasmonic nanostructures [7], for example in plasmonic-enhanced photovoltage generation [8]

1. F. Bonaccorso et al. Nature Photonics 4, 611 (2010)

2. C. Casiraghi et al. Nano Lett. 7, 2711 (2007).

3. R. R. Nair et al. Science 320, 1308 (2008).

4. T. Hasan, et al. Adv. Mat. 21,3874 (2009)

5. Z. Sun et al. ACS Nano 4, 803 (2010); Nano Research 3, 653 (2010)

6. T. Gokus et al. ACS nano 3, 3963 (2009)

7. F. Schedin, *ACS Nano* **4**, 5617 (2010).

8. T.J. Echtermeyer et al, submitted (2011)

9:00am **GR+EM-TuM4 Quantum Mechanics-Based Exploration of Graphene-Like Systems to Model Magnetic Resonators***, X.W. Sha, E.N. Economou, **D.A. Papaconstantopoulos***, George Mason University*, M.R. Pederson, M.J. Mehl,* Naval Research Laboratory*, M. Kafesaki*, University of Crete, Greece

Quasi-circular pieces of graphene as well as nanotubes offer the possibility of acting as magnetic resonators to be used in negative refractive index optical metamaterials. The advantage of these graphene pieces is twofold: (a) they are stable even when their size reaches the tens of nanometers; (b) the induced currents in the presence of an AC magnetic field perpendicular to the graphene plane cancel each other in all the interior hexagons and only an edge circular current remains. This current is expected to be ballistic in nature with almost zero resistance. This analog of the split (in the split ring resonators) is expected to be achieved by the substitutional insertion of foreign atoms (e.g. nitrogen atoms). To explicitly and reliably check these ideas we have used the NRLMOL, a first- principles DFT code, in the presence of an AC magnetic field, to calculate the response of various configurations of quasi-circular pieces of graphene with or without the presence of substitutional foreign atoms. In order to be able to extend our calculations to larger systems, of the order of tens of thousands of atoms, we used the NRL-TB method, in which the TB matrix elements were fitted so as to reproduce the energy levels of our DFT approach. Results for the energy levels, some selected eigenfunctions, and the current distribution for several configurations will be presented and evaluated vis-a-vis the intended use as almost lossless magnetic resonators.

9:20am **GR+EM-TuM5 Infrared Optical Conductance of CVD-grown Graphene***, **J.W. Weber**, M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

The infrared optical conductance of chemical vapour deposited (CVD) graphene is determined from near normal incidence reflection and transmission Fourier transform infrared measurements in the spectral range of 370-7000 cm^{-1}. The real part of the conductance, up to 2500 cm^{-1} , shows both the effect from doping and finite temperature that was shown for exfoliated graphene.[1,2] The conductance for the range 2500-7000 cm^{-1} is increasing from the value for the universal optical conductance ($\pi e^2/2h$) to 1.5 times this value. This could imply that graphene and bilayer graphene have grown in a 1:1 ratio. The graphene is grown via CVD of methane and hydrogen on Cu-foil and transferred to a glass substrate following the procedure of Li *et al*.[3] A three-phase optical model (air/graphene/glass) is used to simultaneously fit the reflection and transmission data and extract the (Kramers-Kronig consistent) optical conductance. The conductance will be used to compare it with the conductance of CVD-graphene that is exposed to a hydrogen plasma.

[1]Mak *et al*. *Phys. Rev. Lett* **101**, 196405 (2008)

[2]Li *et al*. *Nat. Phys*. **4**, 532 (2008)

[3]Li *et al*. *Science* **324**, 1312 (2009)

9:40am **GR+EM-TuM6 Optical Properties of Graphene on MgO and SiC Polytypes Determined by Spectroscopic Ellipsometry***, **A. Boosalis**, T. Hofmann, S. Schoche, P.A. Dowben,* University of Nebraska - Lincoln*, S. Gaddam, C. Vamala, J. Kelber,* University of North Texas*, V. Darakchieva,* Linköping University, Sweden*, D.K. Gaskill,* U.S. Naval Research Laboratory*, M. Schubert*, University of Nebraska - Lincoln

Wafer-scale production of epitaxial graphene has been demonstrated recently. It has been observed, however, that the highest quality graphene is achieved from exfoliation, while epitaxial graphene exhibits less desirable electronic and optical characteristics. Identifying substrate effects on

epitaxial graphene is of paramount contemporary interest for future device production.

We have determined the complex dielectric function of graphene deposited on a number of different substrates using multiple growth techniques. The investigations were performed in the spectral range from 1.5 to 9.5 eV using spectroscopic ellipsometry. The samples studied here include graphene grown on (111) MgO using chemical vapor deposition (CVD) and graphene grown on SiC by sublimation of silicon from the substrate at high temperature. Several different SiC polytypes, including 4H, 3C, and 6H SiC were studied. Distinct differences in the complex dielectric function of graphene are observed as the underlying substrate differs in material composition and polytype. In particular in the spectral region of the exciton absorption peak (4 eV) the complex dielectric function is sensitive to both substrate and growth parameters. We compare our results with those of recent publications of graphene grown by CVD on SiO_2.

10:40am **GR+EM-TuM9 Plasmon Resonance in Individual Nanogap Electrodes Studied Using Graphene Nanoconstrictions as Photodetectors**, ***S.-F. Shi***, Cornell University, *X. Xu,* University of Washington, *P.L. McEuen, D.C. Ralph*, Cornell University

A plasmonic nanostructure can act like an optical antenna, concentrating light into a deep sub-wavelength volume and enabling manipulation of light-electron interactions at the nanometer scale. Achieving efficient coupling from such antennas to functional electrical devices has been challenging, because the region of field enhancement is so small. We achieve direct electrical read out of the wavelength and polarization dependence of the plasmon resonance in individual gold nanogap antennas by positioning a graphene nanoconstriction within the gap as a localized photodetector. The polarization sensitivities can be as large as 99%, while the plasmon-induced photocurrent enhancement is 2-100. The plasmon peak frequency, polarization sensitivity, and photocurrent enhancement all vary between devices, indicating the degree to which the plasmon resonance is sensitive to nanometer-scale irregularities.

11:00am **GR+EM-TuM10 Large Area Graphene Growth for Optoelectronic Applications**, ***C. Edwards***, *C.L. Berrie, J. Liu, J. Wu*, University of Kansas

Graphene shows great promise for numerous applications within the field of optoelectronics due to its high charge mobility, high optical transmittance, chemical inertness, and flexibility. We are focused on developing large-area graphene sheets that sustain or enhance these characteristics currently present in small-area growth. Chemical vapor deposition of graphene onto various copper substrates has been investigated to understand the role of the substrate in graphene epitaxy and its deposition mechanism. With this understanding it will be possible to use the substrate structure to control the density of surface defects, which is high in current methods for large area fabrication. Also, the effect of nanopatterning and doping graphene grown by chemical vapor deposition has been investigated, and observed improvements in light transmittance and electrical conductivity suggest the potential to favorably modify graphene optical and electrical properties for these applications.

11:20am **GR+EM-TuM11 Stable Chemical Doping of Graphene: Transport, Raman Spectroscopy, SEM, and Transmittance Studies**, ***K. Berke***, *S. Tongay, M. Lemaitre, Z. Nasrollahi, D.B. Tanner, B.R. Appleton, A.F. Hebard*, University of Florida

Since becoming experimentally available by mechanical exfoliation, graphene has been used in various devices such as field effect transistors (FETs), Schottky based solar cells and sensing applications. Although graphene based devices with modest characteristics have been reported, in some of the device geometries a lower graphene sheet resistance with different Fermi level values is still desired. To achieve these ends, graphene's physical properties have been adjusted by *n*- or *p*- chemical doping using $AuCl_3$, Br_2, N_2, and organic solutions. However, these techniques have several drawbacks which prevent their use in devices, namely: environmental instabilities, aging effects and a reduction in optical transparency. Here, we describe our use of a hydrophobic organic complex dopant with strong electronegativity, tight bonding, environmental stability and high optical transmittance which is spin cast onto CVD-prepared graphene films. We observe a typical 75% reduction in sheet resistance upon chemical modification of the graphene. Resistance vs. temperature / magnetic field and Hall measurements imply that the modified graphene sheets are doped, and time-dependent resistance measurements show excellent stability. Using a Horiba Micro Raman instrument we confirm the doping of graphene sheets from the shifts in G and 2D peak positions and intensity ratios. We show transmittance and SEM characteristics of the graphene sheets before and after doping. The presented results may serve as a guide for modification of graphene's properties as desired for various applications.

Electronic Materials and Processing Division
Room: 210 - Session EM-TuA

High-k Dielectrics for MOSFETs Part 2
Moderator: A.C. Kummel, University of California San Diego

2:00pm **EM-TuA1 High Mobility Channel Materials and Novel Devices for Scaling of Nanoelectronics beyond the Si Roadmap**, ***M. Heyns***, IMEC, Belgium **INVITED**

The introduction of high-k dielectrics and metal gates in advanced CMOS has opened the door to Ge and III-V compounds as potential replacements for Si to further increase the device performance. Using MOCVD the selective area growth of low-defect InP and InGaAs layers in submicron trenches on Si was demonstrated. These virtual Ge-III/V substrates can be processed in a standard CMOS line. Short channel Ge pMOS devices with high drive currents were fabricated. Strain engineering using GeSn source/drain areas allows to boost the performance of these devices so that they can outperform their strained Si counterparts. One of the key problems in developing III/V devices is the near midgap Fermi level pinning associated with the high density of defect states present at the high-k/III-V interface. The origin of these states is still under debate but there are clear indications that there exists a strong relationship with native antisite point defects. Various sulfide and other treatments were investigated to passivate the surface. The measured distribution of interface states and border traps on typical III/V MOS structures has some special consequences on the electrostatic operation of different transistor designs. Since inversion mode devices do not seem to be the appropriate choice for III/V based logic applications, other device types have been explored. The Implant-Free Quantum Well (IF-QW) device enables VLSI-compatible processing by self-aligned source/drain definition. Strained Implant Free Quantum Well Ge-based pFETs show excellent short channel control and record drive currents. The concept was also used to demonstrate high mobility n-channel InGaAs devices. For III/V pMOS devices GaSb is at present the material of choice. Very encouraging results have been obtained on direct heteroepitaxy of GaSb epilayers on InP(001) combined with *in-situ* deposition of an Al_2O_3 high-κ gate dielectric. The introduction of these advanced materials also allows the development of new device concepts that can fully exploit the properties of these new materials. Tunnel-FETs, where the III/V material may be either introduced only in the source or in the complete device, can provide superior performance at lower power consumption by virtue of their improved subthreshold behavior, allowing to reduce the supply voltages. Vertical surround gate devices can be produced from III/V nanowires directly grown on silicon, allowing the introduction of a wide range of III/V materials and functionalities on Si. This illustrates some of the possibilities that are created by the combination of new materials and devices to allow scaling of nanoelectronics beyond the Si roadmap.

2:40pm **EM-TuA3 Local Profile of the Dielectric Constant Near the Oxygen Vacancy in the GeO_2 Films**, ***J. Nakamura***, *M. Tamura*, The University of Electro-Communications (UEC-Tokyo), Japan

Ge-based metal-oxide-semiconductor (MOS) devices are focused as complementary-MOS devices for the next-generation in the post-Si technology. However, the dielectric properties of GeO_2 gate ultrathin films have not been clarified yet in detail. Our purpose is to clarify the spatial variation of the local dielectric constant for the GeO_2 thin films using first-principles ground-state calculations in external electric fields [1,2]. In particular, we reveal the local profile of the dielectric constant near the oxygen vacancy in the film, focusing on the crystal phase dependence.

We have adopted quartz (0001) and rutile (001) films with/without oxygen vacancies, in which Ge atoms at the topmost surfaces are terminated with H atoms. We have evaluated the optical and the static dielectric constants that are attributed to the electronic polarization and both the lattice and electronic polarizations, respectively.

From the local profile of the dielectric constants for the ideal films, it has been clarified that the dielectric constants change gradually from the surface and approach constant values at the center of the film. Such features have also been confirmed for the Si and SiO_2 films [1,2]. The dielectric constant for the defective model of the quartz film becomes larger locally "at" the oxygen vacancy site compared with that for the ideal model, but at "adjoining" oxygen sites to the vacancy for the rutile film. Such features stem from the difference in the fashion of the chemical bonding between Ge and O atoms: The dielectric constant for the defective quartz model becomes large at the vacancy site where the covalent Ge-Ge bonding is formed. For the rutile, on the other hand, the Ge-O bondings surrounding the vacancy site are softened because of their less ionic character, which results in the larger displacement in external electric fields, leading to the larger lattice polarization around the vacancy.

[1] J. Nakamura *et al*., J. Appl. Phys. 99, 054309 (2006); Appl. Phys. Lett. **89**, 053118 (2006)

[2] S. Wakui *et al.*, J. Vac. Sci. Technol. B **26**, 1579 (2008); ibid 27, 2020 (2009).

3:00pm **EM-TuA4 Two Step Passivation and ALD Monolayer Nucleation on Ge(100)**, ***T. Kaufman-Osborn***, *J.S. Lee, K. Kiantaj, W. Melitz, A.C. Kummel,* University of California San Diego, *A. Delabie, S. Sioncke, M. Caymax, G. Pourtois*, IMEC, Belgium

Germanium is a promising channel material for next generation MOSFET. The best method to passivate Ge(100) is to form a layer of GeO_2, free of Ge suboxides, using high pressure O_2 or O_3. However, there are three challenges: (1) it is difficult to keep a stoichiometric GeO_2 monolayer (ML) at elevated temperatures, (2) the thermal oxidation process creates a rough interface degrading mobility at high field, and (3) scaling the passivation layer to only 1 ML is a challenge. This study presents a process to form a ½ ML of Ge-H and ½ ML of Ge-OH bonds without disrupting the Ge(100) surface. In-situ scanning tunneling microscopy (STM), in-situ scanning tunneling spectroscopy (STS), and in-situ X-ray photoelectron spectroscopy (XPS) were employed to determine the atomic and electronic structure of the passivation monolayer.

Using a differentially-pumped H_2O dosing system, an ordered, flat monolayer of H_2O chemisorption sites on Ge(100) was formed with a low density of unreacted dangling bonds at 300K. STS data showed that the Ge-H and Ge-OH sites removed the bandgap states from the Ge(100) dangling bonds. Annealing the surface between 20°C and 250°C gradually decreased the coverage of H_2O sites. However, even at 300K, the H_2O surface is highly reactive to trimethyl aluminum (TMA) since it contains a half monolayer of Ge–OH which catalyzes the breaking of Al-CH_3 bonds thereby inducing the formation of Al-O bonds, and the Ge-H sites block ALD ligand chemisorptions. STM experiments showed that the H_2O chemisorbed Ge surface provides a half monolayer of nucleation centers with approximately 0.5 nm spacing for TMA dissociative chemisorption at 300K. High resolution XPS experiments indicated that thermally unstable Ge-OH bonds were converted to thermally stable Al-O bonds. Furthermore, passivating the surface with H_2O prior to TMA dosing doubles the aluminum coverage compared to the TMA only dosed Ge(100) surface. The higher nucleation density from the two step functionalization process, TMA + H_2O, should be favorable for pinhole reduction. DFT calculations are consistent with the data showing TMA reaction with either –Ge-H and –Ge-OH is exothermic, but the reaction of TMA on the –Ge-OH site has both a low activation barrier and higher exothermicity (-41.4 kcal/mol) compared to TMA reaction on the –Ge-H site (-10.8 kcal/mol). The calculation is consistent with the key to full monolayer nucleation, the formation of a full monolayer of Ge-OH chemisorption sites, which is being studied with HOOH dosing.

4:00pm **EM-TuA7 Bilayer High-k Gate Stacks on Ge and InGaAs**, ***P.C. McIntyre***, Stanford University **INVITED**

Research on novel channel materials such as Ge and InGaAs for high performance MOSFETs prompts interest in alternative high permittivity gate dielectrics because the thermal stability requirements that led to the adoption of HfO_2-based high-k dielectrics on silicon are relaxed for such channels. We have focused recently on ALD-grown TiO_2/Al_2O_3 bilayer dielectrics that combine large band gap Al_2O_3 interfacial layers (1-2 nm in thickness) with physically thicker but very high k TiO_2 gate dielectrics as a means of scaling gate capacitance and gate leakage current. This bilayer structure relies on the electrical passivity of the Al_2O_3/channel interface to achieve high performance. This presentation will summarize the scaling potential of these bilayer dielectric structures and methods by which low defect density Al_2O_3/Ge and Al_2O_3/InGaAs interfaces can be prepared.

4:40pm **EM-TuA9 Effect of Post Deposition Anneal on the Characteristics of InP MOS Capacitors with High-k Dielectrics**, ***R.V. Galatage***, *B. Brennan, H. Dong, D.M. Zhernokletov, C.L. Hinkle, R.M. Wallace, E.M. Vogel*, The University of Texas at Dallas

Due to high defect density between III-V semiconductors and high-k dielectrics, buried channel structures with InP barrier layers are being considered for CMOS applications1,2. It has been observed that sulfur passivated InP is thermally stable up to ~460° C3. However, little work has been performed to understand the thermal stability of the high-k/InP interface. In this work, the effect of dielectric post deposition anneal (PDA)

on InP MOS capacitors with high-k dielectrics was studied. Temperatures above 450° C result in an increase of the interface trap density.

MOS capacitors were fabricated on both n-type and p-type InP substrates with HfO2 and Al2O3 dielectrics. Room temperature ammonium sulfide was used for surface passivation prior to ALD. Various temperatures ranging from 400° C to 500° C were used for PDA and a control sample without any PDA was used. The surface Fermi level is severely pinned for the p-InP substrate4 and the device does not go into accumulation. This behavior is not observed for the n-InP substrate. Room temperature C-V characteristics for HfO2/n-InP devices show increased interface trap response for the samples with PDA above 450° C. However, low temperature (77 K) C-V measurements show that the samples with PDA have similar *equivalent oxide thickness (*EOT) and their interface trap response can be compared directly. A semi quasi-static method is used to calculate the Dit distribution across the InP band gap. Details of the technique will be presented. The Dit distribution shows a peak located at mid gap for all of the samples which increases with increasing temperature. A similar trend is observed for Al2O3/InP MOS capacitors. Correlation of these results to X-ray photoelectron spectroscopy (XPS) analysis will be presented.

This work is sponsored by SRC FCRP MARCO Materials Structures and Devices Center and the National Science Foundation.

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5:00pm **EM-TuA10 ALD Half Cycle Study of HfO_2 on InP by *In Situ* XPS***, **H. Dong**, D.M. Zhernokletov, B. Brennan, J. Kim, R.M. Wallace*, University of Texas at Dallas

InP attracts significant attention as a high mobility channel material for Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs)-with many excellent electrical measurements reported on InP based devices. It is well known that one of the electrical limitations of surface channel III-V MOSFETs comes from the interface defects generated from surface/interface oxidation between high-k dielectrics and III-V materials, which can cause Fermi level pinning [1]. InP is also considered as a potential buffer layer material for quantum well FETs, which is in direct contact with a gate dielectric [2]. To examine the interfacial chemistry for high-k/InP, we present a half cycle Atomic Layer Deposition (ALD) study on native oxide and wet chemically treated InP (100) samples with Hf (TDMA-Hf precursor) and water by *in-situ* monochromatic X-ray photoelectron spectroscopy (XPS). The "clean up" effect is examined and compared to the results for ALD Al2O3 on InP. The significant reduction of interfacial oxides by pre-ALD wet chemical treatments and the detailed growth rate of HfO2 on various samples are also discussed.

This work is supported by the FCRP MSD Focus Center and NSF (ECCS-0925844).

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5:20pm **EM-TuA11 Nonvolatile Memresistive Nano-Crossbar Switches in Pt/Ta2O5/Cu Solid Electrolytes**, ***P.R. Shrestha**, K.P. Cheung,* National Institute of Standards and Technology (NIST)*, H. Baumgart*, Old Dominion University

Metal filament resistive memory is an excellent candidate for a nanoscale crossbar switch, and such two terminal "memresistive" devices are being considered for next-generation non-volatile memory due to the inherent simplicity, scalability and low cost (1). Additionally, these devices show potential to replace static random access memory (SRAM) as high performance switches for reconfigurable devices .

Memresistive devices operate by changing resistance from high (Roff) to low (Ron) values in response to an applied voltage. Despite a tremendous amount of work in the scientific literature, the actual underlying switching mechanism has yet to be fully explained. Few studies, most of which lack measurement details, have reported on the transient current response and high speed switching characteristics of memresistive devices. The papers suggest the presence of the variety of active current and thermal dissolution of the low resistance filament while switching OFF. The switching ON has been attributed to the movement of the metal ions towards the cathode and being neutralized by the electrons to form the metal filament. Transient current measurements for switching ON have not yet been analyzed in detail in the literature. Another crucial problem in measurements of these devices is due to the preferred values of Ron(<1kΩ) and Roff(>1GΩ). Thus the key obstacle preventing fundamental understanding has been the lack of reliable and accurate measurements of the transient response while switching ON (from Roff to Ron). In this work, we developed a new measurement capability that enables reliable and accurate investigation of the transient switching response, monitoring change from low Ron to high Roff.

In order to address the need to reliably and accurately monitor the device I-V transient response extremely fast, we have designed an amplifier with low-gain and high bandwidth (1.7 GHz) to accommodate much faster (and realistic) "program" voltage pulses. For switching purposes, this amplifier allows for fast transient current monitoring during programming with proficiency but not limited to follow 2 nsec of pulse rise time. The high gain bandwidth of the amplifier allows us to monitor change from low current (Roff) to high current (Ron) accurately.

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5:40pm **EM-TuA12 Metrology for Interfaces and Mass Transport in C-MOS Related Nanofilms***, A. Herrera-Gomez,* ***A. Sanchez-Martinez****, O. Ceballos-Sanchez, M.O. Vazquez-Lepe,* CINVESTAV-Unidad Queretaro, Mexico*, P. Lysaght*, SEMATECH

Interface layers play a fundamental role in determining the electrical properties of CMOS devices because their thicknesses are of a magnitude comparable to that of the dielectric layers currently employed. The main (top) techniques traditionally used for characterizing the chemical depth profile of MOS structures have been XPS-Sputter and Back-Side TOF-SIMS. However, they lack the appropriate resolution to characterize the thickness and composition of nano or sub-nano layers. Due to the lack of appropriate metrology methods, the structure of interface layers is usually assessed indirectly through their effect on the device's capacitance. Another important issue in the processing of MOS devices is the diffusion control of chemical species. To quantify or to simply observe displacements on the order of 2 or 3 nm of low concentration elements with those techniques *is close to impossible*. The semiconductor industry will greatly benefit from a metrology method capable of: (a) characterizing the thickness and composition of the various layers constituting a MOS device, including the interface layers; (b) assessing the effect of process driven diffusion of various critical chemical species present in the film. There is a growing consensus that X-Ray Photoelectron Spectroscopy (XPS), specifically Angle-Resolved XPS (ARXPS), has the appropriate chemical and depth resolution for assessing the depth profile of films between 0 and 8 nm. The precise methodology for applying the technique, however, varies wildly among different groups. In many cases the analysis algorithms of ARXPS data are highly susceptible to noise. Because of this, ARXPS is frequently regarded as qualitative techniques. In this talk we briefly describe a robust ARXPS analysis methodology that *minimizes* the sensitivity to noise. This methodology has been successfully applied to characterize various systems. One example that will be addressed regards the failure mechanism for the degradation of the electrical performance of TiN/HfO2/InGaAs devices during thermal processing. We investigated the change on the structure caused by annealing, such as the possible formation of As, Ga or In oxides, accumulation of these elements in the dielectric, formation of metallic arsenic, and/or any other change on the structure that could be correlated to device degradation. ARXPS experiments were performed on those samples and analyzed using the robust methodology. One important finding was that indium diffuses through the dielectric all the way into the metallic layer upon annealing.

Graphene and Related Materials Focus Topic
Room: 209 - Session GR-TuA

Graphene on Dielectrics, Graphene Transfer to Novel Substrates

Moderator: A. Turchanin, University of Bielefeld, Germany

2:20pm **GR-TuA2 A Scanning Tunneling Microscopy and Spectroscopy Study of Artificially Modified Bilayer Graphene***, **H. Baek**, J. Ha, B. Hwang, J. Kwon,* Seoul National University, Republic of Korea*, J.A. Stroscio,* National Institute of Standards and Technology*, Y. Kuk*, Seoul National University, Republic of Korea

Bilayer graphene has drawn considerable attention due to deviation from Dirac Fermion picture such as anomalous quantum hall effect and a tunable band gap in their spectrum. While a pristine Bernal (AB) stacked bilayer graphene can be synthesized by mechanical exfoliation, growth on a SiC

single crystal and epitaxial growth on metal substrates, separate control of the top and the bottom layers has seldom been performed. In this study, artificially modified 2D layers were demonstrated with individually stacked bilayer graphene. Large-area graphene was grown on a Cu foil by chemical vapor deposition (CVD). CVD-grown graphene layers were transferred successively onto insulating substrates with minimum chemical process for realizing bilayer graphene. In this method the mosaic spread between the top and the bottom graphene layers could be varied and an additional thin layer structure could be inserted between the two layers. Artificial bilayer graphene was investigated using scanning tunneling microscopy and spectroscopy. In topographic images and spatially resolved spectrums of local density of states, defect scattering and the misorientation between two graphene layers suggesting weak interaction compared to the AB stacking were found.

3:00pm **GR-TuA4 Dry Transfer of Single Layer Graphene to Polymers**, ***E.H. Lock**, S.G. Walton, M. Baraket, M. Laskoski, S. Mulvaney, W.K. Lee, P.E. Sheehan,* Naval Research Laboratory (NRL)*, D. Hines,* Laboratory for Physical Sciences (LPS)*, J.T. Robinson,* Naval Research Laboratory (NRL)*, J. Tosado, M. Fuhrer*, University of Maryland, College Park

The ability to grow and transfer large area single-layer graphene is critical from both fundamental and applied points of view. The transfer of large area samples will facilitate fundamental studies of graphene's unique properties. It can also allow for the fabrication of three-dimentional structures, electrically insulated graphene bilayers, graphene on previously unexplored substrates and "curved" graphene with non-trivial geometry. Currently, single layer graphene grown via CVD on metal foils is transferred to other substrates via chemical etching of the foil. The transfer process is time consuming, generates chemical waste, and destroys the foils.

We have developed method for direct dry transfer of graphene grown on Cu foils to polymers. The method relies on the differential adhesion between graphene, the metal foil, and the receiving polymer. A successful print results when the adhesion of graphene to the polymer surface is stronger than its adhesion to the metal foil. Plasma treatment of polymers allowed for the attachment of perfluorophenylazide (PFPA) linker molecule. The transfer printing was performed by placing the PFPA treated polymer surface in contact with graphene covered Cu foil and applying heat and pressure. Then, the polymer substrate with transferred graphene was separated from the Cu foil. In this talk, details of the printing process along with graphene film characterization will be discussed.

This work was supported by the Office of Naval Research. M. Baraket appreciates the NRL/NRC postdoctoral research fellowship.

4:00pm **GR-TuA7 Studies on Ozone Based Atomic Layer Deposition of High-k Dielectrics on Graphene**, ***S. Jandhyala**, G. Mordi, B. Lee, J. Kim,* University of Texas at Dallas*, P.-R. Cha*, Kookmin University, Korea

Graphene, being a two dimensional material, is one of the most promising alternative channel materials for post-Si generation [1-3]. However, being just one atom thick and having an inert surface, it poses a huge challenge to develop a top-gate dielectric process for graphene-based devices. Several techniques are currently being explored for depositing dielectrics including physical-vapor deposition (PVD), chemical-vapor deposition (CVD) and atomic layer deposition (ALD) after chemical 'functionalization' of graphene (using NO_2 or O_3) or after depositing nucleation layers (such as Al, PTCA, PVA) on graphene [3].

Here, we will present a novel technique developed by our group for depositing ALD high-k dielectrics such as Al_2O_3 on graphene through ozone functionalization [4]. Physisorption of ozone has been claimed to be the plausible mechanism for functionalizing the graphene surface [5]. Based on Langmuir adsorption equation, the amount of ozone adsorbed on graphene can be increased by increasing the partial pressure of ozone. By utilizing this, we have been able to precisely control the dielectric thicknesses and successfully scale dielectrics on graphene down to a thickness of ~3 nm. We employed both AFM on HOPG/graphene and in-situ electrical characterization of graphene-FETs in order to understand the adhesion mechanisms of ozone with graphene, enabling the deposition of ALD dielectrics. For in-situ electrical characterization, we used package-level devices with back-gated graphene devices to detect molecules adsorbed on graphene surface. The observed charge scattering mechanisms and effect on mobility due to the interaction of ozone with graphene as a function of temperature and amount of ozone will be presented. In-situ studies regarding the role of TMA (Tri-methyl Aluminum) will also be discussed based on experiments in actual ALD chambers.

Acknowledgement

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4:20pm **GR-TuA8 Fluorine Functionalization of Epitaxial Graphene for Uniform Deposition of Ultrathin High-κ Dielectrics**, ***V.D. Wheeler**, N.Y. Garces, L.O. Nyakiti, R.L. Myers-Ward, J. Culbertson, C.R. Eddy Jr., D.K. Gaskill*, U.S. Naval Research Laboratory

Thermal atomic layer deposition (ALD) is a viable approach to attain high-quality ultrathin dielectric films needed for graphene devices, but the hydrophobic nature of the graphene surface inhibits direct application of thermal ALD oxides. Several methods have been explored to render the surface more susceptible to ALD[1-3], but these techniques often result in graphene mobility degradation and/or shifts in the Dirac voltage due to charge in the gate stack. In this work, we investigated a simple dry chemical approach using $XeF_2$to functionalize the graphene surface prior to ALD which results in conformal ultrathin high-κ oxides without degradation of the underlying graphene electrical properties. Epitaxial graphene samples were grown on semi-insulating, on-axis (0001) 6H-SiC substrates using an Aixtron VP508 SiC reactor at 1650°C for 120 min. Fluorination of the graphene was performed in a Xactix X_3 etcher operating in pulse mode. Optimum fluorine exposure conditions consisted of six, 20s pulses with constant XeF_2 and N_2 carrier gas partial pressures of 1 and 35 torr, respectively. X-ray photoelectron spectroscopy (XPS) was used to chemically analyze the functionalized surface prior to oxide deposition. ALD Al_2O_3 and HfO_2 films (≤ 15 nm) were deposited at temperatures between 150 - 225 °C using TMA or TEMAHf and deionized (DI) water precursors. Growth was initiated with 20 DI water pulses. Oxide coverage was characterized with atomic force microscopy and scanning electron microscopy, while graphene mobility changes were observed with van der Pauw Hall measurements. Capacitance-voltage (C-V) measurements were conducted on Ti/Au C-V dots to extract the dielectric constant and electrical quality of the oxide. Initial results show that 15 nm conformal, uniform Al_2O_3 and HfO_2 films are obtained with an optimized XeF_2 surface treatment prior to ALD. XPS showed that the optimum XeF_2 treatment resulted in ~6% fluorine on the surface and the presence of only C-F bonds which provide ALD reaction sites needed for uniform oxide deposition. Graphene mobilities were maintained, and occasionally increased, implying little impact of the XeF_2 treatment or ALD oxide on the underlying graphene properties. Raman spectroscopy reveals no change in the D/G ratio after XeF_2 and oxide deposition, verifying that the graphene lattice quality is maintained. The viability of the fluorination method for achieving ultrathin films (<10 nm) will be presented along with electrical C-V data to show the electronic quality of the ALD oxides.

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4:40pm **GR-TuA9 Improving Performance of CVD Graphene Field Effect Transistors by Reducing Water Trapped at the Graphene/Substrate Interface**, ***J. Chan**, A. Venugopal, A. Pirkle, S. McDonnell, D. Hinojos,* The Univ. of Texas at Dallas*, C. Magnuson, R.S. Ruoff,* The Univ. of Texas at Austin*, L. Colombo,* Texas Instruments Inc.*, R.M. Wallace, E.M. Vogel*, The Univ. of Texas at Dallas

Graphene grown by chemical vapor deposition (CVD) provides a promising pathway for large area fabrication of graphene field effect transistor (FET). However, the performance of CVD graphene FETs reported to date is poorer than FETs fabricated using exfoliated graphene. CVD graphene FETs often exhibit strong hysteresis accompanied with low mobility, large positive Dirac point (V_{Dirac}) and large intrinsic carrier concentration. CVD graphene is exposed to a number of aqueous solutions and deionized water when it is transferred to a device substrate. We find that the large V_{Dirac} shift and strong hysteresis observed in CVD graphene FET are largely due to water trapped in the graphene/substrate interface during the transfer process.

In this study, CVD graphene grown on copper is transferred to SiO_2 substrates with the following three interfacial conditions: i) normal hydrophilic SiO_2, ii) SiO_2 with 20nm of Al_2O_3, and iii) a hydrophobic surface prepared by coating hexamethyldisilazane (HMDS). Device performance, including mobility, V_{Dirac} and intrinsic carrier concentration are compared in ambient as well as in vacuum. Gate hysteresis is analyzed by measurement of time-resolved channel resistance at various back-gate bias voltages. We find that the gate hysteresis is partially reduced by transferring the graphene onto a substrate coated with HMDS. Vacuum pump down and low temperature (80 °C) annealing can remove the remaining gate hysteresis and V_{Dirac} shift. The resulting hole mobility is

5,420cm^2/Vs, which is high compared to most of the CVD graphene mobility values reported in the literature.

As a control experiment, the CVD graphene FET fabricated on untreated SiO_2 shows a smaller mobility, a larger V_{Dirac} and a stronger hysteresis compared to the HMDS coated sample. Under vacuum the hysteresis is reduced but remains significant. We believe the remaining hysteresis is due to adsorbates trapped at the substrate/graphene interface. A graphene FET prepared on a substrate with an Al_2O_3 interface shows less hysteresis than the sample fabricated on an untreated SiO_2 surface but more than that of the HMDS coated surface. In order to study the influence of water trapped between the graphene and the substrate, water is intentionally replaced by isopropanol at the end of the transfer process before drying. In samples prepared using this method, hysteresis and V_{Dirac} point shift are both reduced. These results indicate that efforts to prevent trapping of water molecules at the graphene/substrate interface during the transfer process will improve the performance of CVD graphene FETs.

This work was supported by the NRI SWAN center, ONR, NSF and Sandia's LDRD program.

5:00pm **GR-TuA10 Improved Performance of Top-Gated Graphene-on-Diamond Devices**, ***A.V. Sumant***, Argonne National Laboratory, *J. Yu, G. Liu, A. Balandin*, University of California, Riverside

Since the discovery of graphene and realization of its exceptional electronic properties in suspended form, there have been many efforts in fabricating FET-type devices based on single and bilayer graphene on SiO2 substrate. However, performance of these devices is found to be inferior to the expected intrinsic properties of graphene. It has been observed that apart from carrier mobility in graphene, which is sensitive to trapped charges, and surface impurities at the graphene-oxide interface, breakdown current density in graphene depends sensitively on the heat dissipation property of the underlying supporting substrate. Although graphene has extremely high intrinsic thermal conductivity, it is reported that in graphene devices, more than 70% of the heat dissipates through the 300 nm SiO2 on silicon directly below the active graphene channel while the remainder is carried to the graphene that extends beyond the device and metallic contacts. Such a distribution of heat in to the substrate cause undesirable effects on the overall performance of the device. We show for the first time that by the use of thin CVD-grown ultrananocrystalline diamond thin films on silicon in graphene-on-diamond configuration, the heat dissipation can be improved substantially leading to the higher breakdown current density of more than 50% as compared to conventional graphene-on-oxide substrates. We also describe the fabrication of the top-gate graphene-on- diamond devices and discuss their performance. The obtained devices had the carrier mobility ~ 2354 cm2V-1S-1 for holes and ~1293 cm2V-1S-1 for electrons. The obtained results are promising for developing high-performance graphene-on-diamond devices and interconnects for future electronics.

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The work in Balandin group at UCR was supported, in part, by DARPA – SRC Center on Functional Engineered Nano Architectonics (FENA).

5:20pm **GR-TuA11 Growth of Turbostratic Graphene on Sapphire**, ***S. Rothwell***, *P.I. Cohen*, University of Minnesota, *M. Kumar*, National Physical Laboratory, India

Large area turbostratic graphene was grown on the (0001) plane of sapphire by thermal decomposition of acetylene. Sapphire is an attractive substrate since it has a symmetry match and close coincidence lattice match to graphene. It is a good insulator, appropriate for electronics applications, and large single crystal wafers are readily available. We have found that only after overcoming nucleation barriers, high quality graphene can be grown directly on sapphire without transfer. The sapphire was first heated to about 1400 C to obtain a reconstructed sqrt 31x31 R9 surface structure. The reconstruction was monitored in real time via reflection high energy electron diffraction, which was possible due to the low Debye-Waller factor. After obtaining a clean reconstructed surface, the sample was cooled to near room temperature and exposed to 10 Torr of acetylene. The sample was then heated to 1400 C in the presence of acetylene, in order to nucleate growth. At these pressures, sufficient acetylene coverage for growth was maintained during the ramp to high temperatures. Continued exposure to acetylene at 1400 C did not result in further growth. We speculate that at high temperature there is not sufficient residence time for incorporation, thus lower temperature is needed for further growth. Controlling pressure and temperature during a cool down phase becomes the fine control for film thickness. For example, 10 nm thick graphene samples were obtained by cooling in 1 – 7 E-7 Torr of acetylene. Transmission electron diffraction showed very sharp, nearly continuous rings, indicating large domains and no preferential azimuthal rotation between planes. X-ray diffraction showed an increased layer separation of 0.345 nm compared to graphite. Electron energy loss spectroscopy showed bulk-like plasmons or interband transitions, indicative of multilayer graphene. Raman spectra showed 2D/G peak intensity ratios of 0.5 to 1, comparable to literature values for turbostratic graphene. The spectra also exhibit the expected broader highly symmetric 2D peak. Thicker films could be easily lifted from the substrate. Films greater than 100 nm thick exhibited macroscopic ripples while 10 nm thick films were flat. Hydrogen was explored as a means to control growth but was found to rapidly etch graphene and to passivate the room temperature reconstructed sapphire surface. The growth was modeled with a simple rate equation analysis. These results offer a route to large area graphene grown directly on single crystal sapphire wafers.

Partially supported by the University of Minnesota IREE and by the National Physical Laboratory, India

5:40pm **GR-TuA12 Scanning Tunneling Microscopy and Nanomanipulation of Graphene-Coated Water on Mica**, ***J.D. Wood***, *K.T. He, E. Pop, J.W. Lyding*, University of Illinois at Urbana Champaign

Graphene on ultraflat substrates such as hexagonal boron nitride has shown to suppress charge puddle formation and give high carrier mobility [1,2]. Transfer of graphene to other ultraflat substrates such as muscovite mica might bring about similar transport characteristics. To that end, we place graphene on mica for scanning tunneling microscopy (STM) studies. We grow monolayer graphene on Cu by chemical vapor deposition and support it with polymethyl methylacrylate (PMMA). We clean the film with water baths and transfer it to mica. In contrast to previous atomic force microscopy (AFM) experiments of dry-transferred exfoliated graphene on mica [3,4], our graphene films trap multiple water layers. After a 700 ºC *in situ* degas, we achieve atomic resolution of graphene on water on mica, and we notice that there are at least 3 layers of ordered, bound water on mica [5], due to the wet transfer and the highly hydrophilic mica. We can atomically image graphene monolayers, bilayers, and grain boundaries regardless of the underlying water structure. Additional water layers on top of the bound water are rough, weakly bound, and amorphous. We notice up to 5 layers of graphene-encapsulated water on mica. Using the STM tip, we can nanomanipulate these amorphous layers at high tunneling conditions (>6 V, 1 nA). These water patterns are highly stable, invariant after several days of scanning. Water nanomanipulation under graphene could help elucidate water's complex bonding structure and charge transfer from graphene to encapsulated species. Further, graphene-coated water can assist in STM-based research of other aqueous-suspended nanostructures.

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Electronic Materials and Processing Division
Room: 210 - Session EM-WeM

Low-k Materials and Devices
Moderator: B. French, Intel Corporation

8:20am **EM-WeM2 Feature-Scale Modeling of Diffusion Barrier and Metal Seed Physical Vapor Deposition Processes**, ***R.A. Arakoni**, J.-P. Trelles, D. Kim, M. Khabibullin, S. Nikonov, D. Zierath*, Intel Corporation

The continuous reduction of critical dimensions and the increasing complexity of interconnect structures has stressed the process requirements of metallization steps (i.e., deposition of diffusion barrier and metal seed, electroplating, chemical-mechanical polishing). Particularly, physical vapor deposition (PVD) of the barrier and seed relies on a limited number of process parameters (e.g., target and bias power, reactor pressure) to satisfy increasingly tighter film requirements (e.g., coverage over high aspect ratio features, control of barrier thickness, proper aperture of the seed to prevent void formation during electroplating). Computational modeling has proven an efficient means to aid the design and development of PVD metallization steps by allowing pre-silicon analysis of the effects of feature geometry and process parameters (e.g., see [1]). A continuum-based process simulator, based on a level-set solver for multi-material topography evolution, is applied to the analysis of 2 successive metallization steps, namely the PVD of barrier-over-ILD and of seed-over-barrier. Primary (e.g., distributed along the domain boundary) as well as secondary (e.g., emitted and reflected from surfaces) fluxes are accounted for through a ray-tracing technique that ensures mass conservation. In contrast to Monte-Carlo methods, which allow the description of gas phase kinetics, our solver is based on the specification of finite-rate surface reactions, which provides smooth topography evolution and is suitable for the analysis of extended domains encompassing multiple features, as needed for the analysis of within-die pattern effects. Sputtering, attachment, and neutralization reactions are accounted for between all the neutral and ionic species and the entire set of surface and bulk species in the film to allow the description of inter-material interactions (e.g., re-deposition of sputtered barrier species over the seed). The simulator is used to analyze the effects of neutral and ionic flux distributions (e.g., athermal neutrals, directional ions dependent on bias power) and the sputtering yield characteristics (i.e., energy and angular dependence) on the obtained film. Figure 1 presents snapshots of simulation results of the two-step process over a dual damascene structure. The results show that the simulation of consecutive steps is essential for the realistic description of inter-process effects.

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8:40am **EM-WeM3 Ultralow-k PECVD pSiCOH Dielectrics and their Implementation in VLSI Interconnects**, ***A. Grill**, S.M. Gates,* IBM Research*, E.T. Ryan,* GlobalFoundries*, S. Nguyen*, IBM Research **INVITED**

The performance of integrated circuits and their density has been improved continuously through the shrinking of the active devices according to Moore's law. At the 0.25 mm technology node it became clear that new materials had to be introduced to reduce the RC of the interconnect which became a barrier to further improvement of the VLSI performance.

After IBM introduced Cu in 1997, low-k PECVD SiCOH dielectrics with a dielectric constant k=3.0 were introduced in 2003-2004 at the 90 nm node, after many other low-k dielectrics failed integration. Reduction or even maintaining of the interconnect capacitance at the decreasing dimensions of later technology nodes required the development of porous ultralow-k pSiCOH. The first generation of pSiCOH dielectrics with k=2.4 has been successfully integrated by IBM in 45 nm products, such as the Power 7 chip released in 2010. Material extendibility of porogen based pSiCOH has been demonstrated to k values as low as 2.0. However, the reduction of the dielectric constant is achieved for a given chemistry by increasing porosity in the films, resulting in a decrease of mechanical properties, degraded integrability of the dielectric, and potentially reduced reliability of the interconnect.

The original chemistry produced the pSiCOH films having a skeleton of mainly O-Si-O bonds, with nanometer sized pores stabilized by Si-CH3 groups (V1 type). These films are damaged by the integration processes and the degree of damage increases with decreasing k and decreasing pattern dimensions with each new technology node. To reduce these problems we developed pSiCOH films using precursors containing Si-CH2-Si bonds, enabling the fabrication of high-carbon (V2 type) films whose skeleton comprises Si-CH2-Si bonds in addition to the Si-O-Si. The high-carbon pSiCOH films have reduced degrees of porosity and improved pore structures as compared to the V1 type films of same k and, as a result, have higher resistance to processing damage and provide improved dimension control during integration compared to V1 pSiCOH of identical k values.

The talk will discuss the evolution of the low-k and ultralow-k dielectrics, the effects of the chemistries on the properties of the different types of the porous pSiCOH, and the behavior of such dielectrics during integration processing.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

9:20am **EM-WeM5 Limitations in Dielectric Constant Scaling for low-k a-SiC(N):H Diffusion Barriers in Nanoelectronic Applications**, ***S. King**, D. Jacob,* Intel Corporation*, M. Liu, D.W. Gidley*, University of Michigan

As the semiconductor industry strives to keep pace with Moore 's Law, new materials with extreme properties are increasingly being introduced and tighter control of these material properties is being demanded. Low dielectric constant (i.e. low-k) materials are one specific example. Lower k (< 6) a-SiC(N):H materials are desired to replace a-SiN_x:H (k > 6.5) as the Cu capping diffusion barrier layer in order to reduce resistance-capacitance (RC) delays in nano-electronic Cu interconnect structures. Typical methods for producing low-k a-SiCN:H materials consist of introducing controlled levels of nano-porosity via carbon doping during plasma enhanced chemical vapor deposition (PECVD) of a-SiN_x:H matrix materials. While lowering k, the introduction of nano-porosity can seriously compromise the moisture and Cu diffusion barrier performance of these materials. In this presentation, we demonstrate that critical thresholds in nano-porosity exist for the diffusion of water through low-k materials. Specifically, we utilize Fourier Transform Infra-Red (FTIR) spectroscopy, to show that the concentration and size of nano-pores formed in low-k a-SiC(N):H dielectric materials is controlled by the concentration of terminal Si-CH_3 bonding versus Si-C/N network bonding. We further combine moisture diffusivity measurements with x-ray reflectivity (XRR) and positron annihilation lifetime spectroscopy (PALS) to demonstrate that low-k a-SiC(N):H dielectrics become poor moisture diffusion barriers at mass densities < 2.0 g/cm^3 and when the pore size approaches that for the molecular diameter of water. The implications of these critical nano-porosity thresholds on continued dielectric constant scaling of low-k a-SiC(N):H diffusion barrier materials will be discussed as well as methods for overcoming these limitations.

9:40am **EM-WeM6 Fundamental Characterization of Amorphous Hydrogenated Boron Carbide Toward its use as a Low-*k* Dielectric Material**, ***B.J. Nordell**, S. Karki, C. Clayton, M.S. Driver, M.M. Paquette, A.N. Caruso*, University of Missouri-Kansas City

The development of stable and low-dielectric-constant (i.e., low-*k*) materials for interlayer dielectrics (ILDs) in ultra-large-scale integrated circuits has become an essential target for the semiconductor industry. Toward this end, several low-Z boron-based materials (e.g., boron nitrides and boron carbonitrides) have been studied due to their exceptional thermal, mechanical, and chemical stability, which have exhibited *k* values as low as 1.9–2.4. Amorphous hydrogenated boron carbide, in turn, may be an even more promising low-*k* boron-based material on the basis of the lower polarity of B–C bonds relative to B–N bonds and the mesoscopically porous icosahedral cage structure of boron-rich carbides which can exhibit significantly lower free volume, particularly for the low-density amorphous hydrogenated variants. Moreover, amorphous hydrogenated boron carbide films grown by plasma-enhanced chemical vapor deposition (PECVD) methods from carborane precursors exhibit resistivity's >1×〖10〗^10 ohm-cm. This talk will describe the causal relationship between the measured dielectric constant, resistivity, breakdown voltage, hardness, Young's Modulus, and mass/density as a function of the PECVD growth parameters (power, pressure, substrate temperature, and gas flow) and film composition (notably hydrogen and oxygen content) in the context of establishing and optimizing amorphous hydrogenated boron carbide as a next-generation durable and resilient low-*k* ILD.

10:40am **EM-WeM9 Robust PECVD Ultra-Low-k Dielectric (κ≤2.55) Development for sub-28nm Generations**, ***D. Kioussis***, *E.T. Ryan,* GLOBALFOUNDRIES, *S.M. Gates,* IBM T.J. Watson Res. Ctr., *A. Madan, N. Klymko, C. Parks, S. Molis,* IBM, *R. Augur,* GLOBALFOUNDRIES, *H. Masuda,* Toshiba America, *D. Restaino,* IBM, *Z. Sun,* GLOBALFOUNDRIES, *S. Hosadurga,* IBM, *S. Cohen,* IBM T.J. Watson Res. Ctr., *K. Virwani,* IBM Almaden Res. Ctr., *A. Grill*, IBM T.J. Watson Res. Ctr. **INVITED**

In the demanding microelectronics industry there is a constant need to increase circuit density in multilevel Copper (Cu) back-end-of line (BEOL) interconnects to improve the operating speed and reduce power consumption. With successive nodeon- node scaling, one approach to meet the capacitance-resistance (RC) requirements for the BEOL is through the introduction of organo silicate glass (SiCOH) materials with low dielectric constants (κ-value) as interlevel dielectrics (ILD). At the 45 nm node, porosity was first introduced into the BEOL interconnect structures in the form of porous organo silicate glass films (p-SiCOH) with ultra low-κ (≤ 2.55) to further minimize the RC delay. These ULK materials incorporate a large number of methyl groups and pores into Si-O based network structures, although the initial precursors and final properties may vary. Both the SiCOH and pSiCOH ILD films are commonly deposited by plasma-enhanced chemical vapor deposition (PECVD). Since their introduction nanoporous ULK films have significantly increased the Cu BEOL fabrication complexity. For example, porous ULK films are mechanically weak and tend to crack as a result of elastic mismatch with the substrate. Meanwhile, pore collapse and carbon depletion occur when ULK is exposed to RF-plasma during etching or ashing. Subsequent moisture adsorption leads to the increase of effective κ-value in Cu interconnects degrading RC performance. Therefore, the integration challenges of ULK are significant, such as plasma damage, chip packaging interaction, and dielectric/metal barrier compatibility issues. Careful optimization of the ULK properties is crucial for successful process integration in the 28 nm BEOL node and beyond.

This presentation will report on the ability to tune the material properties of ULK films with κ ≤ 2.55 through the use of new chemical precursors and simple processing optimization steps to meet the specific integration requirements. Three ULK material classes were evaluated, optimized, and characterized to compare electrical and mechanical properties, pore characteristics, FTIR, XPS, and thermal stability. The effect of UV Cure dose on the ULK film properties and correlation of the degree of plasma damage to the ULK chemical, physical, and structural properties will be discussed. We will show that balancing composition of the film to minimize damage for successful integration needs to be coupled with improving electrical and mechanical integrity for packaging compatibility.

11:20am **EM-WeM11 Molecular Strengthening Mechanisms for Low-k Dielectrics**, ***R.H. Dauskardt***, Stanford University **INVITED**

Hybrid organic-inorganic glass films processed from small organosilane precursors exhibit unique electro-optical properties while maintaining excellent thermal stability. Processed using either sol-gel or plasma-enhanced chemical vapor deposition they have application in emerging CMOS, nanoscience and energy technologies. A fundamental challenge for their integration, however, remains their inherently mechanically fragile nature that derives from the oxide component of the hybrid network and the presence of terminal hydroxyl and organic groups that reduce network connectivity. Also, to achieve ultra-low dielectric properties (i.e $k < 2.4$) nanoporous forms of the hybrid films are required which further reduce mechanical properties. We describe the development of computational methods to address the fundamental relationship between molecular structure and resulting mechanical and fracture properties of organosilicate glasses. Using molecular dynamics and a simulated annealing approach, large distortion-free hybrid glass networks with well-controlled network connectivity can be generated. With this capability along with a novel fracture model and molecular dynamics simulations of elastic deformation, we elucidate the critical effect of network connectivity and nanoporosity on mechanical properties. The accuracy of our computational tools is confirmed through comparison to synthesized hybrid films where the molecular structure, connectivity and nanoporosity is carefully controlled. Having predictive models for how molecular structure affects mechanical properties offers the opportunity for computational design of new glasses and provides a quantitatively accurate rationale for guiding precursor selection. Thus in addition to the fundamental insights gained regarding structure-mechanical property relationships, we will present our efforts to apply these tools to design new neat and nanoporous glasses with exceptional mechanical properties and low density.

Energy Frontiers Focus Topic
Room: 103 - Session EN+EM+NS-WeM

Quantum Dot and Nanowire Solar Cells
Moderator: K. Leschkies, Applied Materials Inc.

8:00am **EN+EM+NS-WeM1 Hybrid Quantum-Dot/Organic Solar Cells Based on Silicon Nanocrystals**, ***U. Kortshagen***, *C.Y. Liu, Z. Holman, J. Yang*, University of Minnesota **INVITED**

Organic solar cells based on bulk heterojunctions between acceptor and donor semiconductors have attracted significant attention due to their low cost, compatibility with roll-to-roll processing, and relative lack of health and environmental concerns. However, the stability of organic semiconductors under solar irradiation remains to be a challenge. Producing bulk heterojunction solar cells based entirely on inorganic materials thus has become an attractive proposition.

In a first step into this direction, we have produced solar cells from silicon nanocrystals (Si NCs) and poly-3-hexylthiophene (P3HT). Silicon NCs 3–5 nm in diameter were synthesized by dissociating silane gas in a nonthermal radio frequency plasma, and collected on a mesh downstream of the plasma. The silicon-hydride terminated NCs were dispersed with P3HT in 1,2-dichlorobenzene. Films of this blend with thicknesses of 100–200nm were spin-cast onto an indium tin oxide (ITO) substrate pre-coated with 50 nm of poly(3,4-ethylenedioxythiophene)/poly (styrenesulfonate) (PEDOT:PSS). Metal electrodes (2mm wide, 100 nm thick) were then evaporated on top of the Si NC/P3HT film.

The Si NCs were found to be efficient electron acceptors. The optimal weight ratio of Si NC to P3HT was 50 wt%. The effects of annealing and different metal electrodes on Si NC/P3HT hybrid solar cells were studied. After annealing at 150 °C, Si NC/P3HT solar cells exhibited power conversion efficiencies as high as 1.47%. The hole mobility in the P3HT phase extracted from space-charge-limited current measurements of hole-only devices increased from $2.5x10^{-10}$ cm^2/V-s to $1.1x10^{-9}$ cm^2/V-s after annealing, resulting in better transport in the solar cells. A quenching of the open-circuit voltage and short-circuit current was observed when high work function metals are deposited as the cathode on Si NC/P3HT hybrid devices.

Devices with silicon-hydride terminated Si NCs were plagued by poor film morphology. Hence we studied functionalizing Si NCs with organic ligands. Functionalization with 1-octene and 1-dodecene led to improved film morphology but the transport in the Si NC network became worse. However, excellent stability with respect to air exposure of these cells was observed. Efforts to improve the dispersability of Si NCs without inhibiting transport in the Si NC network are in progress.

This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0819885 and by the DOE Energy Frontier Research Center for Advanced Solar Photophysics.

8:40am **EN+EM+NS-WeM3 Precision Engineering of Semiconductor Nanowires for Advanced Photovoltaic Devices**, *N. Shin, I.R. Musin, S. Sivaram,* ***M.A. Filler***, Georgia Institute of Technology **INVITED**

Semiconductor nanowires offer exciting opportunities to engineer light absorption and carrier transport for ultrahigh efficiency photovoltaic devices. The precise control of crystal structure and geometry is required to achieve a desired behavior, especially in highly confined nanoscale systems. In the ideal situation, the combination of nanowire diameter, lattice structure (e.g. diamond cubic, wurtzite), crystal orientation (e.g. <111> vs. <110>), and sidewall faceting that yields the most robust device performance would be known and could be rationally synthesized. Unfortunately, an inadequate understanding of nanowire chemistry-structure and structure-property relationships prevents the accomplishment of this task with bottom-up syntheses at the present time. This presentation will provide an overview of our recent efforts to bridge this knowledge gap. In our research, *in-situ* infrared spectroscopy is combined with an ultrahigh vacuum growth environment to fundamentally correlate nanowire chemistry with photophysics, while circumventing the sample degradation that can obscure the intrinsic properties of nanoscale structures. Group IV nanowires and their heterostructures are a model system and are fabricated with the vapor-liquid-solid (VLS) growth technique. The critical influence of surface-bound species near the three-phase boundary and their impact on nanowire crystal structure will be discussed in detail. This fundamental knowledge opens a generic and highly tunable route to engineer multiple classes (e.g. group IV and III-V, etc.) of semiconductor nanowires, heterostructures, and superstructures for advanced photovoltaic device applications.

9:20am **EN+EM+NS-WeM5 Electrophoretic Deposition of CdSe Nanocrystals in Quantum Dot Sensitized Solar Cells**, ***N.J. Smith***, Middle Tennessee State University

Electrophoretic deposition (EPD) of nanocrystal thin films from the solution phase has received increasing attenion due to its simplicity and ability to rapidly create controlled thickness films. In this presentation, we wil discuss the impact of solvent choice, deposition time, and eletrode voltage on the properties of CdSe nanocrystal films deposited by EPD for solar cell applications.

While hexanes are a commonly used solvent for depositing CdSe nanocrystals, resulting film formation by EPD is often not reproducible for different batches of nanocrytals. In this work, we report that adding acetone to solutions of nanocrystals in hexanes enables the consistent deposition of CdSe nanocrystal thin films of controllable thickness. These films form within a few seconds and require comparatively low electrode voltages for the deposition process. The addition of acetone appears to mitigate the effects of impurities in the precursor chemicals, the presence of solvents left over from nanocrystal synthesis, and variable environmental conditions that may otherwise compromise the quality of the resulting EPD nanocrystal films.

Quantum dot sensitized solar cells have been fabricated using the EPD process with CdSe nanocrystals solvated in hexanes with acetone. By modifying the EPD parameters, both the density and thickness of the nanocrystals films deposited on titanium dioxide coated ITO slides were affected. We will discuss the relationship between the EPD parameters and the resulting I-V characteristics and efficiency of the CdSe nanocrystal sensitized solar cells. Preliminary studies suggest that proper choice of EPD parameters can lead to more than one order of magnitude improvement in the solar cell performance metrics.

9:40am **EN+EM+NS-WeM6 Selective and Highly Efficient Photo-Induced Activity Over Nano-Scale Sites in Porous Silicon: Potential Application for Hybrid Organic-Silicon PV**, ***M. Asscher***, The Hebrew University of Jerusalem, Israel, *G. Toker, A. Nahor, O. Berger, S. Yitzchaik, A. Sa'ar*, Hebrew University, Israel

Photo-induced processes over solid surfaces are of great basic and technological interest with applications in e.g. photolithography, sensing, catalysis and photovoltaics. Photo activity within porous silicon (PSi) following UV (193-266nm) irradiation has been studied. Unusually efficient, non-thermal, morphology and wavelength dependent photo-induced desorption (PID) of Xe was recorded. It is a selective process, revealing more than 3 orders of magnitude enhancement within pores, at the vicinity of nano-scale silicon tips, over atoms adsorbed on top of flat surfaces. Remarkably large cross sections up to $\sigma_{PSi} = 2\cdot 10^{-15}cm^2$ were recorded, significantly larger than any previously published photo-induced events on solid surfaces at this wavelength range. Long lived, photo-induced positive charges (holes) located at inner surface nano-tips is proposed to stabilize transient negative Xe adsorbate ions as the precursor for this new photo-desorption process.

These results were utilized for the construction of hybrid conducting polymer-porous silicon photovoltaic cell. Proof of concept and preliminary results are discussed.

10:40am **EN+EM+NS-WeM9 High-Performance, Low-Cost Nanopillar Array Photovoltaics**, ***A. Javey***, University of California Berkeley **INVITED**

Semiconductor nanowires (NWs) hold great promise for fabrication of high-performance, low-cost solar cells. These materials have been extensively studied, both computationally and experimentally. The key advantage of NW solar cells resides in the ability to grow single crystalline NWs non-epitaxially on support substrates. Additionally, by varying the NW geometry, the electrical, optical and mechanical properties of the solar cells c an be controlled, providing opportunities unavailable to planar thin-film solar cells. Here we discuss our work on bottom-up CdS/CdTe nanopillar (NPL) solar cells, optical engineering of NPL arrays, and top-down fabrication of InP solar cells.

Bottom-up NPL solar cells were fabricated on anodized aluminum oxide (AAO) templates. Due to the 3-D geometry, the templated NPL architecture orthogonalizes the light absorption and carrier collection directions, enabling cells to be optimized even for poor quality materials. First-generation CdS/CdTe solar cells on low-cost Al foil exhibited 6% efficiency, 0.6 V open circuit voltage, V_{OC}, and 21 mA/cm^2 short circuit current, J_{SC}, despite significant (>30%) optical reflection from the top contact. Additionally, detailed electronic simulation was used to examine the design trade-offs involved with the NPL architecture. We found that even for a poor quality CdTe absorber layer, through proper design, moderate efficiencies of ~15% could be achieved. Additionally, all the processes used to fabricate the cell were roll-to-roll compatible. Thus, the combination of experiment and modeling show the promise of this method for fabrication of low-cost, high-performance solar cells.

The AAO templated growth enables a high degree of control over the geometry and dimensions of the NPL arrays. For single-diameter Ge NPL arrays embedded in AAO, increasing the Ge material filling ratio both increases the reflectance and decreases the transmittance. The absorbance of an array is shown to strongly increase for increased diameter NPL arrays. Thus, by fabricating arrays of dual-diameter Ge NPL s, ~99% of incident light was absorbed with a film only 2 μ m thick. This behavior is caused by the smaller NPL diameter at the interface between the material and incident light, and the higher diameter base then absorbs the light.

Finally, radial p-n junction solar cells are fabricated from InP NPLs generated from a top-down etching procedure. The main challenge with radial p-n junctions is the ability to form ultra-shallow and conformal junctions along the radial axis. By utilizing a sulfur monolayer doping scheme, conformal junction depths of <10nm with high electrically active dopant concentrations (~10^{19} cm^{-3}) are achieved. The fabricated solar cell exhibited a power conversion efficiency of 8.1%, a V_{OC}=0.54 V, and a J_{SC}=25 mA/cm^2.

In summary, we have presented both top-down and bottom-up approaches for fabricating NPL solar cells, from both crystalline starting materials as well as low-cost Al foil. The templated AAO growth method also enabled optical engineering of NPL arrays, allowing a single material to maximize absorption and minimize reflection. Finally, the utilization of a previously-developed conformal, ultra-shallow doping scheme was shown to enable radial InP solar cells.

11:20am **EN+EM+NS-WeM11 Extremely Thin Absorber Solar Cells Based on CdSe-Coated ZnO Nanowires**, *H. Majidi, T.P. Le, G.W. Guglietta, **J.B. Baxter***, Drexel University

Solar cells can provide an abundant, clean, and sustainable source of electricity, but high costs have limited their implementation. The use of sensitized nanostructured architectures may enable both low-cost processing and high efficiency by decoupling the functions of light harvesting and charge transport into different materials. Sensitized solar cells consist of a bicontinuous interpenetrating network of electron- and hole-transporting materials with an interfacial absorber layer. In this architecture, interfacial recombination is the dominant loss process, so controlling the interfacial chemistry during deposition is critical.

We report on the use of n-type ZnO nanowire arrays sensitized with thin CdSe coatings and covered with p-type CuSCN in extremely thin absorber (ETA) solar cells. Low temperature, solution deposition methods were used for each material, offering the potential for inexpensive and scalable nanomanufacturing. Nanowire arrays provide direct pathways for electron transport as well as sufficient surface area for sensitization. The electrodeposited CdSe coatings are nanocrystalline and conformal with well-controlled thickness. CuSCN is electrodeposited into the pore volume between nanowires. Morphology and microstructure of CdSe and CuSCN depend sensitively on bath chemistry and deposition potential. By controlling nucleation and growth rates, conformal and void-free materials can be deposited.

A combination of solar cell measurements and ex situ materials characterization for both planar thin film stacks and nanowire arrays have been used to direct the selection of optimal ETA cell architectures. For example, ultrafast transient absorption spectroscopy demonstrates that interfacial electron transfer from photoexcited CdSe to the ZnO is much faster than recombination (~3 ps vs ~50 ps) for thin coatings. Planar solar cells were used to identify the optimal coating thickness of ~70 nm for these materials. External quantum efficiency measurements show efficient sensitization throughout the visible region of the solar spectrum. However, interfacial recombination limits overall energy conversion efficiencies.

11:40am **EN+EM+NS-WeM12 Hybrid Photovoltaics Devices Based on Quantum Dot Functionalized ZnO Nanowire Arrays Embedded in a Polymer Matrix**, *N. Harris, L. Butler, G. Shen, N. Dawahre, S. Wilbert, W. Baughman, S. Balci, P. Kung, **S. Kim***, University of Alabama

There is an increasing need to develop new low-cost materials and architectures for high efficiency solar cells in an attempt to provide a cost effective alternative to fossil fuels. Dyes, polymers and quantum dots have received tremendous amounts of attention due to their potential for solution processing and high absorption coefficients. Polymers and quantum dots are an attractive option for replacing dyes as the next generation low-cost absorber material due to their improved electronic properties and increased longevity. Bulk-heterojunction polymer based cells suffer from low carrier mobility and short carrier lifetimes which lead to high recombination rates. Quantum dots are promising sensitizing material because they potentially

have improved stability over polymers and can potentially generate multiple excitons per photon. However, charge transport in solar cells based solely on quantum dots is generally accomplished through the hopping-mechanism and leads to increased recombination rates.

In this talk, we present a hybrid photovoltaic device structure based on quantum dot (QD)-functionalized single crystalline ZnO nanowire arrays embedded into a polymer matrix in order to achieved improved charge collection efficiencies from the QDs and transport through the cell. A number of issues need to be addressed, such as the enhancement of the coverage of the nanowires with quantum dots to increase photon absorption, as well as implementing a hole-transport medium that does not degrade the quantum dots and can potentially serve as a secondary absorber material that could potentially greatly improve device longevity, reproducibility and efficiency.

In this work, the specific photovoltaic device structure consisted of an InP/ZnS core-shell QD functionalized ZnO nanowire array that is embedded into a poly-3(hexylthiophene) (P3HT) hole transport matrix. The QD sensitized ZnO nanowires were characterized by optical absorption, confocal Raman and photoluminescence spectroscopy, as well as high resolution and scanning transmission electron microscopy. In addition, interface between QDs and ZnO NWs were studied by Atom Probe Tomography. QDs with different absorption bands were concurrently functionalized onto the same nanowire arrays in order to broaden the final device absorption bandwidth. The ZnO:P3HT matrix was then planarized using inductively coupled plasma etching. The performance of planarized, quantum dot functionalized devices was subsequently compared to as-deposited and non-functionalized devices and the effect of QDs on device efficiency is presented. These include the study of the charge transfer mechanism using terahertz time domain spectroscopy.

Thin Film Division
Room: 110 - Session TF1+EM-WeM

ALD/MLD: Hybrid Organic Films
Moderator: Q. Peng, Duke University

8:00am **TF1+EM-WeM1 Vapor-Phase Fabrication of Organic-Inorganic Hybrid Thin Films Using Molecular Layer Deposition with Atomic Layer Deposition**, ***M.M. Sung***, Hanyang University, Korea **INVITED**

We report a vapor phase deposition method of high quality organic thin films, called molecular layer deposition (MLD). MLD is a gas phase process analogous to ALD and also relies on sequential saturated surface reactions which result in the formation of a self-assembled monolayer in each sequence. In the MLD method, the high quality organic thin films can be quickly formed with monolayer precision under ALD conditions (temperature, pressure, etc). The MLD method can be combined with ALD to take advantages of the possibility of obtaining organic–inorganic hybrid thin films. The advantages of the MLD technique combined with ALD include accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, multilayer processing capability, sharp interfaces, and excellent film qualities at relatively low temperatures. Additionally, a vast library of materials is accessible by ALD methods, ranging from single elements to compound semiconductors to oxides, nitrides, and sulfides. Therefore, the MLD method with ALD is an ideal fabrication technique for various organic-inorganic nanohybrid superlattices.

8:40am **TF1+EM-WeM3 Metalcone and Metalcone/Metal Oxide Alloys Grown Using Atomic & Molecular Layer Deposition Techniques**, ***B.H. Lee***, *V.R. Anderson, S.M. George*, University of Colorado, Boulder

A new class of films known as the "metalcones" can be grown using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. Metalcones are hybrid organic-inorganic materials derived from the sequential, self-limiting reactions of metal and organic alcohol precursors. The first metalcones were the "alucones" based on trimethylaluminum and ethylene glycol (EG) and the "zincones" based on diethylzinc and EG. Other metalcones can be fabricated with various properties using different metal precursors together with organic alcohols. This talk reports new metalcones known as the "zircones" using zirconium tert-butoxide (ZTB) and EG. In addition, this talk will discuss two new tunable ALD:MLD films based on alloys of alucone MLD/Al2O3 ALD and zircone MLD/ZrO2 ALD. Zircone MLD films were grown by using zirconium tert-butoxide (ZTB) and EG. MLD growth was observed at temperatures ranging from 105 to 195°C. *In situ* quartz crystal microbalance and *ex situ* X-ray reflectivity (XRR) experiments confirmed linear growth of zircone MLD versus number of ZTB/EG reaction cycles. Zircone MLD growth rates decreased versus temperature and varied from 1.6 Å per cycle at 105°C to 0.3 Å per cycle at 195°C. A constant density of ~2.3 g/cm3 was measured for all growth temperatures. XRR measurement also showed that zircone MLD films were very stable under ambient conditions. The metalcones will have useful mechanical, optical and electrical properties that can be tuned by growing alloys of the metalcones and their parent metal oxides. For example, this tuning allows the density of alucone MLD/Al2O3 ALD alloys to be varied from 1.6 g/cm3 to 3.0 g/cm3. The density of zircone MLD/ZrO2 ALD alloys could also be varied from 2.3 g/cm3 to 4.0 g/cm3. The reflective index of zircone MLD/ZrO2 MLD alloys was also tuned continuously between 1.63 and 1.86. These new metalcone materials provide a tool set for engineering the functional properties of thin films. These materials can be grown with atomic control of thickness and excellent conformality. The metalcones and metalcone alloys can also be thermally annealed to remove the organic constituent and create porous metal oxide films.

9:00am **TF1+EM-WeM4 Sequential Vapor Infiltration and Atomic Layer Deposition on Surfactant Films for Mesoporous Metal Oxide**, ***B. Gong***, *D. Kim, G.N. Parsons*, North Carolina State University

Mesoporous materials are critical for applications such as catalyst support, energy storage and conversion, and chemical separations. Conventionally, solution based approaches are employed for the preparation of these materials, and amphiphilic molecules are widely used as templates to form well defined pore size and surface area. In these methods, the interaction between the hydrophilic block of the surfactant molecules and the metal oxide precursors direct the self-assembly of ordered micelles/metal oxide hybrid materials, and porous inorganic structures were recovered after removal of the organic template. Recently, this selective interaction was also discovered during vapor phase sequential vapor infiltration and atomic layer deposition (ALD) of metal oxide onto polymers, where precursor infusion and reaction depends strongly on the interaction between the precursor and polymer starting substrate. We therefore believe that sequential vapor infiltration or ALD on amphiphilc surfactant molecule films could also yield ordered inorganic/organic hybrid materials and porous metal oxides.

In this work, mesoporous aluminum oxide and titanium oxide materials were prepared by the vapor phase infiltration and ALD on two kinds of surfactants: the ionic cetyltrimethylammonium bromide (CTAB) and poly ethylene oxide based nonionic surfactant F127 (PEO-PPO-PEO). The nitrogen adsorption and desorption measurement was employed to measure the specific surface area and the pore size distribution of the resulted material. In-situ FTIR was used to monitor the chemistry change during the vapor infiltration, SEM TEM and XRD were used to characterize the structure and the morphology of the porous material.

We find that both sequential vapor infiltration and ALD produced mesoporous materials. However, the vapor phase infiltrated films show a relative higher specific surface area and narrower pore size distribution. This can be explained by the more uniform distribution of metal oxide into the surfactant layer compared to ALD. These results demostrate a new vapor phase approach for well defined mesoporous materials, which would potentially important for many advanced applications.

9:20am **TF1+EM-WeM5 Flexibility and Water Vapor Transmission Rates for Al-, Hf-, and Zr-based ALD Films and Nanolaminates Utilizing Water and Glycerol Co-Reactants**, ***M.J. Sowa***, *E.W. Deguns*, Cambridge NanoTech, Inc.

Organic electronics constructed on flexible substrates stand to revolutionize the display and lighting markets due to the low potential cost of manufacturing inherent to roll-to-roll manufacturing. A significant downside to organic electronics is their sensitivity to atmospheric oxygen and moisture. Various encapsulation techniques have been demonstrated, some of which have achieved Water Vapor Transmission Rates (WVTR) better than 1e-6 g/m^2/d, which has been suggested to be the maximum allowable rate to give a minimum usable lifetime of 10,000 hours for Organic Light Emitting Diodes (OLEDs). However, most of the encapsulation technologies that provide these low WVTRs lack the flexibility of the underlying plastic substrate or the organic electronics, limiting the actual flexibility of the final product.

Here we will report on the flexibility of aluminum-, hafnium-, and zirconium-based ALD films deposited on representative substrate material samples of polyethylene napthalate(PEN) at 115°C. Metal precursors used were trimethyl aluminum(TMA), tetrakis(dimethylamino)hafnium(TDMAH), and tetrakis(dimethylamino)zirconium(TDMAZ). Water was used as the ALD co-reactant for producing inorganic films while glycerol was utilized as the

co-reactant for depositing hybrid organic films. Various nanolaminate combinations of the inorganic/organic materials were also investigated for their response to various levels of strain. Inorganic Al_2O_3 films subjected to 2% strain were observed to begin cracking at thicknesses below 27nm. A 2% strain did not cause any cracking on organic films deposited with TMA and glycerol to the thickest film studied at 245nm. Organic films were always observed to be more flexible than inorganic films of the same thickness. Nanolaminates were observed to have flexibility intermediate to their pure inorganic and organic constituents.

WVTR measurements were performed on inorganic, organic, and nanolaminate aluminum films. A WVTR of 6.1e-6 g/m^2/day was obtained for a 100nm inorganic Al_2O_3 film. A substantially more flexible 100nm TMA + glycerol film gave a WVTR of 9.2e-6 g/m^2/day.

The technical issues associated with uniformly delivering glycerol to a 115°C ALD reactor will also be discussed.

9:40am **TF1+EM-WeM6 Polymer Wires Containing Quantum Dots with Different Lengths Grown by Molecular Layer Deposition: Potential Applications to Sensitization in Photovoltaics**, ***T. Yoshimura***, *R. Ebihara, A. Oshima*, Tokyo University of Technology, Japan

[Introduction] Molecular layer deposition (MLD) grows tailored polymer wires with designated molecular arrangements by connecting different kinds of molecules with monomolecular steps. We grew polymer wires with quantum dots (QDs), called as “polymer multiple quantum dot (polymer MQD),” by MLD using three kinds of molecules, terephthalaldehyde (TPA), *p*-phenylenediamine (PPDA) and oxalic dihydrazide (ODH), and proposed their potential applications to sensitized photovoltaic devices.

[Polymer MQDs] As a preliminary work, polymer MQDs of OTPTPT, OTPT and OT were grown. In OTPTPT, molecules are connected in a sequence of -ODH-TPA-PPDA-TPA-PPDA-TPA-ODH---. The region between two ODHs is a QD of ~3-nm long. In OTPT, ~2-nm-long QDs are constructed with a molecular sequence of -ODH-TPA-PPDA-TPA-ODH---. In OT, ~0.8-nm-long QDs are constructed by connecting ODH and TPA alternately. A polymer MQD with three kinds of QDs, “3QD-MQD,” in which OT-like QD [OT], OTPT-like QD [OTPT] and OTPTPT-like QD [OTPTPT] are formed in one polymer wire, was grown with a sequence of -ODH-TPA-ODH-TPA-PPDA-TPA-ODH-TPA-PPDA-TPA-PPDA-TPA-ODH---. For polymer MQD growth, we used the carrier-gas type MLD, where carrier gas of nitrogen was employed to give molecular gas blows onto substrates through valves for molecular gas switching.

[Light Absorption Spectra] Light absorption measurements revealed that the peak energy of the absorption spectra shifts toward the high energy side with decreasing the QD length, namely, in the order of OTPTPT, OTPT, and OT. This effect is attributed to the quantum confinement. The absorption spectrum of 3QD-MQD is broad extending from ~480 nm to ~300 nm, which is a superposition of the spectra of [OTPTPT], [OTPT], and [OT]. This result indicates that the polymer MQD with different QD lengths could be an efficient sensitizer. In addition, the molecular orbital calculation confirmed that the electron density is high in the QD regions of 3QD-MQD.

[Proposal of Polymer MQD Sensitization] In the polymer MQD sensitization, polymer MQD is on a ZnO surface as a sensitizer. QDs exhibit narrow absorption bands comparing with bulk semiconductors like Si due to their zero-dimensional characteristics. The absorption peak energy can be adjusted by QD lengths. Therefore, polymer MQD containing different-length QDs enables us to divide the wavelength region for light absorption into narrow regions. Each QD absorbs lights of wavelengths matched to its own energy gap, and injects the excited electrons into ZnO. This might suppress the energy loss arising from the heat generation in the light absorption process. The structure is regarded as a molecular tandem structure.

10:40am **TF1+EM-WeM9 Hybrid Materials by Vapor Phase Infiltration**, ***M. Knez***, Max-Planck-Institut für Mikrostrukturphysik, Germany **INVITED**

Atomic layer deposition (ALD) is a thin film deposition technique which was developed in the 1970s to meet the needs for processing thin film electroluminescent displays (TFEL). Technically and chemically it is similar to chemical vapor deposition (CVD). However, in contrast to CVD, ALD incorporates as a specific feature the separation of the chemical reaction into two half-reactions. The ALD is not only able to perform thin film coatings of inorganic materials, but also allows coatings with organic-inorganic hybrid materials and, due to the separated exposure of the substrate to the precursors, infiltration of soft matter.

This talk will show top-down approaches to hybrid organic-inorganic and bio-inorganic materials obtained by infiltration with metals from the vapor phase. With tiny amounts of metals infiltrated, biological materials, such as spider silk or collagen, can positively change their mechanical properties after being treated with pulsed vapors of metal-organic precursors. The improvement of mechanical properties is related to changes in the molecular structure of the protein-based materials. However, not only biopolymers undergo changes after infiltration. With the example of some synthetic polymers, analogous routes to modify their mechanical properties will be shown.

11:20am **TF1+EM-WeM11 Titanicone Molecular Layer Deposition Using $TiCl_4$ and Sugar Alcohols and Porous TiO_2 Films Produced by Annealing**, ***R.A. Hall***, *A.I. Abdulagatov, S.M. George*, University of Colorado, Boulder

Metalcone molecular layer deposition (MLD) can be performed using metal precursors and organic diols or triols. The first metalcone MLD films were the alucones and zincones grown using trimethylaluminum and diethylzinc, respectively, with ethylene glycol (EG). In this work, we report the growth of titanicone MLD films using $TiCl_4$ and two sugar alcohols: EG and glycerol (GL). The titanicones may have useful photocatalytic properties and may form valuable porous TiO_2 frameworks upon annealing to remove the organic constituent. Titanicone films were grown using $TiCl_4$ and EG at temperatures between 90-135°C. Quartz crystal microbalance (QCM) measurements observed a growth rate of ~83 ng/cm^2-cycle from 90 to 115°C before decreasing significantly at 135°C. X-ray reflectivity (XRR) studies obtained a growth rate of 4.5 Å/cycle with a density of 1.84 g/cm^3 at 115°C. Titanicone films were grown using $TiCl_4$ and GL at higher temperatures between 130-210°C. The GL is believed to lead to more cross-linking that stabilizes the MLD film. QCM measurements observed growth rates that varied slightly with temperature from 49 ng/cm^2-cycle at 130°C to 34 ng/cm^2-cycle at 210°C. XRR studies yielded a growth rate of 2.2 Å/cycle at 150°C. QCM measurements revealed that the surface chemistry for titanicone MLD was self-limiting. XRR studies indicated that the titanicone films were stable in air. The titanicone films were absorptive in the ultraviolet and consistent with an optical bandgap of ~3.5 eV. Annealing the titanicone films removed the carbon component and yielded porous TiO_2 films. Ultraviolet exposures also appear to be able to produce porous TiO_2 films. The ability to deposit conformal porous TiO_2 films on high surface area substrates could produce “super” high surface area substrates. These substrates may serve as TiO_2 scaffolds for dye-sensitized solar cells or photocatalytic membranes.

Electronic Materials and Processing Division
Room: 210 - Session EM-WeA

Defects in Electronic Materials
Moderator: B.D. Schultz, University of California, Santa Barbara

2:00pm **EM-WeA1 Controlling Schottky Barriers and Doping with Native Point Defects**, ***L.J. Brillson***, *Y. Dong,* The Ohio State Univ., *F. Tuomisto,* Helsinki Univ. of Tech., Finland, *B. Svensson, A.Yu. Kuznetsov,* Univ. of Oslo, Norway, *D. Doutt,* The Ohio State Univ., *H.L. Mosbacker,* Traycer Diagnostic, *G. Cantwell, J. Zhang, J.J. Song,* ZN Technology, *Z.-Q. Fang,* Univ. of Dayton, *D.C. Look*, Air Force Research Lab **INVITED**

Native point defects in semiconductors have until now not been considered a major factor in Schottky barrier formation or doping due to their relatively low bulk densities. Likewise, efforts to control doping type and density usually treat point defects as passive, compensating donors or acceptors. Recent advances in the rapidly emerging semiconductor ZnO include a deeper understanding into the nature of native point defects at its surfaces, interfaces, and epitaxial films. Key to ZnO Schottky barrier formation is a massive redistribution of native point defects near its surfaces and interfaces. It is now possible to measure the energies, densities and in many cases the type of point defects below the semiconductor free surface and its metal interface with nanoscale precision. Using depth-resolved cathodoluminescence spectroscopy (DRCLS) of deep level emissions calibrated with electrical techniques, we find that native point defects can (i) increase by orders-of-magnitude in densities within tens of nanometers of the semiconductor surface, (ii) alter free carrier concentrations and band profiles within the surface space charge region, (iii) dominate the Schottky barrier formation for metal contacts to ZnO, and (iv) play an active role in semiconductor doping. Among major roadblocks to ZnO optoelectronics have been the difficulty of both n- and p-type doping. Oxygen vacancies (V_O), V_O complexes, Zn interstitial-related complexes, and residual impurities such as H and Al are all believed to be shallow donors in ZnO, while Zn vacancies (V_{Zn}) and their complexes are acceptors. While their impact on free carrier compensation and recombination is recognized, the physical nature of the donors and acceptors dominating carrier densities in ZnO and their effect of carrier injection at contacts is unresolved. How these defects impact ZnO optoelectronics at the nanoscale is only now being explored. We address these issues using a combination of depth-resolved and scanned probe techniques to clearly identify the optical transitions and energies of V_{Zn} and V_{Zn} clusters, Li on Zn sites, Ga on Zn site donors, the effects of different annealing methods on their spatial distributions in ion-implanted as well as Ga grown-in ZnO, and how V_{Zn}, V_{Zn} clusters, and V_O complexes contribute to near- and sub-surface carrier density. Defects also couple to nanostructures, which form spontaneously on ZnO polar surfaces and create sub-surface V_{Zn} locally with Zn diffusion that feeds the growth. These results reveal the interplay between ZnO electronic defects, dopants, polarity, and surface nanostructure, and they highlight new ways to control ZnO Schottky barriers and doping.

2:40pm **EM-WeA3 High Level of Mg Alloying Effects on the Deep Level Defects in $Mg_xZn_{1-x}O$**, ***E. Gur***, The Ohio State University, *G. Tabares,* Ciudad Universitaria, Spain, *A. Arehart,* The Ohio State University, *J.M. Chauveau,* University of Nice Sophia Antipolis, France, *A. Hierro,* Ciudad Universitaria, Spain, *S.A. Ringel*, The Ohio State University

The $Mg_xZn_{1-x}O$ material system is very promising for ultraviolet emission and detection applications because of its direct band-gap, band-gap tunability, low lattice mismatch, and low polarization field. Using molecular beam epitaxy, a-plane 1.5 micron thick *n*-type $Mg_xZn_{1-x}O$ films (x=0, 0.26, 0.36, 0.43, 0.52) were grown on r-plane sapphire. Semi-transparent 100 Å thick Au Schottky contacts were used for deep level optical spectroscopy measurements (DLOS). The Schottky diodes (SD) exhibited rectification with low leakage currents and barrier heights between 1.00-1.19 eV from $Mg_{0.52}Zn_{0.48}O$ to ZnO. The frequency dependence of the capacitance caused by the high series resistance of the SDs required low frequency lock-in based capacitance measurements for accurate determination of capacitance. Lock-in 1kHz DLOS measurements revealed six deep levels in $Mg_xZn_{1-x}O$ samples while only three deep levels were observed in ZnO. In all samples, the energy of the deep levels relative to the conduction or valence band was independent of Mg content. The ~Ec-1.4 eV, ~Ec-1.85 eV, and ~Ec-2.50 eV levels follow the conduction band while ~Ev+1.20 eV, ~Ev+0.60eV, and ~Ev+0.28 eV follow the valence band. Because of high concentration of two dominant deep levels, lighted capacitance-voltage measurements was applied on all the samples in order to obtain true values of the concentration of the traps. The concentration of the two dominant compensating centers at ~E_v+0.28 eV and ~E_v+0.60 eV are ~$3x10^{16}$ cm^{-3} and ~$1x10^{16}$ cm^{-3}, respectively.

3:00pm **EM-WeA4 Comparative Depth Resolved Cathodoluminescence and X-ray Excited Optical Luminescence Studies of $SrTiO_3$**, ***R.A. Rosenberg***, *Y. Choi, V. Kalyanaraman,* Argonne National Laboratory, *M. Kareev, J. Tchakhalian,* University of Arkansas at Fayetteville, *S. Balaz, L.J. Brillson*, Ohio State University

$SrTiO_3$ and related perovskite materials are increasingly being utilized in a wide range of electrical applications. Furthermore, $SrTiO_3$ is often used as a substrate for growth of thin film structures. Thus, knowledge of its defect structure and, in particular, their depth dependence is crucial for understanding their impact on conductivity and optical phenomena. In the present work we utilize the limited penetration depth of x-rays to study the near-surface properties of $SrTiO_3$ substrates and epilayers and compare the results to analogous measurements using electrons. For an incidence angle of 10 degrees, the x-ray penetration depth varies between 22 and 207 nm as the energy changes from 600 to 1500 eV. For electrons the mean penetration depth varies from 3 to 90 nm as the energy changes from 0.5 to 5 keV. Thus, by obtaining x-ray excited optical luminescence (XEOL) and cathodoluminescence (CL) spectra as a function of x-ray or electron energy, it is possible to probe the near-surface region with nm-scale resolution. We will present energy-dependent XEOL and CL data from several $SrTiO_3$ samples. The luminescence spectra show features that can be assigned to Ti^{3+} (~1.6 eV) and oxygen-related (1.9-2.9 eV) defects, but the relative intensities differ between XEOL and CL. We will discuss the results in terms of the respective mechanisms, previous CL studies [1,2] and theoretical models.

This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357. We gratefully acknowledge

Ohio State University support from Army Research Office Grant

W911NF-10-1-0220

1. J. Zhang, et al, J. Vac. Sci. Technol. B 26, 1456 (2008).

2. J. Zhang, et al, Appl. Phys. Lett. 94, 092904 (2009).

4:00pm **EM-WeA7 Quantifying the Surface Generation Rate for Bulk Point Defects in TiO_2**, ***K. Pangan-Okimoto***, *A. Hollister, P. Gorai, E.G. Seebauer*, University of Illinois at Urbana Champaign

The defect and surface properties of titania have been well-studied for its potential use in memory resistors and nanoelectronic gas sensors but the control of these properties in such fields has still not been fully realized. Such control of defect mobility and concentration in titania is essential for improving the operation of these technologies. Previous work in our research group has found that controlling the rutile (110) surface has opened up a new pathway for oxygen self-diffusion via an oxygen-interstitial mechanism in conditions where oxygen vacancies and titanium interstitials are thought to dominate. The present work models the detailed diffusion-reaction network of point defects in rutile to simulate interstitial-mediated self-diffusion of oxygen and to calculate a generation rate of bulk point defects at the surface. The model explicitly incorporates gas adsorption onto the (110) surface, interstitial generation at the surface/near surface, and diffusion of the oxygen in an interstitial-mediated mechanism through the bulk. In addition, the model employs techniques drawn from systems engineering to estimate the key kinetic parameters. Simulated diffusion profiles were compared to experimental profiles obtained by exposing annealing single-crystal rutile to isotopically labeled oxygen gas and then measuring isotopic oxygen concentration with secondary ion mass spectrometry. The simulated diffusion profiles matched experimental results, verifying that oxygen interstitials do indeed mediate oxygen self-diffusion in our experiment. More importantly, our model allows us to calculate the oxygen interstitial generation rate at the (110) surface, a first for titania.

4:20pm **EM-WeA8 Metastable Defects and Recoverable Degradation in InAs/AlSb HEMTs**, ***X. Shen***, *S. DasGupta, R.A. Reed, R.D. Schrimpf, D.M. Fleetwood, S.T. Pantelides*, Vanderbilt University

It is known that some defects undergo a structural transformation to a metastable configuration when capturing a carrier. However, their roles in affecting device performance are not widely recognized. Here we show that metastable oxygen defects can cause recoverable degradation of InAs/AlSb HEMTs (high-electron mobility transistors).

Recently, we performed electrical stress tests on InAs/AlSb HEMTs and observed a recoverable degradation in some of the devices. The degradation is manifested as negative shifts of the transconductance peak and threshold voltage, which nearly completely recover after two days at room temperature. The recoverable nature of the degradation suggests that metastable defects are involved. The threshold shift indicates an increase of donor concentration or a decrease of acceptor concentration in the device. No degradation of mobility in the channel is observed, indicating that the responsible defects are in the AlSb barrier instead of the InAs channel.

We propose that the recoverable degradation is caused by a pre-existing defect in the top AlSb barrier being converted into more positive metastable configurations upon capturing the injected holes that are generated by impact-ionization in the channel. To identify the responsible defects, we performed a thorough survey of the defects in AlSb such as intrinsic defects, dopants, and contaminants, using first-principles calculations. We found that among all the candidates, oxygen impurities, both substitutional and interstitial, can account for the observed degradation. More specifically, both oxygen defects undergo large structural changes upon capturing two holes and the resulting states are metastable.

It is notable that the metastability of the oxygen defects in these devices does not originate from an energy barrier, but instead from a totally different mechanism. The Fermi level in the AlSb layer is pinned in the lower part of its band gap by the adjacent InAs layer, which ensures low electron concentration in AlSb. This leads to slow electron capture by the metastable defects. Furthermore, upon capturing two holes, the emptied electronic level associated with an oxygen defect is shifted far above the Fermi level due to the large structural relaxation. This energy-level shift ensures slow hole emission from the defect and slow electron tunneling from the adjacent layer. This mechanism results in lifetimes of metastable defects that are consistent with the experiments, and is further confirmed by additional annealing experiments that are done under bias.

The work was supported by ONR MURI under Grant No. N-00014-08-10665 and by the McMinn Endowment at Vanderbilt University.

4:40pm **EM-WeA9 Room-Temperature Native Defect Diffusion in Semiconductors**,
***K.H. Warnick**, Y.S. Puzyrev, T. Roy, D.M. Fleetwood, R.D. Schrimpf,* Vanderbilt University, *S.T. Pantelides*, Vanderbilt University and ORNL

Diffusion mediated by native point defects does not generally occur in semiconductors at room temperature (RT) because of high activation energies. However, recent observations of plastic deformation in AlGaN/GaN High Electron Mobilty Transistors (HEMTs) in AlGaN epilayers on GaN in the presence of strain and electric fields have been attributed to diffusive processes. Here we report the results of first-principles density-functional calculations of formation and migration energies of vacancies under strain and electric fields that allowed us to identify the enablers of self-diffusion at RT in AlGaN/GaN structures: triply-negative cation vacancies with near-zero formation energy, driven by an electrostatic potential gradient. We show that the formation energies of Ga and Al vacancies in unstrained n-type AlGaN are near zero but their migration energies are too large, >1.5 eV, for appreciable diffusion at RT (typically the diffusion activation energy, i.e., sum of formation and migration energies, must be ~1 eV or lower for diffusive processes to be appreciable at RT). We find that application of strain, even at substantial levels, has little effect on either formation or migration energies. However, the Ga and Al vacancies are triply negative, and application of an electric field lowers the barrier for migration by more than 0.5 eV. At the observed critical values of the field, the net activation energy is lowered down to approximately 1 eV which makes thermally-activated atomic migration possible at RT. Simulation of the AlGaN/GaN HEMT shows that the electric field is highest in the region where the plastic deformation is observed. These results provide a mechanism for plastic deformation mediated by vacancies, much like Nabarro-Herring creep and dislocation climb, but with an electric field being the main driver (vacancy drift). In addition, unusually high local strain can also lead to dislocation glide and further dislocation formation via strain relaxation, compounding the role of vacancy migration processes.

The work was supported in part by ONR MURI grant N-00014-08-1-0655 and by the McMinn Endowment at Vanderbilt University.

5:00pm **EM-WeA10 Defect Interactions at Grain Boundaries in Polycrystalline Graphene**,
***Y.S. Puzyrev**, B. Wang,* Vanderbilt University, *S.T. Pantelides*, Vanderbilt University and ORNL

The properties of polycrystalline graphene largely depend on the properties of the grain boundaries (GB) [1,2]. Classical molecular dynamics simulations coupled with density functional calculations of vacancies and self-interstitials at grain boundaries show that lower formation energies are induced by the local strain near the GB. The vacancies interact with each other as well as the interstitials. Vacancies and interstitials [3] can diffuse in graphene due to their low migration barrier. We investigated the time scale of vacancy and interstitial dynamics in pristine graphene and at grain boundaries at the distances where defect-defect and defect-GB interactions are found to be significant. GB-558 consists of pentagon and octagon pairs, whereas GB-575 is formed by repeated pentagon-heptagon pairs. We show that recombination of vacancies and interstitials can occur at grain boundaries resulting in efficient annealing of defects. The compression (stretch) for GB-558 is up to 3%, while in GB-575, the stretch reaches 9% at the C-C bonds between pentagon and heptagon or between hexagon and heptagon. We find that single vacancies can diffuse towards a grain boundary, attach to a pentagon, then merge into the grain boundary to release the compressive strain and cause local reconstruction. Molecular dynamics simulations show that if a single vacancy exits at 1nm from the grain boundary GB-558, it diffuses towards the grain boundary and attaches at the pentagon ring after 160 ps at 3000 K. It takes another 40 ps to merge into the grain boundary. Similar phenomena occur in GB-575. Stretched C-C bonds at the heptagon, on the other hand, accumulate interstitials. An interstitial that was initially positioned 7 Å above the graphene sheet, was adsorbed on the grain boundary. Once the vacancy coalesces into the grain boundary, the carbon adatom fills the reconstructed vacancy and recovers the original grain boundary structure. This recombination takes only ~ 0.5 ns at 2000 K. The results suggest a new mechanism of defect annealing with a two-step procedure, i.e. point defects (single vacancies and interstitials) diffuse and recombine locally at grain boundaries. This work was supported by DTRA Grant No. HDTRA1-10-1-0016, the US Department of Energy, Basic energy Sciences, and the William A. and Nancy F. McMinn Endowment at Vanderbilt University. The calculations were performed at ORNL's Center for Computational Sciences and the Air Force Research Laboratory DoD Supercomputing Resource Center

[1] P. Y. Huang et. al, *Nature 469*, 389-393, 2011.

[2] Q. X. Pei, Y. Z. Zhang, V. B. Shenoy, *Carbon 48*, 898-904, 2010.

[3] A. Hashimoto, et. al, *Nature 430*, 870-873, 2004.

5:20pm **EM-WeA11 X-ray Induced Defect Formation in Graphene**,
***E.X. Zhang**, A.K.M. Newaz, S. Bhandaru, M.L. Alles, D.M. Fleetwood, R.D. Schrimpf, K. Bolotin, R.A. Reed, R.A. Weller, S.M. Weiss, S.T. Pantelides*, Vanderbilt University

Graphene is a truly two-dimensional material that consists of carbon atoms connected by sp^2 bonding and arranged in a honeycomb lattice. Due to its unique properties and potential applications in future electronic devices, graphene has received much attention recently from the scientific community. Initial studies of the effects of electron-beam and proton irradiation have been performed on graphene materials, but there remain significant questions about the nature of the conductivity and of the defects.

In this work, the responses of graphene materials to 10-keV x-ray radiation are evaluated with Raman spectroscopy. A defect related peak (D-peak) appears (~1345 cm^{-1}) after x-ray irradiation in air; the intensity of the D-peak increases with increasing total dose, and decreases with post-irradiation vacuum annealing at 350 °C. (See supplemental figures.) These results suggest that new defects can be created and/or that weak bonds at defect precursor sites can be scissioned and decorated with impurities (e.g., H, O) during x-ray exposure. The charge neutral point of graphene transistors made from similar material shifts positively with increasing x-ray dose, suggesting that similar defects may contribute to shifts in the Dirac point and degradation in the conductivity.

It has been shown previously that ozone can react with C-C bonds to degrade graphene layers. We have measured significant ozone generation during x-ray irradiation, suggesting that the x-rays may not directly create the defects sensed by Raman, but that x-ray generated ozone may lead to at least some of the observed defects. However, it is likely that there is an additional source of degradation, since in previous work the ozone reaction typically has been shown to lead to irreversible degradation, but we find that vacuum annealing at elevated temperature leads to partial recovery. Hydrogen annealing treatments of graphene have shown reversible degradation. Thus, it seems likely that hydrogen released by x-ray exposure in the SiO_2 substrate reacts with defect precursors (e.g., weak bond sites) in the graphene. Hydrogen reactions with C-C bonds can enhance the intervalley scattering, thereby increasing the D line intensity. Much of the hydrogen may be driven out by annealing in vacuum at 350 °C, leading to recovery of the degradation, consistent with our experimental results.

This work was supported by the DTRA Basic Research Program through Grants HDTRA1-10-1-0016 and HDTRA1-10-1-0041.

5:40pm **EM-WeA12 Influence of Point Defects on the Properties of Highly Mismatched Alloys**, *R.L. Field III, T. Dannecker, Y. Jin, C. Kurdak, C. Uher,* ***R.S. Goldman***, University of Michigan

It has been suggested that alloy films composed of highly immiscible solute atoms in a solvent, termed "highly-mismatched alloys" (HMAs), are promising for energy conversion devices due to their ability to efficiently absorb light and heat, and to subsequently transport charge carriers. The properties of HMAs are often described with models focusing on the influence of individual solute atoms, assuming that all solute atoms "see" the same atomic environment. In the case of GaAsN alloys, the single local environment models predict a N composition-dependence of the energy band gap which agrees *qualitatively* with experiment. However, such models do not *quantitatively* explain several extraordinary electronic and optical properties. In this talk, I will discuss our investigations of the growth [1], structure [2-3], and properties [4-6] of GaAsN alloys. I will focus on correlations between the presence of N-N, N-As, and N-Si pairs [2,5-6] and extraordinary physical phenomena, including non-monotonic composition-dependent effective masses [7] and persistent photoconductivity [8]. I will also discuss our preliminary work on complementary alloys in the GaAsBi system.

[1] M. Reason, et al, *J. Appl. Phys.* **101**, 083520 (2007).

[2] M. Reason, et al, *Appl. Phys. Lett.* **85**, 1692 (2004).

[3] M. Reason, et al, J. Appl. Phys. 97, 103523 (2005).

[4] M. Reason, et al, *J. Appl. Phys.* **102**, 103710 (2007).

[5] Y. Jin, et al, *Appl. Phys. Lett.* 95, 062109 (2009).

[6] Y. Jin, et al. *Appl. Phys. Lett.* 95, 092109 (2009).

[7] T. Dannecker, et al. *Phys. Rev. B* 82, 125203 (2010).

[8] R.L. Field III, et al., to be submitted (2011).

Thin Film Division
Room: 109 - Session TF1+EM-WeA

Nonvolatile Memory
Moderator: T. Karabacak, University of Arkansas at Little Rock

2:00pm **TF1+EM-WeA1 Application of Amorphous Zinc Tin Oxide for Memristor Devices**, ***G.S. Herman***, *J.S. Rajachidambaram, S. Murali, J. Conley,* Oregon State University, *S.P. Sanghavi, P. Nachimuthu, V. Shutthanandan, T. Varga, S. Thevuthasan*, Pacific Northwest National Laboratory

Amorphous zinc tin oxide semiconductor materials have been studied primarily as the active semiconducting material for thin film transistors with applications including transparent and flexible electronics. Due to the amorphous nature of these materials excellent uniformity can be obtained over a large area, while still having reasonably high electron mobilities (>10 cm^2/Vs). Furthermore, considerable control over the electrical properties can be maintained, where insulating, semiconducting, and conductive properties can be obtained by varying the processing conditions. We have recently used sputter-deposited zinc tin oxide as a bipolar switching element in memristor devices. Memristors are a two-terminal nonvolatile data memory device that is very promising for the replacement of silicon-based Flash. A significant benefit is that memristors can be manufactured with high areal densities with potentially low manufacturing costs. A variety of oxide-based materials are being evaluated for memristors, however many of these are nanocrystalline which can lead to non-uniformity of devices. We have found that the switching properties of zinc tin oxide are closely related to the process conditions, the electrical test conditions, and the electrode materials. In this presentation we will discuss the physical and electrical characterization of the zinc tin oxide films and the switching mechanisms for these materials.

2:20pm **TF1+EM-WeA2 PE-MOCVD of GeTe Materials for Phase Change Memory Applications**, ***E. Despiau-Pujo***, *L. Dussault, C. Vallée,* LTM/CNRS-UJF, France, *E. Gourvest,* ST Microelectronics, France, *D. Jourde, S. Maitrejean, P. Michallon*, CEA Leti Minatec Campus, France

Phase-Change Random Access Memories (PCRAM) are very promising candidates for next generation of non-volatile memories. Those devices store information using the high electrical contrast between the amorphous and crystalline phases of chalcogenide alloys such as $Ge_2Sb_2Te_5$ (also called GST) which are mainly deposited by physical vapor deposition (PVD) [1]. However, two important drawbacks have to be overcome: a too short archival life for GST at high operating temperatures and a too high power consumption. The binary compound GeTe seems to be a promising candidate for high temperature applications since it has an estimated archival life up to ten years at 110°C. A pronounced increase in thermal stability of N- and C-doped GeTe was also demonstrated [2].

Concerning the power consumption, it was shown that a way to reduce the high operating currents is to confine the material. In this way, several groups try to develop a new deposition process to achieve the gap filling of the confined structure. Atomic Layer Deposition (ALD) of GST has shown very good step coverage but the deposition rate remains very low. Therefore, we proposed to study the deposition of GeTe in a shower-head type 200mm plasma-enhanced pulsed liquid injection CVD reactor (AltaCVD200). Ge and Te liquid precursors are introduced into the deposition chamber as vapours through a pulsed injection system and an evaporating furnace. A capacitively-coupled RF plasma is applied between the shower head and the substrate heater to decompose the precursors. Chamber walls are maintained at 70°C to avoid condensation of precursors vapours. The deposition chamber is mounted on a cluster tool which allows quasi *in situ* analysis of the deposited films by angle-resolved XPS while the plasma is analyzed by optical emission spectroscopy (OES).

In this paper, we investigate the optical emission spectra of high pressure (2-20 Torr) Ge- and Te-containing plasmas. Reference UV-visible emission spectra (200-800 nm) are recorded for various conditions of RF power, pressure, and flow rate. The role of electrons and H atoms in the decomposition of Ge and Te precursors is discussed by correlating the OES of the plasma with the chemico-physical properties of the deposited material. It is shown that H atoms induce a competitive effect between deposition (due to the decomposition of the precursors) and etching of Ge and Te atoms at the growing film surface. Role of C contamination in the phase change properties is also discussed and phase transitions of plasma deposited GeTe-C materials are compared with sputtered GeTe-C.

[1] G. W. Burr et al, J. Vac. Soc. Technol. B 2010, 28 (223)

[2] A. Fantini et al, IEDM 2010

2:40pm **TF1+EM-WeA3 Embedded HfO_2 based 1T1R Cells for Future RRAM Applications**, ***Ch. Wenger***, *T. Bertaud, Ch. Walczyk, D. Walczyk, M. Malgorzata*, IHP, Germany **INVITED**

The integration of various functionality to (Bi)CMOS circuits is in the focus of the "More than Moore" approach. Here, we demonstrate the incorporation of nonvolatile memories (NVM) into the Back end of line (BEOL) of Bi(CMOS) circuits. The added functionalities open new technological possibilities for high value microelectronics systems.

Embedded nonvolatile memories (NVM) with high-density, high-speed, and low-power are attractive for a growing number of applications. One promising candidate for next-generation nonvolatile memories is based on the electrically switchable resistance change between a high (OFF-state) and a low (ON-state) resistive state of a metal-insulator-metal (MIM) structure. This approach is often termed resistance random access memory (RRAM) technologies. Due to the cost effectivity and BEOL compatibility with (Bi)CMOS technologies, this approach is highly attractive. By combining the MIM devices (R) with selection transistors (T), the 1T-1R cells offer good scalability, long retention time, and rapid read/write times. In this letter, the reliable bipolar resistive switching of TiN/HfO_2/Ti/TiN devices embedded into 1T-1R cells is demonstrated.

The current-voltage (I-V) characteristics of the TiN/HfO_2/Ti/TiN diodes and 1T-1R cells were studied by DC voltage sweep measurements. By applying a positive voltage at the top electrode, the resistance is reduced for $V > V_{Set}$. The device can be switched back into the OFF-state when a negative voltage is applied beyond V_{Reset}. In case of the 1T-1R cell, the forming and set processes can be controlled by changing the gate voltage (V_G) of the select transistor.

4:00pm **TF1+EM-WeA7 Synthesis and Characterization of Multiferroic Oxides by Radical Enhanced Atomic Layer Deposition**, ***C.D. Pham***, *J.H. Choi, J.P. Chang*, University of California Los Angeles

Multiferroic materials exhibit two or more forms of ferroic order such as (anti)ferroelectricity, (anti)ferromagnetism, ferroelasticity, or ferrotoroidicity. Materials containing both ferroelectricity and ferromagnetism will exhibit some amount of magnetoelectric coupling which is a desirable aspect for the future of non-volatile memory, as these materials could potentially be used for devices that will be written magnetically and read electronically or vice versa, as well as the prospect of four-state memory devices. Materials which exhibit magnetoelectric coupling have been well studied, however, the synthesis methods may not easily translate into large scale integration.

One possible route for synthesis on a commercial scale, atomic layer deposition (ALD) is a thin-film processing technique which involves

alternatively flowing non-self reacting precursor vapors or gases onto a substrate. As a result of the self limiting reaction, the precursors only form a single monolayer per cycle. The sequential and self-limiting nature of the deposition is used to deposit thin films with good compositional control, high conformity, high uniformity, and excellent thickness control.

To create multiferroic crystal structures, a 1:1 stoichiometric ratio between cations is desired with low contamination by organic ligands in order to form the crystal phases that permit multiferroicity. Therefore, in this work, multiferroic $YMnO_3$ and $BiFeO_3$ on various substrates are synthesized by radical enhanced atomic layer deposition (RE-ALD) using $Y(tmhd)_3$ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), $Mn(tmhd)_3$, $Fe(tmhd)_3$, and $Bi(tmhd)_3$ as metal precursors and oxygen radicals as the oxidizer. By varying the cycle sequences, controlled composition is demonstrated and verified through XPS. Growth rates are shown on a thickness per cycle basis as a function of deposition temperature, precursor pulse times, and substrate. The crystal structure as well as atomic environment are examined by XRD and extended x-ray absorption fine structure spectroscopy (EXAFS) respectively and are accompanied by TEM micrographs. Finally, magnetic measurements made by a super conducting quantum interference device (SQUID) magnetometer, zero-field cooled and field cooled (ZFC-FC) M vs. T and M vs. H, are shown on 1:1 $YMnO_3$ stoichiometric films showing a Néel temperature T_N = ~45 K and a coercive magnetic field H_C = 130 Oe for Si(111) and H_C = 300 Oe for YSZ(111).

4:20pm **TF1+EM-WeA8 Perpendicular Magnetic Tunnel Junctions based on Thin CoFeB Free Layer and Co-based Multilayer SAF Pinned Layers**, ***A. Natarajarathinam***, *S. Gupta*, University of Alabama

We have previously reported on fully perpendicular Co/Pd multilayers (ML)-based CoFeB/MgO/CoFeB magnetic tunnel junctions (MTJ's)1, 2. However, Co/Pd ML-based MTJ's have rarely exhibited TMR ratios greater than about 10%. This has been attributed to the inability to pull a sufficiently thick CoFeB layer perpendicular on top of MgO, as well as the incomplete bcc templating of CoFeB from MgO owing to the adjacent fcc Co/Pd ML's3. Recent results3-7 have generated great interest in MTJ's with pinned perpendicular synthetic antiferromagnets (SAF), of the form AP1/Ru/AP2 where AP1 and AP2 are Co-based multilayers, for instance, Co/Ni or Co/Pd. We report on fully perpendicular MTJ's with a thin CoFeB free layer and a Co/Pd(Pt) ML-based SAF pinned layer. For Co/Pd ML SAF's, strong antiferromagnetic coupling was seen at tRu of 1.1nm, with a coupling strength of 0.017 mJ/m2. For Co/Pt ML SAF's the optimum antiferromagnetic coupling was found at slightly higher Ru thickness of 1.3 nm, with a coupling strength of 0.013 mJ/m2. Improved MTJ properties are expected from using a thin Ta-seeded CoFeB bottom free layer, along with a thin, amorphous Ta layer used to transition from bcc CoFeB to fcc Co/Pd(Pt) for the top pinned layer6. The full stack is of the form: bottom lead/Ta (2)/CoFeB(1)/MgO(1.6)/CoFeB(0.8)/Ta(0.3)/[{Co(0.3/Pd(1)}5/Co(0.3) or {Co(0.5)/(Pt(2)}5/Co(0.5)/Ru1.1 or 1.3/[Co(0.3/Pd(1) or Co(0.5)/(Pt(2)]9/top lead. CIPT measurements indicated TMR values as high as 20% for as-deposited stacks. Magnetometry of blanket stacks showed a large separation in the switching fields of free and pinned layers, with free layer switching close to zero field and pinned layer switching at 0.8-1.8 kOe (Fig.1). This symmetric extended plateau of constant magnetization offers a large dynamic range over which the magnetic configuration remains stable7. The stacks were patterned into MTJ's, annealed at 240◦ C in an in-plane field of 0.5 T, and characterized magnetically and electrically.

Acknowledgements:

This work is partially supported by a U.S. Department of Defense DARPA-MTO STT-RAM Universal Memory contract, and Grandis Technology, Milpitas. Dr. David Abraham of IBM is gratefully acknowledged for CIPT measurements.

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4:40pm **TF1+EM-WeA9 Characterizing the Effects of Processing on Materials for Phase Change and Spin Torque based Non-Volatile Memory Technologies**, ***E.A. Joseph***, *R.M. Martin, J.S. Washington, D.W. Abraham, S. Raoux, J.L. Jordan-Sweet,* IBM T.J. Watson Res. Ctr.*, D. Miller,* IBM Almaden Res. Ctr.*, H.-Y. Cheng,* Macronix International Co., Ltd, Taiwan, R.O.C.*, M.C. Gaidis, M. Gajek, M. Breitwisch,* IBM T.J. Watson Res. Ctr.*, S.-C. Lai,* Macronix International Co., Ltd, Taiwan, R.O.C.*, Y. Zhu, R. Dasaka, R. Sawant, D. Neumayer,* IBM T.J. Watson Res. Ctr.*, R.M. Shelby,* IBM Almaden Res. Ctr.*, H.-L. Lung,* Macronix International Co., Ltd, Taiwan, R.O.C.*, C.H. Lam, N.C.M. Fuller*, IBM T.J. Watson Res. Ctr. **INVITED**

Phase change memory (PCM) and spin-torque magnetic random access memory (ST-MRAM) have recently garnered significant interest for future non-volatile memory applications due to their promise for scalability beyond that of conventional DRAM and flash memory technologies. In addition, both PCM and ST-MRAM have potential to enable improvements in programming speed, low voltage operation and high endurance, as compared to current devices. However, the introduction of each technology not only brings with it new device challenges, but the fabrication process itself can also alter the properties of the materials, leading to performance degradation. In this work, we explore the effects of integration and processing on $Ge_2Sb_2Te_5$ (GST) and CoFeB for PCM and ST-MRAM devices respectively, with relevance towards scaling to the 14nm node and beyond. Using multiple analysis techniques including time resolved laser reflectivity and X-ray diffraction, we determine that exposure to various etch and ash plasma chemistries can cause a significant reduction in the (re)crystallization speed of GST, while concurrently increasing the transition temperature from the rocksalt to the hexagonal phase. Furthermore, by utilizing optical emission spectroscopy, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) we are able to link the changes in crystallization to etch-induced modification of the GST stoichiometry. For CoFeB materials, vibrating sample magnetometry is used to determine the effect that plasma exposure (as used for both patterning and encapsulation) has on the magnetic moment. We find that even when relatively thick capping layers are present, magnetic moment can still be significantly degraded. The severity of this effect is heavily dependent on plasma chemistry. Further results of process-induced material modification and device degradation as a function of etch, encapsulation, and thermal processing will be presented, focusing primarily on the impact on scaling of these technologies. Finally, potential integration and processing solutions to circumvent these issues will also be discussed.

Thin Film Division
Room: 110 - Session TF2+EM-WeA

Nanostructuring Thin Films
Moderator: A.V. Melechko, North Carolina State University

2:00pm **TF2+EM-WeA1 Templated Solid-State Dewetting for Patterning of Films**, ***C.V. Thompson***, *J. Ye, A.L. Giermann*, Massachusetts Institute of Technology **INVITED**

Most crystalline thin films are metastable in the as-deposited state, and will dewet to form islands when they are heated to temperatures that lead to sufficiently high atomic mobilities. This can happen well below the melting temperature of the film, so that the material remains in the form of a crystalline solid throughout the dewetting process. When unpatterned films dewet on flat substrates, the resulting islands have widely varying sizes and spacings. However, we have shown that substrate patterning can be used to control the solid-state dewetting process and to produce ordered arrays of monodispersed and crystallographically aligned islands from polycrystalline films. Recent experiments on patterned single-crystal films have allowed independent study of the various mechanisms that control structure evolution during solid-state dewetting. These include fingering instabilities, edge faceting, corner instabilities, pinch-off processes, and Rayleigh-like instabilities. Surface energy anisotropy plays a very important role in these processes, and for single-crystal films, leads to the formation of crystallographically aligned complex patterns of lines and islands that can be reproducibly controlled through pre-patterning.

2:40pm **TF2+EM-WeA3 Dynamics of Solid Thin-Film Dewetting in the Silicon-On-Insulator System**, ***E. Bussmann***, *F. Cheynis, F. Leroy, P. Müller*, CINaM-CNRS, France

Thin-film dewetting is a process wherein a film on a substrate spontaneously agglomerates into 3D islands, which in some instances are ordered. A detailed understanding of the mechanism and dynamics of dewetting is crucial, either to avoid the agglomeration, or to engineer

organized arrays of nanostructures. Silicon-on-Insulator (SOI) films, which are promising substrates for microelectronics, undergo dewetting when annealed at >700°C under ultrahigh vacuum conditions. The Si film spontaneously transforms into an assembly of ordered nano-sized Si islands. Previous *ex-situ* studies of dewetted SOI films provided a qualitative description of the dewetting process [1-4]. However, the dewetting dynamics, as well as the thermodynamic driving forces and atomistic mechanisms at work, remained largely unclear. We simultaneously measure the real-time dewetting dynamics and the motion of surface atomic-steps (surface self-diffusion) using low-energy electron microscopy (LEEM) [5]. We observe the following scenario: (i) dewetting voids nucleate at defects in the Si(001) layer. In the early stages of dewetting, the area of the opening voids grows linearly with time, and the Si ejected from the voids accrues into a rim surrounding the dewetted area. (ii) As dewetting progresses, the rim undergoes an instability that leads to the formation of elongated Si fingers. Once the first fingers have formed, the void area grows as the square of time. (iii) Finally, the Si fingers undergo a Plateau-Rayleigh instability, breaking apart into 3D Si nano-islands. We compare our measurements of the morphological evolution of dewetting to a simple analytical model for dewetting void growth (based on surface diffusion, nucleation on the top of the 3D structures, and mass-conservation), and to Kinetic Monte Carlo simulations. The KMC simulations reproduce the qualitative features of the complex void shape evolution in detail, while the analytical model of void growth allows us to connect the void growth rate with the dewetting driving force. These approaches unambiguously show that the SOI dewetting process is surface-diffusion-limited and driven by surface and interface free-energy-minimization.

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3:00pm **TF2+EM-WeA4 Self and Directed Assembly of Thin Metallic Films by Pulsed Laser Induced Dewetting**,
Y. Wu, University of Tennessee, *J.D. Fowlkes,* Oak Ridge National Laboratory, *L. Kondic,* New Jersey Institute of Technology, *J. Diez,* Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Argentina, *N.A. Roberts, P.D. Rack*, University of Tennessee

The synthesis and assembly of functional metallic nanomaterials is critical for realizing many important applications of nanoscience and nanotechnology, and metallic thin film dewetting has been an effective and low-cost approach to this end. In this study, we investigated dewetting of metal thin films via pulsed nanosecond laser melting. We also explore the dewetting and nanopattern formation of nanolithographically pre-patterned thin films of various shapes to understand initial and boundary conditions in guiding the assembly. More recently, nanolithography was used to impose the perturbation which ultimately led to an organized nanoparticle array. Specifically, liquid–phase pulsed laser induced dewetting (PLiD) was used to transform metallic thin film strips into nanoparticle arrays. We demonstrated that the assembly accuracy and precision could be drastically improved by merely imposing a synthetic sinusoidal perturbation onto the lateral surfaces of the thin film strip. The synthetic perturbations in the strip translated into an unstable varicose oscillation on the rivulet during retraction – a precise nanoparticle diameter and pitch emerged thereby superseding the otherwise naturally evolving modes predicted by the modified Rayleigh-Plateau instability. A nanoscale, synthetic perturbation was usefully imposed to “nudge” the natural, self–assembly dispersion toward significantly higher order.

4:00pm **TF2+EM-WeA7 Directed Self-Assembly of Ge Heteroepitaxial Quantum Dots with sub-35nm Spacing**,
C. Petz, University of Virginia, *D. Yang, J. Levy,* University of Pittsburgh, *J.A. Floro*, University of Virginia

Artificially ordered Ge quantum dot (QD) arrays, where confined carriers can interact via spin coupling, may create unique functionalities such as spintronic bandgap systems. Development of such arrays for quantum computing requires fine control over QD size and spatial arrangement on the sub-35 nm length scale. We employ fine-probe electron-beam irradiation to locally decompose ambient hydrocarbons onto a bare Si (001) surface. These carbonaceous patterns are annealed in UHV, forming ordered arrays of nanoscale SiC precipitates that serve as templates for subsequent Ge quantum dot nucleation via strain-induced self-assembly during heteroepitaxy. The nanoprecipitates effectively reduce the critical thickness for Ge QD formation to below the 3-4 monolayers typical of Stranski-Krastanov growth in the Ge/Si (001) system. Thus, Ge QDs in the SiC-patterned regions nucleate prior to formation of randomly located QDs in the unpatterned areas. It is critically important to ascertain the variability in Ge QD size and placement, and ultimately to determine the crystalline quality and interface properties of these ultrasmall Ge dots on SiC nanoprecipitates. Using atomic force microscopy and cross-sectional transmission electron microscopy, we investigate the patterned surface morphology and internal structure of patterned QDs to develop a fundamental understanding of the Ge adatom behavior in the vicinity of local high lattice-mismatch nanoprecipitates. We find that Ge self-assembly at SiC sites depends on QD spacing and that the QD size is surface diffusion limited, suggesting that local alteration of the intermediate Si surface may repel Ge to higher lattice mismatched SiC sites. Support from the DOE Office of Basic Energy Sciences is gratefully acknowledged under grant number: DE-FG02-07ER46421.

4:20pm **TF2+EM-WeA8 Surface Functionalization of Zeolites and Nanoparticles: Understanding and Applying Plasma Modification Strategies for Unusually Shaped Particles**,
J.C. Shearer, *E.R. Fisher*, Colorado State University

Unusually shaped micron- and nanometer-sized particles are becoming key components in catalytic and biological applications. Zeolite particles are typically modified for ion-exchange and catalytic applications. Fe_2O_3 nanoparticles are widely used in biological applications such as MRI imaging and site-specific drug delivery, thereby creating a need for surface functionalization techniques to ensure biocompatibility. Plasma processing can effectively modify and implant functional groups onto flat substrates, and is non-directional. Thus, the primary focus here is on applying these plasma processes to unusually shaped materials and understanding the gas-phase chemistry and surface reactions that make these coatings viable. Previous work in our lab employed plasma-enhanced chemical vapor deposition to create composite SiO_2/TiO_2 nanoparticles. Here, we use plasma processing methods for the modification of zeolite surfaces and functionalization of Fe_2O_3 nanoparticles. Compositional and morphological data demonstrate that the conformal treatment of particles was achieved and that the use of PECVD methods allowed for advanced control over surface modification and specific tailoring of the structure, composition, and growth characteristics of any deposited film. Insight into the modification and deposition process is provided by actinometric optical emission spectroscopy (AOES) and laser induced fluorescence spectroscopy (LIF), which allow characterization of the gas-phase species and their energetics (i.e. internal energies) for each system. To further investigate the functionalization of nanoparticle surfaces, additional studies explore the contributions of gas-phase OH radicals to the creation of SiO_2/Fe_2O_3 composite nanoparticles. Scatter coefficients and gas-phase density measurements derived from our imaging of radicals interacting with surfaces technique (IRIS) provides additional insight on the molecular-level chemistry occurring at the interface between gaseous plasma species and nanoparticle substrates. The operation and design of an in-house rotating drum reactor will be discussed as a potential method for adapting the composite nanoparticle fabrication to an industrial scale.

4:40pm **TF2+EM-WeA9 Role of Ion Flux on Alignment of Carbon Nanofibers Synthesized by DC Plasma on Transparent Insulating Substrates**,
R.C. Pearce, North Carolina State University, *A.W. Vasenkov,* CFD Research Corporation, *D.K. Hensley, M.L. Simpson, T.E. McKnight,* Oak Ridge National Laboratory, *A.V. Melechko*, North Carolina State University

A key factor to the implementation of vertically aligned carbon nanofibers (VACNFs) in devices is a more fundamental understanding of how to control fluctuations in the growth direction of the fibers. It has previously been hypothesized that the electric field is the primary factor in determining the orientation of fibers grown catalytically using plasma enhanced chemical vapor deposition (PECVD). Here we present results of carbon nanofiber synthesis on insulating substrates by dc plasma in the vicinity of grid electrodes. To perform these observations, VACNFS were synthesized on a fused silica substrate using direct current PECVD. To maintain continuous glow discharge above the substrate, a metal grid electrode layer (Cr) was deposited over silica with windows of exposed silica ranging in size from 200 µm to 1 mm. Observed trends in nanofiber alignment at the window-electrode interface suggests that the alignment is governed by the direction of the ion flux rather than the electric field at the substrate level. The proposed alignment mechanism is that ion sputtering of the carbon film on a catalyst particle the growth direction of the nanofibers. With this development, fiber growth direction can be better manipulated through changes in ionic flux direction, opening the possibility for growth of nanofibers on substrates with unique geometries.

5:00pm **TF2+EM-WeA10 High-Performance Poly-3-alkylthiophene-Carbon Nanotube Composites for Transparent Electrodes***,* ***S.L. Hellstrom****, R.Z. Jin, R.M. Stoltenberg, Z. Bao*, Stanford University

Flexible transparent electrodes are crucial for flat panel display and solar cell technologies. While carbon nanotube network electrodes show promise, their fabrication often involves insulating surfactants which worsen conductivity. As an alternative, we show that small amounts of conjugated semiconducting polymer added to nanotube dispersions enables straightforward solution deposition of uniform electrodes by spin-coating or drop casting. After doping, electrodes as good as 120 ohm/sq with 81% transmittance at 550 nm are obtained. Tuning system chemistry and deposition parameters allows control of tube bundle size, density, and alignment, and these may be correlated with electrode performance.

We also employ the selectivity of P3HT:CNT composites in wetting of and adhesion to different dielectric surfaces, to simultaneously fabricate and pattern organic electrodes with unprecedented nanotube density gradients and excellent feature resolution. We employ these to drive pentacene and C_{60} transistors that are competitive with those made using Au electrodes. We thereby suggest that this material system and fabrication technique has promise in applications requiring flexible, semitransparent, low-cost complementary circuits.

5:20pm **TF2+EM-WeA11 SiGe Nanomembranes: Defect-Free Single-Crystalline Growth Substrates for High- Quality Strained Epitaxial Materials***,* ***D.M. Paskiewicz****, B. Tanto, D.E. Savage, M.G. Lagally*, University of Wisconsin Madison

Silicon-Germanium semiconductor alloys are important in improving Group IV opto- and microelectronics. Typically, SiGe is used as a stressor to introduce strain into Si, thereby altering the electronic band structure [1, 2] or changing optical properties [3]. The SiGe stressor can be incorporated locally to strain small areas of Si uniaxially [2], or relaxed SiGe can be used as a substrate for growth of biaxially strained Si over large areas [1]. We will focus on the latter: using relaxed SiGe to induce global biaxial strain in Si. Conventional methods for creating relaxed SiGe substrates involve epitaxial growth on Si substrates and relaxation of the alloy *via* dislocations. The density of defects that reach the top relaxed SiGe layer can be limited though various techniques [4], but strain inhomogeneities and surface roughness created by the dislocations remain. We demonstrate the fabrication of SiGe nanomembranes (NM): fully *elastically* relaxed, smooth, single-crystalline sheets of SiGe alloy. A thin SiGe layer (less than the kinetic critical thickness for dislocation formation) is grown on a silicon-on-insulator (SOI) substrate with molecular beam epitaxy (MBE), followed by a Si capping layer of similar thickness to the Si template layer of the SOI. The SiO_2 layer of the SOI is selectively etched away, leaving the Si/SiGe/Si trilayer heterostructure free to strain share [5]. The Si layers of the trilayer are then selectively etched away, leaving a fully elastically relaxed SiGe NM. These SiGe NMs can be transferred to new handling substrates, bonded, and used as templates for growth of new defect-free materials.

A specific application involving strained Si/relaxed SiGe heterostructures is fabrication of 2-dimensional electron gas devices (2DEGs) that can be patterned and gated to confine individual electrons into quantum qubits with long spin coherence times [6]. These devices are very sensitive to changes in the electrostatic potential and thus require superb material quality. We compare the material quality of strained Si/SiGe heterostructures grown on SiGe NMs with those created on SiGe substrates relaxed *via* dislocations.

Research supported by DOE. Facilities support from NSF-MRSEC is acknowledged. DMP is supported by a NSF Graduate Research Fellowship.

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5:40pm **TF2+EM-WeA12 Multilayer Barrier Coatings for Organic Photovoltaics***,* ***A.M. Coclite****, K.K. Gleason*, Massachusetts Institute of Technology

Barrier coatings, which prevent the permeation of water into OPV devices fabricated on flexible plastic substrates, are essential to extend the device lifetime. Such protective coatings are made of multilayer stacks where multiple dense, inorganic layers are alternated with soft, organic ones. The inorganic layer contains inevitably some pinholes and defects. The roles of the organic layer are (i) creating a tortuous and longer path among the defects of two successive inorganic layers (ii) filling the pores of the inorganic underlayer limiting the propagation of defects from one inorganic layer to the other and (iii) smoothening the substrate surface roughness.

In the past, we obtained good barrier properties (WVTR= 10^{-2} g/cm^2/day) with a hexalayer obtained by coupling initiated CVD (iCVD) and plasma enhanced CVD (PECVD). iCVD layers resulted in effective defect decoupling and good planarization of the substrate.[1]

Now a similar approach is investigated for the multilayer deposition in a large-area reactor (0.16 m^3), maintaining the same organosilicon precursor and the same reactor configuration for both deposition of silica-like and organosilicon layers.

SiO_x layers were deposited through PECVD in MW plasma at high power and high oxygen dilution. The silanol and organic groups were not detectable by IR spectroscopy, resulting in denser film if compared with the previous results.

A new process was used for the formation of organosilicon polymers with enhanced monomer structure retention compared to a conventional plasma deposition and faster deposition rate if compared to conventional iCVD processes from organosilicon monomer. We demonstrate that the monomer molecule remains substantially preserved in fact the C/Si ratio calculated from XPS data on the polymer was 4.3, close to the 3.7 C/Si elemental ratio of the monomer molecule.

The deposition of smoothening organic layers is demonstrated by depositing the coating on the top of a microsphere (1 µm in diameter) monolayer deposited over silicon wafers. Increasing the thickness of the coating, the degree of planarization (DP), both local (DLP) and global (DGP), increases. The DLP increases much faster than the DGP: when the coating is 1µm-thick the DLP is already 99%, for the global planarization instead a 1.8µm-thick-coating is needed to reach DGP= 99%.

The high density of the inorganic layer, the smoothness and planarization properties of the organic one make this approach particularly promising for the deposition of effective multilayer barrier coatings.

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Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-ThM

Spectroscopic Ellipsometry of Biological Materials and Organic Films

Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands, K.G. Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **EL+AS+EM+MS+PS+TF-ThM1 Application of Various Spectroscopic Ellipsometry Techniques for In Situ Studies of Thin Polymer Films on Solid Substrates**, ***K.-J. Eichhorn***, Leibniz-Institut für Polymerforschung Dresden e.V., Germany **INVITED**

Thin films of functional polymers are not only widely integrated into modern micro- and nanoelectronic devices, but also used to modify solid surfaces for biosensor, biomedical and antifouling applications.

Therefore, in the first part I will report on improved temperature-dependent spectroscopic Vis-ellipsometry experiments to study confinement effects on the polymer dynamics in thin films to address a question which is controversially discussed in the polymer physics community for a long time past: Is there really a significant change of the glass transition temperature Tg of polymers when confined in nanoscopic films (studied here down to about 10 nm thickness)? We compared well-known linear polystyrenes of different molecular weights /1/ and hyperbranched polyesters having different architectures and functional groups /2/. Films of different thickness were prepared by spin-coating on silicon wafers, carefully equilibrated and measured in dependence on temperature (up to 250°C) in an inert gas atmosphere. The Tg data were determined from the ellipsometric results and discussed.

In the second part, “smart” surfaces will be presented which can be used for controlled adsorption and release of biomolecules. For that, different types of stimuli-responsive polymer brushes were prepared on solid substrates by a “grafting-to” procedure. The brush properties (e.g. swelling/collapsing) as well as the resulting adsorption/desorption of model proteins (e.g. Human Serum Albumin, Chymotrypsin) can be switched in an appropriate aqueous medium with temperature (PNIPAAM) and/or pH (PAA-P2VP). The corresponding processes at the solid-liquid interface were studied in-situ by spectroscopic Vis- and IR-ellipsometry /3,4/.

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8:40am **EL+AS+EM+MS+PS+TF-ThM3 Hard Matter Meets Thin Polymer Films-Spectroscopic Ellipsometry as a Versatile Tool to Investigate Properties of Responsive Poly(N-isopropylacrylamide) Systems with Incorporated Magnetic Nanoparticles**, ***S. Rauch***, Leibniz-Institut für Polymerforschung Dresden e. V., Germany

Responsive polymer systems designed by using polymer brushes or hydrogels are interesting systems, which can exhibit reversible or irreversible changes in their physical and structural properties to special environmental conditions (e.g. temperature or magnetic fields). The temperature responsive poly(*N*-isopropylacrylamide) (PNiPAAm) is one of such polymers. It undergoes a phase transition in aqueous solution at its lower critical solution temperature (LCST) of 32 °C which induces an increase in hydrophobicity. Combined with the properties of magnetic nanoparticles (NP) (e.g. Fe_3O_4 or $CoFe_2O_4$) these systems can lead to new surface functionalities with new interesting properties for many applications, as sensing, wettability or (bio)adhesion.

For the design of such thin film systems a basic knowledge of the film characteristics is essential. Therefore it is first necessary to know how much nanoparticles are inside or attached to the system. By using spectroscopic Vis-Ellipsometry (SE) it is not only possible to investigate optical properties of these films but also the composition of it, e.g. volume fraction of Fe_3O_4-NP.

We studied two types of films and present results for a thin NP-composite film prepared by pre-mixing of the PNiPAAm with hydrophobic Fe_3O_4-NP, spin-coated and grafted to a silicon substrate (System 1) and a film prepared by adsorption of hydrophilic functionalized Fe_3O_4-NP onto PNiPAAm brushes (System 2). The former system was chosen to develop an optical model starting from a simple two component effective-medium-approach (Maxwell-Garnett-EMA) using the optical constants of the pure polymer measured by SE and of Fe_3O_4 with averaged data taken from three different publications. The SE best fit-results were validated against scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

After transferring this optical model to System 2, the adsorption of hydrophilic functionalized Fe_3O_4-NP onto PNiPAAm brushes was investigated and will be discussed with additional results obtained from contact angle (CA) and phase transition (LCST) measurements.

9:00am **EL+AS+EM+MS+PS+TF-ThM4 The White Scarab Beetle *Cyphochilus insulanus* –Scattering and Polarization Properties**, ***C. Akerlind,*** Swedish Defence Research Agency / Linköping University, Sweden, *H. Arwin,* Linköping University, Sweden, *T. Hallberg, H. Kariis,* Swedish Defence Research Agency, Sweden, *J. Landin, K. Järrendahl*, Linköping University, Sweden

Three methods were used to characterize the optical properties of the light scattering white scarab beetle *Cyphochilus insulanus*. Spectral directional hemispherical (DH) reflectance measurements in the wavelength region 250 nm to 25 µm were performed using integrating spheres. The general spectral appearance shows a relatively strong reflectance band in the range 400 - 1600 nm. The Bidirectional Reflection Distribution Function (BRDF) was measured over a semi-circle in the plane of incidence at the wavelengths 633 nm and 3.39 µm, using s- and p-polarized light. In the visible the BRDF data shows a near Lambertian behaviour with a constant BRDF for most angles, *i.e.* the light is diffusely scattered. For large incident angles and in the infrared the BRDF is more specular. Full Mueller-matrix spectroscopic ellipsometry (MMSE) measurements were performed in the wavelength range 250 - 1000 nm at angles of incidence between 45° and 75° using a dual rotating compensator ellipsometer. The Mueller data show that the reflected light in general has a high degree of polarization *P* even for nonpolarized incident light. The angular dependence of *P* was pronounced for incident p-polarized light and was very low near the Brewster angle. In comparison, *P* was high for all measured angles for incident s-polarized light. Close to the Brewster angle, the reflected light showed a high ellipticity for incident p-polarized light. The optical data is used to model the structure and optical response of the beetle cuticle. With input from the DH and BRDF-data analysis of the Mueller Matrix data was made using Fresnel-based layer modelling. 2-, 3- and n-phase models are compared. The obtained optical properties are also used to calculate color data in terms of chromaticity and whiteness. The scattering properties of the *Cyphochilus insulanus* cuticle are also discussed by combining the BRDF and MMSE data as well as recently obtained Mueller matrix imaging polarimetry results.

9:20am **EL+AS+EM+MS+PS+TF-ThM5 Real-time Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation Characterization of Biomolecule Adsorption within Sculptured Thin Films**, *T. Kasputis, D. Schmidt,* ***K.B. Rodenhausen***, *H. Wang, A.K. Pannier, M. Schubert*, University of Nebraska - Lincoln

Recent improvements in nanofabrication strategies have led to the development of precisely crafted nanostructures with intricate features. Incorporating biomolecules such as proteins, DNA, drugs, and even whole cells could allow for functionalization of nanostructured surfaces for biological applications including biosensing, tissue engineering scaffolds, and drug and gene delivery. Along with the nanofabrication of biological devices, there is a need to develop instrumentation capable of probing and characterizing the dynamic evolution of these bio-functionalized interfaces. Spectroscopic ellipsometry combined with quartz crystal microbalance with dissipation (SE/QCM-D) is a non-destructive optical/mechanical characterization technique that reveals dynamic properties, including average film thickness (with sub-angstrom resolution), adsorbed mass, and porosity.

Nanostructures in the form of sculptured thin films (STF) were fabricated by glancing angle deposition via electron beam evaporation of titanium onto gold-coated quartz sensors. The sensors were then mounted within an SE/QCM-D liquid cell, and proteins of varying sizes were deposited and characterized, *in-situ*. Protein adsorption was detected shortly after introducing the protein solutions by SE and QCM-D as a change in the optical response and decrease of vibration frequency, respectively. QCM-D reported greater adsorbed mass for larger proteins (fibronectin) than smaller

proteins (bovine serum albumin). The adsorbed mass of proteins within the nanostructured scaffold exceeded that of proteins on flat surfaces, confirming that the STFs are capable of trapping proteins. Analysis of the anisotropic optical response from the nanostructures, which is very sensitive to environmental changes, adds complementary information on protein adsorption; the optical quantification is in agreement with QCM-D results. In addition, the adsorption of other biomolecules, such as cells and DNA complexes, has also been accomplished. The use of combinatorial SE/QCM-D to characterize and monitor the attachment of biomolecules on complex nanotopographies will improve the design and fabrication strategies for a wide array of biotechnological devices.

9:40am **EL+AS+EM+MS+PS+TF-ThM6 Characterization of Multilayer Organic Thin Film for Use as an Aptamer Biosensor with Hybrid Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation**, ***J.Y. Gerasimov****, K.B. Rodenhausen, H. Wang, R.Y. Lai, M. Schubert*, University of Nebraska - Lincoln

DNA aptamer molecules passivated by alkanethiols can be used for biological detection and screening. Through the use of spectroscopic ellipsometry (SE, optical) and quartz crystal microbalance with dissipation (QCM-D, mechanical) techniques, selective binding of analytes to chemisorbed aptamer probes can be observed *in-situ*. The system analyzed consists of a gold-coated quartz substrate, a multilayer organic thin film (containing aptamer probe, alkanethiol, and single-stranded DNA analyte), and physiological buffer solution. The attachment and detachment of material, the hybridization efficiency of the aptamer probes, and changes in the porosity of the multilayer organic thin film were all determined by SE/QCM-D.

In this contribution, we present the real-time SE/QCM-D characterization of (a) the formation of the aptamer probe layer, (b) the subsequent chemisorption of alkanethiol, and (c) the interrogation of single-stranded DNA that is non-complementary or complementary to the sequence found on the aptamer probe. The aptamer DNA sequence encodes codon 12 of the *K-ras* gene; mutations of this gene are frequently found among pancreatic cancer patients. We found that introduction of either complementary or non-complementary DNA caused increases of the multilayer organic thin film thickness. However, our SE/QCM-D analysis showed that the porosity of the multilayer organic thin film responded differently depending on the compatibility of the DNA analyte. The SE/QCM-D technique provides evidence for different surface attachment mechanisms and can be useful in characterizing biological interfaces.

10:40am **EL+AS+EM+MS+PS+TF-ThM9 Contamination Processes of EUV Optics Characterized by Spectroscopic Ellipsometry**, ***L.J. Richter****, C. Tarrio, S. Grantham, S.B. Hill, T.B. Lucatorto,* National Institute of Standards and Technology*, N.S. Faradzhev*, University of Virginia

Extreme ultraviolet (EUV) lithography using 13.5 nm light is emerging as a viable tool for semiconductor fabrication at design rules below 32 nm. Tool performance critically depends on limiting and mitigating degradation of the EUV optical elements. A primary degradation mechanism is the EUV induced deposition of carbon from ambient species originating from outgassing of the unbaked vacuum system and/or outgassing from the EUV irradiation of the resist. Using the high brightness of the Synchrotron Ultraviolet Radiation Facility (SURF-III) at NIST both fundamental studies of EUV induced contamination and practical (“witness plate”) studies of resist out gassing are performed. Typical deposits are hydrogenated amorphous carbon features with peak thicknesses of about 1 nm and nominal lateral extent of 1 mm. Both ex-situ, small spot mapping spectroscopic ellipsometry (SE) and in situ single-wavelength imaging nulling-ellipsometry are used for rapid, sensitive, contamination metrology. Fundamental studies of contamination by admitted gases indicate that the process is a complex function of both gas pressure and photon dose. Correlations between SE and XPS are suggestive that, at high EUV fluxes, densification can occur resulting in spatial variation in the deposit dielectric function. The use of principal component analysis of the SE images to highlight the spatial diversity will be discussed.

11:00am **EL+AS+EM+MS+PS+TF-ThM10 Characterization of Organic Solar Cells Materials and Structures by Spectroscopic Ellipsometry**, *J.P. Piel,* ***L. Kitzinger****, A. Bondaz, C. Defranoux*, SEMILAB-SOPRALAB, France

Spectroscopic Ellipsometry (S.E) is a well known optical technique widely used for the characterisation of all types of thin films for determination of film thickness and optical indices on glass or plastic substrates.

S.E. is also being applied to the characterization of materials and multilayer structures of organic materials like organic light-emitting diodes (OLEDs) or Organic Solar Cells.

We present the determination of the refractive indices of organic Solar Cells materials like P3HT, PCBM, Pentacene, Perylene, and their blends. Complex organic materials can be analyzed accurately and fully characterized from their absorption bands in the visible and UV range (190nm to 900nm).

Transmission and absorption can be also measured at the same time and be used to determine the optical properties of these materials.

Using these refractive indices, analysis of real multi-layer stacks can be done. The refractive indices can be used afterwards to automatically optimise and balance the energy flow dissipation Q inside an organic solar cell composed of a thin film stack. We present an example performed on a single cell and on a tandem bi-layer cell structure.

Since these materials are sensitive to moisture and pollution, it can be necessary to measure their optical properties and thickness values through an encapsulated media. We will demonstrate how we can measure single layer properties and multi-layer stacks, through encapsulated samples, from the back side of the substrate. This technique can be applied to test structure or real Organic Solar Cell monitoring. Backside measurement combined with a water vapour cell used for ellipsometry porosimetry is used to test the efficiency of the thin film encapsulation.

We also present the characterization of ITO and ZnO transparent electrodes by S.E. and how near infra-red ellipsometry is used to determine the ITO resistance, without contact, by using the Drude behaviour on encapsulated samples.

Electronic Materials and Processing Division
Room: 210 - Session EM+TF-ThM

Hybrid Electronic Materials and Interfaces
Moderator: A.J. Muscat, University of Arizona

8:00am **EM+TF-ThM1 Chemical Modification of Surfaces for Biological Applications**, ***W.G. McGimpsey***, Kent State University **INVITED**

The chemical and physical characteristics of surfaces can have profound and useful effects on the behavior of biological systems. We describe here several methods for modifying the surfaces of a variety of biocompatible materials, including metals, glass and polymers, in order to produce desired chemical and physical properties. The effects of surface chemistry and surface morphology on the growth and proliferation of mammalian cells as well as bacteria are also reported. Applications investigated include control of the growth of microbial biofilms, the growth of three-dimensional tissue assemblies, the patterned growth of neurons and other cell types and the functionality of primary neurons deposited on surfaces.

8:40am **EM+TF-ThM3 Modification of Oxide-Free Silicon Surfaces with Phosphonic Acid Self-Assembled Monolayers**, ***P. Thissen****, T. Peixoto, A. Vega, Y.J. Chabal*, University of Texas at Dallas

Phosphonic acid self-assembled monolayers (SAMs) are being considered as versatile surface modification agents due to their ability to attach to surfaces in different configurations, including mono-, bi- or even tri-dentate arrangements. Different chemical strategies for grafting SAMs on oxide-free silicon have been developed. Recently, a novel method for preparing OH-terminated, on otherwise oxide-free silicon has been reported [1] and further expanded for this work. This atomically flat surface contains precisely 1/3 OH and 2/3 H termination groups.

Using this model surface, we demonstrate that the phosphonic group of organic molecules can be chemically grafted to the OH group on the surface using a single chemical step, leaving the Si-H termination unaffected, without oxidation of the Si surface. We also show that the nature of solvents is important as they can act as a catalyst. The perfection of the surface (that remains atomically flat throughout the modification) makes it possible to use first principles DFT-based calculations to model the IR and XPS data obtained for this surface. Thus, a detailed structure for the SAMs can be derived on an atomic level. It is found that phosphonic acids are chemically attached to the Si(111) surface as mono-dentate via Si-O-P bond upon reaction with the OH groups. The remaining groups of P=O and P-OH are further oriented by forming a 2D network of hydrogen bonds.

[1] D. J. Michalak, S. R. Amy, D. Aureau, M. Dai, A. Esteve and Y. J. Chabal, Nanopatterning Si(111) surfaces as a selective surface-chemistry route, NATURE MATERIALS, Vol. 9, March 2010

9:00am **EM+TF-ThM4 Competing Effects of Interfacial Organic Layers on the Nucleation of Inorganic Thin Films Deposited Via Atomic Layer Deposition**, *K.J. Hughes,* ***J.R. Engstrom***, Cornell University

Over the past several years a number of groups have been investigating the use of interfacial organic layers (IOLs) in the form of self-assembled monolayers (SAMs) and/or surface grown or bound oligomers to promote the subsequent growth of inorganic thin films. Work in our group has initially focused on determining the relative importance of the type, density and dimensionality of the organic functional groups present in IOLs on the subsequent growth of the thin film, particularly via ALD[1]. Here we shall report on two perhaps less well-studied aspects concerning the use of SAMs or IOLs to promote nucleation and growth via ALD: (*i*) the effects of the underlying substrate on the IOL, and its ability to promote growth; and (*ii*) given the same IOL|substrate combination, the effects on ALD for a series of inorganic thin film deposition processes. To examine these systems we have made use of a variety of experimental tools, including a conventional viscous flow ALD tool, and also an ultrahigh vacuum (UHV) molecular beam based ALD process, where we employ *in situ* x-ray photoelectron spectroscopy. Concerning the first of these, we have examined the effect of a thin (< 10 Å) organic layer, poly(ethylene-imine) (PEI) on the ALD growth of TaN_x, where the underlying substrate is a chemically oxidized SiO_2 thin film, or a porous SiO_2 based low-κ dielectric thin film. Here we observe essentially the same result from conventional viscous flow, and molecular beam UHV ALD: PEI acts to attenuate TaN_x ALD on SiO_2, while it enhances growth on a low-κ dielectric thin film. From a practical point of view, most importantly, we find that PEI stops infiltration/penetration of the TaN_x ALD thin film into the porous low-κ dielectric. Concerning the second major issue, we have examined the effect of PEI on the subsequent growth via ALD of a series of inorganic thin films, namely: Al_2O_3, HfO_2, Ta_2O_5, and TaN_x. Here PEI has the effect of attenuating growth to different degrees depending on the subsequently grown ALD thin film, leading to no attenuation of growth for Al_2O_3, but significant incubation periods, in increasing order, for Ta_2O_5, HfO_2 and TaN_x. The length of the incubation time is found to correlate with both the total enthalpy change of the overall ALD reaction, as well as the net internal energy change of a single ligand exchange reaction representative of the second half of the ALD reaction, suggesting that these factors associated with the ALD process play a key role in determining the length of the incubation period caused by PEI.

[1] K. J. Hughes and J. R. Engstrom, J. Vac. Sci. Technol. A **28**, 1033-1059 (2010)

9:20am **EM+TF-ThM5 Towards Molecular Electronics: Solution-Based Methods for Selective Deposition of Metals and Semiconductors**, *Z. Shi, J. Yang, P. Lu,* ***A.V. Walker***, University of Texas at Dallas

Robust methods for the chemically selective deposition of metals, semiconductors, biomolecules and other substances are developed and applied in the construction of complex two- and three-dimensional structures. This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. These methods are easily parallelized, afford precise nanoscale placement and are compatible with photolithography. Two examples are discussed in detail: the chemical bath deposition (CBD) of CdSe on functionalized self-assembled monolayers (SAMs), and the electroless deposition of Ni nanowires on micron-scale patterned surfaces.

CBD is a solution-based method for the controlled deposition of semiconductors. The formation of CdSe nanocrystals are of particular interest for a wide range of applications because their photoluminescence spans visible wavelengths. Using CdSe chemical bath deposition (CBD) we demonstrate the selective growth and deposition of monodisperse nanoparticles on functionalized self-assembled monolayers (SAMs). On –COOH terminated SAMs strongly adherent CdSe nanoparticles form via a mixed ion-by-ion and cluster-by-cluster mechanism. Initially, Cd^{2+} ions form complexes with the terminal carboxylate groups. The Cd^{2+}-carboxylate complexes then act as the nucleation sites for the ion-by-ion growth of CdSe. After a sufficient concentration of Se^{2-} has formed in solution via the hydrolysis of selenosulfate ions, the deposition mechanism switches to cluster-by-cluster deposition. On –OH and $–CH_3$ terminated SAMs monodisperse CdSe nanoparticles are deposited via cluster-by-cluster deposition and they do not strongly to the surface. Thus under the appropriate experimental conditions CdSe nanoparticles can be selectively deposited onto -COOH terminated SAMs. We illustrate this by selectively depositing CdSe on a patterned $-COOH/-CH_3$ terminated SAM surface.

Our approach for the construction of Ni nanowires begins with a single SAM layer deposited and UV-photopatterned using standard techniques. We exploit the different deposition rates of nickel electroless deposition on $–CH_3$ and –OH terminated SAMs to deposit nanowires. The deposited nanowires are long (centimeters) and uniform in diameter, and can be patterned in arbitrary shapes. SAMs are ideal for the construction of nano- and micro- structures since their surface chemistry can be easily tuned to form the needed structures. Further the micron-scale UV photopatterning of SAMs does not require a clean room or expensive lithography equipment.

9:40am **EM+TF-ThM6 Sensing Mechanism for Peroxide and Hydroperoxide Vapors in Phthalocyanine Thin Film Transistors**, ***J. Royer****, E. Kappe, W. Trogler, A.C. Kummel*, University of California San Diego

Organic thin-film transistors (OTFTs) are promising candidates for selective chemical sensors due to numerous chemical and electrical parameters which govern sensor response. Analyte selectivity can be obtained using multiparameter electrical monitoring of a single OTFT which is sensitive to changes in mobility, I_{on}/I_{off} ratio, and/or threshold voltage. The present study demonstrates selective hydrogen peroxide and organic peroxide sensors based on irreversible metal-phthalocyanine (MPc) OTFT threshold voltage shifts. The irreversible threshold voltage shift is not evident with non-oxidizing analytes such as di-methyl methylphosphonate (DMMP) and common background analytes such as water vapor. Furthermore, the threshold voltage shift responds linearly to the dose time which permits dosimetric sensing analysis. A proposed mechanism for peroxide sensing is determined using simultaneous monitoring of mobility and threshold voltage. The data reveal reversible mobility and irreversible threshold voltage response. Mobility response time is fast and saturates quickly whereas threshold voltage response is dosimetric, and irreversible, suggesting an accumulation of uncompensated positive charge in the MPc film. The results are consistent with a dual response adsorption/decomposition mechanism in which the peroxide reversibly decreases mobility through a molecular chemisorption event and irreversibly shifts threshold voltage due to electron transfer from the MPc to peroxide. The electron transfer from the MPc to peroxide dissociates the peroxide to form hydroxyl products and leaves an uncompensated MPc^+. This detection method is exclusive for the OTFT platform and permits high selectivity at low peroxide concentrations.

10:40am **EM+TF-ThM9 Organic/Oxide Hybrid Thin-Film Applications for Photo-detector Cells and Complementary Inverters**, ***S.I. Im***, Yonsei University, Republic of Korea **INVITED**

Due to the distinct advantages and functionalities, oxide and organic devices on glass or flexible substrates have extensively been studied in such basic forms as thin-film transistors (TFTs) and light emitting diodes. As a more revolutionary approach to realize advanced thin-film devices using both oxide and organic layers, organic/inorganic hybrid layer techniques were also employed, so that hybrid p-n diodes, image sensors, nonvolatile memory, and complementary inverters have recently been demonstrated. *These hybrid approaches are an interesting and attractive way to extract a unique device performance which may not be possible with organics or with inorganics alone, compensating some weakness of organics with inorganics or vice versa*. The most representative example among the organic/inorganic hybrid devices may be complementary thin-film transistor (CTFT) inverters with an organic p-channel thin-film transistor (TFT) and an oxide n-channel TFT. In particular, a vertically stacked CTFT (VS-CTFT) inverter for logic operation on a glass substrate is very impressive since the vertical stacking of organic p-TFT on oxide n-TFT improves device integration or device area reduction. For the VS-CTFT inverter for logic and photo-gating, we used a thermally-evapotated p-channel pentacene layer, sputter-deposited n-channel GaZnSn-based oxide (GZTO), and atomic layer deposited (ALD) Al_2O_3 dielectric. Our VS-CTFT inverter nicely displays effective photo- and electrical-gating with a high voltage gain, dynamically operating in the low-voltage regime of 3, 5, and 8 V (the thin pentacene channel receives blue photons). As a more advanced hybrid approach, we have successfully fabricated transparent image pixels that operate at 3 V as composed of pentacene thin-film transistor (TFT) and semitransparent pentacene/ZnO photodiode with a transparent top electrode in the interest of a light detectable smart functional windows. Our transparent pixels was equipped with an additional 6,13-pentacenequinone phosphor layer as deposited on the pentacene/ZnO photodiode. The organic phosphor transmits most of visible photons but absorbs ultra-violet (UV) photons to convert them to yellow-green photons, so that the emitted yellow-green lights excite the pentacene/ZnO diode under a reverse bias state. Our approach to the transparent pixel adopting such an organic phosphor layer certainly makes the pixel operations efficient under not only visible photons but also UV, protecting the organic pentacene from direct UV.

11:20am **EM+TF-ThM11 Near-ideal Schottky-Mott Behavior of n-Si / Hg Diodes with Hydroquinone-Alcohol Monolayers**, ***A. Vilan****, R. Har-Lavan, O. Yaffe, P. Joshi, R. Kazaz, D. Cahen*, Weizmann Institute of Science, Rehovot Israel

The Schottky-Mott model predicts that the eventual energy barrier formed when metal and semiconductor are brought into intimate contact, will be equal to the difference between the metal work function and the

semiconductor's electron affinity (for n-type). 60 years of extensive experiments have clearly shown that this ideal picture, that seems to hold for wide bandgap ionic semiconductors such as ZnO, GaS etc., is far from being adequate for the more covalent narrow bandgap Si, Ge, InP, and GaAs. Following Bardeen, who attributed this deviation from the model to surface states energetically located within the semiconductor's forbidden gap, different explanation were raised as for the source of those surface states.

One commonly used model for surface states formation at the interface of semiconductor and metal is the intrinsic Metal Induced Gap State (MIGS) model, stating that gap states are inevitably formed due to the decay of metal electronic states' wavefunction into the semiconductor's bandgap.

We have examined the presence of such MIGS using Hg, which is one of the few metals that doesn't interact chemically with Si, as an electrode. Furthermore, in order to eliminate surface states which are just due to Si dangling bonds, we have used state of the art mixed molecular monolayers of hydroquinone and alcohols that were shown to be the best chemical passivation for Si surfaces.

Using alcohols of different alkyl chain lengths we succeeded to effectively change the electron affinity of the Si over 400 mV range while maintaining firm surface passivation. Current-voltage measurements of diodes formed that way, with Hg on organically modified n-Si surface, demonstrated near ideal Schottky-Mott characteristics with index of interface behavior S=0.9 (compared to a common value for Si S=0.1).

11:40am **EM+TF-ThM12 Electroless Deposition of Metals on SiO_2 Surfaces Modified by a Self-Assembled Monolayer**, ***R. Jain***, *A. Ng*, *A.J. Muscat*, University of Arizona

Self-assembled monolayers (SAMs) are used to both chemically activate and deactivate semiconductor surfaces. For instance, octadecyltrichlorosilane prevents atomic layer deposition of high-k films, and 3-aminopropyltriethoxysilane promotes metal deposition. The formation of a uniform and defect free monolayer is essential for nano-scale device fabrication. SAMs could serve as an adhesion layer, which is required for the electroless deposition of metals on some dielectric surfaces. Electroless deposition processes in particular are known to be sensitive to the surface termination and are not robust. In this work, the thickness and density of an aminosilane SAM formed on a SiO_2 surface were monitored as a function of solvent, concentration, and time, and the metal to N ratio was quantified.

A 3-aminopropyltrimethoxysilane (APTMS) SAM was formed on a well-hydroxylated SiO_2 surface. SAM formation was studied as a function of solvent (methanol and toluene), APTMS concentration (5.72 mM and 57.2 mM), immersion time, solution agitation (stirring and sonication), and post-deposition rinsing in methanol or chloroform depending on the solvent used. The thickness of the APTMS SAM using ellipsometry was 7.8±0.2 Å after 15 min when prepared by stirring an APTMS-methanol solution. This thickness corresponds to the expected length of an APTMS molecule. The roughness was 0.3±0.1 nm measured over 2×2 μm^2 regions using atomic force microscopy. These thickness and roughness values indicate that thin, uniform layers were formed using this method. The absence of a peak for methoxy groups in the high resolution C 1s x-ray photoelectron spectroscopy (XPS) spectrum suggests that all of the methoxy groups were hydrolyzed on the APTMS molecules that reacted with the surface. A single peak in the N 1s spectrum at 399.7 eV indicates the presence of a primary amine when the SAM was prepared in methanol. A second peak was also observed at 400.4 eV corresponding to a hydrogen-bonded amine when the SAM was prepared in toluene. These results suggest that all the SAM molecules were bonded to the surface by siloxane (Si-O-Si) linkages and that amine groups were directed away from the surface with the methanol solvent. Based on XPS peak areas, the molecular density in the SAM layer was 5.4±1.9 molecules/nm^2. A layer of Pd atoms was successfully deposited by immersing the APTMS SAM surfaces in an 80 mM $PdCl_2$-HCl solution for 2 min, yielding one Pd atom bonded to two amine groups based on XPS peak areas. These results demonstrate that an adhesion layer can be formed that will bind metal. Future work will be done to determine how strongly the metal layer adheres to the SAM.

Transparent Conductors and Printable Electronics Focus Topic
Room: 106 - Session TC+AS+EM-ThM

Transparent / Printable Electronics Part 1
Moderator: R. Haasch, University of Illinois at Urbana Champaign

8:00am **TC+AS+EM-ThM1 Growth Characteristic and Films Properties of Ga doped ZnO (GZO) by Low Temperature Atomic Layer Deposition**, ***T.W. Nam***, *JM. Kim*, *W.S. Lee*, *H. Kim*, Yonsei University, Republic of Korea

Atomic layer deposition (ALD) has great benefits over other deposition techniques since its growth mechanism controlled by a self-limited surface reaction exhibits excellent conformality, large area uniformity, and atomic scale thickness controllability. In particular, ALD becomes increasingly more promising thin film deposition method for future flexible electronics. Recently, there have been many research efforts on the investigation of doped ZnO for transparent conducting oxides (TCOs) due to their higher mobility than that of undoped ZnO. Ga doped ZnO (GZO) is one of the promising material for substitution of ZnO. As a representative TCO for applications to the transparent thin film transistor (TTFT) or flexible electronic, GZO thin films by PVD or CVD have been extensively studied. Nevertheless studies on GZO films grown by ALD at low temperature condition which can be applied to flexible devices were still not carried out as far as we know in spite of its potential importance. Hence, for this study, we investigated the growth characteristics and film properties of low temperature ALD (LT-ALD) GZO films by varying deposition method. Field emission scanning electron microscopy (FE-SEM) observation of the GZO films deposited on 5:1 via patterns showed that the film has excellent conformality with over 95 % coverage even at room temperature growth. Additionally, the chemical and microstructural analysis was studied by various analytical techniques including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscope (AFM). Also spectrophotometer was used to measure a transmittance of the film and showed high transmittance that could be applicable to transparent devices.

8:20am **TC+AS+EM-ThM2 Enhancement of C-Axis Orientation of Ga-doped ZnO Films Deposited on Unintentionally Heated Glass Substrates using Nanosheet Seed Layers**, ***H. Makino***, Kochi Univ. of Tech., Japan, *T. Shibata*, NIMS, Japan, *N. Yamamoto*, Kochi Univ. of Tech., Japan, *T. Sasaki*, NIMS, Japan, *T. Yamamoto*, Kochi Univ. of Tech., Japan

Ga-doped ZnO (GZO) film is one of promising candidates as substitute for ITO transparent electrodes in optoelectronic devices. Control of structural properties, especially c-axis orientation, is crucial issue to improve electrical properties of polycrystalline GZO films on glass or plastic substrates [1]. Recently, nanosheet seed layers were proposed to control crystal orientation of oxide films on amorphous substrates [2]. In this study, we employed a seed layer of tungsten oxide nanosheets with two-dimensional hexagonal lattice structure for deposition of GZO thin films on unintentionally heated glass substrates.

The nanosheets were assembled on glass substrates by Langmuir-Blodgett method. The GZO films with thickness of 100 nm were deposited by an ion-plating with direct current arc discharge on unintentionally heated glass substrates with and without the nanosheet seed layers.

The crystal structural properties were characterized by x-ray diffraction measurements. The c-axis orientation of the GZO films was drastically enhanced by the nanosheet seed layers. The intensity of (002) diffraction peak of GZO films deposited with the seed layers was about 40 times as strong as that deposited without the seed layers. The degree of c-axis orientation was evaluated by the (002) x-ray rocking curve (XRC). The full-width half-maximum of XRC of the GZO films on the nanosheet seed layers was 2.6 °, which is even lower than that of GZO films deposited on bare glass substrate at 200 °C.

The electrical properties were characterized by Hall effect measurements at room temperature. The GZO films deposited on the nanosheet seed layers showed the resistivity of 2.9×10^{-4} Ωcm with the Hall mobility of 24 cm^2/Vs and the carrier concentration of 9.0×10^{20} cm^{-3}. On the other hand, the GZO film deposited without the nanosheet seed layers showed the resistivity of 5.0×10^{-4} Ωcm with the Hall mobility of 17 cm^2/Vs and the carrier concentration of 7.2×10^{20} cm^{-3}. Both the Hall mobility and the carrier concentration were improved by the nanosheet seed layers.

[1] T. Yamada et al., J. Appl. Phys. 107, 123534 (2010). [2] T. Shibata et al., Adv. Mater. 20, 231 (2008).

8:40am **TC+AS+EM-ThM3 Multi-component Transparent Conducting Oxides: Progress in Materials Modeling**, ***S.-H. Wei***, National Renewable Energy Laboratory **INVITED**

Transparent conducting oxides (TCOs) play an essential role in modern optoelectronic devices through their combination of electrical conductivity and optical transparency. We review recent progress in our understanding of multi-component TCOs formed from solid solutions of ZnO, In2O3, Ga2O3 and Al2O3, with a particular emphasis on the contributions of materials modeling, primarily based on Density Functional Theory. In particular, we highlight three major results from our work: (i) the fundamental principles governing the crystal structures of multi-component oxide structures including (In2O3)(ZnO)n, named IZO, and (In2O3)m(Ga2O3)l(ZnO)n, named IGZO; (ii) the relationship between elemental composition and optical and electrical behavior; (iii) the origin of high-performance of amorphous oxide semiconductors. From these advances, the challenge of the rational design of novel electroceramic materials is discussed.

9:20am **TC+AS+EM-ThM5 Composition Control of Electron Beam Deposited Nb-TiO$_2$ Thin Films**, ***N.A. Beckers***, *R.T. Tucker,* University of Alberta, Canada*, M.D. Fleischauer,* NRC-National Institute for Nanotechnology, Canada*, M.J. Brett*, University of Alberta, Canada

Nb-doped TiO$_2$ has been identified as a potential indium-free transparent conductor, and has been fabricated by pulsed laser deposition and sputtering with good success.[1,2] Other deposition methods, such as electron beam evaporation, are of interest for this material but have had limited demonstration to date. It would be advantageous to be able to use electron beam evaporation because in addition to planar films, the collimated flux allows for structured thin films via glancing angle deposition (GLAD). Composition control is essential for doped functional materials, which is typically difficult to obtain through physical mixing of source materials. Here we show that using a sol gel approach to prepare the source materials provides a possible route to circumvent this issue. The facile, solution based sol gel process for the synthesis of ceramic and glassy materials allows for precise composition control by controlling the amounts and ratios of the metal oxide precursors. A sol gel methodology was used to prepare a series of Nb-doped TiO$_2$ deposition source materials with the following compositions: $Nb_{0.06}Ti_{0.94}O_2$, $Nb_{0.12}Ti_{0.88}O_2$, and $Nb_{0.24}Ti_{0.76}O_2$. We will show that XPS results confirm the composition of the electron beam deposited films and reflects the composition of the source materials. Premixed powders of Nb_2O_5 and TiO$_2$ do not show the same translation of composition as the sol-gel derived source material. Details on the effects of the post-deposition annealing environment on the thin film optical and electrical properties will also be presented.

References:

1. Yamada, N.; Hitosugi, T.; Hoang, N. L. H.; Furubayashi, Y.; Hirose, Y.; Konuma, S.; Shimada, T.; Hasegawa, T. *Thin Solid Films* **2008**, *516*, 5754-5757.

2. Ishida, T.; Okada, M.; Tsuchiya, T.; Murakami, T.; Nakano, M. *Thin Solid Films* **2011**, *519*, 1934-1942.

9:40am **TC+AS+EM-ThM6 Laboratory and Production-Scale Low-Temperature Transparent Conducting Oxide Deposition**, ***E. Ritz***, University of Illinois at Urbana Champaign*, G.B. Rayner,* Kurt J. Lesker Company*, D. Andruczyk,* University of Illinois at Urbana Champaign*, T. Dockstader,* Kurt J. Lesker Company*, D.N. Ruzic*, University of Illinois at Urbana Champaign

Transparent conducting oxides (TCOs) are a class of materials that are becoming increasingly ingrained in our daily lives due to their use in electronic displays and mobile devices. There is a strong need to develop an economical deposition technique that allows for high transparency films with high electrical conductivity while replacing costly materials such as Indium Tin Oxide (ITO) with alternatives such as Aluminum-doped Zinc Oxide (AZO). In addition, a low-temperature deposition method would allow creation of TCOs on flexible plastic substrates, such as polyethylene terephthalate (PET). By using a dual DC magnetron system with a secondary RF antenna running at 13.56 MHz, a process has been developed that can deposit TCO films without significantly heating the substrate while maintaining high transmission and electrical properties. This capability has been demonstrated on a small-scale experimental setup utilizing 3-inch diameter circular magnetrons as well as a prototype production-scale chamber operating with 18x3.5 inch rectangular mangetrons aimed at flexible photovoltaic manufacturing. Using an immersed inductive RF antenna, ionization fraction can be increased to over 80%, measured by a gridded energy analyzer, and plasma density increased by an order of magnitude from 10^{10} cm^{-3} to 10^{11} cm^{-3}, as measured by Langmuir probe. The secondary plasma deposits energy in the film without heating the substrate above 100°C while still achieving film resistivity on the order of 10^{-3}-10^{-4} Ohm-cm (measured by four-point probe method) and transparency of greater than 90% in the visible wavelengths (measured by spectrophotometry.) Adjusting the RF power (0-1000W) and the oxygen content (0-5%) in the plasma enables the ability to tune the film transparency and conductivity to desired levels. Crystal formation of films analyzed by x-ray diffraction (XRD) and elemental composition determined by x-ray photoelectron spectroscopy (XPS).

10:40am **TC+AS+EM-ThM9 Optical and Electronic Properties of Photonic Crystal Based Transparent Conductors**, ***S. Narayanan***, *M. Bockstaller, L. Porter*, Carnegie Mellon University

Transparent conductors are becoming ubiquitous in a host of civil and military applications, including transparent electrical contacts in solar cells and LEDs, heated glass for aircraft and automobile windows, and electrochromic devices and smart windows. However, finding abundant materials with optimal electrical and optical properties and that can be produced economically is a particular challenge. Moreover, limited supply and large demand, of late, for indium has inspired focused research on finding alternatives to ITO as a transparent conductor. We report here a novel approach to control optical properties such as absorption, transmission and reflection in multilayered structures (based on [1-2]) with absorbing components. Appropriate combination of materials could, among others, allow for applications like transparent electrodes, transparent electromagnetic shielding, flexible transparent conductors, etc. Through this study, we have demonstrated the validity of this approach using a few different materials combinations including polymer/metal and metal/ceramic systems. In these realizations the approach was shown to increase the transparency in the visible frequency range by ~ 3 orders of magnitude as compared to the reference materials. For example, transmittances of 30-50% of incident light in the visible region were measured for films containing a polymer (polystyrene – PS) and an amount of metal (gold – Au) that was 3-4 times as thick as its skin depth (~ 40-50 nm). We have also found compatibility between the observed experimental results and numerical simulations. Apart from enhanced optical transmittance, resisitivity values of ~ 10^{-4} Ωcm (comparable to Au films having ~ 10^{-5} Ωcm) have also been discovered in structures having insulating components. Our ongoing and future work is focused on alternative structures to enhance conductivity in the transverse direction as well as incorporate flexibility in the same. **References:** [1] M. Scalora *et al.*, *J. Appl. Phys.* **83** 5 (1998) 2377-2383 [2] M. Scalora, M. J. Bloemer, C. M. Bowden, *Optics and Photonics News* **10** 9 (1999) 24-27

11:00am **TC+AS+EM-ThM10 Effect of Plasma Treatment and Annealing on the Electrical Properties of Spin-Coated Colloidal ITO Films**, ***S.M. Joshi***, *G.W. Book, R.A. Gerhardt*, Georgia Institute of Technology

Colloidal ITO based inks may be an attractive route to direct writing transparent circuits and also be useful for the fabrication of transparent conductive ITO films on complex shaped substrates. The presence of stabilizing ligands and minimal contact between the ITO nanoparticles in the deposited films can be a challenge in obtaining the optimum electrical properties. This study investigates the effect of plasma treatment and annealing on the electrical properties of colloidal ITO films. Crystalline colloidal ITO nanoparticles were synthesized in-house by a non-aqueous technique. The solutions were spin coated onto glass and quartz substrates and their electrical and optical properties were evaluated. All films were found to be completely transparent, while the as-deposited films had resistivities more than 10^8 ohm-cm. Plasma treatments were shown to be effective in removing residual organics in the films, and even without annealing, some recipes were able to reduce the film resistivity by more than four orders of magnitude. Plasma treatments, when done in combination with annealing, resulted in films with resistivities less than 1 ohm-cm.

11:20am **TC+AS+EM-ThM11 Hybrid Organic/Inorganic Materials and Devices for Flexible Electronics Applications**, ***M.A. Quevedo-Lopez***, *J.I. Mejia, A. Salas-Villasenor, A. Carrillo-Castillo, B.E. Gnade,* University of Texas at Dallas*, D. Allee*, Arizona State University **INVITED**

The field of flexible electronics has expanded tremendously over the past few years. Similar to what happened in silicon integrated circuit technology 40 years ago; flexible electronics are now at a point where system design and process integration will drive the technology. Flexible electronics will likely push the limits of material performance, process integration, circuit design, and system integration to demonstrate the full potential of flexible electronics. In general, key components for any flexible electronic application include thin film transistors. In order to be competitive with state-of-the-art a:Si:H thin film transistors, any other thin film transistor technology must show reproducible transistor parameters such as mobility, threshold voltage, drive current and reliability.

A grand challenge in flexible, thin-film-transistor (TFT) circuitry is the development of complementary metal oxide semiconductor (CMOS)

circuits. Although flexible digital circuits, flexible sensors, flexible batteries and solar cells have already been demonstrated, the missing technology piece that must be developed is flexible analog circuitry. For example, an operational amplifier will enable the interface to most sensors and actuators, significantly expanding the functionality of flexible electronic systems. In this paper, we will present n- and p-type chalcogenide-based materials that can be used as the building blocks for analog CMOS-based circuits. In particular, we will introduce the use of chemical bath deposition as an alternative to deposit these materials and will discuss the correlation between device characteristics and materials properties. Photolithography-based chalcogenide-based TFTs processed by chemical bath deposition achieved mobilities in the order of 10-25 cm2/V-s. In addition, we demonstrate hybrid CMOS for a:Si-Pentacence, CdS-Pentacene and CdS-TIPS Pentacene.

We also present the impact of semiconductor thickness, gate dielectrics and contact in device performance. In addition, NAND, NOR and Inverters are demonstrated using chalcogenide-based materials integrated with either a-Si or pentacene. Device processing is carried out at a maximum processing temperature of 110oC, which is compatible with most plastic substrates.

Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-ThA

Spectroscopic Ellipsometry for Photovoltaics, Metals and Oxide Thin Films
Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands

2:00pm **EL+AS+EM+MS+PS+TF-ThA1 Applications of Ellipsometry in Photovoltaics**, ***D. Levi***, National Renewable Energy Laboratory **INVITED**

With the growing possibility of anthropomorphic-induced climate change there has come increasing concern over energy-related emissions of carbon dioxide into the atmosphere. The search for low or no-carbon energy sources has intensified. This has lead to a twenty first century gold rush into photovoltaics research and technology startups. Although the PV industry has maintained its exponential growth rate through the global economic downturn, electricity from photovoltaics is still a long ways from economic competitiveness with fossil fuel-based electricity sources. The U.S. Department of Energy recently announced the Sunshot program, with the expressed goal of $1/Watt installed cost for utility scale PV plants by 2017. This aggressive goal will require radical advances in new and existing PV technologies.

This presentation will begin with an overview of the major PV technologies and the state of the rapidly evolving global photovoltaics industry. Photovoltaics is a natural arena for application of spectroscopic ellipsometry. Nearly all PV devices are made of multiple thin films of semiconductors and transparent conducting oxides. New materials are constantly being introduced. Film thickness, optical properties, interfaces, electronic properties, and film growth dynamics are all critical aspects of these devices and lend themselves to investigation through the use of spectroscopic ellipsometry. I will present several case studies of how we have applied spectroscopic ellipsometry in our research in photovoltaics at the National Renewable Energy Laboratory.

2:40pm **EL+AS+EM+MS+PS+TF-ThA3 Comparison between Ex Situ and Real Time Spectroscopic Ellipsometry Measurements of Structurally Graded Si:H Thin Films**, ***N.J. Podraza***, University of Toledo

Analysis of spectroscopic ellipsometry measurements of graded thin films remains challenging, although analysis procedures and software have improved over the past several decades. Practical use of these processes remains somewhat time consuming and is often not fully utilized by the casual user. In this work, ex situ ellipsometric spectra collected for static samples and real time spectroscopic ellipsometry (RTSE) measurements collected during film growth will be compared to illustrate differences in results arising from the measurement procedures and analysis. As an application, consider hydrogenated silicon (Si:H) thin films used for solar cells. Devices typically incorporate either amorphous silicon (a-Si:H) or "nanocrystalline" silicon (nc-Si:H) absorber layers, although the best "nanocrystalline" absorber layers actually consist of mixed-phase amorphous+nanocrystalline (a+nc) material. Si:H thin films may initially (i) nucleate as amorphous and remain amorphous throughout growth; (ii) immediately nucleate as nanocrystallites; or (iii) initially evolve in the amorphous regime but nucleate crystallites which subsequently grow preferentially over the surrounding amorphous material until nanocrystallite coalescence. Analysis of ellipsometric spectra collected for (i) or (ii) simply involve using a substrate / bulk film / surface roughness model and complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) for the bulk material. For (iii), RTSE is ideally used to monitor the growth of Si:H that evolves through the amorphous, nanocrystalline, and mixed-phase regimes and a virtual interface analysis (VIA) procedure is used to extract ε for the amorphous and nanocrystalline components, the bulk and surface roughness thicknesses versus time, and the nanocrystalline fraction depth profile in the (a+nc) growth regime. For (a+nc)-Si:H films only measured with a single static ex situ measurement at the end of the deposition, obtaining ε and structural parameters of the film become less precise. Specifically, sensitivity to the variation in the nanocrystallite fraction with thickness may be lost and inaccurate ε for the component materials may be obtained. This works seeks to compare the structural and optical properties of (a+nc)-Si:H obtained by RTSE and VIA with those from analysis of static ex situ spectra with models using different structures, parameterizations in ε, and spectral range restrictions. These comparisons will be used to identify appropriate structural and dielectric function models to more accurately analyze structurally graded thin films under different material and measurement circumstances.

3:00pm **EL+AS+EM+MS+PS+TF-ThA4 Real-Time Spectroscopic Ellipsometry of $Cu(In,Ga)Se_2$ Thin Film Deposition: Copper Transition in 3-Stage Co-Evaporation Process**, ***D. Attygalle***, University of Toledo*, V. Ranjan,* Old Dominion University*, P. Aryal,* University of Toledo*, S. Marsillac,* Old Dominion University*, R.W. Collins*, University of Toledo

With record efficiencies above 20%, $Cu(In,Ga)Se_2$ (CIGS) based solar cells have shown the greatest potential for success among the thin film photovoltaics technologies. Thermal co-evaporation of individual elements has proven to produce extremely high quality CIGS materials, provides a high level of flexibility, but also generates greater challenges in process optimization. The limitations of existing process monitoring capabilities, hence the challenge of correcting process fluctuations in real time, has led the industrial community toward more controllable CIGS deposition processes. Real time spectroscopic ellipsometry (RTSE) can be used successfully in the monitoring of complicated processes -- including CIGS film preparation by co-evaporation using precursor films of $(In_xGa_{1-x})_2Se_3$. Information extracted from RTSE includes the evolution of bulk layer and surface roughness layer thicknesses, the composition and phase, as well as the layer dielectric functions, all of which can assist in understanding the fabrication process and in optimizing solar cells. In this study, the focus is on the transitions of Cu-poor to Cu-rich CIGS and vice versa by observing the changes in (ψ, Δ) spectra obtained by RTSE. The commonly used monitoring method, which involves observing the changes in emissivity of the film, largely depends on the apparatus design, the substrate, and the bulk layer thickness. When a CIGS film is prepared by exposing a precursor film of $(In_x,Ga_{1-x})_2Se_3$ to Cu and Se fluxes, thereby becoming Cu-rich, a semi-liquid $Cu_{2-x}Se$ phase is believed to form on top of a bulk layer consisting of mixed phases of $Cu(In,Ga)Se_2$ and $Cu_{2-x}Se$ [1]. A multilayer optical model, with appropriate effective medium approximation layers to represent this scenario, has shown good agreement with the observed (ψ, Δ) spectra. Since RTSE is highly sensitive to monolayer-level changes in the top-most layer, RTSE gives superior sensitivity in Cu-rich to Cu-poor end point detection, which occurs when the top $Cu_{2-x}Se$ phase drops below detectable limits. Furthermore this method is less affected by the substrate and bulk layer thickness. Although careful analysis of RTSE can give a wealth of information about CIGS material properties and their evolution, this type of end point detection can be successful simply by monitoring the real time changes in the (ψ, Δ) spectra.

[1] J. AbuShama, R. Noufi, Y. Yan, K. Jones, B. Keyes, P. Dippo, M. Romero, M. Al-Jassim, J. Alleman, and D.L. Williamson, "$Cu(In,Ga)Se_2$ Thin-film evolution during growth from $(In,Ga)_2Se_3$ precursors", *Mat. Res. Soc. Symp. Proc.* paper H7.2.1, (2001).

3:40pm **EL+AS+EM+MS+PS+TF-ThA6 Bulk Hetrojunction Solar Cell Characterization by Phase Modulated Spectroscopic Ellipsometry**, ***K. Uppireddi****, L. Yan*, HORIBA Scientific

The blend morphology, phase separation as well as crystallinity of organic photovoltaic solar cell are important properties to increase the efficiency. The performance of such cells is strongly influenced by blend composition and thermal annealing conditions. In this work we demonstrate the use of ellipsometry as a powerful and sensitive metrology means of monitoring organic solar cell based on the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-buytric acid methyl ester (PCBM). Ellipsometric measurements were performed on P3HT/c-Si, PCBM/c-Si and P3HT:PCBM/c-Si at an angle of incidence of 70 degree, across the spectral range 190 – 2100 nm (0.6-6.5 eV). Two different analysis protocols were used to model the P3HT:PCBM blend structure. In the first protocol effective medium theory was used to represent the optical constant of layer, where as in the second one the blend was treated as one single homogenous material. The approach renders investigation of final morphology and composition.

4:00pm **EL+AS+EM+MS+PS+TF-ThA7 *In Situ* Spectroscopic Ellipsometry during Atomic Layer Deposition of Pt, Pd and Ru**, ***N. Leick****, J.W. Weber, M.J. Weber, A.J.M. Mackus, H.C.M. Knoops, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The precise thickness control of atomic layer deposition (ALD) and its conformal growth make ALD the method of choice for nanometer thin film deposition. Platinum-group metals such as Pt, Pd and Ru have many applications in the areas of nanoelectronics and catalysis and recently there has been considerable interest to deposit films of these materials by ALD. Spectroscopic ellipsometry (SE) is a powerful, noninvasive optical technique that can be used *in situ* during ALD to precisely monitor the thickness of the films. SE also provides information on the optical and

electrical properties of the films which is very relevant for their applications. Choi et al. [1] previously investigated the dielectric functions of Pt-group metal films with a thickness of ~400 nm as prepared by physical vapor deposition. For the aforementioned applications, however, the films are required to be much thinner, which leads to differences in film morphology as well as to dielectric functions that can be different from those of bulk films. In the spectroscopic ellipsometry work to be presented in this contribution we have therefore focused on films with thicknesses from 5 nm to 35 nm. *In situ* data was obtained during ALD in the photon energy range of 0.7 – 6.5 eV. Using a Kramers-Kronig consistent B-spline model to account for the thickness-dependent dielectric functions, we were able to obtain accurate ALD growth-per-cycle values for Ru, Pt and Pd (1.00 ± 0.06 Å, 0.47 ± 0.04 Å, 0.14 ± 0.02 Å). Furthermore, the contributions from free-carriers (Drude term) and interband absorptions (Lorentz-oscillator contributions) were investigated by combining the SE data with FT-IR reflectance data such that the photon energy range of 0.04 eV – 6.5 eV was covered. In this range, it was possible to represent each film with a unique Drude-Lorentz model although some ambiguities about the Lorentz oscillator contributions remained in the case of Ru. It will be shown that the extracted thicknesses and electrical resistivities from this model are in line with data obtained from X-ray reflectometry and four-point probe measurements (for example Ru: ρ_{SE} ~23 μΩ.cm and ρ_{FPP} ~16 μΩ.cm). Furthermore, in the case of Ru also the influence of the film roughness will be addressed.

[1] Choi *et al.*, Phys. Rev. B **74**, 205117 (2006)

4:20pm **EL+AS+EM+MS+PS+TF-ThA8 Manipulating the Optical Properties of Metals: Sculptured Thin Films Coated by Atomic Layer Deposition**, *D. Schmidt, N. Ianno, E. Schubert,* ***M. Schubert***, University of Nebraska - Lincoln

The fabrication of three-dimensional metal nanostructures with tailored geometry is one of the central challenges of nanotechnology because geometrical and material parameters are responsible for the optical, electrical, mechanical, chemical, or magnetic properties of such nanostructured thin films. Engineered artificial sculptured thin films (STFs) with designed anisotropies are potential candidates for applications in various fields such as optics, magneto-optics, as well as chemical and biological sensing and detection. However, in order to utilize metallic nanostructures for novel applications their size-, structure-, and material-driven physical properties have to be understood and quantified.

We utilize glancing angle electron-beam deposition, which exploits physical atomic-scale shadowing and dynamically varying particle flux azimuth for fabrication of three-dimensional highly spatially coherent STFs with different morphologies. Subsequently, nanostructures are individually covered with a thin conformal coating (cladding) by means of atomic layer deposition (ALD).

We will present the anisotropic optical properties of highly anisotropic ALD coated metal STFs determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region. The analysis of our multilayer slanted columnar thin films deposited at glancing angle (θ_i = 85°) revealed that such STFs possess monoclinic optical properties, and the optical response may be described by an effective medium dielectric homogenization approach. It will be discussed how the anisotropic Bruggeman effective medium approximation (AB-EMA) allows for determination of structural parameters as well as fractions of individual film constituents. Furthermore, the AB-EMA analysis reveals that the anisotropic dielectric properties of the metal core changes upon deposition of a dielectric cladding.

4:40pm **EL+AS+EM+MS+PS+TF-ThA9 Ellipsometric Characterisation of Porous Aluminium Oxide Supports**, *W. Ogieglo, N.E. Benes,* ***H. Wormeester***, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Porous aluminium oxide is widely used as a support material for thin film inorganic micro- and mesoporous membranes. Such membranes are used in energy-efficient gas separation, pervaporation and nanofiltration processes. Ellipsometry can be used to determine material properties of the thin membrane films, as well as the penetrant loading [1]. Interpretation of the ellipsometry data requires a detailed knowledge of the porous aluminium oxide support. This support is made of aluminium oxide particles that are sintered together. In between the particles voids are present that amount to 38% porosity. We have studied the influence of the size of the voids on the optical response of the support material. For this study, voids with a diameter of around 60, 80 and 160 nm were used. We noted a strong decrease of the normal incidence specular reflection with void size and a subsequent increase in off specular reflection. In ellipsometry, only a limited depolarization of the specular reflected light was noted in the wavelength range between 300 and 1750 nm. The angle dependent ellipsometry measurements showed that the optical properties of these supports can not be obtained from a direct inversion. The reason for this is that at the interface the more or less spherical voids are cut, which leads to a distribution of openings at the surface, i.e., a substrate with a very rough surface. This roughness was modelled with a graded porosity changing from 38% in the bulk to 75% at the outer surface. This measured variation in porosity is very similar to the cumulative height distribution of the surface layer obtained from AFM. The validity of this graded porosity model was verified from the analysis of a sample with a thin polysulfone (PSU) layer deposited on the support. The PSU layer partly fills the open pores at the surface. This results in an interface with a graded variation in aluminium oxide, void and PSU.

The proper treatment of the surface layer also provides the optical properties of the porous aluminium oxide bulk material itself. These optical properties can in a limited wavelength range be modelled with Bruggeman's effective medium approximation. As a consequence of the size of the inclusions, their diameter is no longer negligible with respect to the wavelength of light in the UV part of the spectrum. For the material with the largest pore size, also a large part of the visible range has to be excluded. A more elaborate approach than the standard effective medium approach has to be used in this case.

[1] H. Wormeester, N.E. Benes, G.I. Spijksma, H. Verweij and B. Poelsema Thin Solid Films **455-456**, 747-751 (2004)

5:00pm **EL+AS+EM+MS+PS+TF-ThA10 Optical Properties and Structure of Vanadium Oxide Thin Films**, ***M.A. Motyka****, M.W. Horn,* Pennsylvania State University*, N.J. Podraza*, University of Toledo

Vanadium oxide (VO_x) thin films are common materials used as imaging layers in uncooled microbolometer based thermal imaging devices. These films are used in this application largely due to the controllable resistivity of the film (ρ), the high temperature coefficient of resistance (TCR), and the low electrical noise. One of the main difficulties of this material system relates to the multiple valence states of vanadium, each of which results in materials with different electrical properties. Bolometer quality VO_x may consist of a composite of nanocrystalline face centered cubic (FCC) VO phase and amorphous materials. The thin film oxygen content via Rutherford back scattering (RBS) has suggested that the typical ratio V:O should be near 1:1.7-2.0, significantly higher than the stability window of the FCC phase. This off-stoichiometry ratio suggests that the amorphous material is a mixture of higher oxygen valence states similar to V_2O_5 and VO_2. The higher quality VO_x thin film material also has been observed via transmission electron microscopy (TEM) to contain VO/V_2O_3 nano-twin crystalline domains. The presence of each of these phases impacts the electrical and optical properties of the resulting VO_x film. Films with various oxygen contents and structures were studied with spectroscopic ellipsometry (SE) over a spectral range of 0.05 to 5.15 eV using a multichannel dual rotating compensator near-ultraviolet to near infrared instrument in conjunction with Fourier transform infrared spectroscopic ellipsometry (FTIR-SE). Thus, the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) can be obtained for these materials over the full spectral range. Differences in ε due to variations in the film structure are observed as functions of processing, indicating that SE is a means of probing the material composition and structure. Specifically, ε are compared for various film composites fabricated by unbiased pulsed DC magnetron sputtering as well as composite films prepared by reactive ion beam sputtering and pulsed DC magnetron sputtering with a substrate bias. The microstructure and ε are correlated with films exhibiting the desirable device electrical properties. In situ real time spectroscopic ellipsometry (RTSE) has shown that environmental conditions alter the as-deposited VO_x thin films grown via pulsed DC-magnetron reactive sputtering of a metallic vanadium target. In order to prevent undesired atmospheric effects to the thin film, it is a common practice to encapsulate the thin film with a more environmentally stable material. In this study, the material chosen was SiO_2 grown in the same deposition chamber, pre-atmospheric exposure, via rf sputtering.

5:20pm **EL+AS+EM+MS+PS+TF-ThA11 Sensitivity of Dielectric Properties of Vanadium Dioxide Thin Films to Growth Conditions***, D.W. Ferrara,* ***R.E. Marvel****, J. Nag, R.F. Haglund*, Vanderbilt University

Vanadium dioxide (VO_2) is a strongly-correlated electron material with a well-known semiconductor-to-metal transition (SMT) that can be induced thermally (T_c = 68°C), optically, or electrically. Recently, VO_2 films have attracted attention as a component in active metamaterials, especially in conjunction with metal nanostructures. Since these structures are highly sensitive to the dielectric properties of the embedding material, the SMT of VO_2 can be used to tune the optical response of the structure. Accurately modeling the behavior of these structures requires detailed knowledge of the dielectric function of VO_2 as it undergoes the SMT; however, previous measurements of the optical constants of VO_2 reveal significant variations between experiments.

To understand systematic variations due to growth conditions, films of VO_2 were deposited on either silicon, glass, or sapphire substrates by pulsed laser ablation of vanadium metal targets in 10 mTorr oxygen (O_2) background gas, followed by annealing at 450°C in 250 mTorr of O_2. Anneal times were varied from 30 to 90 depending on film thickness; deposition thickness was varied from 20 nm to 200 nm. For each sample, temperature-dependent spectroscopic ellipsometry measurements at optical and near-infrared wavelengths were conducted to determine the dependence of the optical constants on film thickness, substrate and crystallinity, and temperature.

Bruggeman and Maxwell-Garnett effective-medium formulations were used to account for three constituent materials: semiconducting VO_2, metallic VO_2, and vanadium pentoxide (V_2O_5). The effective dielectric functions were modeled using Lorentz and Tauc-Lorentz oscillators. Our results show that the contribution of V_2O_5 to the effective dielectric function increases with annealing time, consistent with previous studies. The results are also substantiated using Rutherford backscattering, X-ray photoelectron spectroscopy and X-ray diffraction.

Transparent Conductors and Printable Electronics Focus Topic
Room: 106 - Session TC+EM+NS-ThA

Transparent / Printable Electronics Part 2
Moderator: S. Durbin, University at Buffalo

2:00pm **TC+EM+NS-ThA1 ZnO-based Schottky Diodes and Their Utilization in Transparent Electronics**, ***H. von Wenckstern***, Universität Leipzig, Germany **INVITED**

Transparent conducting oxides (TCO) have found application as electrode in emerging markets like that of thin films solar cells or flat panel displays. For this passive functionality the TCO material must combine high transparency preferentially over a wide spectral range and high conductivity. In the last years active transparent devices like photodetectors, transistors or a complete transparent circuitry are envisioned and rely on semiconducting properties of the material. Besides a precise control of the doping level in the active part of devices the creation of space charge regions by rectifying contacts is a prerequisite for active devices. In the emerging field of transparent electronics, only metal-insulator-semiconductor field-effect transistors (MISFETs) were considered so far. In this contribution transparent, high-performance MESFETs, inverters etc. based on ZnO and related ternaries are presented. We discuss design prospects as well as limitations regarding device performance, reliability and stability.

The influence of the contact metal and dielectric passivation layers on the properties of ZnO Schottky diode, used as gate electrode within the MESFETs, as well as sources of non-idealities will be highlighted.

2:40pm **TC+EM+NS-ThA3 Photoresponse of Amorphous In-Ga-Zn-O / Pt Schottky Junction**, ***D.H. Lee***, *K. Nomura, T. Kamiya, H. Hosono*, Tokyo Institute of Technology, Japan

Amorphous oxide semiconductors (AOSs) are expected as an alternative to amorphous/poly-Si for thin-film transistors (TFTs) in next-generation flat-panel displays (FPDs) because AOS TFTs have many advantages such as large field-effect mobilities (>10 $cm^2(Vs)^{-1}$) and low-temperature process [1]. For more advancing AOS optoelectronic technology, it is important to develop more various devices other than TFTs, and to study some remaining issues such as operation characteristics of AOS devices under light illumination.

In this study, we fabricated good and stable metal-AOS Schottky contacts made of amorphous In-Ga-Zn-O (a-IGZO) and bottom Pt electrodes at temperatures below 200°C even though it is generally difficult to make high performance oxide Schottky junctions [2]. It was found that the a-IGZO/Pt Schottky contacts have an ideality factor n ~ 1.1 and a Schottky barrier height ϕ_b ~ 0.9 eV, which were evaluated from their J-V curves using the thermionic emission model. From C-V results, the Schottky junctions operate at the full-depletion condition, whose C corresponds to the geometrical capacitance of the a-IGZO layer, and relative permittivity ε_s of a-IGZO was obtained approximately 13. However, the results of temperature dependences of J-V characteristics were unexplained if we take a simple uniform Schottky barrier model; we found that the barrier potential fluctuations model [3] explained them well, and the mean barrier height $\phi_{b,m}$ of 1.2 eV and the net electron affinity χ_s of a-IGZO of 4.2 eV were obtained. On the other hand, the Schottky contacts showed very small open circuit voltages (V_{OC}'s) < 0.1 V under 100 $mWcm^{-2}$ AM1.5 light illumination, which are far smaller than the built-in potential (V_{bi} ~ 0.4 eV) estimated from the C-V measurements in dark. We also observed that V_{OC} decays with time after starting the light illumination. We will discuss the mechanism of the small V_{OC} based on these results.

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3:00pm **TC+EM+NS-ThA4 Novel Metal-organic Precursors for Printed Electronics - Synthesis, Implementation, and Properties**, ***J.A. Belot***, *R.A. Potash, R.D. McCullough, K.A. Singh, L. Porter*, Carnegie Mellon University

Printed electronics is a rapidly growing industry and within this emerging field there are three required material categories critical to fabricating active and passive circuitry – insulators (dielectrics), semiconductors (polymers), and conductors (metals). The increased interest in printable electronics as alternatives to silicon-based technologies is fueled by the promise of large-area, flexible, and ultra-low-cost devices. To enable the growing demands of printing processes this work develops metal-containing inks for the deposition of the coinage metals - copper, silver, and gold. These metals are chip components ranging from interconnects to source and drain contacts in organic field effect transistors. The liquid ink approach is based on fundamental advances in coordination chemistry to fabricate discrete metal complexes that can be heated or irradiated to yield metallic films. Ultimately inkjet printing technologies were employed to deposit these metal inks in specific, predetermined patterns that were directly transformed into active and passive devices. The versatility of this approach holds the possibility of printing any metallic design and pattern on virtually any type of substrate.

3:40pm **TC+EM+NS-ThA6 A New Application for a-IGZO TFTs: An Addressable Microfluidic Electrowetting Channel Device**, ***J. Noh***, *J.H. Noh,* University of Tennessee*, E. Kreit, J. Heikenfeld,* University of Cincinnati*, P.D. Rack*, University of Tennessee

An electrowetting (EW) microfluidic platform designed for control and transport of aqueous and polar species has been fabricated on passive electrodes as well as an active matrix thin film transistor (TFT) array. To drive the EW devices we integrated the micro fluidic platform on a base-plane of transparent TFTs. Specifically, we have used an InGaZnO (IGZO) active layer for the TFT device which has superior performance and offers the benefit of transparent devices for biological and display applications. The TFTs are fabricated with a bottom-gate staggered structure with Cr gate and SiO2 gate dielectrics deposited via plasma enhanced chemical vapor deposition (PECVD). The a-IGZO semiconducting active layers are deposited using rf magnetron sputtering in a reactive Ar-O2 atmosphere. Finally, source and drain electrodes are formed by e-beam evaporating Ti/Au. Finally the device is annealed in an N2ambient for electrical activation. For the EW device integration, Al electrodes are have been deposited various passivation layers. Subsequently a top dielectric and a hydrophobic Fluoropel layer are applied. In this presentation we will review the process flow and will discuss the materials integration issues of EW device and its effect on the TFT performance. We will illustrate the EW characteristics based on standard planar electrowetting on dielectric (EWOD) platforms and compare them to a new concept we have termed the "Laplace Barrier" which includes post arrays and enhances electrowetting characteristics.

4:00pm **TC+EM+NS-ThA7 Amorphous Oxide Semiconductor Thin-Film Transistors**, ***J.F. Wager***, *K. Hoshino,* Oregon State University*, B. Yeh, R.L. Hoffman*, Hewlett-Packard Company **INVITED**

Amorphous oxide semiconductor (AOS) thin-film transistors (TFTs) are transitioning towards commercialization for active-matrix liquid crystal display flat-panel display backplane applications. They also appear to be well-positioned to meet the more demanding challenges associated with active-matrix organic light-emitting device backplanes. Additionally, AOS TFTs offer an attractive approach to printed electronics. The primary focus of this talk will be to discus our novel approach to top-side passivation of bottom-gate indium gallium zinc oxide (IGZO) and zinc tin oxide (ZTO) AOS TFTs. Device performance between passivated and unpassivated AOS TFTs will be compared. Passivation mechanisms will be considered in the context of induced-gap state and device physics electrostatic modeling.

4:40pm **TC+EM+NS-ThA9 Why Optimum Oxygen Pressure Range Exists for Fabricating Amorphous In-Ga-Zn-O Thin-Film Transistor and How it Should be Optimized**, ***K. Ide***, *K. Nomura, T. Kamiya, H. Hosono*, Tokyo Institute of Technology, Japan

Amorphous oxide semiconductors (AOSs) represented by amorphous In-Ga-Zn-O (a-IGZO) are expected for large-area high-performance flexible electronic devices, because AOSs have large electron mobilities greater than

10 $cm^2(Vs)^{-1}$ even if fabricated at room temperature (RT). In particular, a-IGZO has good controllablities of carrier concentration, and their thin-film transistors (TFTs) exhibit superior properties including long-term stability.

In this study, we investigated effects of oxidation on operation characteristics of a-IGZO TFTs. Bottom gate, top-contact a-IGZO TFTs were fabricated on SiO_2/c-Si substrates by RF magnetron sputtering. Sputtering conditions were the RF power of 70 W and the total pressure of 0.55Pa. Two oxidation treatments were examined; (i) ozone annealing and (ii) varying a mixing gas ratio of Ar : O_2 from 18 : 2 to 19.8 : 0.2 in standard cc per minute (sccm) during the channel deposition.

For the ozone annealed TFTs, annealing at ≤ 250°C produced good TFTs, while those annealed at 300°C caused large hysteresis and S slope. After applying a high V_{GS} larger than 40 V, the transfer characteristics showed the large V_{th} of 40V and the small hysteresis. Trap state around Fermi level of the large S state and the large V_{th} state were ~4x10^{17} and ~1x10^{17} $cm^{-3}eV^{-1}$, which were estimated by C-V analysis. The large V_{th} state is very stable in the dark, but the TFT recovers to the initial large S state by light illumination. The photoresponse measurements revealed that deep trap states were formed at 2.3 eV below the conduction band minimum by applying a high $V_{GS.}$ Thermal desorption spectra showed that weakly-bonded excess oxygens were incorporated in the a-IGZO layer. From these results, we built a subgap DOS model of the trap states of the excess oxygens. We also confirmed similar behaviors in a-IGZO TFTs fabricated in high oxygen pressure conditions.

This study reveals that the control of oxygen stoichiometry is important for obtaining good performance and stability of AOS TFTs.

5:00pm **TC+EM+NS-ThA10 Effects of Low-Temperature Annealing and Deep Traps in Operation Characteristics of Amorphous In-Ga-Zn-O Thin-Film Transistors**, ***T. Kamiya***, *Y. Kikuchi, K. Ide, K. Nomura, H. Hosono*, Tokyo Institute of Technology, Japan

Amorphous oxide semiconductors (AOSs) represented by a-In-Ga-Zn-O (a-IGZO) are expected for channel materials in thin-film transistors (TFTs) for next-generation flat-panel displays such as jumbo-size / fast / ultrahigh-resolution liquid-crystal displays and organic light-emitting diode displays. These are also expected for flexible electronics devices because they may be fabricated on unheated substrates, and thus produce flexible displays and circuits on inexpensive plastic substrates such as PET. On the other hand, it is known that, although room-temperature fabrication is possible for AOS TFTs, post-deposition thermal annealing at ≥300°C is better employed to obtain good stability. To employ this technology to the flexible electronics, the annealing temperature should be lowered to 200°C or far below. We reported that wet O_2 annealing produces the best performance TFTs when annealed at ≥300°C, while it caused serious negative threshold voltage (V_{th}) shift at ≤200C. In this paper, we report the origin of the negative V_{th} shift by employing photoresponse spectroscopy of TFT characteristics. It revealed that the near-valence band maximum (VBM) states are reduced significantly even by the low-temperature 200C annealing, and implied that the negative V_{th} shift originates from free electrons released by annihilation of the near-VBM states.

5:20pm **TC+EM+NS-ThA11 β-alumina (SBA): A Promising High Dielectric Constant Gate Material for Solution Processed, Transparent and Low Voltage Transistor Devices**, ***B. Zhang***, *Y. Liu, H. Katz*, Johns Hopkins University

β-alumina (SBA) has been discovered as a promising high dielectric constant gate material for solution processed, transparent and low voltage transistor devices. Some experimental evidence indicates that the mobile Na ion within two spinel blocks made by Al and O is responsible for the high dielectric constant. Transistors (W/L ratio 10) using SBA as gate layer and zinc tin oxide (ZTO) as active layer only need 2V to obtain 0.7mA output current. SBA material is compatible with organic semiconductors such as PQT12 and pentacene as well. Some key issues regarding using SBA for real applications, such as device stability in the ambient atmosphere, response under high frequency, and threshold voltage shift under gate bias have also been studied. It is found that encapsulating the device with CYTOP fluorinated polymer is an effective way to increase the operational stability of the devices in the ambient environment.

Thin Film Division
Room: 110 - Session TF+EM+SS-ThA

Applications of Self Assembled Monolayers
Moderator: M.R. Linford, Brigham Young University

2:00pm **TF+EM+SS-ThA1 Organic Monolayers on Silicon-rich Substrates: Methods and Mechanisms**, ***H. Zuilhof***, Wageningen University, Netherlands **INVITED**

SAMs on silicon-containing substrates including silicon, silicon nitride and glass widely expand the applicability of such materials. The presentation will focus on 3 recent developments:

1) The surface modification of H-terminated Si has functioned as a stepping-stone for the construction of a wide-range of hybrid materials. Recent synthetic improvements and detailed mechanistic studies have shown how to optimally construct such modified substrates. These results will be presented in the light of further developments.

2) Silicon nitride can be modified by covalent SAM attachment to achieve chemically highly robust systems. Biofunctionalization thereof with oligosaccharides and antibodies provides novel diagnostic applications in terms of specific bacterial capture in combination with generally antifouling substrates when combined with lithographic structuring of the material. Proof-of-principle and remaining challenges will be demonstrated based on recent experimental progress.

3) A photochemical method we recently developed to modify glass (SiO2), and the application thereof within the field of modified glass microchannels will be shown, e.g. via the on-chip embedding of enzymatic cascade reactions using a combination of local SAM attachment and DNA-enzyme hybrids. Finally, generalizations to the modification of other oxidic surfaces will be provided.

Key references:

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2:40pm **TF+EM+SS-ThA3 Molecularly Modulated Electrical Transport at Chemically Passivated Silicon Surfaces**, ***G. Dubey***, NRC-SIMS, Canada, *F. Rosei*, INRS-EMT, Canada, *G.P. Lopinski*, NRC-SIMS, Canada

Adsorption of charged or polar species on semiconductor surfaces can modulate the electrical properties through long-range field effects. Hydrogen-terminated silicon-on-insulator (SOI-H) is an interesting model system for investigating this sensitivity to surface processes [1,2]. Accumulation mode SOI-H pseudo-MOSFETs [3] have been used to probe molecular adsorption and reaction events. Current-voltage characteristics of such *n*-channel devices are found to be sensitive to the environment, with the accumulation threshold voltage, or flat-band voltage (V_{FB}), exhibiting large reversible changes upon cycling between ambient atmosphere, high vacuum (<10^{-5} Torr) and exposure to water and pyridine vapour at pressures in the torr range. Both these adsorbates act as effective electron donors, shifting the flat band potential to more negative values. The field-effect mobility is found to be comparatively less affected through these transitions. Adsorption of the well known electron acceptor tetracyanoethylene (TCNE), is shown to cause depletion, with ppm levels of TCNE vapour in ambient atmosphere found to rapidly decrease the saturation current by over two orders of magnitude. The effect is only partially reversible on the hydrogen terminated surface, due to the accumulation of strongly bound TCNE molecules on the surface. In addition, oxidation of the H-terminated surface is seen to result in irreversible shifts in both the flat-band voltage and field-effect mobility. In order to passivate the surface from these irreversible processes, a photochemical gas phase reaction [4] with decene was used to form a decyl monolayer on the SOI(100)-H surface. Formation of this monolayer is found to result in a relatively small shift of threshold voltage and only a slight degradation of the field effect mobility. Decyl passivation only slightly decreases the response of the FET to TCNE adsorption while significantly improving the reversibility of the response. These results suggest that alkyl monolayer dielectrics formed by the gas phase photochemical method can function as good passivating dielectrics in field effect sensing applications.

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3:00pm **TF+EM+SS-ThA4 Micrometer- and Nanometer-Scale Patterning of Azide-Functionalized Self-assembled Monolayers on Gold and Aluminum Oxide Surfaces**, ***O. El Zubir**, I. Barlow, G. Leggett, N. Williams*, University of Sheffield, UK

Self-assembled monolayers (SAMs) have been prepared by the adsorption of [11-(4-azido-benzoylamino)-undecyl] phosphonic acid on aluminum oxide and by the adsorption of 11-(4-azido-benzoylamino)-undecylthiol. Exposure to near UV radiation causes elimination of nitrogen and the creation of a reactive nitrene species. Quantitative studies by X-ray photoelectron spectroscopy (XPS) and contact angle measurement show that the reaction is complete after an exposure of 20 J cm–2. The reaction enables selective introduction of primary amines to the surface. By exposure of the azide under a solution of the amine, derivatization may be carried out with high efficiency, providing a simple pathway for the creation of a variety of multiple-component surface chemical patterns. Micropatterned surfaces were fabricated by exposure the SAMs to UV-laser (λ=325 nm) through a mask in presence of amines. Photopatterning was carried out at the nanometer scale by using scanning near-field photolithography (SNP) in which a scanning near-field optical microscope (SNOM) coupled to a UV laser (λ=325 nm) is utilized as the light source. Selective modification of azide terminated monolayers on aluminum oxide by protein-resistant molecules enabled the fabrication of protein nanopatterns that could be imaged by fluorescence microscopy.

3:40pm **TF+EM+SS-ThA6 Free-standing, SAM-based, Hybrid Biocompatible Nanomembranes for Biological Applications**, ***N. Meyerbröker**, W. Eck, M. Zharnikov*, Universität Heidelberg, Germany

Functional monomolecular films - so-called self-assembled monolayers (SAMs) - represent a broad platform for nanofabrication, sensor design, and molecular electronics, as well as a framework for Chemical Lithography, and a model system for organic interfaces and molecular, macromolecular and biological assemblies. These films can be prepared on different substrates which provide necessary support and guarantee the persistence of the 2D molecular assembly. Since the intermolecular interaction within the SAMs is relatively weak, such films cannot exist without support, dissipating into the individual constituents upon the separation from the substrate. However, as far as the individual molecules within a SAM can be cross-linked extensively by physical means such as electron irradiation, the resulting quasi-polymer film can be separated from the substrate and exist as a free-standing monomolecular membrane on its own. In this presentation we describe the formation of such free-standing membranes on the basis of aromatic SAMs. In contrast to the previous work, we used not only non-substituted but nitro- and nitrile-substituted SAM constituents which, due to either nitro-to-amine or nitrile-to-amine transformation, become chemically reactive after the irradiation treatment and can be subsequently coupled to further species. As such species we used oligo(ethylene glycol)-based molecules with a specific anchor group providing the coupling to the amine groups of the monomolecular template. After the attachment, these templates and respective hybrid membranes become protein-repelling and as such can be used as a non-disruptive and highly transparent support for proteins and cells in transmission electron microscopy (TEM) experiments. Whereas the ultimate thinness of this support guarantees a high imaging quality, protein-repelling ensures the lack of protein denaturing, which extents essentially the possibilities of TEM experiments in their specific application to sensitive biological targets.

4:00pm **TF+EM+SS-ThA7 Development of Nanoscale Heterostructures: From Single Component Nanostructures to Multicomponent Nanosystems**, ***N. Chopra***, The University of Alabama, Tuscaloosa **INVITED**

Chemical vapor deposition (CVD) and solution synthesis was coupled to realize a unique surfactant-free approach for the direct nucleation of nanoparticles on 1-D nanostructures. Towards this end, skeleton nanostructures such as carbon nanotubes and oxide nanowires were successfully utilized as a selective nucleation sites for nanoparticles. Carbon nanotubes (CNTs)–Ni/NiO nanoparticles and oxide nanowires -(Au or Co_3O_4) nanoparticles were synthesized. Morphological evolution of nanoparticles as a function of various growth parameters was studied using TEM, SEM, and XRD. New kinds of lattice relationships, interfaces, and morphologies were established. For example, CuO nanowire-Co_3O_4 nanoparticles showed unique optical characteristics leading to enhanced absorbance in visible light. Growth mechanisms of heterostructures revealed various competing phenomena at nanoscale including thermodynamic stability and chemical potential, and surface migration of nanoparticles on high curvature 1-D nanostructures as opposed to flat surface. These heterostructures also hold great promise as novel sensors and energy technologies.

4:40pm **TF+EM+SS-ThA9 Physical and Electrical Characterization of Metal Incorporated SAM-based Molecular Electronic Junctions**, ***S. Pookpanratana**, M.A. Walsh, C.A. Richter, C.A. Hacker*, National Institute of Standards and Technology

Molecular electronics is attractive for next-generation applications because of the flexibility in tailoring the organic functionality and the facile formation of uniform monolayers by using thiol-Au chemistry for self-assembly. Added functionality can be achieved by using thiol self-assembled monolayers (SAMs) containing terminal carboxylic acid functional groups to chelate with metal ions [1], and thus can incorporate d-orbital transition metals with the SAMs. One challenge in molecular electronics has been the reliable formation of a top contact to the organic layer. Fabrication techniques involving metal evaporation of the top contact often result in penetration to the substrate [2] or into the SAM [3], either of which influences the measured electrical properties across the junction. Here, we utilize flip chip lamination (FCL), a soft metallization technique by nanotransfer printing, to form a top contact onto SAMs on Au [4].

Based on previous work by Ulman et al. [5] and Allara et al. [6], we have incorporated metal ions (Cu and Ni) with mercaptohexadecanoic acid (MHA) and formed a molecular junction by FCL. SAMs of MHA were prepared on Au on Si and Au on polyethylene terephthalate (PET) substrates. The MHA/Au/Si was exposed to metal ion (M) containing solution. The M-MHA/Au/Si samples were then laminated to MHA/Au/PET to create a 'molecular sandwich' which resulted in the following structure: PET/Au/MHA-M-MHA/Au/Si where the PET substrate is removable.

The SAMs on Au were investigated by using X-ray photoelectron spectroscopy (XPS) and p-polarized reflection absorption infrared spectroscopy (p-RAIRS), and both methods confirm the initial presence of carboxylic acid on the (pre-FCL) surface. Successful incorporation of metal ions into the SAM were directly confirmed by XPS (occupying 30-50% of the –COOH sites), and indirectly by p-RAIRS with the appearance of C=O bands in an acid salt environment. Electrical and physical characterization (using backside p-RAIRS and near edge X-ray absorption fine structure (NEXAFS)) measurements to investigate the monolayer after FCL are currently ongoing. With these results, we are able to obtain a thorough picture linking electrical properties with physical characterization of the buried molecular junctions.

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5:00pm **TF+EM+SS-ThA10 Examining the Role of Laminin-Derived Peptides in Neuronal Attachment**, ***N.A. LaFranzo**, J.A. Maurer*, Washington University in St. Louis

Laminin-1 is a 900kD glycoprotein that is a major component of the extracellular matrix (ECM). Laminin is known to be involved in many cellular processes including cell adhesion, migration and differentiation *in vivo* and is often used in *in vitro* experiments to encourage neuronal attachment. While laminin contains some integrin-receptor binding sites, multiple domains on the protein including the peptide sequences IKVAV, YIGSR and RGD have also been shown to bind to non-integrin neuronal receptors, encourage cell adhesion, and encourage neurite outgrowth in the absence of the full protein structure. However, previous experiments performed using these peptides as substrates for neuronal culture fail to consider the effects of excretion of the cells own ECM proteins onto the surface, which we have shown can occur on surfaces with high peptide concentrations. By utilizing self-assembled monolayers (SAMs), we have created a substrate that prevents the non-specific adsorption of proteins excreted by neurons, while introducing a low-concentration of the peptide sequences to encourage neuronal attachment.

A pair of alkane-thiol monomers for assembly on a gold substrate have been designed which contain a tetra-ethylene glycol moiety at the tail to prevent the non-specific adsorption of proteins. One of the monomers is terminated with an azide moiety that can be used to specifically attach molecules with an alkyne group by a copper-mediated azide-alkyne cycloaddition (CuAAC) reaction, also known as the "click" reaction. By introducing 5-pentynoic acid at the N-terminus of each of the peptides during synthesis, we have introduced a bioorthogonal attachment point for reaction with the

azide-terminated monomers on the surface. Once prepared, these surfaces have been confirmed to be resistant to adsorption of proteins by quartz-crystal microbalance (QCM) experiments. Primary culture neurons dissected from embryonic mice have been cultured on the surface and the effects of the peptides on neurite outgrowth have been quantified. To better understand the role of these peptides in cell adhesion, neurons transfected with a plasmid encoding EGFP-vinculin or EGFP-paxillin have been cultured on the surface and the focal adhesion morphologies have been observed in live-cell imaging experiments. These results are compared to those observed for a surface where the full laminin protein has been adsorbed. Together, these experiments help to design a surface resistant to non-specific protein adsorption that allows for neuronal adhesion, sheds light on laminin-mediated attachment, and aids in developing better small-molecule mimics of receptor-mediated cellular adhesion.

5:20pm **TF+EM+SS-ThA11 Contact-Free Electrical Characterization of Molecular Layers using CREM**, ***H. Cohen***, Weizmann Inst. of Science, Israel

While generally recognized as a powerful analytical tool, XPS is insensitive to hydrogen atoms and, in many cases, to fine variations in the environment of carbon atoms. As such, XPS characterization of organic molecular layers is rather limited, in particular under demands for high overlayer quality. On the other hand, a recent XPS-based technique for chemically resolved electrical measurements (CREM) proposes high sensitivity to even small amounts of defects or organization imperfections [1,2].

Here, CREM application to monolayers self-assembled on metallic or semiconducting substrates is overviewed, demonstrating some of the unique capabilities offered by this non-contact probe. Damage evolution under irradiation is specifically discussed; two of its extreme limits being modeled, yielding the effect of corresponding defect sites on the CREM-derived I-V curves. Potential applications to molecular electronics, approaching ***atomic*** resolution in the electrical data, will be discussed.

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Electronic Materials and Processing Division
Room: East Exhibit Hall - Session EM-ThP

Electronic Materials and Processing Poster Session

EM-ThP1 Novel Quantized Edge States on Ag(111), ***A.R. DiLullo***, Ohio University, *D. Acharya,* Pacific Northwest National Laboratory, *N. Takeuchi,* Universidad Nacional Autonoma de Mexico, *S. Ulloa, S.-W. Hla*, Ohio University

A one-dimensional electronic edge state has previously been observed using ultra-high-vacuum low-temperature scanning tunneling microscopy (UHV-LT-STM) methods at a sample tunneling bias of approximately 4V on Cu(111) and explained in terms of an image state at the step with energy modified by a dipolar potential[1]. Presented here are new measurements using sample bias dependent UHV-LT-STM imaging techniques of step edges on a Ag(111) surface which show numerous higher order states with correlated energy spacing. Measurements are additionally made at tip induced vacancy locations (holes in the surface) to examine effects of confinement on the newly observed one dimensional states. Experimental results are supported by density functional theory (DFT) calculations, and a framework for explanation of the newly observed energy correlated one dimensional and confined states is explored.

Supporting funding is supplied in part by the grants DOE DE-FG02-02ER46012 and NSF OSIE 0730257.

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EM-ThP2 Fabrication of Multilayered Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$ Thin Film Cooling Devices, ***M. Hines***, *J. Lenhardt,* Alabama A&M University, *M. Lu,* Brookhaven National Laboratory, *Z. Xiao*, Alabama A&M University

In this paper, we report to fabricate multilayered Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$thin film cooling devices using the microfabrication techniques. The multilayered Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$thin films will be grown using the e-beam evaporation. The in-plane and cross-plane micro cooling devices will be fabricated using the standard integrated circuit (IC) fabrication process; pn junction diodes will be fabricated as thermometers for the measurement of temperature in the devices. The electrical and thermal properties of the e-beam-grown Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$thin films and the cooling efficiency of the fabricated cooling devices will be measured, and the measurement results will be reported in the conference. The developed devices could be a good candidate for the application of high-efficiency solid-state micro-cooling.

EM-ThP3 Solution-Based High Performance and Fully Patterned Chalcogenide Thin Film Transistors, ***J.I. Mejia***, *A. Salas-Villasenor, A. Carrillo-Castillo, B.E. Gnade, M.A. Quevedo-Lopez*, University of Texas at Dallas

In recent years, the development of novel processes for inexpensive and flexible electronics has become an increasing research area where low-cost and low temperature deposition techniques are key point to fabricate large area and flexible circuits. Here, we demonstrate fully photolithography defined thin film transistors using cadmium sulfide (CdS) and lead sulfide (PbS) as n-type and p-type semiconductors, respectively. These chalcogenides materials are deposited using chemical bath deposition (CBD) which is a low cost solution-based process that requires temperatures below 70° C. Extracted mobility for CdS was 25 cm^2/V-s and 0.14 cm^2/V-s for PbS. These mobilities are among the highest reported for a fully patterned TFT made with either CdS or PbS as semiconductor. The maximum temperature used in the complete fabrication process was kept below 100° C. In addition, we studied how the device performance (mobility, threshold voltage and contact resistance) is affected depending on the semiconductor thickness, thermal annealing and the metal used as drain-source electrodes. Our fabrication approach can be integrated in complex designs such as CMOS logic gates, pixel arrays, etc., complying with all the requirements for a flexible electronics technology.

EM-ThP4 Novel Materials and Device Structures for Solid-State Charged Particle Detectors, ***J.W. Murphy***, *J.I. Mejia, B.E. Gnade, M.A. Quevedo-Lopez*, University of Texas at Dallas

Detectors for charged particle spectroscopy are typically fabricated from crystalline silicon, germanium, or gallium arsenide, which are high-cost materials. However, if the purpose of the device is particle detection rather than spectroscopy, then it is possible to use less expensive materials and deposition techniques to fabricate electrically-sensing, solid-state particle detectors. Particularly, we are interested in detecting alpha particles emitted from a 210-Polonium source. In this work we investigate ZnO nanostructures in combination with poly(3-hexylthiophene) (P3HT) to form hybrid inorganic/organic p-n diodes which are as charged particle sensors. The ZnO nanostructures are grown from solution on a Cr electrode, and the P3HT is subsequently deposited via the drop-casting technique to achieve bi-layer film thicknesses on the order of microns. We evaluate the devices' performance in terms of leakage current, capacitance, and alpha particle detection efficiency as a function of thickness, DC bias, and annealing treatment. The structures are investigated using x-ray diffraction and cross-sectional electron microscopy. We also study the materials degradation upon exposure to radiation by monitoring the leakage current.

EM-ThP5 Structural and Electrical Characteristics of TaN Film Deposited by DC Sputtering for MOS Capacitor and Schottky Diode Upper Electrodes, ***L.P.B. Lima***, *J.A. Diniz,* State University of Campinas, Brazil, *C. Radtke,* Federal University of Rio Grande do Sul, Brazil, *I. Doi, J. Miyoshi, A.R. Silva, J. Godoy Fo*, State University of Campinas, Brazil

Tantalum nitride (TaN) films have been obtained by DC sputtering deposition in a nitrogen/argon ambient on Si substrates. TaN film have been used as gate electrodes in MOS capacitors and in Schoktty diodes on Si substrates. 20nm and 100nm thick TaN layers were deposited by DC sputtering in N_2:Ar (20:60 sccm) ambient, with a sputtering power of 1000 W. These films presented electrical resistivity of 327 Ω.cm and poly crystalline strucure. XPS analysis evidence TaN and Ta_2O_5 formation in both 20 nm (Fig. 1) and 100 nm (Fig. 2) thick films. Ta_2O_5 formation could be related with the exposure the metal electrode to air. To get MOS capacitors with $TaN/SiO_2/Si/Al$ and $Al/TaN/SiO_2/Si/Al$ structures, the Si substrates were used and were cleaned with a standard RCA method. After, dry thermal oxidation at 1000°C for 2 min was carried out and a 8 nm thick SiO_2 layer on Si was obtained. 20 nm and 100nm thick TaN layer was deposited on SiO_2/Si by DC sputtering. Finally, in some devices a 200nm thick alumininum (Al) layer was deposited on TaN layer by DC sputtering, in order to reduce these contamination of the metal electrode. MOS capacitor pattern was defined by a mask composed of an array of 200 µm diameter dots. These devices were sintered in conventional furnace in forming gas at 450 °C for 30 minutes and were electrical characterized by capacitance-voltage (C-V) measurements. Figure 3 and 4 presents MOS capacitor C-V characteristics. TaN work function values and flat-band voltage were extracted from all C-V measurements using CVC software and $1/C^2$ method. The extracted TaN work function values and flat-band voltage were between 4.3 and 4.4 eV (Fig. 3-4), 0.1 and 0.2 V (Fig. 3-4), respectively. The variations on work function values are related with the dipole variations due the interface between metal and dielectric. To investigate the TaN work function, Schoktty diodes were fabricated in the same substrate of MOS capacitors. TaN layer were deposited by DC sputtering in a N_2:Ar (20:60 sccm) ambient, with a sputtering power of 1000 W. TaN/Si/Al and Al/TaN/Si/Al diodes were formed with TaN (20nm and 100nm) gate electrodes and Al layer (200nm) were deposited by DC sputtering process. These diodes were sintered in conventional furnace in forming gas at 450 °C for 30 minutes. The electrodes were patterned with a mask composed of an array of 200 µm diameter dots. These diodes were electrical characterized by current-voltage (I-V) measurements, and the ideality factor between 1.1 and 1.5, and work function values between 4.4 and 4.5 eV were extracted, which is near the work function values for mid-gap electrode application.

EM-ThP6 TiAlO and TiAlON Obtained by e-Beam Evaporation with Additional Electron Cyclotron Resonance (ECR) Plasma Oxidation and Oxynitridation on Si for MOS Gate Dielectric, ***J. Miyoshi***, *A.R. Silva, F.A. Cavarsan, J.A. Diniz, L.P.B. Lima*, State University of Campinas, Brazil

Titanium-Aluminum Oxide (TiAlO) and Titanium-Aluminum Oxynitride (TiAlON) high *k* films have received considerable attention due to their electrical and physical properties, which are from the composition of Titanium Oxide and Aluminum Oxide properties, such as higher permittivity (k~80) and higher band gap (Eg~8.8 eV), respectively, than others high *k* (such as HfO_2 and ZrO_2) films [1,2]. Furthermore, this composition can reduce the undesirable effects on sub-32 nm MOS devices, which are high leakage current, due to the value of band offset of 2.8 eV to Al_2O_3, and EOT higher than 2 nm, due to relatively low *k* between 8 and 10, respectively. In this work, Titanium-Aluminum Oxide (TiAlO) and Titanium-Aluminum Oxynitride (TiAlON) were obtained on Si wafers as follow: 0.75 nm Titanium (Ti) and 0.25 nm Aluminum (Al) were sequentially deposited by vacuum e-beam evaporation, without any substrate heating. The evaporation pressure was $3x10^{-8}$ Torr, and the Ti and

Al evaporation rates were of 0.1 nm/min, resulting in Al/Ti/Si structures. ECR (electron cyclotron resonance) plasma oxidation and oxynitridation process were carried out on these strucures using O_2/Ar and O_2/N_2/Ar gases, respectively, to get the TiAlO and TiAlON films on Si. Physical thickness values between 6.3 and 6.9 nm were determined by ellipsometry. XPS (X-Ray Photoelectron Spectroscopy) analysis was performed and the formation of TiAlO and TiAlON films was confirmed. These films were used as gate insulators in MOS capacitors fabricated with TiN (20nm)/Al (180 nm) electrodes, and they were used to obtain capacitance–voltage (C–V) measurements. A relative dielectric constant of 3.9 was adopted to extract the equivalent oxide thickness (EOT) of films from C–V curves under strong accumulation condition, resulting in values between 0.5 and 1.4 nm, and effective charge densities of about 10^{11} cm^{-2}. Because of these results, nMOSFETs with TiN/Al gate electrode and TAON gate dielectric were fabricated and characterized by current–voltage (I–V) curves. These results indicate that the obtained TiAlON and TiAlO films are suitable gate insulator for the next generation (MOS) devices.

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EM-ThP7 Exploring Thermal Reduction Efficiency of Reduced Graphene Oxide with Alcohols Studied by First - Principles Calculations and Infrared Spectroscopy, ***R.M. Abolfath***, *C.G. Gong, M. Acik, Y.J. Chabal, K. Cho*, The University of Texas at Dallas

Graphite oxide (GO) is convenient to be used as a precursor for functionalization studies and explore the chemistry in solution. Since GO is solution-processable and hygroscopic, tuning the chemical properties by reduction therefore tailors the electronic and electric properties of thermally/chemically reduced GO. The reduction processes of GO sheets have gained much interest since improvement and systematic investigation of the graphitic structure-electrical property relationship is particularly required for graphene nanoelectronics applications. The excellent electrical conductivity of the reduced GO sheets therefore promises potential electronic applications.

It was reported by Su *et al.* in (ACS Nano, 4, 5285-5292, 2010) that the use of high-temperature alcohol vapor for reducing GO increases the conductivity dramatically which improves the graphitic domains. However, details of understanding reduction mechanisms behind the interactions of alcohol molecules within the reduced defective sites of reduced GO still remains elusive.

One of our recent study in (ACS Nano 4, 5861-5868, 2010) shows that trapped water molecules intercalate in the interlayers of as-synthesized GO and interacts with the carbon dangling bonds of the etch holes upon reduction. In this study, formation of carbonyl groups and production of CO2from the structural decomposition is a key experimental observation. Replacing intercalated water with methanol and ethanol and performing thermal reduction of GO at 60-300°C, *in-situ* infrared spectroscopy measurements in transmission demonstrate that the thermal reduction efficiency of reduced GO changes dramatically within two different alcohol environment. In the presence of methanol in the interlayers of reduced GO, an increase of infrared absorption could be observed which is attributed to a stable carbonyl concentration during annealing. In contrast, compared with methanol, carbonyl formation at ~1750-1850 cm-1 is absent when there is ethanol in the interlayers of reduced GO. To understand differences in these experimental observations, we simulate the reduction mechanisms by both MD and DFT calculations which show a faster diffusion of methanol in the interlayer of GO that facilitate its reaction with etch holes, inducing a competing mechanism. In the case of ethanol intercalation, simulations confirm that the carbonyl formation which tends to enlarge the etch hole upon annealing can be blocked.

EM-ThP8 Characterization of Ion Implantation-Induced Vacancy Defects and Graphitization in Diamond Lattices by Coherent Acoustic Phonon Spectroscopy, ***J.M. Gregory***, *A.D. Steigerwald,* Vanderbilt University*, H. Takahashi,* Japan Advanced Institute of Science and Technology, Japan*, N.H. Tolk*, Vanderbilt University

We describe implantation damage experiments on single-crystal diamond samples and subsequent characterization using optical pump-probe techniques. Samples are irradiated using He^+ ions with energies on the order of 1 MeV, generating lattice defects and buried layers of graphitic carbon under high pressure. Using the time-resolved optical technique known as coherent acoustic phonon spectroscopy, these samples are characterized in a depth-dependent manner. The resulting oscillation patterns reveal clues about the optical and electronic structure of the defects and the graphitic layers.

EM-ThP9 New Reconstruction Mechanism of Dense SiC(111) on Sparse Si(110) Interface, ***E. Abavare,*** University of Tokyo, Japan*, J.-I. Iwata,* University of Tsukuba, Japan*, A. Oshiyama*, University of Tokyo, Japan

SiC grown on Si substrates is a promising candidate for mass production of Graphene, an emerging material in technology. SiC(111) on Si (110) with particular alignments of the two planes offers almost perfect matching of the lattice periodicity, albeit dense SiC and sparse Si. We here report the total-energy electronic-structure calculations based on the Real-Space Density Functional Theory (RSDFT), that elucidate new reconstruction mechanism of the dense 3C-SiC(111) on the sparse Si(110) interface with the relaxed superstructures displaying undulating structures near the interface. We have explored a variety of candidate interface structures and reached two distinctive types called type I and II which shows bistability at the interface. In type I, the silicon-silicon interface energy is calculated as 9.57 eV whereas that of silicon-carbon is 10.41 eV. Similarly, in type II, silicon-silicon interface energy is 9.89 eV and that of silicon-carbon is 10.84 eV. We argue that in both types, the silicon-silicon interface is energetically favorable compared with the silicon-carbon interface.

EM-ThP10 The Influence of the Layer Thickness on the Optoelectronic Properties of InN, *M.K.I. Senevirathna, S. Gamage, R. Atalay,* Georgia State University*, J. Hong,* Georgia Institute of Technology*, **N. Dietz**, A.G.U. Perera*, Georgia State University

Indium nitride (InN) and indium-rich group III-nitride alloys may have great potential for high efficient energy conversion devices such as solar cells, high speed optoelectronic devices, and various types of light emitting device structures. Scientists are exploring several different growth methods and various characterization methods to improve the material quality and to understand the optical, structural, and electronic properties of these epilayers. However, till today, the growth of high quality InN alloys and epilayers is still a challenge, mainly due to low InN dissociation temperature and due to stoichiometry instabilities at optimum growth conditions. InN epilayers exhibit significant different physical properties depending on the growth techniques (PAMBE, MBE, MOCVD, etc.) and the substrate material used. At present, low-pressure CVD based growth methods are limited to InN growth temperatures at or below 600°C, which creates problems related to a suited nitrogen precursor, since the ammonia decomposition at these growth temperatures is insufficient. To stabilize InN at higher growth temperature, we explored the growth of InN by high-pressure chemical vapor deposition (HPCVD) at 10 bar and 15 bar reactor pressures. Under these growth conditions the growth temperature can be increased to around 800 °C, resulting in improved ammonia decomposition and smaller group III/N precursor ratio.

This contribution presents results on the effect of the layer thickness on the physical properties of epitaxial InN layers. All InN layers where grown on GaN/sapphire (0001) templates under identical growth conditions, only the growth time was varied. Fourier transform IR reflectance (FTIR) spectroscopy was used to analyze the film thickness and the optoelectronic layer properties. We will present results on the free carrier concentration and mobility as a function of layer thickness. The reflectance spectra were simulated using a Lorentz-Drude model and a multilayer stack model, which allows determining the phonon frequencies, dielectric function, plasma frequency, and damping parameters. From these, the free carrier concentration and mobility for each layer can be calculated. The crystalline quality of the epilayers has been characterized by XRD 2theta- omega scans and by Raman spectroscopy analysis.

EM-ThP11 The Effect of Reactor Pressure on the Optoelectronic Properties of InN Epilayers Grown by HPCVD, ***M.K.I. Senevirathna***, *S. Gamage, M. Buegler, R. Atalay,* Georgia State University*, J. Hong,* Georgia Institute of Technology*, N. Dietz, A.G.U. Perera*, Georgia State University

The dependency of the optoelectronic and structural properties of InN epilayers on the reactor pressure is presented. The InN epilayers were grown by high-pressure chemical vapor deposition (HPCVD) varying the reactor pressure from atmospheric pressure to 18.5 bar. The optoelectronic properties such as free carrier concentration and mobility have been studied using Fourier transform IR reflection spectroscopy. The film thickness, growth rate, free carrier concentration and carrier mobility of the InN layer are obtained by simulating the IR reflectance spectra, using a multilayer stack layer model and a Lorentz-Drude model. XRD 2theta- omega scans and Raman spectroscopy were used to evaluate the structural properties of the epilayers.

EM-ThP12 Effect of Buffer Layers on Structural and Optical Properties of InN Films by RF-MOMBE, ***W.C. Chen**,* National Applied Research Laboratories, Taiwan, Republic of China*, S.Y. Kuo,* Chang Gung University, Taiwan, Republic of China*, F.-I. Lai,* Yuan-Ze University, Taiwan, Republic of China*, C.-T. Lee, C.N. Hsiao, D.P. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China

Hexagonal InN films were prepared on sapphire by RF-MOMBE using AlN, GaN and ZnO buffer layers. Also, we have investigated the effect of buffer layers on optical, structural and electrical properties of InN films. The crystalline quality of the InN film is sensitive to the underlying buffer layer when the film is grown under the high effect V/III ratio condition. The structural, optical and electrical properties of InN films were investigated by X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), UV/VIS/IR spectrum measurements, and Hall effect, respectively. The XRD pattern indicated all InN films along c-axis growth. Optical absorption edge by spectrophotometer confirms that the band gap of wurtzite InN films were 1 to 1.2 eV. A Hall mobility of more than 170 cm^2/V-s with a carrier concentration of 9.2×10^{19} cm^{-3} at room temperature can be routinely obtained on InN/GaN film. Also, the average later thicknesses range measured about 800 to 1000 nm, and high growth rate about 1.6 mm/hr at InN/GaN, 2 mm/hr at InN/ZnO and 1 mm/hr at InN/AlN, respectively. We suggest that the reduced lattice mismatch between the InN epilayer and top buffer layer is responsible for improvement of sample quality using the buffer-layer technique.

EM-ThP13 The Influence of Ammonia - MO Precursors Pulse Separation on the Gallium Incorporation in Indium-Rich $In_xGa_{1-x}N$ Epilayers, ***S. Gamage**, R. Atalay, M.K.I. Senevirathna,* Georgia State University*, J. Hong,* Georgia Institute of Technology*, J.S. Tweedie, R. Collazo,* North Carolina State University*, N. Dietz*, Georgia State University

Ternary $In_xGa_{1-x}N$ alloys and embedded epilayers are of great interest due to their large band gap tenability, which enables new applications in the fields of advanced optoelectronic devices. Here, the growth of ternary $In_xGa_{1-x}N$ epilayers is explored by high-pressure chemical vapor deposition (HPCVD) and pulsed precursor injection in order to reduce the temperature gap between the binary alloys GaN and InN and to improve the phase stability on the ternary alloys. In the pulsed precursor injection approach, the precursor separation times between the metal organic (MO) sources (TMI and TMG) and ammonia (S_1), and ammonia and MO (S_2) are two critical process parameters. Previous studies on InN growth showed that the precursors separation critically influences the surface chemistry and the resulting structural and physical layer properties.

In this contribution, we present results on indium-rich InGaN epilayers grown by simultaneous MO injection and with different S_2 timings, with the aim to find the optimum S_2 separation for high quality, single-phase InGaN epilayers. We will show that the S_2 separation is critical for the incorporation of gallium into the epilayers. In order to maintain single-phase epilayers, the S_2 separation has to be increased from S_2=400 ms for InN to over 1200 ms for $In_xGa_{1-x}N$ with x=0.2. Raman spectroscopy and X-ray diffraction (XRD) are used to study the structural properties and the Fourier Transform Infra-red (FTIR) and transmission spectroscopy are used to study the electrical and optical properties of the epilayers.

EM-ThP14 Thermal Stability of HPCVD Grown InN Epilayers, *A.R. Acharya, S. Gamage, N. Dietz, **B.D. Thoms***, Georgia State University

The thermal stability of InN layers grown on sapphire by high-pressure chemical vapor deposition (HPCVD) was studied using isothermal desorption measurements and Auger electron spectroscopy (AES). The desorption of hydrogen-, carbon-, and nitrogen-containing species was analyzed using a differentially-pumped mass spectrometer while the sample temperature was ramped from room temperature to a target value, where it was held constant for ten minutes before cooling back to room temperature. Experiments were performed with increasing target temperatures from 500 °C and 700 °C. No significant evaporation of nitrogen and other species was observed until the samples were annealed to 600 °C. However, during isothermal heating to 650 °C or above, the evaporation of molecular nitrogen commenced around 450 °C and an abrupt increase occurred above 600 °C indicating serious degradation of the film. The stability of InN layers was found to be dependent on V/III ratio, being more stable for the film grown in higher V/III ratio growth conditions. After annealing to 700 °C, the AES spectra showed carbon, oxygen, and traces of indium but no nitrogen indicating the complete desorption of nitrogen from the InN film.

EM-ThP15 Substrate Template and V/III-Ratio Effects on the Surface and Structural Properties of HPCVD Grown InN Films, ***A.R. Acharya**, M. Buegler, R. Atalay, S. Gamage,* Georgia State University*, J.S. Tweedie, R. Collazo,* North Carolina State University*, N. Dietz, B.D. Thoms*, Georgia State University

Nucleation and growth processes in chemical vapor deposition determine the crystalline quality and orientation which also affect the surface configuration. The bulk and surface structural properties of InN layers grown by high-pressure chemical vapor deposition (HPCVD) were investigated by Raman spectroscopy, x-ray diffraction (XRD), and high resolution electron energy loss spectroscopy (HREELS). HREEL spectra of InN grown on GaN/sapphire with a group V/III precursor ratio of 630 showed surface NH species and nitrogen-termination. For this layer Raman spectroscopy and x-ray diffraction (XRD) showed c-axis film orientation. In contrast, HREEL spectra of InN grown directly on sapphire with a higher group V/III precursor ratio of 3000 revealed that the dominant surface species is NH_2. For this sample, the Raman and XRD analysis indicate the existence of micro-crystallites oriented in the (01-11) direction. Two factors suggested to account for the appearance of these tilted planes are slower surface diffusion under more nitrogen-rich conditions and strain due to the larger lattice mismatch when growing on sapphire substrates.

EM-ThP16 P-Si / N-type GaN Heterojunction, ***J. Kim**, J. Ahn*, Korea University, Republic of Korea

P-N heterojunction from P-Si thin film / N-GaN microstructures have been demonstrated. To control the position of GaN microstructures, a mechanical method or electric-field assisted method was employed. Firstly, thermally-grown SiO2(300nm) on top of p-Si substrate was wet-etched to define the mesa structures. Then, the metal was deposited on both front (on top of the SiO2) and backside. Finally, GaN microstructures were moved to form p-n heterojunction. When P-Si thin film / N-GaN microstructures were forward-biased, the electroluminescence from p-n heterojunction was observed. The details of the fabrication and the characterizations of P-Si thin film / N-GaN microstructures will be presented.

EM-ThP17 CIGS Thin Film Prepared by One-Step Sputtering Process by Using a Powder Target, ***S. Oh**, G. Cho, N. Kim*, Chosun University, Republic of Korea

CIGS thin film with cells reported the highest efficiency up to 20% in the thin film solar cells, which is generally considered as the most promising thin film solar cell. It has been fabricated by using the three stage process in evaporation process with four sources of Cu, In, Ga, and Se pure elements. This preparation method requires very strict controls during the deposition process of CIGS thin film. Recently, there are two widely used methods for CIGS thin film fabrication: selenization with H_2Se or Se after sputtering and thermal co-evaporation. Although the sputtering process was the most suitable method for the deposition of CIGS thin film over the large area with a good uniformity, the two-step selenization shows the critical drawbacks including the additional manufacturing steps, higher materials costs, and the less efficiency. The co-evaporation for CIGS thin film is hard to manage the sources in sequence and to deposit over the large area. For this reason, the novel method for CIGS preparation was demonstrated by using the sputtering process with the powder target. This method has the advantages of the production of target, change of stoichiometry, and easy doping of impurities. The composition of the powder-sputtered CIGS thin film with 1 µm-thickness were analyzed and compared to that of the starting powder target with a composition of Cu, In, Ga, and Se at 25, 15, 10, and 50 at% by electron probe microanalysis (EPMA). The crystal structure, surface morphology, optical properties, and electrical characteristics of CIGS thin film were analyzed by using X-ray diffraction (XRD), atomic force microscope (AFM), UV-Visible spectrophotometer, and a Hall effect measurement system.

EM-ThP18 Effects of Ta Addition on the Characteristics of ITO Thin Film Transistors by Sputtering, ***S.M. Chung**, J.H. Shin, C.H. Hong, W.S. Cheong*, ETRI, Republic of Korea

Thin-film transistors (TFTs) using amorphous oxide semiconductors (AOSs) as an active layer have shown remarkable performances including low-temperature processing, high transparency, environmental stability, and high mobility for alternative display backplanes of active-matrix organic light emitting displays (AM-OLEDs), thin-film-transistor liquid crystal displays (TFT-LCDs) and opto-electronic components. Oxide material combinations such as InZnO (IZO), InGaZnO (IGZO), ZnSnO (ZTO), and GaZnSnO (GZTO) have been vastly studied for enhancing the mobility and stability. Though the mobility of the amorphous oxide TFTs has been much improved for several years, the instability under prolonged on-current status is still critical issue to substitute for Si-based technology. Recently, other elements of high oxygen affinity such as Al, Zr, Si, and Hf were added to oxide based TFTs for improving the stability characteristics, which, however, results in a mobility reduction problem. In order to overcome the

problem, we used Ta dopant. This work reports on the characteristics of bottom-gate Ta-doped InSnO (ITO) TFTs. An amorphous ITO:Ta channel layer was deposited at room temperature by sputtering. The devices were annealed at 50 ~ 200℃ in oxygen condition for 1 hours. Optical transmittance data in the visible range reveal average transmittance higher than 80% including the glass substrate. The field-effect mobility of 15.9 cm^2/V-s, the ON/OFF ratio of >10^8, and the sub-threshold slope of 0.81 V/decade are achieved in the n-channel ITO:Ta TFTs. Effects of ITO:Ta preparation conditions on the resulting TFT performances were discussed. Stability experiments and further device optimizations through processes are under investigation. The detailed results will be revealed in this presentation.

EM-ThP19 Infrared Absorption Enhancement in Silicon via Silicidation and Nanoparticle Incorporation, ***C.M. Gonzalez**, R. Sachan, G. Duscher, R. Kalyanaraman, P.D. Rack*, University of Tennessee, Knoxville

Conventional silicon photovoltaics lack the ability to absorb the full electromagnetic spectrum arriving from the sun. Nickel silicides are small band-gap semiconductors that effectively engage the near-infrared region, whereas bare silicon does not. Ultra-thin (<100nm) silicon structures incorporated with nickel silicides have been synthesized and characterized and have shown enhanced absorption from 750-3000nm wavelengths. Four different structures were constructed via a combination of sputtering, co-sputtering and laser irradiation and their optical and electrical characteristics were compared. In one case, the nickel is deposited and reacted between the p and the n+ silicon regions; in another, nickel is co-sputtered along with p-Si and co-sputtered with n+ silicon; and finally nickel is co-sputtered with silicon followed by laser irradiation to form nickel silicide nanoparticles via pulsed laser induced dewetting. This last structure contains non-patterned nanoparticles (<50nm) in close proximity to a pn junction after capping the former with the p and n+ silicon. In this presentation we will correlate the material composition and micro and nanostructure by STEM and EELS to the observed optical and photovoltaic responses and demonstrate effective media approximations for the observed optical properties.

EM-ThP20 Fabrication of Shape-Controlled Metal Nanodot Array by Electrostatistically-Driven Self-Assembly as well as their Charge Injection Properties, ***R. Sumi**, Nagoya University, Japan, T. Hosoi, H. Watanabe,* Osaka University, Japan, *X. Hu, O. Takai, N. Saito, N. Zettsu*, Nagoya University, Japan

Nanometer-sized inorganic particles play an important role in modern nanotechnology owing to their superior characteristics that can lead to fascinating function that are difficult to be realized using conventional used bulk materials. Recently the development of shape-controlled synthesis techniques make possible to obtain various well-defined shapes of nanoparticles with high yield. To determine their surface-to-volume ratio and crystal structure are expected to lead to improvement in performance in given application.

In this paper, we demonstrated fabrication of various metal nanodots MOS capacitors for floating nanodot gate memory using a evaporation-based colloidal self-assembly in order to attain a tight control over the size, shape, and density of metal nanodots, as well as the study of their effects on the charge injection characteristics of the nanodot arrays.

We synthesized Au nanoparticles with 2nm diameter by solution plasma processing in aqueous solution. The surface was modified with organic surfactants which tuned their zeta-potential to be approximately -40mV. We have recently proposed a versatile method for the fabrication of self-assembled metallic nanodot arrays onto a SiO2/Si substrate with dimension of 50 x 100mm2 by using a newly developed electrostatistically-driven self-assembly. The substrate surface was modified with amino-silane agents prior to use assembly. In order to make MOS capacitor containing Au nanodot array as a charge trapping layer, the Au nanodot array was embedded in a gate oxide.

By precise control of the velocity of the leading edge of a liquid slug, the volume ratio of the particles, and the deposition rate, we were able to reproducibly form an array consisting of a single layer of Au nanodot array with density of 1012particles/cm2. We further demonstrated the charge injection characteristics of the Au nanodot array, embedded in the ultra-thin SiO2 layer consisting of both thermally grown tunnel oxide and RF-driven sputtered control oxide layer. Counterclockwise hysteresis was observed reproducibly, whereas there was no hysteresis in the C-V curve of the MOS capacitor without Au nanodots. This hysteresis indicates the charging and discharging of the embedded Au nanodots. This electron confinement caused the flat-band voltage shift observed as the capacitance hysteresis.

EM-ThP21 Small-Molecule Scaffolds for Directed Self-Assembly, ***P. Mancheno-Posso**, A.J. Muscat*, University of Arizona

Self-assembled monolayers (SAMs) are often used as scaffolds for the deposition of a subsequent layer. This process allows the surface properties to be tailored to a specific application and facilitates the construction of functional nanostructures. For instance, copper electrodes and graphene have been deposited on carboxyl-terminated and on 3-aminopropyltriethoxysilane (APTES) monolayers, to create metallic electrodes for electronic devices and a lubricating layer for nanoelectromechanical systems, respectively. Small silane molecules in particular could be used to direct the self-assembly of another layer and keep it in close proximity to a silicon surface. Vinyltrichlorosilane (VTCS, CH_2=CH-$SiCl_3$) is a candidate and contains a carbon-carbon double bond. A vinyl C=C bond is a versatile functional group because it can be reacted in situ to generate a variety of terminations, including –COOH, –SH, and –NH_2, and could also direct the assembly of new molecules on the surface. While VTCS SAMs have been studied previously, a reproducible and self-limiting process to form a single monolayer from solution has not yet been achieved. In this work we adsorbed VTCS from solution on a Si(100) substrate and characterized the layer with ellipsometry, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). Silicon wafers were cleaned and hydroxylated in a piranha solution. After drying, the samples were dipped for different times into a 1:1000 solution of VTCS in toluene, hexane, chloroform and acetone. The thickness of the monolayer was monitored ex situ using ellipsometry. Toluene and hexane yielded multilayers with a thickness greater than 10 Å, whereas chloroform and acetone produced more consistent monolayers with a thickness of about 6 Å. A bromination was performed to demonstrate the presence of the unsaturated bond. We are in the process of making XPS and AFM measurements to determine whether VTCS is covalently attached to the Si substrate and to assess whether the vinyl group is suitable to graft molecules to the substrate.

EM-ThP22 Deposition of Organic and Inorganic Hybrid Laminates using Ozone Based ALD (Atomic Layer Deposition), ***S. Lee**, NCD Technology, J. Huang, M. Lee,* University of Texas at Dallas, *P.-R. Cha,* University of Texas at Dallas and Kookmin Univ., Korea, *J. Kim*, University of Texas at Dallas

Recently, organic materials have been attracting attention due to the large area, low cost, and flexibility. On the other hand, inorganic conducting materials have several benefits such as high conductivity, functional properties, and rigid characteristics, etc. A novel technique for building an organic and inorganic hybrid stack has been introduced by M. M. Sung et al. using a modified ALD method.[1] It has advantages to minimize the defects during growth of organic and inorganic films because hybrid films are deposited by an in-situ process through the sequential self-limiting surface reaction like atomic layer deposition (ALD), while maintaining their flexibility and functionality.

In this study, we investigate the growth characteristics of organic/inorganic conducting material, ZnO, and 7-octenytrichlorosilane (7-OTS) thin film using an ozone based ALD. 7-OTS is grown by exchange reaction between functional group and water and then the terminal vinyl group of 7-OTS is converted into a carboxylic group through ozone activation.[1] The deposition rate and the contact angle of the organic films are about 7Å/cycle and 60°, respectively. In case of the ZnO, it is deposited using diethylzinc (DEZ) source and H_2O oxidant under the temperature of 120°C. The deposition rate is about 2 Å/cycle. The organic/inorganic hybrid laminate films will be analyzed by TEM, AFM, Ellipsometer and FTIR. The electrical characteristics of laminate structure will be discussed.

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EM-ThP23 Simple Methods to High Quality Self-Assembled Monolayers of Alkylsilanes on Oxides, ***B.D. Gates**, Y. Gong, A. Liu, H.W. Ng, M. Wang*, Simon Fraser University, Canada

The interfacial properties of a material can be easily modified by modifying its surfaces with self-assembled monolayers. These single-molecule thick coatings can be used to prevent non-specific adsorption of biomolecules, protect the underlying material from chemical attack, serve as a masking layer to prevent or direct the deposition of a coating material, and reduce friction between two materials. Interest in the use of self-assembled monolayers continues to grow. The applications being pursued for these molecular coatings are increasingly interested in the robustness and uniformity of these films. An important aspect of their resilience is the density and size of defects within the monolayers, which can have a large role in their overall performance. One type of monolayer for which it is particularly challenging to achieve high quality coatings are those films

based on the assembly of alkylsilane molecules. Often these coatings are pursued for the modification of oxidized surfaces, but form either a sub-monolayer or a multilayered film. A primary goal of the work that will be presented is to further optimize the conditions in which monochloro alkylsilane-based molecules are assembled into monolayers. Considerations for the development of these refined methods include the ease of scaling the technique to cover larger areas and the ability to avoid stringent requirements for environmental control during growth of the monolayer. Additional work is being pursued to identify and repair defects within the silane-based films. One approach that will be discussed uses solvent extraction techniques to remove adsorbed molecules, followed by further assembly of alkylsilane molecules onto the unprotected regions of these surfaces. The 'repaired' surfaces exhibit improved resistance to chemical attack. A key aspect of this work has been the development of new analytical methods for determining the density and size of the defects. These methods are used to also monitor the success of repairing the defects. The talk will cover these and other aspects of our progress towards developing simple methods that will produce high quality monolayers of alkylsilane-based molecules.

EM-ThP24 Deposition and Characterization of Hydrophobic Coatings on Electronic Devices*, **V. Gupta**, S.C. Kunzler, M.R. Linford*, Brigham Young University

More cell phones are damaged by water than by any other means, and this damage often requires the devices to be discarded. The number of damaged phones is also increasing because these phones are now taken almost everywhere. Chemical vapor deposition may provide a solution to this problem, which is large (100.9 million Smartphones were shipped in Q4 2010). For example, the phones may be coated with a hydrophobic monolayer or multilayer of fluorosilanes. Bonding of the fluorosilane may be improved using of a primary adhesion layer, which may be a different silane monolayer, e.g., an isocyanatosilane, and/or by introduction of hydroxyl groups via plasma treatment. The latter process is typically rapid and economical and can take place both on oxide and polymeric materials. The presence of OH groups can be assayed by XPS, ToF-SIMS and ATR-FTIR. The density of surface hydroxyl groups can be varied by changing the proportions of etch gases, the time and intensity of the plasma treatment, and the system base pressure. The hydrophobicity of the surface can be characterized by contact angle goniometry and XPS and ToF-SIMS analysis of fluorine. Resistance to abrasion can be tested with a Martindale abrasion tester. This work can be further extended to touch screen panels in equipment used under water.

EM-ThP25 Impact of Substrate Type on the Formation of Si Nanocrystals in the Annealed SiO_x and SiO_x:Er,F Films*, A.S. Nikolenko, M.V. Sopinskyy, V.V. Strelchuk, L.I. Veligura,* ***N.A. Vlasenko***, V. Lashkaryov Institute of Semiconductor Physics, Ukraine

Erbium doped nc-Si/SiO_2 nanosystems are considered as possible candidates for the manufacturing of light emitting sources compatible with silicon technology [1]. Fluorine, like other halogens, has a tendency to enhance recrystallization processes. Therefore, one could hope that introduction of F will intensify the transformation of amorphous silicon nanoinclusions formed on initial stage of SiO_x thermal decomposition into Si nanocrystallines, and reduce the low-temperature threshold of this process. Lowering of the process temperature is the essential advantage of every technology. In case of SiO_x:ErF_3 films this is principally important because at $T_{ann} > 900°C$ the segregation of erbium ions into metallic clusters takes place. Consequently, the final stage of forming the erbium-doped light-emitting system should not exceed 1000 °C.

In this work the silicon nanoparticle formation due to the structural-phase transformations in the SiO_x and SiO_x:Er,F films evaporated onto c-Si and sapphire substrates is studied. These transformations are induced by moderate temperatures annealing (650–1000°C). For this study the methods of Micro-Raman scattering and multi-angle ellipsometry are used. It was established that more intensive formation of a-Si nanoparticles takes place in the doped films as compared to undoped SiO_x films on both c-Si and sapphire substrates. Besides, it was found that the crystallization of a-Si nanoparticles is much more intensive and occurs at lower temperatures (≥ 750°C) in the annealed SiO_x:Er,F films on sapphire substrate as compared to the annealed SiO_x:Er,F films on c-Si substrate.

Analysis of available literature data which deal with behaviour of Er and F in silicon, Si−O, and Al−O systems allows explaining the obtained results by the influence of F. In our opinion, the mechanism of F influence on the crystallization of a-Si nanoparticles is similar to the mechanism of h ydrogen-induced crystallization of amorphous Si thin films [1]. Fluorine diffuses into Si−O and c-Si extremely fast. Therefore, during the annealing of SiO_x:Er,F films deposited on c-Si the significant part of mobile fluorine easily diffuses into c-Si substrate and its concentration in the film drops considerably. On the contrary, F very slowly diffuses into Al_2O_3 – even the thin native aluminum oxide layer provides very good protection against fluorine diffusion. Accordingly, fluorine concentration in the film on sapphire substrate stays significant, and its crystallization action manifests itself stronger.

Conclusions.

1) It is shown that the formation of erbium doped nc-Si/SiO_2 nanosystems at the temperatures ≥ 750°C is possible by annealing of SiO_x:Er,F films on sapphire substrate.

2) This work, together with the work [2], demonstrates the wide variety of mechanisms by which a substrate can impact upon the formation of nc-Si–SiO_x nanosystems.

[1] S. Sriraman, M. S. Valipa, E. S. Aydil, and D . Maroudas . J. Appl. Phys. 100,

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Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-FrM

Spectroscopic Ellipsometry: Future Directions and New Techniques
Moderator: H. Wormeester, MESA, The Netherlands

8:20am **EL+AS+EM+MS+PS+TF-FrM1 Current Trends and Future Outlook for Spectroscopic Ellipsometry**, ***J.N. Hilfiker****, B. Johs, C.M. Herzinger, T.E. Tiwald*, J.A. Woollam Co., Inc. **INVITED**

This talk reviews the significant developments in spectroscopic ellipsometry (SE) in areas including extending spectral range, improving accuracy, and enhancing speed. Current SE applications owe much to hardware and software developments of the past. Thus, today's research efforts may reach full potential for applications years or even decades from now. With this in mind, we point to the current state-of-the-art and what this may mean for future SE applications.

Three important areas will be explored. First, there has been a continual trend to expand SE wavelength range. This has included extensions to both shorter and longer wavelengths. For the latter, there is current development into the THz. More immediate benefit may come from smaller SE extensions from the ultraviolet to the near infrared. For example, further near-infrared extensions help to characterize modern transparent conductive oxides (TCOs), used in both inorganic and organic photovoltaic stacks.

Second, we look at the search for improved SE accuracy. Substantial improvements have come with the development of new ellipsometer technologies, progressing from rotating analyzer/polarizer to rotating compensator and now dual-rotating compensator ellipsometers. In addition to improved accuracy, this technology provides advanced measurements, including the complete Mueller-matrix. This will open SE characterization to new applications of anisotropic, nanostructured, and even patterned thin films. Accuracy enhancements must be compatible with the expanding SE spectral range. Infrared SE has overcome many non-ideal optical components to provide measurements competitive to standard FTIR measurements.

Third, we look at the quest for improved measurement speed. This development is constrained by the previous requirements. The benefits of a wide spectral range generally outweigh speed requirements; otherwise laser-based ellipsometry would still have a strong foot-hold. Thus, compromises are made depending on application. Current instrumentation typically utilizes detector arrays for multi-channel SE measurements.

To conclude, we will look at the SE outlook and how it may take advantage of wavelength range, accuracy, and speed. In-line and in-situ SE measurements show special promise. Significant improvements in instrumentation, computing speed, and software are now making these applications more feasible. In addition, there are novel ideas to provide sample access and overcome non-ideal measurement conditions for in-line and in-situ SE. Significant progress in many different areas promises to extend ellipsometry into new areas – many of which are being studied by researchers today.

9:00am **EL+AS+EM+MS+PS+TF-FrM3 THz Optical Hall-effect and MIR-VUV Ellipsometry Characterization of 2DEG Properties in a HfO_2 Passivated AlGaN/GaN HEMT Structure**, ***S. Schöche****,* U. of Nebraska - Lincoln*, J. Shi,* Cornell U.*, A. Boosalis, P. Kühne,* U. of Nebraska - Lincoln*, C.M. Herzinger, J.A. Woollam,* J.A. Woollam Co., Inc.*, W.J. Schaff, L.F. Eastman,* Cornell U.*, V. Darakchieva,* Linkoping U., Sweden*, M. Schubert, T. Hofmann*, U. of Nebraska - Lincoln

Nitride based high electron mobility transistors (HEMT) utilize the formation of a two-dimensional electron gas (2DEG) at the interface between GaN and AlGaN due to a difference in spontaneous polarization. It is known that surface traps significantly influence the electrical properties of this 2DEG. Accurate knowledge about the influence of surface passivation on the channel properties is crucial. The device performance is governed by the mobility, the sheet charge density, and the effective mass of electrons in the 2DEG. These parameters are typically determined by electrical Hall effect (EHE), Shubnikov-de Haas (SdH), or cyclotron resonance (CR) measurements. Commonly these experiments require very low temperatures and high magnetic fields. Complex contact configurations are required for SdH and EHE and the ability to locate the 2DEG and possible parallel current paths is limited.

We present non-contact, optical measurements of free-charge carrier mobility, sheet density, and effective mass parameters of the 2DEG for a HfO_2-passivated AlGaN/GaN HEMT structure at room temperature. Spectroscopic ellipsometry in the spectral range from THz and Mid-IR to VUV and THz optical Hall-effect (generalized ellipsometry in magnetic field) (OHE) are employed.

The MIR measurements are performed for analysis of the heterostructure constituents' layer thickness, phonon modes, and volume free charge carriers. The phonon mode parameters were found to be in excellent agreement with literature values and the existence of significant volume charge carrier concentrations could be excluded. NIR to VUV ellipsometry is used to determine the thickness of the thin top layers. From a line-shape analysis in the VUV spectral range the optical constants of the HfO_2 passivation layer could be extracted. An amorphous structure of the HfO2 passivation layer could be confirmed by comparison with existing studies in literature.

OHE in the THz spectral range is performed for characterization of the 2DEG channel parameters. A classical Drude model for free charge carrier contribution to the dielectric function was applied to determine the sheet density, the carrier mobility, and the effective mass of the 2DEG electrons. The electron effective mass of $(0.22\pm0.04)\ m_0$ extracted here using OHE corroborates the values found in previous SdH and CR studies. The values for the high-frequency sheet density and carrier mobility obtained by the optical investigations in the THz spectral range are in excellent agreement with results from dc EHE measurements indicative within linear Boltzmann transport theory for frequency-independent carrier scattering mechanisms of the 2D carrier distribution.

9:20am **EL+AS+EM+MS+PS+TF-FrM4 Vector-Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films**, ***D. Schmidt****, C. Briley, E. Schubert, M. Schubert*, University of Nebraska - Lincoln

Sculptured thin films are self-organized and self-assembled three-dimensional nanostructures with tunable geometries. These artificial nanostructured thin films exhibit highly anisotropic physical properties, which mainly depend on their specific geometry.

Slanted, highly-spatially coherent, columnar nanostructure samples were prepared by glancing angle electron-beam deposition. Glancing angle deposition is a bottom-up fabrication technique that employs a physical vapor deposition process at oblique angles where the trajectory of the incoming particle flux is not parallel to the substrate normal. The technique allows to engineer the columnar film structure and is today amongst the most promising self-organized fabrication processes in micro- and nanotechnology.

We present and discuss the novel approach of vector-magneto-optical generalized ellipsometry on ferromagnetic permalloy nanostructured thin films carried out at room temperature. Investigations have shown that the metal alloy thin films are highly transparent, reveal strong form-induced birefringence, and exhibit intriguing magneto-optical anisotropy. Spatial magnetization orientation hysteresis and magnetization magnitude hysteresis properties are studied using a three-dimensional Helmholtz coil arrangement. This particular octupole setup allows for arbitrary magnetic field directions at the sample position with field strengths up to 200 mT while optical access is granted for reflection and transmission-type ellipsometry measurements. Analysis of data obtained within this unique vector-magneto-optic setup reveals magnetization anisotropy of the permalloy slanted nanocolumns and gives insight into switching behavior of confined magnetic domains.

9:40am **EL+AS+EM+MS+PS+TF-FrM5 THz Dielectric Anisotropy of Metal Slanted Columnar Thin Films**, ***T. Hofmann****, D. Schmidt, A. Boosalis, P. Kühne, R. Skomski,* University of Nebraska-Lincoln*, C.M. Herzinger, J.A. Woollam,* J.A. Woollam Co., Inc.*, M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Sculptured thin films (STFs) present an interesting class of self-organized, artificially made materials with three-dimensional, highly spatially coherent arrangements of nanostructures. Contemporary interest in materials for terahertz (THz) electronic, optoelectronic, and optical applications is redrawing attention to STFs that may enable designed optical properties for the THz frequency region.

We report on the anisotropic optical dielectric functions of a metal (cobalt) slanted columnar thin film deposited by electron-beam glancing angle deposition for the THz frequency domain using generalized spectroscopic ellipsometry. A simple anisotropic Bruggeman effective medium dielectric function homogenization approach is successfully employed to describe the observed optical response. This approach describes isolated, electrically conductive columns which render the thin film biaxial (orthorhombic). The anisotropy induced by the columnar film structure is very large. The anisotropic Bruggeman effective medium approach predicts upon slight modifications of Drude, fraction and/or depolarization parameters that

targeted optical properties of STF in the THz range can be achieved by variation of slanting angle, lateral column density, and material.

10:00am **EL+AS+EM+MS+PS+TF-FrM6 A Compact High-speed Spectroscopic Ellipsometer**, ***G. Chin***, ULVAC Inc., Japan

Recently, we developed a compact, high-speed spectroscopic ellipsometer. It analyzes the spectrums obtained from the polarization interference occurring between two multiple-order retarders which snapshot the wavelength distribution of the sample's spectroscopic polarization parameters. This innovative spectroscopic ellipsometer can measure the thickness and optical constants of thin films at a dramatically fast speed. Its acquisition time is as short as 10 ms. It does not require the conventional complex mechanical or active components for polarization-control, such as a rotating compensator and an electro-optical modulator. It can open great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. For example, it was integrated into the deposition tool and successfully measured thin films in the vacuum chamber.

This paper describes the principle, system configuration and our innovative efforts on developing the compact high-speed spectroscopic ellipsometer. Some typical application data will be also introduced, such as in line and in situ measurements for photovoltaic, flat panel display and semiconductor industries.

10:20am **EL+AS+EM+MS+PS+TF-FrM7 Ellipsometry Porosimetry (EP): In Situ Spectroscopic Ellipsometry Measurements Coupled with Pressure Controlled Adsorption of Organic Vapors to Study Properties of Nano-Porous Thin Films**, *J.P. Piel, L. Kitzinger,* ***A. Bondaz****, C. Defranoux*, SEMILAB-SOPRALAB, France

Ellipsometric porosimetry (EP) is a non contact, non destructive technique that is cited as a reference technique for porous thin film analysis [1, 2]. As it is based on a spectroscopic ellipsometric measurement, the technique allows the precise determination of the refractive indices and thickness of the porous films. The advantage of these EP tools is that the combination of this well established spectroscopic ellipsometric (SE) technique with a suitably adapted adsorption chamber permits access to all the information obtained by classic adsorption experiments (e.g. BET) on thin films with an excellent sensitivity. Information such as open and closed porosity, pore size distribution etc... can be thus obtained.

In addition the EP allows access to a multitude of information that the classic equipment does not. For example, Spectroscopic Ellipsometry allows to follow the variation of the sample thickness during the adsorption experiment, leading to the determination of the Young's Modulus for the thin films. This will be presented. The technique is highly sensitive to the detection of interfaces; it is thus possible to detect a porosity gradient or to study a multilayer structure and thereafter simultaneously plot the two corresponding adsorption isotherms [3]. In the same manner, the instrument permits the use of a range of different gases adsorptive in order to tailor the probe molecule to the morphology and to the chemistry of the porous layer at ambient temperature [4]. We thus obtain information on the chemistry of the pores within the layer, before, during and after the adsorption experiment. Recent developments include the implementation of the FTIR interferometer SE extension to the EP system. It allows a precise characterization of the chemistry of the pores within the layer. We thus obtain information on the chemical bonds present in the layers before, during and after the adsorption experiment. Preliminary results will be presented.

Specifically, this fundamental technique permits the thorough characterization of porous thin film samples. We will demonstrate some of the different features of the EP technique with regards to the morphological and chemical properties of the porous thin films. Additionally, we will illustrate the technique for various thin film applications such as solgel thin films, nanofilms for catalysis, photovoltaic cells, fuel cells, optical sensors, and bio-compatible materials to name but a few.

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Electronic Materials and Processing Division
Room: 210 - Session EM+SS-FrM

Surfaces and Materials for Next Generation Electronics
Moderator: E.X. Zhang, Vanderbilt University, L. Porter, Carnegie Mellon University

8:20am **EM+SS-FrM1 Growth of 3C-SiC Epitaxial Layers on 4H-SiC Step-Free Mesas**, ***R.L. Myers-Ward****, E.A. Imhoff, J.D. Caldwell, L.O. Nyakiti, V.D. Wheeler, K.D. Hobart, C.R. Eddy, Jr., D.K. Gaskill*, Naval Research Laboratory (NRL)

To avoid defects such as polytype inclusions or dislocations, the epitaxial growth of 3C-SiC requires a lattice-matched, perfect substrate. One solution to this problem is to use step-free mesas of 4H-SiC as 3C-SiC lattice templates [1]. In this work, we describe the formation of large area step-free mesas and the subsequent nucleation and growth of 3C-SiC layers. A powerful array of tools were utilized to characterize the properties of these layers including Nomarski microscopy, secondary electron microscopy (SEM), atomic force microscopy and X-Ray diffractometry. Micro-photoluminescence (μ-PL) was employed to investigate the presence of electronic defects and identification of polytype, enabling us to obtain information about the structural and electronic properties on a micron-sized length scale.

On-axis 4H-SiC substrates were initially patterned and reactive ion etched to produce hexagonal and square shaped mesas with varying widths ranging from 40 to 400 μm (400% greater area than previous reports), and heights from 2 to 5 μm. Homoepitaxial layers were grown on the mesas in an Aixtron VP508 horizontal hot-wall chemical vapor deposition reactor using the standard chemistry of silane and propane in order to grow out the steps on the mesas. The homoepitaxial layers were terminated at the mesa step edge and further growth is prohibited. The films were grown at 2μm/hr and the pressure and temperature were 100 mbar and 1580°C, respectively. The yields of 200 μm width 4H-SiC step-free mesas was ~95%. Heteroepitaxial 3C-SiC was grown 2 μm thick on the homoepitaxy (4H-SiC) by means of reducing the growth temperature to 1450°C, while maintaining 100mbar.

Under Nomarski evaluation, ~ 18% of the 200 μm wide 3C-SiC mesas appeared to be step-free. Micro-PL maps were used to confirm the presence of 3C-SiC, where uniform 3C-SiC was detected across the entire mesas. X-ray rocking curves also indicated 3C-SiC, with the FWHM of the SiC (111) being ~21", indicating good quality material.

Yield maps for the 200 and 400 μm mesas will be presented. In addition, real color PL imaging will be used to determine the types of defects within the mesas which displayed lower PL intensity regions of 3C-SiC. Lastly, initial results of Schottky rectifiers performance made on the layers will given.

References

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8:40am **EM+SS-FrM2 Growth of Epitaxial Rare Earth Nanostructures in III-V Semiconductors**, ***B.D. Schultz****, J.K. Kawasaki, C.J. Palmstrøm*, University of California, Santa Barbara

Highly ordered embedded nanostructures of rare-earth monopnictides can be formed within III-V semiconductor heterostructures providing a new degree of control over the structural and transport properties of the heterostructures. Materials such as ErAs and ErSb are thermodynamically stable with GaAs and GaSb respectively, and in both cases a common group-V sublattice is maintained throughout the heterostructures. In both the arsenides and antimonides, co-deposition at concentrations above a few atomic percent results in the formation of nanoparticles and nanorods. The shape of the nanostructures is strongly dependent of the growth surface including reconstructions, stoichiometry, temperature, and crystallographic orientation. Codeposition of Er with GaAs can produce nanoparticles or ordered nanorods oriented along either the [111] or [211] directions depending on aforementioned conditions[1]. While codeposition of Er with GaSb produces either particles or nanorods oriented primarily along the [100] direction. STM of the GaAs(311)A and B surfaces during the initial stages of nucleation show that following the deposition of a fractional monolayer of ErAs, embedded growth of ErAs particles are observed on the B surface, while the A surface shows primarily surface cluster formation. MBE growth of GaAs on (311)A and B orientations produces relatively flat surfaces with uniquely different (8×1) reconstructions. Codeposition of Er with GaAs results in significant roughening of the surface during growth due to anisotropic diffusion of Ga and Er along the <233> and <011> directions and the general tendency of GaAs not to wet ErAs(100) surfaces. The [211] orientation of the ErAs nanorods on the surface is found to result from preferential growth along the (1 -1 -1) plane on Ga-polar A surfaces. While the angle between the (1 -1 -1) and surface normal remains less than

or equal to 90º, the [211] orientated growth is supported. The {111} surface of the rocksalt ErAs is typically a high-energy surface; however, the Ga-rich (1 -1 -1) plane provides a flux mediated epitaxial growth surface for the ErAs analogous to a vapor-liquid-solid type of growth. *In-situ* RHEED, LEED and STM surface studies will be presented along with a detailed growth model to explain differences in the growth process and in nanorod formation for different substrates and substrate orientations.

Supported by AFOSR FA9550-10-1-0119 and ARO W911NF-07-1-0547.

[1] T.E. Buehl, C.J. Palmstrøm, and A.C. Gossard, J. Vac. Sci. Technol. B **29**, 03C108-1, 2011.

9:00am **EM+SS-FrM3 Bulk Topological Insulators and Superconductors: Discovery and the Frontier**, ***M.Z. Hasan***, Princeton University **INVITED**

While most known phases of matter are characterized by broken symmetries, the discovery of quantum Hall effects (1980s) revealed that there exists an organizational principle based on topology rather than broken symmetry. In the past few years, theory and experiments have suggested that new types of topological states of matter exist in certain insulators without any applied magnetic field. These topological insulators are characterized by a full band gap in their bulk and gap-less conducting edge or surface states protected by time-reversal symmetry. Unlike the quantum Hall systems, the topological insulators can be doped into superconductors and magnets revealing the interplay between topological order and broken symmetry order. In this talk, I will briefly review the basic theory and highlight the experimental developments in topological insulators. I will then conclude by drawing connections b etween the emergent novel physics and their potential applications.

10:20am **EM+SS-FrM7 Inter-band GaN/InGaN/GaN Tunnel Diodes**, ***S. Krishnamoorthy***, *D.N. Nath, S. Bajaj, S. Rajan*, Ohio State University

The III-Nitride material system has demonstrated its potential for a broad range of optoelectronic and electronic applications. However there are no reports of efficient III-Nitride tunnel junctions due to the large band gaps in this material system. In this work, we show that with unique properties such as the polarization, tunneling can be enhanced using band bending over smaller distances in nitride heterostructures, leading to record reverse and forward tunneling current density for the III-nitride material system.

We have designed and demonstrated GaN/InGaN/GaN tunnel junction with a record high current density of 118 A/cm^2 at a reverse bias of 1 V by utilizing a 6.4 nm thin $In_{0.33}Ga_{0.67}N$ barrier material. N-polar p-GaN/$In_{0.33}Ga_{0.67}N$/n-GaN heterostructure designed for tunneling close to zero bias was grown by plasma assisted molecular beam epitaxy by choosing the critical thickness of InGaN barrier appropriately. The tunnel junction sample shows five orders of magnitude higher current at a reverse bias of 1 V as compared to a standard p+/n+ GaN sample indicating efficient tunneling across the InGaN barrier. The tunneling turn-on close to zero bias, and maximum current density of 9.1 kA/cm^2 achieved in this work demonstrates the potential of polarization-engineered tunnel junctions.

Two distinct regimes of transport are identified based on the temperature dependent I-V measurements. At lower reverse bias, defect assisted tunneling with strong temperature dependence is found to dominate. In this regime, a plot of ln (J/E) vs $E^{1/2}$ shows a linear behavior suggesting a Frenkel- Poole emission mechanism due to the high field in the InGaN quantum well. A direct band to band tunneling regime resulting in weak temperature dependence that arises from band gap variation with temperature is observed from a reverse bias of 1 V. A decrease in current density is observed with increase in temperature in the range of 77- 150 K and this can be attributed to the presence of band tail states which has been observed previously in In face InGaN.

We discuss the design of these quantum well tunnel junctions. Athough higher indium compositions yield higher band to band tunneling probability, calculations using a simplified Kane model reveal that the wider depletion region in n GaN due to higher band offset considerably reduces the net tunneling probability. Calculations also reveal the need for very high doping in the n GaN layer so as to minimize the depletion region thickness in order to achieve very high current densities in such polarization charge assisted tunnel junctions. These calculations can guide future tunnel junctions with better performance characteristics.

10:40am **EM+SS-FrM8 Probing Surface-Induced Fluctuations in Organic Materials using an Atomic Force Microscope**, ***N.C. Hoepker***, *S. Lekkala, R.F. Loring, J.A. Marohn*, Cornell University

The development of organic electronics calls for new tools to study organic thin films. By measuring the frequency noise experienced by a cantilever near a surface, we are able to microscopically probe organic materials. In previous work, we used an Atomic Force Microscope to measure frequency noise due to dielectric fluctuations as a function of cantilever height and voltage over a thin film of polyvinyl acetate. In parallel, we have developed a zero-free parameter linear-response theory of thermally induced dielectric fluctuations that successfully describes our observations.[1]

Having understood dielectric fluctuations, we are now investigating fluctuations induced by carrier motion in polymeric semiconductors. Charge transport in these devices is not well understood. Previous work indicates that the ratio of diffusion constant to mobility in these materials violates what is predicted by the Einstein relation. In addition, there is an ongoing controversy on the charge density and electric field dependence of mobility. While the correlated-disorder model correctly predicts the electric field dependence of mobility, models that predict a density dependence of mobility rely on uncorrelated site-to-site energies.

A resolution of these controversies calls for new tools to study carrier motion in organic semiconductors. By measuring the frequency fluctuations experienced by a cantilever near a surface, we are able to microscopically probe carrier motion in organic materials. Comparing our observations over a poly(3-hexylthiophene) transistor to a calculation based on free diffusion, we find that while theory overestimates the observed fluctuations, it predicts the correct spectral shape and distance dependence of the fluctuations. Even at high gate bias, the observed cantilever frequency fluctuations differ from what we expect based on free diffusion and on the measured carrier mobility. This discrepancy indicates a breakdown of the Einstein relation. Further we present a number of different charge hopping models. We find that the predicted cantilever frequency noise is very sensitive to the details of the model, indicating that frequency noise spectra are a vital tool for selecting appropriate charge transport models.

[1] Nikolas Hoepker, Swapna Lekkala, Roger F. Loring, John A. Marohn (manuscript in preparation). *Quantifying Dielectric Fluctuations over Polymer Films Using an Atomic Force Microscope*.

11:00am **EM+SS-FrM9 2011 AVS Albert Nerken Award Lecture - Electron Spectroscopy of Reconstructed Surfaces: From Silicon to Graphene**, ***J.E. Rowe****, North Carolina State University **INVITED**

Surface reconstruction of silicon (and other materials) refers to the process by which atoms at the surface of a crystal assume a different structure than that of the bulk and has been extensively discussed and reported at a number of AVS meeting from the early 1960's until present time. In the 1970's a number of electron spectroscopy methods were applied to study this effect and many atomic models were proposed. Early 1970's experiments using electron energy loss spectroscopy and photoemission spectroscopy are described which along with modern theory methods led to the now accepted dimer model (later confirmed by STM) for the Si(100)2x1 and most other reconstructed (100) semiconductor surfaces. Additional core-level synchrotron spectra are described along with very recent studies which include adsorbate-induced surface reconstruction and the role of interface reconstruction of SiC(0001) used for the growth of graphene and studied by STM and STS. Spectroscopy has continued to play an important role even during the past 25 years after the discovery of atomic--scale imaging by STM of the Si(111)7x7 reconstruction. Both early and more recent studies of reconstruction by the author are reviewed.

11:40am **EM+SS-FrM11 Molecular Motion Confined to Self-Assembled Quantum Corrals**, ***E. Yitamben***, *R.A. Rosenberg, N.P. Guisinger*, Argonne National Laboratory

Engineering molecular superstructures on metals opens great possibilities for the control and exploration of complex nanosystems for technological applications. Of particular interest is the use of chiral molecules, such as alanine, to build self-assembled nanoscale structures for the trapping of the two-dimensional free electron gas of a metal. In the present work, molecules of D- or L-alanine were deposited on Cu(111). Scanning tunneling microscopy and spectroscopy revealed the formation of a uniform network of hexagonal pores of average diameter ~1.2 nm. Each pore acts as a quantum corral by confining the two-dimensional electron gas of the Cu(111) surface state. Furthermore, excess alanine molecules were trapped at the inner perimeter of the hexagonal pore, and were observed as rotating or immobile spatial states. This study demonstrates the engineering of one of the smallest quantum confined structure, and the dynamics of molecular motion within these potential wells.

Acknowledgements: This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

* Albert Nerken Award Winner

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+MS+EM-FrM

Graphene Device Physics and Applications
Moderator: M. Arnold, University of Wisconsin-Madison

8:20am **GR+MS+EM-FrM1 Fabrication and Characterization of Graphene p-n Junction Devices**, ***J.U. Lee***, University at Albany-SUNY **INVITED**

Graphene is a newly discovered material composed of two-dimensional array of hexagonal carbon atoms. It has a number of unique electronic properties, the most remarkable of which is the zero band-gap light-like linear electronic dispersion, giving rise to Dirac fermions. This feature can be used to make devices based on previously unexplored physical properties. For example, in analogy to optics, we describe new devices based on *optics-like manipulation of electrons*.

Our devices are based on graphene and bi-layer graphene *p-n* junctions doped using electrostatic doping techniques from buried split gates. In the present context, graphene *p-n* junctions do not rectify, i.e. behave as semiconductor diodes. Instead, in graphene p-n junctions, carriers launched from a point contact from one side of the junction are able to refocus back to a point on the other side of the junction. This behavior, known as the Veselago effect, can be the basis for new logic devices for replacing Si CMOS. In addition, using the same platform, we describe interconnect structures that can be reconfigured. Together, we envision a new circuit paradigm based on components that seamlessly reconfigure between devices and interconnect components.

In this talk, we describe the details of graphene *p-n* junction fabrication and characterization, and circuits that are enabled by the *p-n* junction devices. The devices are fabricated at CNSE's state-of-the-art 300mm Si wafer fabrication line using processing techniques that leave atomically flat top oxide surface above the patterned split gates. For characterizing the p-n junctions, we perform transport and SPM measurements.

9:00am **GR+MS+EM-FrM3 Assembled Bilayer Graphene for Electronic Applications**, ***G.G. Jernigan***, *T.J. Anderson, J.T. Robinson, J.D. Caldwell, M.D. Ancona, V.D. Wheeler, L.O. Nyakiti, J. Culbertson, A.L. Davidson, A.L. Friedman, P.M. Campbell, D.K. Gaskill*, U.S. Naval Research Laboratory

Graphene has shown successful application in RF transistors and frequency doublers where its high mobility and high saturation velocity translate into operation at high frequencies while utilizing little power. However, a major detraction to graphene development for other device applications is that it does not have a band gap. The lack of a band gap means that graphene's current cannot be turned off. Bilayer graphene is regarded as one possible solution to this problem, since bilayer graphene is capable of developing a band gap if the symmetry of the system can be broken. That said, bilayer graphene (from exfoliation or growth) forms a highly ordered A-B stack of the two graphene sheets resulting in little to no band gap, unless a high electric field can be applied.

In this presentation, we will demonstrate a novel method for creating bilayer graphene where a single layer of CVD graphene grown on Cu is bonded to a single layer of epitaxial graphene grown on Si-face SiC. This process results in a bilayer system that has a built-in asymmetry that yields unique physical and electrical properties not previously observed. For example, we demonstrate that the transfer of CVD graphene to epitaxial graphene results in a smoother morphology than transfer onto SiO2 and that bonding of CVD graphene to epitaxial graphene can avoid the damage caused by the drying step necessary in the poly (methyl methacrylate) transfer method. X-ray photoelectron spectroscopy and Raman microscopy demonstrate that the sheets are coupled together but strained differently, in contrast to a naturally formed bilayer. Electrical characterization of Hall devices fabricated on the novel bilayer show higher mobilities and lower carrier concentrations than the individual CVD graphene or epitaxial graphene sheets alone. Modeling of the electric field produced by opposite doping in the graphene sheets will also be presented, as CVD graphene is typically p-type and epitaxial graphene is typically n-type.

10:00am **GR+MS+EM-FrM6 Rectification at Graphene / Semiconductor Junctions: Applications Beyond Silicon Based Devices**, ***S. Tongay***, *X. Miao, K. Berke, M. Lemaitre, B.R. Appleton, A.F. Hebard*, University of Florida

Schottky barriers are crucial and necessary device components of metal-semiconductor field effect transistors (MESFETs) and high electron mobility transistors (HEMTs). Here, we report on the formation of Schottky barriers at graphene-multilayer graphene/semiconductor junction interfaces which have been characterized by current density vs. voltage (J-V) and capacitance vs. voltage (C-V) measurements. After graphene transfer onto various semiconductors such as Si, GaAs, GaN and SiC, we observe a strong rectification at the interface, i.e., high (low) resistance in the reverse (forward) bias directions. The J-V characteristics have been analyzed using thermionic emission theory and the extracted barrier height values are consistent with the Schottky-Mott model. When capacitance is plotted as $1/C^2$ vs V, a linear dependence is observed, which by extrapolation to the intercept identifies a built in potential that is consistent with the Schottky barrier height extracted from J-V measurements. Graphene's low Fermi energy together with its robust thermal, chemical, structural and physical properties provide numerous advantages when used to form Schottky barriers in device applications: namely, voltage tunability of the Schottky barrier height, stability to high temperatures, resistance to impurity diffusion across the interface, and the use of absorbates to chemically tune the Fermi energy and hence the Schottky barrier height.

10:20am **GR+MS+EM-FrM7 Imaging of Electron Beam Induced Current in Epitaxial Graphene**, ***S. Mou***, *J. Boeckl, W.C. Mitchel, J.H. Park,* Air Force Research Laboratory*, S. Tetlak,* Wyle Laboratories*, W. Lu*, Fisk University

It has been known and observed that there forms a Schottky junction between graphene and SiC in epitaxial graphene due to the work function difference and the charge transfer between them. As a result, it is viable to apply the electron beam induce current (EBIC) technique on the epitaxial graphene directly due to the fact that it needs a built-in field and ample electron generation volume to generate EBIC. EBIC is an important characterization technique, which identifies electrically active impurities/defects, detects local built-in field, and measures minority carrier diffusion length. In this paper, we use a FEI SEM equipped with a current amplifier to investigate the spatial mapping of EBIC generation and collection in a two terminal geometry. The incident electron beam generates excited electron-hole pairs in SiC and the minority carriers are collected through the Schottky junction before flowing into graphene. EBIC imaging reveals mesoscopic domains of bright and dark contrast areas due to local EBIC polarity and magnitude, which is believed to be the result of spatial fluctuation in the carrier density in graphene. We also investigate the electron energy dependence, which modulates the EBIC magnitude. With an analytical drift-diffusion current model, we are able to extract the minority carrier diffusion length in the SiC, which is on the order of micro meter and agrees well with other published data.

10:40am **GR+MS+EM-FrM8 Potassium-Ion Sensors Based on Valinomycin-Modified Graphene Field-Effect Transistors**, ***Y. Sofue***, *Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, The Institute of Scientific and Industrial Research, Osaka University, Japan

Highly sensitive ion sensors based on valinomycin-modified graphene field-effect transistors (VGFETs) have been developed to selectively detect K ions, which are an essential element for biological activity including human life. Graphene single-layers were obtained by mechanical exfoliation. Graphene FETs were fabricated by conventional e-beam lithography and lift-off method on a thermally grown SiO_2 layer. To demonstrate selective detection of K ions, the graphene channels were covered with ion selective membrane, which consisted of polyvinyl chloride and valinomycin. Transfer characteristics of VGFETs in a 100 mM Tris-HCl buffer solution with various KCl concentrations over the range from 10 nM to 1.0mM. With increasing K ion concentration, the solution-gated voltage at the Dirac point shifted toward negative direction. The shifts are due to the accumulation of positively charged K ions surrounded by valinomycin on the graphene surfaces. The electrostatic potential of graphene surfaces exhibit a rather linear dependence on log[K]. These results indicate that VGFETs effectively detected K ions with concentration from 10 nM to 1.0 mM. To investigate selectivity in VGFETs, Na-ion concentration dependence was also measured. The transfer characteristic in VGFETs remained almost constant over the Na ion concentration range between 10 nM and 1.0 mM. These results indicate that VGFET selectively detected K ions with high sensitivity.

11:00am **GR+MS+EM-FrM9 Band-gap Generation by using Ionic-Liquid Gate in Bilayer Graphene**, ***Y. Yamashiro***, *Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, Osaka University, Japan

Electric fields were applied to a bilayer graphene to generate a band gap using an ionic-liquid gate instead of the general top-gate structures. The ionic-liquid gate can apply higher electric field than other type of the gates because of its large capacitance and electric strength. In this abstract, the graphene layers were extracted from kish graphite by a mechanical exfoliation and were put on highly *n*-doped Si substrates covered with a 300-nm-thick SiO_2 layer. Side-gate electrodes were patterned approximately 20 mm away from the channels. An ionic liquid (DEME-TFSI) was put on the bilayer graphene and the side-gate electrode. Electrical characteristics at 300 K revealed that the electrical double layer in the ionic-liquid, which

works as a very thin insulator, had 200 times larger capacitance than a 300-nm-thick SiO_2 layer. The thickness of electrical double layer was estimated to be 3.75 nm. In electric field dependence measurements, an increase in a sheet resistance of the bilayer grapheme channel was clearly observed with increasing the magnitude of electric field in bilayer graphene. On the other hand, the increase in the sheet resistance didn't appear in the monolayer- and trilayer- graphene. That is why the increasing of the sheet resistance was caused by a band gap generated in ionic-liquid gated bilayer graphene by the electric field.

11:20am **GR+MS+EM-FrM10 Electronic Transport in Hydrogenated Graphene Films**, ***B.R. Matis****, J.S. Burgess,* NRC/NRL Postdoctoral Associate*, A.L. Friedman, J.T. Robinson,* Naval Research Laboratory (NRL)*, F.A. Bulat,* Sotera Defense Solutions, Inc.*, B.H. Houston, J.W. Baldwin*, Naval Research Laboratory (NRL)

Graphene films grown by chemical vapor deposition on copper foils and exfoliated graphene flakes were hydrogenated using low kinetic energy plasma processing. The film sheet resistance can be tuned over a wide range (1 kΩ/square – 300 kΩ/square), increasing proportionally with hydrogen coverage. Variable temperature measurements demonstrate a transition from semi-metallic behavior for graphene to semiconducting behavior for hydrogenated graphene. Sheet resistance measurements as a function of temperature also suggest the emergence of a band gap in the hydrogenated graphene films. Interesting surface doping effects will be discussed in conjunction with the location of the charge neutrality point. This work was supported by the Office of Naval Research.

11:40am **GR+MS+EM-FrM11 First-principles Study of Electronic Properties of Two Dimensional Carbon and Boron Nitride Nanomaterials***,* ***S. Mukherjee***, S.N. Bose National Centre for Basic Sciences, India

First principles pseudopotential plane wave method was used to study ground state electronic properties of Graphene, hexagonal Boron Nitride (h-BN), Graphene doped with Boron and Nitrogen, and multilayers of Graphene and h-BN. Our results on doped Graphene indicate that upon electron (hole) doping, the Dirac-point in the electronic bandstructure shifts below (above) the Fermi level and a gap appears at the high-symmetric K-point. Upon co-doping of Graphene by both Boron and Nitrogen a small energy gap between the conduction and valence band appears at the Fermi level, making the CBN nanomaterial a narrow band semiconductor. The energy gap depends sensitively on the degree of doping and on the thickness of CBN layer. These results are in agreement with recent experimental measurements [1,2]. Our bandstructure calculations on the multilayers of Graphene and h-BN indicate that these nanostructured multilayers exhibit semiconducting behaviour with band gap in the range 60-600 meV depending on the relative orientation and thickness of the layers. (Author: Sugata Mukherjee, work done in collaboration with T.P. Kaloni)

1. X. wang et al, Science **324**, 768 (2009)

2. L. Cie et al, Nature Materials **9**, 430 (2010).

Surface Science Division
Room: 107 - Session SS-FrM

Surface Science on Graphene
Moderator: I.I. Oleynik, University of South Florida

8:20am **SS-FrM1 Towards Controlled Growth of a Single-Layer of MoS_2**, ***D. Sun****, W. Lu, D. Kim, J. Mann, L. Bartels*, University of California, Riverside

MoS2 is a semiconducting material consisting of sulfur-molybenum-sulfur tripledecker layers loose bound by van der Waals interactions. MoS2 has been used technologically for a long time, for instance as lubricant, where similar to graphite its layered character was employed. Recently, its electronic characteristics have attained increased attention with the finding that it transitions from an indirect bandgap semiconductor at 1.6eV gap to a direct bandgap one at 1.9eV gap at the transition from multilayers to a single layer. A transistor has been constructed from a MoS2 and shown appreciable properties. The increased bandgap and high fluorescence yield may also suggest applications of the material for photonic or photocatalytic applications.

MoS2 can be exfoliated mechanically similar to graphene. While this method is simple, it is hard to control and not amendable to mass production of thin films. Solution-based processes have been proposed and may provide a scalable source of a mixture of single and multilayer material. Here we show an alternative avenue for the fabrication of MoS2 monolayers: growth of MoS2 on a sulfur-preloaded copper surface. In contrast to all other methods, this route has the potential of providing exclusively monolayer material, as the sulfur source is only available until the substrate is covered. Practically, this approach is related to the growth of graphene monolayers on copper or ruthenium films, where segregation of carbon to the surface is employed in aggregating a carbonaceous layer that transforms into graphene under the correct conditions.

Small MoS2 triangles of a few nanometers in size have been grown previously on gold in a dilute H2S athmosphere. Here we show significantly larger patches, tens of nanometers in size. In contrast to gold, copper forms a multitude of sulfur surface coverages and also readily absorbs sulfur into the bulk. Thus, we can preload the substrate with a specific amount sulfur using an easy to handle liquid precursor, benzenethiol. In previous work we have shown that heating to below 400K removes the phenyl group of benzenethiol reliably from copper leaving sulfur coverages behind.

8:40am **SS-FrM2 Oxygen Adsorption on Electronically Modified Graphite Surfaces Studied by Molecular Beam Scattering***,* ***J.P. Oh****, T. Kondo, K. Arakawa, Y. Saito, J. Nakamura*, University of Tsukuba, Japan

The graphite surface consists of π conjugated system. When the π conjugated system is broken, the non-bonding π electronic states are known to form on the surface. Recently, the non-bonding π electronic states at the Fermi level of the graphite-related materials are expected to the active sites for the specific chemical reaction such as oxygen-reduction reaction in the fuel cell [1]. It is thus important to understand the interaction between an oxygen molecule and the graphite surface for the efficient usage of the graphite-related materials. We have reported previously that the defects induced by Ar^+ ion bombardment on the graphite surface significantly affects the gas-graphite interaction based on the measurements of the angular intensity distributions of He and Ar beam scattered from the pristine and the defect induced graphite surfaces [2]. The difference in the gas-surface interaction has been ascribed to the local breaking of the π conjugated system of graphite by defect formation. To further investigate the effect of the modification of the graphite electronic states on the gas-surface interaction, especially for the oxygen adsorption, we have measured angular intensity distributions of O_2 from electronically modified graphite surfaces, namely potassium intercalated graphite, nitrogen-doped graphite (graphite bombarded by N_2^+ ion) and defective graphite (graphite bombarded by Ar^+ ion). The detail of scattering features as well as the effects of the electronic modification of graphite on the oxygen adsorption will be discussed in detail with our recent STM and STS results.

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[1] S.F. Huang, K. Terakura, T. Ozaki, T. Ikeda, M. Boero, M. Oshima, J. Ozaki and S. Miyata, *Phys. Rev. B*, **80**, 235410 (2009).

[2] J. Oh, T. Kondo, D. Hatake, Y. Honma, K. Arakawa, T. Machida, J. Nakamura, *J. Phys.: Condens. Matter*, **22**, 304008 (2010).

9:00am **SS-FrM3 Interaction and Thermal Stability of Oxygen Species in Graphene Oxide and Graphene Defects***, M. Acik, C. Gong, G. Lee, K. Cho, C. Mattevi, M. Chhowalla,* ***Y.J. Chabal***, University of Texas at Dallas **INVITED**

Graphene devices are based on finite size flakes (e.g. nanoribbons) in contact with dielectrics or other materials, and therefore require control of edges and depend on the control of processing methods (often involving vapor or wet chemistry). Graphene oxide (GO) represents an interesting system from which much can be learned about oxygen interaction with graphene. Furthermore, studying the reduction of GO provides a powerful way to understand the stability of oxygen species and the role of trapped molecules. We have studied both the thermal and chemical reduction of single- and multi-layer GO using *in situ* infrared (IR) absorption spectroscopy under a variety of conditions. For the commonly used as-synthesized GO, we find that water molecules play an important role in both defect formation (evident from CO_2 evolution)[1] and carbonyl-termination of defect edges at intermediate annealing temperatures (150-250 C).[2] We also find that a very stable edge configuration appears after high temperature anneals (> 850C), involving edge-ether termination of atomically straight zigzag edges and characterized by an anomalously strong IR absorption.[3] The situation is dramatically different when water is replaced by alcohols or more complex molecules (e.g. ionic liquids). In general, defect formation is greatly suppressed (no CO_2 evolution) with less carbonyl formation and a reduced density of atomically straight, edge-ether terminated edges. This talk will summarize the current understanding of the mechanisms involved in thermal reduction and suggest pathways for developing stable graphene nanostructures with reasonable electrical properties.

1. Acik et al., Generation and capture of CO_2 and CO in graphite oxide stacks during thermal reduction Mater. Res. Soc. Symp. Proc**.**, **1205E**, 1205 (2010).

2. Acik et al., The Role of Intercalated Water in Multilayered Graphene Oxide. ACS Nano **4**, 5861 (2010).

3. Acik et al.,Unusual infrared-absorption mechanism in thermally reduced GO. Nature Materials **9**, 840 (2010).

9:40am **SS-FrM5 Graphene on Pt(111) as a Template for Pt Nanocluster Formation**, ***Z. Liang****, H. Khosravian, A. Uhl, R. Meyer, M. Trenary*, University of Illinois at Chicago

Graphene on transition metal substrates often forms superlattices that are manifested as Moiré patterns in scanning tunneling microscopy (STM) images. Such graphene superlattices can serve as templates for the formation of periodic arrays of metal nanoclusters with a uniform size distribution, a situation that is ideal for model catalyst studies. We have used an ultra high vacuum (UHV) STM to investigate graphene growth on Pt(111) from precursor hydrocarbon species. Different periodicities in the Moiré patterns are observed corresponding to different orientations of the graphene layer with respect to the Pt(111) lattice. Various graphene orientations are possible because of a relatively weak graphene-Pt interaction. Following Pt deposition onto the graphene-covered areas of the surface, small Pt nanoclusters were observed. While graphene on Pt(111) only weakly interacts with the substrate, which leads to a weak corrugation in the superlattice compared to other transition metals, such as Ru, our results show that even this weak corrugation is sufficient to serve as a template for the formation of mono-dispersed Pt nanoclusters. These Pt nanoclusters are relatively stable and only undergo agglomeration for annealing temperatures above 600 K.

10:00am **SS-FrM6 Ripening Behavior of Pt Clusters on Monolayer Graphene Supported by Ru(0001) and the System's Thermal Stability**, ***C.U. Lorenz****, A.K. Engstfeld,* Ulm University, Germany*, H.E. Hoster,* Technische Universität München, Germany*, R.J. Behm*, Ulm University, Germany

The Moiré-type nm-scale patterns of graphene monolayers supported by metal single crystals were recently used for the fabrication of ordered arrays metal nanoclusters by metal vapor deposition under ultrahigh vacuum UHV conditions [1-3]. The corrugation within the adsorption potential of the graphene layer result in virtually monodisperse clusters. These are important for model (electro-)catalysis studies investigating the size dependency of Pt clusters on carbon support.

In this study we analyze the ripening behavior of Pt clusters (formed at room temperature) on monolayer graphene supported by Ru(0001) at temperatures above 450 K by means of STM. The size distribution change of the clusters gives insight into the rate determining step and into the mechanism of the ripening process. Two different annealing step methods (i: a single sample was successively heated to higher temperatures and ii: individual samples reproducibly prepared in the same manner annealed to certain temperatures; both methods using the same heating period of 10 min) bring us to the conclusion that Pt cluster ripening between 450 K and 725 K occurs via a mechanism proposed by M. Smoluchowski. Above 725 K we observe indications for a change in the ripening mechanism, where Smoluchowski ripening is likely in competition with Ostwald ripening. Also above 725 K, we observed an adverse influence of the Pt on the stability of the monolayer graphene. Single defects in the otherwise well ordered graphene appeared, which were absent after annealing to lower temperatures.

[1] A.T. N'Diaye et al., New J. Phys. 11, 2009, 103045. [2] Yi Pan et al., Appl. Phys. Lett. 95, 2009, 093106. [3] K. Donner and P. Jakob, J. Chem. Phys. 131, 2009, 164701.

10:20am **SS-FrM7 Mechanisms of Graphene Growth on Metals**, ***N.C. Bartelt***, Sandia National Laboratories **INVITED**

Growth on metal substrates is a promising route for synthesizing high-quality graphene films. In addition, moving electronic applications into the real world requires understanding and controlling the properties of graphene in contact with metals. This talk will focus on the properties and growth mechanisms on several metals distinguished by varying binding strengths to graphene sheets. Mechanistic insight comes from observing growth directly using low-energy electron microscopy (LEEM). On the relatively strongly interacting substrate Ru(0001), graphene grows with a single in-plane orientation from a highly supersaturated sea of C adatoms. On the less interacting substrates Ir(111) and Pd(111), graphene forms several but discrete in-plane orientations. Small but significant differences in graphene's electronic properties (i.e., band structure and work function) result from changes in orientation. On Cu foils, graphene islands nucleate with a large range of orientation. Thus, the weak film-Cu interaction leads to a high defect density. Finally, the mechanism of bilayer graphene growth has been explored. Diffraction analysis reveals that the second graphene layer on Ir(111) grows next to the substrate, not on top of the first layer. This "underlayer" growth mechanism occurs when the carbon source is either segregation from the substrate or deposition on top of the first layer. How this unusual mechanism affects thickness uniformity will be discussed.

This work was supported by the Office of Basic Energy Sciences, Division of Materials and Engineering Sciences of the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

11:00am **SS-FrM9 Graphene Moiré Polymorphism on Hydrogenated Ruthenium Surfaces**, ***B. Diaconescu***, University of New Hampshire*, F. Hagelberg,* East Tennessee State University*, K. Pohl*, University of New Hampshire

Graphene has aroused tremendous interest due to its remarkable electronic and mechanical properties. The lack of a band-gap, however, causes a serious challenge for implementing graphene as a material for electrical switches and therefore creative ways of inducing this band-gap are needed. We will present a STM/LEED/DFT study of the monolayer graphene on Ru(0001) system in the presence of hydrogen. STM reveals a diverse array of Moiré superlattice sizes ranging from 0.9 to 2.4 nm in the presence of hydrogen adlayer structures, as confirmed by LEED. Density functional theory calculations show a correlation between the Moiré superstructure sizes and the hydrogen coverage and the opening of a band-gap in the graphene/H/Ru(0001) system for some of the Moiré/hydrogen adlayer coverages.

This work was supported by the Nanoscale Science and Engineering Center for High-rate Nanomanufacturing (NSF NSEC-425826) and NSF DMR-1006863.

11:20am **SS-FrM10 Modifying Ni(111)/Graphene Interfaces by Sn-Ni Interface Alloy Formation**, ***R.Q. Addou****, A. Dahal, L. Adamska, I.I. Oleynik, M. Batzill*, University of South Florida

Graphene growth on metal surfaces (Ni, Pt, Ir, Rh and Cu) has been studied extensively [1]. Ni(111) is special among these metals because it is closely lattice matched with graphene ($a_{graphene}$= 0.246 nm vs. $a_{Ni(111)}$= 0.249 nm) allowing the growth of graphene with a single domain and in registry with the substrate [2]. However, compared to most other metal substrates the interaction between Ni and graphene is rather large, resulting in a small metal-carbon distance and a large shift of the graphene π-band compared to freestanding graphene. In order to de-couple graphene from the Ni-substrate other weaker interacting metals such as Cu and Au have been successfully intercalated between the graphene and Ni-substrate [3]. These metals have, however, a different lattice parameter and consequently the registry between the substrate and graphene is lost. Here we demonstrate a new approach that weakens the metal-graphene interaction without destroying the lattice registry. By intercalating Sn-atoms an ordered $\sqrt{3} \times \sqrt{3}$ R30° Sn-Ni alloy is formed at the interface. The Sn intercalation process is characterized by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). In this alloy Sn substitutes for surface Ni atoms without changing the lattice parameter of the substrate and consequently the registry between the metal substrate and graphene is maintained. DFT simulations indicate that Sn alloying with Ni weakens the interaction of graphene with the metal substrate and consequently increasing the graphene-substrate distance and restoring the graphene π-band close to the position of free-standing graphene. Atomic-resolution scanning tunneling microscopy (STM) imaging reveals that the alloy periodicity is reproduced in the graphene layer, i.e. a $\sqrt{3} \times \sqrt{3}$ R30° superstructure is imposed on the graphene by the alloy substrate. This indicates a variation of the local density of states for C-atoms located on top of Sn-substrate sites compared to Ni-sites. Further experimental and theoretical characterization of the influence of the substrate on the electronic and structural properties of graphene is ongoing.

[1] J. Wintterlin and M.-L. Bocquet, Surf. Sci. ***603****, 1841-1852 (2009)*

[2] J. Lahiri et al., Nano Lett. ***11****, 518-522 (2010)*

[3] A. Varykhalov et al., Phys. Rev. Lett., ***101****, 157601 (2008)*

11:40am **SS-FrM11 Silicene Epitaxial Sheets: Silicon New Start**, *P. Vogt,* Aix Marseille Univ, CNRS-CINaM, France and Technische Universität Berlin, Germany*, P. De Padova, C. Quaresima,* CNR-ISM, Italy*, J. Avila, E. Frantzeskakis, M.C. Asensio,* Synchrotron SOLEIL, France*, B. Ealet,* Aix Marseille Univ, CNRS-CINaM, France*,* ***G. Le Lay***, Aix Marseille Univ, CNRS-CINaM, France and CNR-ISM, Italy

We have just synthesized in Marseille silicene sheets [1], i.e., atom-thin two-dimensional graphene-like silicon layers with an in-plane Si-Si interatomic distance of 0.23 nm [2], upon in-situ epitaxial growth on silver (111) surfaces. The honeycomb atomic structure is revealed in Scanning Tunnelling Microscopy, while the long-range epitaxial order is confirmed by sharp 4x4 Low Energy Electron Diffraction patterns. Dirac cones at the

K and K' points of the silicene Brillouin zone, evidenced in High-Resolution Synchrotron Radiation Angle-Resolved PhotoElectron Spectroscopy measurements, point to massless relativistic fermions with a Fermi velocity of 1.3E6 m/s, as theoretically predicted [3], quite the same as graphene, and four times higher than previously obtained on a one-dimensional grating of silicene nano-ribbons [4]. Density Functional Theory calculations *including the Ag(111) substrate* confirm the stability of the epitaxial arrangement. The demonstration that silicon can form sheets of silicene, a two dimensional honeycomb structure, which does not exist in Nature, is tantalizing for new Physics. Silicon being the workhorse of electronics industry, this synthesis could have a major impact for novel devices because of the compatibility with existing Si technologies.

[1] P. Vogt , P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M.C. Asensio and G. Le Lay, submitted

[2] G. G. Guzman-Verri and L.C. Lew Yan Voon, Phys. Rev. B 76, 75132 (2007).

[3] M. Houssa, G. Pourtois, M. Heyns, V.V. Afanas'ev, and A. Stesmans,

J. Electrochem. Soc. 158, H107 (2011)

[4] P. De Padova et al., Appl. Phys. Lett., 96, 261905 (2010)

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Baughman, W.: EN+EM+NS-WeM12, 22
Baumgart, H.: EM-TuA11, 17
Baxter, J.B.: EN+EM+NS-WeM11, **22**
Beckers, N.A.: TC+AS+EM-ThM5, **35**
Behm, R.J.: SS-FrM6, 53
Belot, J.A.: TC+EM+NS-ThA4, **39**
Benes, N.E.: EL+AS+EM+MS+PS+TF-ThA9, 38
Berger, O.: EN+EM+NS-WeM6, 22
Berke, K.: GR+EM-TuM11, **15**; GR+MS+EM-FrM6, 51
Berrie, C.L.: GR+EM-TuM10, 15
Bersch, E.J.: EM+TF-TuM6, **11**
Bersuker, G.: EM+TF-TuM4, 11
Bertaud, T.: TF1+EM-WeA3, 27
Bhandaru, S.: EM-WeA11, 26
Bhaviripudi, S.: ET+EM+NS+GR-TuM2, 12
Bockstaller, M.: TC+AS+EM-ThM9, 35
Boeckl, J.: GR+MS+EM-FrM7, 51
Bolotin, K.: EM-WeA11, 26
Bondaz, A.: EL+AS+EM+MS+PS+TF-FrM7, **49**; EL+AS+EM+MS+PS+TF-ThM10, 32
Bonvalot, M.: EM2-MoA9, **8**
Book, G.W.: TC+AS+EM-ThM10, 35
Boosalis, A.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, 48; GR+EM-TuM6, **14**
Breitwisch, M.: TF1+EM-WeA9, 28
Brennan, B.: EM+TF-TuM2, **11**; EM+TF-TuM3, 11; EM-TuA10, 17; EM-TuA9, 16
Brett, M.J.: TC+AS+EM-ThM5, 35
Briley, C.: EL+AS+EM+MS+PS+TF-FrM4, 48
Brillson, L.J.: EM-WeA1, **25**; EM-WeA4, 25
Brown, D.: NS+EM-MoM6, 4
Buegler, M.: EM1-MoA4, 6; EM-ThP11, 44; EM-ThP15, 45
Bulat, F.A.: GR+MS+EM-FrM10, 52
Burek, G.B.: EM-MoM2, 1
Burgess, J.S.: GR+MS+EM-FrM10, 52
Bussmann, E.: TF2+EM-WeA3, **28**
Butler, L.: EN+EM+NS-WeM12, 22

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Cahen, D.: EM+TF-ThM11, 33
Caldwell, J.D.: EM+SS-FrM1, 49; GR+MS+EM-FrM3, 51
Campbell, P.M.: GR+MS+EM-FrM3, 51
Cantwell, G.: EM-WeA1, 25
Carnevale, S.D.: NS+EM-MoM2, **3**
Carrillo-Castillo, A.: EM-ThP3, 43; TC+AS+EM-ThM11, 35
Carter, A.D.: EM-MoM2, 1
Caruso, A.N.: EM-WeM6, 20
Cavarsan, F.A.: EM-ThP6, 43
Caymax, M.: EM-TuA4, 16
Ceballos-Sanchez, O.: EM-TuA12, 17
Cha, P.-R.: EM-ThP22, 46; GR-TuA7, 18
Chabal, Y.J.: EM+TF-ThM3, 32; EM-ThP7, 44; SS-FrM3, **52**
Chae, S.-D.: EM-MoM8, 2
Chan, J.: GR-TuA9, **18**
Chang, J.P.: TF1+EM-WeA7, 27
Chang, Y.C.: EM+TF-TuM9, 12
Chauveau, J.M.: EM-WeA3, 25
Chawla, J.S.: ET+EM+NS+GR-TuM11, 13
Chen, C.: EN+EM+NS-MoA9, **10**
Chen, W.C.: EM-ThP12, **45**
Cheng, H.-Y.: TF1+EM-WeA9, 28
Cheong, W.S.: EM-ThP18, 45
Cheung, K.P.: EM-TuA11, 17
Cheynis, F.: TF2+EM-WeA3, 28
Chhowalla, M.: SS-FrM3, 52
Chin, G.: EL+AS+EM+MS+PS+TF-FrM6, **49**
Cho, G.: EM-ThP17, 45
Cho, K.: EM-ThP7, 44; NS+EM-MoM5, 4; SS-FrM3, 52
Choi, B.L.: NS+EM-MoM5, 4
Choi, H.J.: NS+EM-MoM1, 3
Choi, J.H.: TF1+EM-WeA7, 27
Choi, Y.: EM-WeA4, 25
Chopra, N.: TF+EM+SS-ThA7, **41**
Chung, S.M.: EM-ThP18, **45**
Clark, K.: ET+EM+NS+GR-TuM1, **12**
Clark, R.D.: EM+TF-TuM6, 11
Clayton, C.: EM-WeM6, 20
Clearfield, R.: NS+EM-MoM10, **4**
Coclite, A.M.: TF2+EM-WeA12, **30**
Cohen, H.: TF+EM+SS-ThA11, **42**
Cohen, P.I.: GR-TuA11, 19
Cohen, S.: EM-WeM9, 21
Collazo, R.: EM1-MoA4, 6; EM-ThP13, 45; EM-ThP15, 45
Collins, R.W.: EL+AS+EM+MS+PS+TF-ThA4, 37
Colombo, L.: GR-TuA9, 18
Conley, J.: TF1+EM-WeA1, 27
Consiglio, S.P.: EM+TF-TuM6, 11
Cook, B.: ET+EM+SS-MoM11, **3**
Cronin, S.: ET+EM+NS+GR-TuM3, **13**
Cui, D.: EM-MoM3, 1
Culbertson, J.: GR+MS+EM-FrM3, 51; GR-TuA8, 18
Cunningham, G.: EM1-MoA11, 7; EN+EM+NS-MoA3, 9

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Dadmun, M.: EM1-MoA6, **7**
Dahal, A.: SS-FrM10, 53
Dannecker, T.: EM-WeA12, 27
Darakchieva, V.: EL+AS+EM+MS+PS+TF-FrM3, 48; GR+EM-TuM6, 14
Dasaka, R.: TF1+EM-WeA9, 28
DasGupta, S.: EM-WeA8, 25
Dauskardt, R.H.: EM-WeM11, **21**
Davidson, A.L.: GR+MS+EM-FrM3, 51
Davis, R.F.: EM1-MoA2, 6
Dawahre, N.: EN+EM+NS-WeM12, 22
De Padova, P.: SS-FrM11, 53
Defranoux, C.: EL+AS+EM+MS+PS+TF-FrM7, 49; EL+AS+EM+MS+PS+TF-ThM10, 32
Deguns, E.W.: TF1+EM-WeM5, 23
Delabie, A.: EM-TuA4, 16
Despiau-Pujo, E.: TF1+EM-WeA2, **27**
Diaconescu, B.: SS-FrM9, **53**
Diebold, A.C.: EM+TF-TuM6, 11
Dietz, N.: EM1-MoA4, 6; EM-ThP10, **44**; EM-ThP11, 44; EM-ThP13, 45; EM-ThP14, 45; EM-ThP15, 45
Diez, J.: TF2+EM-WeA4, 29
Dignard, P.: ET+EM+SS-MoM11, 3
DiLullo, A.R.: EM-ThP1, **43**
Dingemans, G.: EM+TF-TuM11, 12
Diniz, J.A.: EM-ThP5, 43; EM-ThP6, 43
Dockstader, T.: TC+AS+EM-ThM6, 35
Doi, I.: EM-ThP5, 43
Dong, H.: EM+TF-TuM2, 11; EM+TF-TuM3, 11; EM-TuA10, **17**; EM-TuA9, 16
Dong, Y.: EM-WeA1, 25
Doutt, D.: EM-WeA1, 25
Dowben, P.A.: GR+EM-TuM6, 14
Dresselhaus, M.S.: ET+EM+NS+GR-TuM2, 12
Driver, M.S.: EM-WeM6, 20
Dubey, G.: TF+EM+SS-ThA3, **40**
Duscher, G.: EM-ThP19, 46
Dussault, L.: TF1+EM-WeA2, 27

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Ealet, B.: SS-FrM11, 53
Eastman, L.F.: EL+AS+EM+MS+PS+TF-FrM3, 48
Ebihara, R.: TF1+EM-WeM6, 24
Eck, W.: TF+EM+SS-ThA6, 41
Economou, E.N.: GR+EM-TuM4, 14
Eddy Jr., C.R.: GR-TuA8, 18
Eddy, Jr., C.R.: EM+SS-FrM1, 49
Edwards, C.: GR+EM-TuM10, **15**
Eichhorn, K.-J.: EL+AS+EM+MS+PS+TF-ThM1, **31**
Einabad, O.: ET+EM+NS+GR-TuM12, 14
El Zubir, O.: TF+EM+SS-ThA4, **41**
Endoh, T.: EM-MoM10, **2**
Endres, J.: ET+EM+NS+GR-TuM5, 13
Engstfeld, A.K.: SS-FrM6, 53
Engstrom, J.R.: EM+TF-ThM4, **33**
Eriksson, M.: ET+EM+NS+GR-TuM5, 13
Esposto, M.: EM+TF-TuM12, 12; NS+EM-MoM6, 4
Evans, K.R.: EM1-MoA2, 6

— F —

Fang, Z.-Q.: EM-WeA1, 25
Faradzhev, N.S.: EL+AS+EM+MS+PS+TF-ThM9, 32
Fay, P.: EM-MoM8, 2
Feenstra, R.M.: ET+EM+NS+GR-TuM1, 12
Ferguson, J.D.: EM1-MoA3, **6**

Ferrara, D.W.: EL+AS+EM+MS+PS+TF-ThA11, 38
Ferrari, A.C.: GR+EM-TuM1, **14**
Field III, R.L.: EM-WeA12, 27
Filler, M.A.: EN+EM+NS-MoA7, 9; EN+EM+NS-WeM3, **21**
Fisher, E.R.: TF2+EM-WeA8, 29
Fleetwood, D.M.: EM-WeA11, 26; EM-WeA8, 25; EM-WeA9, 26
Fleischauer, M.D.: TC+AS+EM-ThM5, 35
Floro, J.A.: TF2+EM-WeA7, 29
Fowlkes, J.D.: NS+EM-MoM10, 4; TF2+EM-WeA4, 29
Frantzeskakis, E.: SS-FrM11, 53
Friedman, A.L.: GR+MS+EM-FrM10, 52; GR+MS+EM-FrM3, 51
Fu, W.: ET+EM+NS+GR-TuM6, 13
Fuhrer, M.: GR-TuA4, 18
Fuller, N.C.M.: TF1+EM-WeA9, 28

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Gaddam, S.: GR+EM-TuM6, 14
Gaidis, M.C.: TF1+EM-WeA9, 28
Gajek, M.: TF1+EM-WeA9, 28
Galatage, R.V.: EM+TF-TuM2, 11; EM+TF-TuM4, 11; EM-TuA9, **16**
Gall, D.: ET+EM+NS+GR-TuM11, **13**
Gamage, S.: EM1-MoA4, 6; EM-ThP10, 44; EM-ThP11, 44; EM-ThP13, **45**; EM-ThP14, 45; EM-ThP15, 45
Garces, N.Y.: GR-TuA8, 18
Gaskill, D.K.: EM+SS-FrM1, 49; GR+EM-TuM6, 14; GR+MS+EM-FrM3, 51; GR-TuA8, 18
Gates, B.D.: EM-ThP23, **46**
Gates, S.M.: EM-WeM3, 20; EM-WeM9, 21
George, S.M.: TF1+EM-WeM11, 24; TF1+EM-WeM3, 23
Gerasimov, J.Y.: EL+AS+EM+MS+PS+TF-ThM6, **32**
Gerhardt, R.A.: TC+AS+EM-ThM10, 35
Gidley, D.W.: EM-MoM5, 1; EM-WeM5, 20
Giermann, A.L.: TF2+EM-WeA1, 28
Gleason, K.K.: TF2+EM-WeA12, 30
Gnade, B.E.: EM-ThP3, 43; EM-ThP4, 43; TC+AS+EM-ThM11, 35
Gocalinska, A.: EM+TF-TuM4, 11
Godoy Fo, J.: EM-ThP5, 43
Goel, N.: EM+TF-TuM4, 11
Goldman, R.S.: EM-WeA12, **27**
Gong, B.: TF1+EM-WeM4, **23**
Gong, C.: SS-FrM3, 52
Gong, C.G.: EM-ThP7, 44
Gong, Y.: EM-ThP23, 46
Gonon, P.: EM2-MoA9, 8
Gonzalez, C.M.: EM-ThP19, **46**
Gorai, P.: EM-WeA7, 25
Gossard, A.C.: EM-MoM2, 1
Gourvest, E.: TF1+EM-WeA2, 27
Grampeix, H.: EM2-MoA9, 8
Grantham, S.: EL+AS+EM+MS+PS+TF-ThM9, 32
Gregory, C.: EM1-MoA11, 7; EN+EM+NS-MoA3, 9
Gregory, J.M.: EM-ThP8, **44**
Grill, A.: EM-WeM3, **20**; EM-WeM9, 21
Gu, G.: ET+EM+NS+GR-TuM1, 12
Guglietta, G.W.: EN+EM+NS-WeM11, 22
Guisinger, N.P.: EM+SS-FrM11, 50
Gupta, S.: TF1+EM-WeA8, 28
Gupta, V.: EM-ThP24, **47**
Gur, E.: EM-WeA3, **25**

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Ha, J.: GR-TuA2, 17
Ha, R.: NS+EM-MoM1, 3
Hacker, C.A.: TF+EM+SS-ThA9, 41
Hagelberg, F.: SS-FrM9, 53
Haglund, R.F.: EL+AS+EM+MS+PS+TF-ThA11, 38
Hall, R.A.: TF1+EM-WeM11, **24**
Hallberg, T.: EL+AS+EM+MS+PS+TF-ThM4, 31
Har-Lavan, R.: EM+TF-ThM11, 33
Harris, N.: EN+EM+NS-WeM12, 22
Hasan, M.Z.: EM+SS-FrM3, **50**
Hasegawa, S.: ET+EM+SS-MoM1, **2**
He, G.: ET+EM+NS+GR-TuM1, 12
He, K.T.: GR-TuA12, 19
Hebard, A.F.: GR+EM-TuM11, 15; GR+MS+EM-FrM6, 51
Heikenfeld, J.: TC+EM+NS-ThA6, 39
Hellstrom, S.L.: ET+EM+NS+GR-TuM6, 13; TF2+EM-WeA10, **30**
Hensley, D.K.: TF2+EM-WeA9, 29
Herman, G.S.: TF1+EM-WeA1, **27**
Herrera-Gomez, A.: EM-TuA12, 17
Herzinger, C.M.: EL+AS+EM+MS+PS+TF-FrM1, 48; EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, 48
Heyns, M.: EM-TuA1, **16**
Hierro, A.: EM-WeA3, 25
Hilfiker, J.N.: EL+AS+EM+MS+PS+TF-FrM1, **48**
Hill, S.B.: EL+AS+EM+MS+PS+TF-ThM9, 32
Hines, D.: GR-TuA4, 18
Hines, M.: EM-ThP2, **43**
Hinkle, C.L.: EM+TF-TuM4, 11; EM-TuA9, 16
Hinojos, D.: GR-TuA9, 18
Hirahara, T.: ET+EM+SS-MoM1, 2
Hla, S.-W.: EM-ThP1, 43
Hobart, K.D.: EM+SS-FrM1, 49
Hoepker, N.C.: EM+SS-FrM8, **50**
Hoffman, R.L.: TC+EM+NS-ThA7, 39
Hofmann, T.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, **48**; GR+EM-TuM6, 14
Hollister, A.: EM-WeA7, 25
Holloway, P.H.: EN+EM+NS-MoA8, 9
Holman, Z.: EN+EM+NS-WeM1, 21
Hong, C.H.: EM-ThP18, 45
Hong, J.: EM-ThP10, 44; EM-ThP11, 44; EM-ThP13, 45
Hong, M.: EM+TF-TuM9, **12**
Horn, M.W.: EL+AS+EM+MS+PS+TF-ThA10, 38
Hosadurga, S.: EM-WeM9, 21
Hoshino, K.: TC+EM+NS-ThA7, 39
Hosoi, T.: EM-ThP20, 46
Hosono, H.: TC+EM+NS-ThA10, 40; TC+EM+NS-ThA3, 39; TC+EM+NS-ThA9, 39
Hoster, H.E.: SS-FrM6, 53
Houston, B.H.: GR+MS+EM-FrM10, 52
Hsiao, C.N.: EM-ThP12, 45
Hu, X.: EM-ThP20, 46
Huang, C.-H.: EN+EM+NS-MoA1, 9
Huang, J.: EM+TF-TuM4, 11; EM-ThP22, 46
Huang, L.: EM1-MoA2, 6
Huang, M.L.: EM+TF-TuM9, 12
Hughes, K.J.: EM+TF-ThM4, 33
Hung, T.-H.: EM+TF-TuM12, **12**
Hurley, P.K.: EM+TF-TuM4, 11
Hwang, B.: GR-TuA2, 17
Hwang, J.: EN+EM+NS-MoA9, 10
Hwang, W.-S.: EM-MoM8, 2

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Iagarashi, M.: EN+EM+NS-MoA1, 9
Ianno, N.: EL+AS+EM+MS+PS+TF-ThA8, 38
Ide, K.: TC+EM+NS-ThA10, 40; TC+EM+NS-ThA9, **39**
Im, S.I.: EM+TF-ThM9, **33**; NS+EM-MoM1, 3
Imhoff, E.A.: EM+SS-FrM1, 49
Inoue, K.: GR+MS+EM-FrM8, 51; GR+MS+EM-FrM9, 51
Iwata, J.-I.: EM-ThP9, 44

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Jacob, D.: EM-WeM5, 20
Jain, R.: EM+TF-ThM12, **34**
Jandhyala, S.: GR-TuA7, **18**
Järrendahl, K.: EL+AS+EM+MS+PS+TF-ThM4, 31
Javey, A.: EN+EM+NS-WeM9, **22**
Jernigan, G.G.: GR+MS+EM-FrM3, **51**
Jia, X.T.: ET+EM+NS+GR-TuM2, 12
Jin, R.Z.: TF2+EM-WeA10, 30
Jin, Y.: EM-WeA12, 27
Johs, B.: EL+AS+EM+MS+PS+TF-FrM1, 48
Jordan-Sweet, J.L.: TF1+EM-WeA9, 28
Joseph, E.A.: TF1+EM-WeA9, **28**
Joshi, P.: EM+TF-ThM11, 33
Joshi, S.M.: TC+AS+EM-ThM10, **35**
Jourde, D.: TF1+EM-WeA2, 27
Jousseaume, V.: EM2-MoA9, 8
Juang, B.: EN+EM+NS-MoA9, 10
Jur, J.S.: EM1-MoA9, **7**

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Kafesaki, M.: GR+EM-TuM4, 14
Kalyanaraman, R.: EM-ThP19, 46
Kalyanaraman, V.: EM-WeA4, 25
Kamiya, T.: TC+EM+NS-ThA10, **40**; TC+EM+NS-ThA3, 39; TC+EM+NS-ThA9, 39
Kappe, E.: EM+TF-ThM6, 33
Kareev, M.: EM-WeA4, 25
Kariis, H.: EL+AS+EM+MS+PS+TF-ThM4, 31
Karki, S.: EM-WeM6, 20
Kasputis, T.: EL+AS+EM+MS+PS+TF-ThM5, 31
Katz, H.: TC+EM+NS-ThA11, 40
Kau, D.: EM2-MoA6, **8**
Kaufman-Osborn, T.: EM-TuA4, **16**
Kavanagh, K.L.: ET+EM+NS+GR-TuM12, 14
Kawasaki, J.K.: EM+SS-FrM2, 49
Kazaz, R.: EM+TF-ThM11, 33
Keating, C.D.: NS+EM-MoM8, 4
Kelber, J.: EM1-MoA8, 7; GR+EM-TuM6, 14
Keller, S.: NS+EM-MoM6, 4
Kent, T.: EM-MoM1, 1
Kent, T.F.: NS+EM-MoM2, 3
Kessels, W.M.M.: EL+AS+EM+MS+PS+TF-ThA7, 37; EM+TF-TuM11, 12
Khabibullin, M.: EM-WeM2, 20
Khalili, P.: EM2-MoA1, 8
Khosravian, H.: SS-FrM5, 53
Kiantaj, K.: EM-TuA4, 16
Kikuchi, Y.: TC+EM+NS-ThA10, 40
Kim, D.: EM-WeM2, 20; SS-FrM1, 52; TF1+EM-WeM4, 23
Kim, H.: EM1-MoA1, **6**; TC+AS+EM-ThM1, 34
Kim, J.: EM+TF-TuM2, 11; EM+TF-TuM3, 11; EM-ThP16, **45**; EM-ThP22, 46; EM-TuA10, 17; GR-TuA7, 18; NS+EM-MoM8, 4
Kim, J.K.: NS+EM-MoM1, 3
Kim, JM.: TC+AS+EM-ThM1, 34
Kim, N.: EM-ThP17, 45
Kim, S.: EN+EM+NS-MoA9, 10; EN+EM+NS-WeM12, **22**
Kim, T.H.: ET+EM+NS+GR-TuM6, 13; ET+EM+SS-MoM8, **3**
King, S.: EM-WeM5, **20**
Kioussis, D.: EM-WeM9, **21**
Kirk, W.P.: EM+TF-TuM4, 11
Kitzinger, L.: EL+AS+EM+MS+PS+TF-FrM7, 49; EL+AS+EM+MS+PS+TF-ThM10, **32**
Klem, E.J.D.: EM1-MoA11, 7; EN+EM+NS-MoA3, **9**
Klymko, N.: EM-WeM9, 21
Knez, M.: TF1+EM-WeM9, **24**
Knezevic, I.: ET+EM+NS+GR-TuM5, 13
Knoops, H.C.M.: EL+AS+EM+MS+PS+TF-ThA7, 37
Kondic, L.: TF2+EM-WeA4, 29
Kondo, T.: SS-FrM2, 52
Kong, J.: ET+EM+NS+GR-TuM2, 12
Kortshagen, U.: EN+EM+NS-WeM1, **21**
Kosel, T.: EM-MoM8, 2
Kreit, E.: TC+EM+NS-ThA6, 39
Krishnamoorthy, S.: EM+SS-FrM7, **50**; EM+TF-TuM12, 12
Kuchibhatla, S.V.N.T.: EM1-MoA2, 6

Kühne, P.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, 48
Kuk, Y.: GR-TuA2, 17; NS+EM-MoM5, 4
Kumar, M.: GR-TuA11, 19
Kummel, A.C.: EM+TF-ThM6, 33; EM-MoM1, 1; EM-TuA4, 16
Kung, P.: EN+EM+NS-WeM12, 22
Kunzler, S.C.: EM-ThP24, 47
Kuo, S.Y.: EM-ThP12, 45
Kurdak, C.: EM-WeA12, 27
Kuznetsov, A.Yu.: EM-WeA1, 25
Kwo, J.: EM+TF-TuM9, 12
Kwon, J.: GR-TuA2, 17; NS+EM-MoM5, 4

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LaFranzo, N.A.: TF+EM+SS-ThA10, **41**
Lagally, M.G.: ET+EM+NS+GR-TuM5, 13; TF2+EM-WeA11, 30
Lai, F.-I.: EM-ThP12, 45
Lai, R.Y.: EL+AS+EM+MS+PS+TF-ThM6, 32
Lai, S.-C.: TF1+EM-WeA9, 28
Lam, C.H.: TF1+EM-WeA9, 28
Landin, J.: EL+AS+EM+MS+PS+TF-ThM4, 31
LaRose, J.D.: EM+TF-TuM6, 11
Laskoski, M.: GR-TuA4, 18
Law, J.J.M.: EM-MoM2, **1**
Le Lay, G.: SS-FrM11, **53**
Le, T.P.: EN+EM+NS-WeM11, 22
Lee, B.: GR-TuA7, 18
Lee, B.H.: TF1+EM-WeM3, **23**
Lee, C.-T.: EM-ThP12, 45
Lee, D.H.: TC+EM+NS-ThA3, **39**
Lee, G.: SS-FrM3, 52
Lee, J.S.: EM-TuA4, 16
Lee, J.U.: GR+MS+EM-FrM1, **51**
Lee, M.: EM-ThP22, 46
Lee, S.: EM-ThP22, **46**
Lee, W.C.: EM+TF-TuM9, 12
Lee, W.K.: GR-TuA4, 18
Lee, W.S.: TC+AS+EM-ThM1, 34
Lee, Y.T.: NS+EM-MoM1, **3**
Leggett, G.: TF+EM+SS-ThA4, 41
Leick, N.: EL+AS+EM+MS+PS+TF-ThA7, **37**
Lekkala, S.: EM+SS-FrM8, 50
Lemaitre, M.: GR+EM-TuM11, 15; GR+MS+EM-FrM6, 51
Lenhardt, J.: EM-ThP2, 43
Leroy, F.: TF2+EM-WeA3, 28
Leusink, G.J.: EM+TF-TuM6, 11
Levi, D.: EL+AS+EM+MS+PS+TF-ThA1, **37**
Levy, J.: TF2+EM-WeA7, 29
Lewis, J.: EM1-MoA11, **7**; EN+EM+NS-MoA3, 9
Li, A.-P.: ET+EM+NS+GR-TuM1, 12; ET+EM+NS+GR-TuM6, 13
Li, M.: NS+EM-MoM8, 4
Li, R.: EM-MoM8, 2
Liang, W.: ET+EM+NS+GR-TuM6, 13
Liang, Z.: SS-FrM5, **53**
Liddell, K.: NS+EM-MoM8, 4
Lim, S.J.: NS+EM-MoM5, **4**
Lima, L.P.B.: EM-ThP5, **43**; EM-ThP6, 43
Lin, S.-H.: EN+EM+NS-MoA1, **9**
Lin, T.D.: EM+TF-TuM9, 12
Linford, M.R.: EM-ThP24, 47
Liu, A.: EM-ThP23, 46
Liu, C.: ET+EM+NS+GR-TuM12, **14**
Liu, C.Y.: EN+EM+NS-WeM1, 21
Liu, F.: EM1-MoA2, **6**
Liu, G.: GR-TuA10, 19
Liu, J.: GR+EM-TuM10, 15
Liu, L.: ET+EM+NS+GR-TuM6, 13
Liu, M.: EM-MoM5, 1; EM-WeM5, 20
Liu, Q.: EM-MoM8, 2
Liu, Y.: TC+EM+NS-ThA11, 40
Lock, E.H.: GR-TuA4, **18**
Look, D.C.: EM-WeA1, 25
Lopinski, G.P.: TF+EM+SS-ThA3, 40
Lorenz, C.U.: SS-FrM6, **53**
Loring, R.F.: EM+SS-FrM8, 50
Lu, M.: EM-ThP2, 43
Lu, P.: EM+TF-ThM5, 33
Lu, W.: EM1-MoA1, 6; GR+MS+EM-FrM7, 51; SS-FrM1, 52
Lu, Y.: EM-MoM8, 2
Lucatorto, T.B.: EL+AS+EM+MS+PS+TF-ThM9, 32
Lung, H.-L.: TF1+EM-WeA9, 28
Lyding, J.W.: GR-TuA12, 19
Lysaght, P.: EM-TuA12, 17

— M —

Mackus, A.J.M.: EL+AS+EM+MS+PS+TF-ThA7, 37
Madan, A.: EM-WeM9, 21
Maehashi, K.: GR+MS+EM-FrM8, 51; GR+MS+EM-FrM9, 51
Magnuson, C.: GR-TuA9, 18
Maitrejean, S.: TF1+EM-WeA2, 27
Majidi, H.: EN+EM+NS-WeM11, 22
Makino, H.: TC+AS+EM-ThM2, **34**
Malgorzata, M.: TF1+EM-WeA3, 27
Mancheno-Posso, P.: EM-ThP21, **46**
Mandoc, M.M.: EM+TF-TuM11, 12
Mann, J.: SS-FrM1, 52
Mannequin, C.: EM2-MoA9, 8
Marohn, J.A.: EM+SS-FrM8, 50
Marsillac, S.: EL+AS+EM+MS+PS+TF-ThA4, 37
Martin, R.M.: TF1+EM-WeA9, 28
Marvel, R.E.: EL+AS+EM+MS+PS+TF-ThA11, **38**
Masuda, H.: EM-WeM9, 21
Matis, B.R.: GR+MS+EM-FrM10, **52**
Matsumoto, K.: GR+MS+EM-FrM8, 51; GR+MS+EM-FrM9, 51
Mattevi, C.: SS-FrM3, 52
Maurer, J.A.: TF+EM+SS-ThA10, 41
Mayer, J.S.: NS+EM-MoM8, 4
Mayer, T.S.: NS+EM-MoM8, **4**
McCullough, R.D.: TC+EM+NS-ThA4, 39
McDonnell, S.: GR-TuA9, 18
McEuen, P.L.: GR+EM-TuM9, 15
McGimpsey, W.G.: EM+TF-ThM1, **32**
McIntyre, P.C.: EM-TuA7, **16**
McKnight, T.E.: TF2+EM-WeA9, 29
Mebarki, B.: EM-MoM3, 1
Mehl, M.J.: GR+EM-TuM4, 14
Mejia, J.I.: EM-ThP3, **43**; EM-ThP4, 43; TC+AS+EM-ThM11, 35
Melechko, A.V.: NS+EM-MoM10, 4; TF2+EM-WeA9, 29
Melitz, W.: EM-MoM1, **1**; EM-TuA4, 16
Meunier, V.: ET+EM+NS+GR-TuM2, 12
Meyer, R.: SS-FrM5, 53
Meyerbröker, N.: TF+EM+SS-ThA6, **41**
Miao, X.: GR+MS+EM-FrM6, 51
Michallon, P.: TF1+EM-WeA2, 27
Miller, D.: TF1+EM-WeA9, 28
Miller, S.: EM1-MoA10, **7**
Mills, M.J.: NS+EM-MoM2, 3
Mishra, U.K.: NS+EM-MoM6, 4
Mitchel, W.C.: GR+MS+EM-FrM7, 51
Miyoshi, J.: EM-ThP5, 43; EM-ThP6, **43**
Molas, G.: EM2-MoA3, **8**
Molis, S.: EM-WeM9, 21
Mordi, G.: GR-TuA7, 18
Morrow, T.: NS+EM-MoM8, 4
Mosbacker, H.L.: EM-WeA1, 25
Motyka, M.A.: EL+AS+EM+MS+PS+TF-ThA10, **38**
Mou, S.: GR+MS+EM-FrM7, **51**
Mukherjee, S.: GR+MS+EM-FrM11, **52**
Müller, P.: TF2+EM-WeA3, 28
Mulvaney, S.: GR-TuA4, 18
Murali, S.: TF1+EM-WeA1, 27
Murayama, A.: EN+EM+NS-MoA1, 9
Murphy, J.W.: EM-ThP4, **43**
Muscat, A.J.: EM+TF-ThM12, 34; EM1-MoA10, 7; EM-ThP21, 46
Musin, I.R.: EN+EM+NS-WeM3, 21
Myers, R.C.: NS+EM-MoM2, 3
Myers-Ward, R.L.: EM+SS-FrM1, **49**; GR-TuA8, 18

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Nachimuthu, P.: TF1+EM-WeA1, 27
Nag, J.: EL+AS+EM+MS+PS+TF-ThA11, 38
Nagpal, P.: EN+EM+NS-MoA6, **9**
Nahor, A.: EN+EM+NS-WeM6, 22
Naik, M.: EM-MoM3, 1
Nakamura, J.: EM-TuA3, **16**; SS-FrM2, 52
Nam, T.W.: TC+AS+EM-ThM1, **34**
Narayanan, S.: TC+AS+EM-ThM9, **35**
Nasrollahi, Z.: GR+EM-TuM11, 15
Natarajarathinam, A.: TF1+EM-WeA8, **28**
Nath, D.N.: EM+SS-FrM7, 50; EM+TF-TuM12, 12; NS+EM-MoM6, **4**
Neumayer, D.: TF1+EM-WeA9, 28
Newaz, A.K.M.: EM-WeA11, 26
Ng, A.: EM+TF-ThM12, 34
Ng, H.W.: EM-ThP23, 46
Nguyen, S.: EM-WeM3, 20
Nguyen, V.: EM-MoM3, 1
Nikolenko, A.S.: EM-ThP25, 47
Nikonov, S.: EM-WeM2, 20
Noh, J.: TC+EM+NS-ThA6, **39**
Noh, J.H.: TC+EM+NS-ThA6, 39
Nomura, K.: TC+EM+NS-ThA10, 40; TC+EM+NS-ThA3, 39; TC+EM+NS-ThA9, 39
Nordell, B.J.: EM-WeM6, **20**
Nyakiti, L.O.: EM+SS-FrM1, 49; GR+MS+EM-FrM3, 51; GR-TuA8, 18

— O —

Ogieglo, W.: EL+AS+EM+MS+PS+TF-ThA9, 38
Oh, J.P.: SS-FrM2, **52**
Oh, S.: EM-ThP17, **45**
Oh, Y.: NS+EM-MoM5, 4
Ohno, Y.: EN+EM+NS-MoA1, 9; GR+MS+EM-FrM8, 51; GR+MS+EM-FrM9, 51
Oldham, C.J.: EM1-MoA9, 7
Oleynik, I.I.: SS-FrM10, 53
Oshima, A.: TF1+EM-WeM6, 24
Oshiyama, A.: EM-ThP9, 44

— P —

Palmstrøm, C.J.: EM+SS-FrM2, 49
Pan, M.H.: ET+EM+NS+GR-TuM2, **12**
Pan, X.: EN+EM+NS-MoA9, 10
Pangan-Okimoto, K.: EM-WeA7, **25**
Pannier, A.K.: EL+AS+EM+MS+PS+TF-ThM5, 31
Pantelides, S.T.: EM-WeA10, 26; EM-WeA11, 26; EM-WeA8, 25; EM-WeA9, 26
Papaconstantopoulos, D.A.: GR+EM-TuM4, **14**
Paquette, M.M.: EM-WeM6, 20
Park, J.H.: GR+MS+EM-FrM7, 51
Park, P.S.: NS+EM-MoM6, 4
Parks, C.: EM-WeM9, 21
Parsons, G.N.: EM1-MoA9, 7; TF1+EM-WeM4, 23
Paskiewicz, D.M.: TF2+EM-WeA11, **30**
Paskova, T.: EM1-MoA2, 6
Pasquale, F.: EM1-MoA8, **7**
Pearce, R.C.: TF2+EM-WeA9, **29**
Pederson, M.R.: GR+EM-TuM4, 14
Peixoto, T.: EM+TF-ThM3, 32
Pelucchi, E.: EM+TF-TuM4, 11
Pender, J.: EM-MoM3, 1
Peng, W.N.: ET+EM+NS+GR-TuM5, **13**
Perera, A.G.U.: EM1-MoA4, 6; EM-ThP10, 44; EM-ThP11, 44
Petz, C.: TF2+EM-WeA7, **29**
Pham, C.D.: TF1+EM-WeA7, **27**
Phillips, J.: EN+EM+NS-MoA9, 10
Phillips, P.J.: NS+EM-MoM2, 3
Pi, T.W.: EM+TF-TuM9, 12
Piel, J.P.: EL+AS+EM+MS+PS+TF-FrM7, 49; EL+AS+EM+MS+PS+TF-ThM10, 32
Pirkle, A.: GR-TuA9, 18
Plaisant, M.: EN+EM+NS-MoA8, **9**

Podraza, N.J.: EL+AS+EM+MS+PS+TF-ThA10, 38; EL+AS+EM+MS+PS+TF-ThA3, **37**
Pohl, K.: SS-FrM9, 53
Pookpanratana, S.: TF+EM+SS-ThA9, **41**
Pop, E.: GR-TuA12, 19
Porter, L.: EM1-MoA2, 6; TC+AS+EM-ThM9, 35; TC+EM+NS-ThA4, 39
Potash, R.A.: TC+EM+NS-ThA4, 39
Pourtois, G.: EM-TuA4, 16
Preble, E.A.: EM1-MoA2, 6
Puzyrev, Y.S.: EM-WeA10, **26**; EM-WeA9, 26

— Q —

Qin, S.: ET+EM+NS+GR-TuM1, 12; ET+EM+NS+GR-TuM6, **13**
Quaresima, C.: SS-FrM11, 53
Quevedo-Lopez, M.A.: EM-ThP3, 43; EM-ThP4, 43; TC+AS+EM-ThM11, **35**

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Rack, P.D.: EM-ThP19, 46; NS+EM-MoM10, 4; TC+EM+NS-ThA6, 39; TF2+EM-WeA4, 29
Radtke, C.: EM-ThP5, 43
Rajachidambaram, J.S.: TF1+EM-WeA1, 27
Rajan, S.: EM+SS-FrM7, 50; EM+TF-TuM12, 12; NS+EM-MoM6, 4
Ralph, D.C.: GR+EM-TuM9, 15
Ranjan, V.: EL+AS+EM+MS+PS+TF-ThA4, 37
Raoux, S.: TF1+EM-WeA9, 28
Rauch, S.: EL+AS+EM+MS+PS+TF-ThM3, **31**
Rayner, G.B.: TC+AS+EM-ThM6, 35
Reed, R.A.: EM-WeA11, 26; EM-WeA8, 25
Reshchikov, M.A.: EM1-MoA3, 6
Restaino, D.: EM-WeM9, 21
Richter, C.A.: TF+EM+SS-ThA9, 41
Richter, L.J.: EL+AS+EM+MS+PS+TF-ThM9, **32**
Ringel, S.A.: EM-WeA3, 25
Ritz, E.: TC+AS+EM-ThM6, **35**
Ro, H.W.: EM-MoM5, 1
Roberts, N.A.: TF2+EM-WeA4, 29
Robinson, J.T.: GR+MS+EM-FrM10, 52; GR+MS+EM-FrM3, 51; GR-TuA4, 18
Rodenhausen, K.B.: EL+AS+EM+MS+PS+TF-ThM5, **31**; EL+AS+EM+MS+PS+TF-ThM6, 32
Rodwell, M.J.W.: EM-MoM2, 1
Rosei, F.: TF+EM+SS-ThA3, 40
Rosenberg, R.A.: EM+SS-FrM11, 50; EM-WeA4, **25**
Rothwell, S.: GR-TuA11, **19**
Rowe, J.E.: EM+SS-FrM9, **50**
Roy, T.: EM-WeA9, 26
Royer, J.: EM+TF-ThM6, **33**
Ruoff, R.S.: GR-TuA9, 18
Ruzic, D.N.: TC+AS+EM-ThM6, 35
Ryan, E.T.: EM-WeM3, 20; EM-WeM9, 21

— S —

Sa'ar, A.: EN+EM+NS-WeM6, 22
Sachan, R.: EM-ThP19, 46
Saito, N.: EM-ThP20, 46
Saito, Y.: SS-FrM2, 52
Salas-Villasenor, A.: EM-ThP3, 43; TC+AS+EM-ThM11, 35
Samatova, N.: NS+EM-MoM10, 4
Samukawa, S.: EN+EM+NS-MoA1, 9
Sanchez-Martinez, A.: EM-TuA12, **17**
Sanghavi, S.P.: TF1+EM-WeA1, 27
Sasaki, T.: TC+AS+EM-ThM2, 34
Savage, D.E.: ET+EM+NS+GR-TuM5, 13; TF2+EM-WeA11, 30
Sawant, R.: TF1+EM-WeA9, 28
Schaff, W.J.: EL+AS+EM+MS+PS+TF-FrM3, 48
Schmidt, D.: EL+AS+EM+MS+PS+TF-FrM4, **48**; EL+AS+EM+MS+PS+TF-FrM5, 48; EL+AS+EM+MS+PS+TF-ThA8, 38; EL+AS+EM+MS+PS+TF-ThM5, 31
Schoche, S.: GR+EM-TuM6, 14
Schöche, S.: EL+AS+EM+MS+PS+TF-FrM3, **48**
Schreiber, D.K.: EM1-MoA2, 6
Schrimpf, R.D.: EM-WeA11, 26; EM-WeA8, 25; EM-WeA9, 26
Schubert, E.: EL+AS+EM+MS+PS+TF-FrM4, 48; EL+AS+EM+MS+PS+TF-FrM5, 48; EL+AS+EM+MS+PS+TF-ThA8, 38
Schubert, M.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM4, 48; EL+AS+EM+MS+PS+TF-FrM5, 48; EL+AS+EM+MS+PS+TF-ThA8, **38**; EL+AS+EM+MS+PS+TF-ThM5, 31; EL+AS+EM+MS+PS+TF-ThM6, 32; GR+EM-TuM6, 14
Schuette, M.: EM1-MoA1, 6
Schultz, B.D.: EM+SS-FrM2, **49**
Scott, S.: ET+EM+NS+GR-TuM5, 13
Seabaugh, A.: EM-MoM8, **2**
Seebauer, E.G.: EM-WeA7, 25
Senevirathna, I.: EM1-MoA4, 6
Senevirathna, M.K.I.: EM-ThP10, 44; EM-ThP11, **44**; EM-ThP13, 45
Sha, X.W.: GR+EM-TuM4, 14
Shearer, J.C.: TF2+EM-WeA8, **29**
Sheehan, P.E.: GR-TuA4, 18
Shelby, R.M.: TF1+EM-WeA9, 28
Shen, G.: EN+EM+NS-WeM12, 22
Shen, J.: EM-MoM1, 1
Shen, X.: EM-WeA8, **25**
Shi, J.: EL+AS+EM+MS+PS+TF-FrM3, 48
Shi, S.-F.: GR+EM-TuM9, **15**
Shi, Z.: EM+TF-ThM5, 33
Shibata, T.: TC+AS+EM-ThM2, 34
Shin, J.H.: EM-ThP18, 45
Shin, N.: EN+EM+NS-WeM3, 21
Shrestha, P.R.: EM-TuA11, **17**
Shutthanandan, V.: TF1+EM-WeA1, 27
Silva, A.R.: EM-ThP5, 43; EM-ThP6, 43
Sim, J.H.: EM-MoM5, 1
Simpson, M.L.: TF2+EM-WeA9, 29
Singh, K.A.: TC+EM+NS-ThA4, 39
Sioncke, S.: EM-TuA4, 16
Sivaram, S.: EN+EM+NS-MoA7, **9**; EN+EM+NS-WeM3, 21
Skomski, R.: EL+AS+EM+MS+PS+TF-FrM5, 48
Smith, N.J.: EN+EM+NS-WeM5, **22**
Sofue, Y.: GR+MS+EM-FrM8, **51**
Soles, C.L.: EM-MoM5, 1
Song, J.J.: EM-WeA1, 25
Sonnet, A.M.: EM+TF-TuM4, 11
Sopinskyy, M.V.: EM-ThP25, 47
Sowa, M.J.: TF1+EM-WeM5, **23**
Steigerwald, A.D.: EM-ThP8, 44
Stoltenberg, R.M.: TF2+EM-WeA10, 30
Strelchuk, V.V.: EM-ThP25, 47
Stroscio, J.A.: GR-TuA2, 17
Sumant, A.V.: GR-TuA10, **19**
Sumi, R.: EM-ThP20, **46**
Sun, D.: SS-FrM1, **52**
Sun, K.: NS+EM-MoM8, 4
Sun, Z.: EM-WeM9, 21
Sung, M.M.: TF1+EM-WeM1, **23**
Svensson, B.: EM-WeA1, 25
Sweet, W.: EM1-MoA9, 7

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Tabares, G.: EM-WeA3, 25
Takahashi, H.: EM-ThP8, 44
Takai, O.: EM-ThP20, 46
Takeuchi, N.: EM-ThP1, 43
Tamura, M.: EM-TuA3, 16
Tanner, D.B.: GR+EM-TuM11, 15
Tanto, B.: TF2+EM-WeA11, 30
Tapily, K.N.: EM+TF-TuM6, 11
Tarrio, C.: EL+AS+EM+MS+PS+TF-ThM9, 32
Tchakhalian, J.: EM-WeA4, 25
Temple, D.: EM1-MoA11, 7; EN+EM+NS-MoA3, 9
Terlinden, N.M.: EM+TF-TuM11, **12**
Tetlak, S.: GR+MS+EM-FrM7, 51
Thevuthasan, S.: TF1+EM-WeA1, 27
Thibeault, B.: EM-MoM2, 1
Thissen, P.: EM+TF-ThM3, **32**
Thomas, K.: EM+TF-TuM4, 11
Thompson, C.V.: TF2+EM-WeA1, **28**
Thoms, B.D.: EM-ThP14, **45**; EM-ThP15, 45
Tiwald, T.E.: EL+AS+EM+MS+PS+TF-FrM1, 48
Toker, G.: EN+EM+NS-WeM6, 22
Tolk, N.H.: EM-ThP8, 44
Tongay, S.: GR+EM-TuM11, 15; GR+MS+EM-FrM6, **51**
Tosado, J.: GR-TuA4, 18
Trelles, J.-P.: EM-WeM2, 20
Trenary, M.: SS-FrM5, 53
Trogler, W.: EM+TF-ThM6, 33
Tsai, D.P.: EM-ThP12, 45
Tucker, R.T.: TC+AS+EM-ThM5, 35
Tuomisto, F.: EM-WeA1, 25
Tweedie, J.S.: EM1-MoA4, 6; EM-ThP13, 45; EM-ThP15, 45

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Uher, C.: EM-WeA12, 27
Uhl, A.: SS-FrM5, 53
Ulloa, S.: EM-ThP1, 43
Uppireddi, K.: EL+AS+EM+MS+PS+TF-ThA6, **37**

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Vallee, C.: EM2-MoA9, 8
Vallée, C.: TF1+EM-WeA2, 27
Vamala, C.: GR+EM-TuM6, 14
van de Sanden, M.C.M.: EM+TF-TuM11, 12; GR+EM-TuM5, 14
Varga, K.: ET+EM+SS-MoM11, 3
Varga, T.: TF1+EM-WeA1, 27
Vasen, T.: EM-MoM8, 2
Vasenkov, A.W.: TF2+EM-WeA9, 29
Vazquez-Lepe, M.O.: EM-TuA12, 17
Vega, A.: EM+TF-ThM3, 32
Veligura, L.I.: EM-ThP25, 47
Venugopal, A.: GR-TuA9, 18
Vilan, A.: EM+TF-ThM11, **33**
Virwani, K.: EM-WeM9, 21
Vlasenko, N.A.: EM-ThP25, **47**
Vogel, E.M.: EM+TF-TuM2, 11; EM+TF-TuM4, **11**; EM-TuA9, 16; GR-TuA9, 18
Vogt, P.: SS-FrM11, 53
von Wenckstern, H.: TC+EM+NS-ThA1, **39**

— W —

Wager, J.F.: TC+EM+NS-ThA7, **39**
Walczyk, Ch.: TF1+EM-WeA3, 27
Walczyk, D.: TF1+EM-WeA3, 27
Walker, A.V.: EM+TF-ThM5, **33**
Wallace, R.M.: EM+TF-TuM2, 11; EM+TF-TuM3, 11; EM-MoM8, 2; EM-TuA10, 17; EM-TuA9, 16; GR-TuA9, 18
Walsh, M.A.: TF+EM+SS-ThA9, 41
Walton, S.G.: GR-TuA4, 18
Wang, B.: EM-WeA10, 26
Wang, E.: ET+EM+NS+GR-TuM6, 13
Wang, H.: EL+AS+EM+MS+PS+TF-ThM5, 31; EL+AS+EM+MS+PS+TF-ThM6, 32
Wang, K.L.: EM2-MoA1, **8**
Wang, M.: EM-ThP23, 46
Wang, W.: ET+EM+NS+GR-TuM6, 13
Wang, X.-Y.: EN+EM+NS-MoA1, 9
Warnick, K.H.: EM-WeA9, **26**
Washington, J.S.: TF1+EM-WeA9, 28
Watanabe, H.: EM-ThP20, 46
Watkins, S.: ET+EM+NS+GR-TuM12, 14
Weber, J.W.: EL+AS+EM+MS+PS+TF-ThA7, 37; GR+EM-TuM5, **14**
Weber, M.J.: EL+AS+EM+MS+PS+TF-ThA7, 37
Wei, S.-H.: TC+AS+EM-ThM3, **35**
Weiss, S.M.: EM-WeA11, 26
Weitering, H.H.: ET+EM+SS-MoM5, **3**
Weller, R.A.: EM-WeA11, 26
Wells, I.B.: EM+TF-TuM6, 11
Wenger, Ch.: TF1+EM-WeA3, **27**
Wernersson, L.-E.: NS+EM-MoM3, **4**

Wheeler, V.D.: EM+SS-FrM1, 49; GR+MS+EM-FrM3, 51; GR-TuA8, **18**
Wilbert, S.: EN+EM+NS-WeM12, 22
Williams, N.: TF+EM+SS-ThA4, 41
Wistey, M.: EM-MoM8, 2
Won, B.: NS+EM-MoM8, 4
Wood, J.D.: GR-TuA12, **19**
Woollam, J.A.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, 48
Wormeester, H.: EL+AS+EM+MS+PS+TF-ThA9, **38**
Wu, J.: GR+EM-TuM10, 15
Wu, Y.: TF2+EM-WeA4, **29**

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Xia, L.Q.: EM-MoM3, 1
Xiang, T.: ET+EM+SS-MoM10, 3
Xiao, K.: EM1-MoA6, 7
Xiao, Z.: EM-ThP2, 43
Xing, H.: EM-MoM8, 2
Xiu, F.: EM2-MoA1, 8
Xu, X.: GR+EM-TuM9, 15

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Yaffe, O.: EM+TF-ThM11, 33
Yamamoto, N.: TC+AS+EM-ThM2, 34
Yamamoto, T.: TC+AS+EM-ThM2, 34
Yamashiro, Y.: GR+MS+EM-FrM9, **51**
Yan, L.: EL+AS+EM+MS+PS+TF-ThA6, 37
Yang, D.: TF2+EM-WeA7, 29
Yang, J.: EM+TF-ThM5, 33; EN+EM+NS-WeM1, 21; NS+EM-MoM2, 3
Ye, J.: TF2+EM-WeA1, 28
Yeh, B.: TC+EM+NS-ThA7, 39
Yin, W.: EM1-MoA6, 7
Yitamben, E.: EM+SS-FrM11, **50**
Yitzchaik, S.: EN+EM+NS-WeM6, 22
Yoon, D.Y.: EM-MoM5, **1**
Yoshimura, T.: TF1+EM-WeM6, **24**
Yu, J.: GR-TuA10, 19

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Zettsu, N.: EM-ThP20, 46
Zhang, B.: TC+EM+NS-ThA11, **40**
Zhang, E.X.: EM-WeA11, **26**
Zhang, J.: EM-WeA1, 25
Zhang, M.: EM1-MoA2, 6
Zhang, Q.: EM-MoM8, 2
Zhang, X.-G.: ET+EM+SS-MoM10, **3**
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