

Electronic Materials and Photonics

Room 102A - Session EM+NS+PS+SS+TF-MoM

Growth and Devices Technology of Group III-Nitrides

Moderators: Nikolaus Dietz, Georgia State University, Shalini Gupta, Northrop Grumman ES

8:20am **EM+NS+PS+SS+TF-MoM1 Development of AlGaIn based UV Laser Diodes**, *Ronny Kirste*, Adroit Materials; *B. Sakar, A. Franke*, NCSU; *J. Tweedie*, Adroit Materials; *Z. Bryan, I. Bryan*, NCSU; *S. Mita*, Adroit Materials; *R. Collazo, Z. Sitar*, NCSU

INVITED

UV laser diodes are widely desired for many important applications such as chemical and biological sensing, non-line of sight communications, and DNA tagging. Design and fabrication of AlGaIn based laser diodes is the most promising pathway for next generation UV lasers but challenges for these devices are many including low n- and p-conductivity, absorbing injection layers, and non-ohmic contacts. Here, we present recent advances in the growth and fabrications of UV laser diodes. The presentation will cover the most important steps that are necessary to achieve electrically injected UV laser diodes. These include: AlGaIn epitaxy, doping, fabrication, and design.

As an advancement over most existing approaches, we pursue the growth of our device structures on single crystalline AlN substrates which allows for low dislocation densities $< 10^4$ cm⁻². Any such device fabrication is started with the growth of an AlN homoepitaxial layer. It is demonstrated that this epitaxial layer can be grown with a dislocation density that follows that of the substrate and no interface between layer and substrate is observed in TEM, which indicates true homoepitaxy. Subsequent growth of AlGaIn layers with Al content ranging 50-85% is shown to be pseudomorphic. An excellent control of the AlGaIn surface morphology is demonstrated using a supersaturation scheme and bilayer steps as needed for highly efficient MQWs are achieved. MQWs for emission at wavelengths ranging 240-280 nm are discussed and optically pumped lasing in this region is demonstrated. The chosen approach to grow on AlN is validated by realizing MQWs with an IQE exceeding 90%. In order to achieve electrically injected UV lasing, Al-rich AlGaIn is doped and free electron concentrations for the n-cladding with 80% Al-content is shown to be around 8×10^{18} cm⁻³. In contrast, p-doping of AlGaIn is much more challenging because of the high activation energy of the Mg acceptor. Consequently, achievable free hole concentration and conductivity of the p-cladding are low. We discuss how these epitaxial layers can be used for realizing laser diodes. Experimental work is supported by simulations and used to direct the UV laser design. Finally, we present electrical data and electroluminescence spectra from fully fabricated diodes and discuss the future challenges that need to be addressed to demonstrate the first electrically injected UV laser diode.

9:00am **EM+NS+PS+SS+TF-MoM3 Low-Temperature PA-ALD Growth Technology for Group III-Nitride Nano-heterostructures and their (Opto)Electronic Device Applications**, *Necmi Biyikli, A. Haider, S. Kizir, P. Deminskyi, M. Yilmaz, S. Bolat, A. Celebioglu, A.K. Okyay, T. Uyar*, Bilkent University, Turkey; *F. Buyukserin, S. Altuntas*, TOBB University of Economics and Technology, Turkey; *J. Yilmaz, K. Khaled*, Turgut Ozal University, Turkey

INVITED

Being initially developed for an entire different area of use, atomic layer deposition (ALD) became a widespread tool to grow functional films and conformal ultra-thin coatings for numerous applications. Based on self-limiting surface reactions, ALD enabled the low-temperature growth of various materials including dielectrics, semiconductors, and metals. Featuring the capability to deposit wafer-scale uniform semiconductor films at relatively low-temperatures with sub-monolayer thickness control and ultimate conformality makes ALD attractive for the semiconductor community. Towards this end, precursors and growth recipes are developed to deposit crystalline thin films for compound and elemental semiconductors. Conventional thermal ALD techniques as well as plasma-assisted and radical-enhanced ALD techniques have been exploited to achieve decent film quality compatible with device applications.

In this presentation, we give an overview of our research efforts on plasma-assisted ALD-based nanoscale semiconductor research focusing on III-nitrides. We have combined our low-temperature thin-film growth recipes with various nanoscale templates and exploited the conformality feature of ALD technique to fabricate nitride nanostructures. Electrospun polymeric nanofibers have been used to produce flexible polymer/III-nitride core-

shell structures which might be used for flexible optoelectronics. In addition, hollow-core multi-shell III-nitride nano-heterostructures are demonstrated as well. Anodized alumina (AAO) templates were utilized to fabricate large-area ordered III-nitride nanostructures including radial heterostructures. Extensive growth and fabrication recipe development and materials characterization details will be presented.

The synthesized III-nitride nanoscale semiconductor materials might find applications in a vast amount of applications including physical and chemical sensing, piezo-electric energy harvesting, photocatalysis, nanoscale and flexible (opto)electronics. As proof-of-principle device demonstrations, we have shown nanofibrous GaN/InN-based photocatalysis, GaN/InN-based chemical (gas) sensing, and nanoscale GaN-based UV photodetectors.

9:40am **EM+NS+PS+SS+TF-MoM5 Structural Qualities of GaN Grown on AlN Buffer Layer by MEPA-MOCVD**, *Daniel Seidlitz, I. Senevirathna, A. Fali, Y. Abate, N. Dietz*, Georgia State University; *A. Hoffmann*, Technical University Berlin, Germany

This study focuses on the influence of Aluminum nitride (AlN) buffer layers on the structural and optoelectronic properties of subsequent overgrown Gallium nitride (GaN) layers, using Migration Enhanced Plasma-Assisted Metal Organic Chemical Vapor Deposition (MEPA-MOCVD).

One challenge in group-III nitride growth is the lattice mismatch between the substrate (e.g. sapphire (Al₂O₃), silicon or silicon carbide) and the group III-Nitride layer as for example GaN. Lattice mismatch imposes compressive strain/stress and influences the crystal quality of subsequent grown group-III nitrides. Inserting an AlN interlayer between the sapphire substrate and the GaN epilayer, transitions the oxygen surface chemistry to a nitrogen surface chemistry, separating surface chemistry related defects from lattice mismatch induced defects, which leads to an improved crystalline quality of the overgrowing GaN layer.

All group III-Nitride layers are grown on sapphire substrates using MEPA-MOCVD. The system design allows the growth of GaN at lower temperatures by using plasma activated nitrogen species (N*/NH*/NH_x*) as nitrogen precursor, which are generated by a radio-frequency hollow cathode plasma source (MEAgrow™) scalable from 20W up to 600W. The tunable nitrogen plasma source enables to control the kinetic energies of the active nitrogen species in the afterglow region to be directed at the growth surface, where they interact with metalorganic (MO) precursors. The growth process parameter set includes: reactor pressure, growth temperature, pulsed injection of MO- and nitrogen plasma fluxes, plasma species and their energies.

The structural properties of the AlN buffer layers (e.g. local ordering, grain size, surface topography) are analyzed by Atomic Force Microscopy (AFM) and Raman spectroscopy. The film thickness and optoelectronic properties of the AlN and GaN layers are studied Fourier Transform infrared (FTIR) and reflectance spectroscopy. Results are presented on the structural and optoelectronic properties of the GaN layers as function of the process parameters and the properties of the underlying AlN buffer layer.

10:00am **EM+NS+PS+SS+TF-MoM6 Optical and Electrical Characteristics of Gamma-ray Irradiated AlGaIn/GaN Heterostructures**, *MinPrasad Khanal, B. Ozden, K. Kim, S. Uprety, V. Mirkhani, L. Shen, K. Yapabandara, A.C. Ahyi, M. Park*, Auburn University

AlGaIn/GaN high electron mobility transistors (HEMTs) show their potential immunity toward high energy radiation related damages, making them promising candidates for the radiation hard electronics. The degradation in performance of these devices under radiation exposed environment might be due to different possible effects in the device structure such as strain/stress, generation of dislocation, carrier removal and reduction in two-dimensional-electron-gas (2DEG) concentration. The AlGaIn/GaN epi structures grown on 6 inch Si wafer were used and irradiated with 120 MRad doses of gamma-ray produced from ⁶⁰Co source. The semi-transparent (with 10-15 nm thickness) Ni Schottky diodes and circular HEMT devices were fabricated using un-irradiated and gamma-ray irradiated AlGaIn/GaN epi structures. In the case of HEMT devices, Ti/Al/Ni (30/180/40 nm thickness) for the ohmic contact and Ir (15 nm thickness) for the gate contact formation were deposited using dc magnetron sputtering system. Spectroscopic photo current-voltage (IV) measurements both with sub-band gap and above band-gap illumination, micro-Raman/photoluminescence spectroscopy, and transistor characterizations were performed. The spectroscopic photo IV measurements were carried out by applying the variable wavelength ultra-violet (UV) and visible light from Xenon lamp source under reverse bias condition. Sub-bandgap illumination (800 nm-400 nm) provided the information about sub-

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bandgap energy levels of defects by relating the change in photocurrent level in response to the applied light spectrum. On the other hand, above bandgap illumination (280 nm-400 nm) utilizes the fact that the penetration depth of a light varies as a function of wavelength. The result showed reduction in photocurrent on the gamma-ray irradiated samples in comparison to the un-irradiated samples, revealing the possibility of creation of extra defects, and hence, decreasing the carrier concentration in the 2DEG. Micro-Raman and photoluminescence (PL) spectroscopic analysis on both the samples were also performed and the results show no substantial change in their spectra, supporting the conclusion from previous scientific reports of radiation resistance of the HEMTs on their bulk structure level. Decrease in drain current and transconductance were observed from the transistor IV measurements, indicating a possible reduction in carrier concentration. It can be concluded that the reduction on photocurrent, drain current level and transconductance after the gamma-ray irradiation are due to the possible creation of some extra defects and decrease of carrier concentration on 2DEG channel.

10:40am **EM+NS+PS+SS+TF-MoM8 Seeded Regrowth for Production of AlN and GaN Substrates by HVPE**, *Jacob Leach, K. Udvary, G. Dodson, K. Gentry, P. Quayle, T. Schneider, H. Splawn, K. Evans*, Kyma Technologies, Inc. **INVITED**

Freestanding GaN and freestanding AlN remain the substrates of choice for the highest performing vertical high voltage switching devices (>1200V) and UV optoelectronics, respectively. However, the cost of these substrates remains high, availability remains low, and the crystalline quality of these substrates varies depending on the growth technique employed. In particular, the electrical quality of GaN substrates and the UV transparency of AlN substrates depend on the specific growth conditions utilized and it remains a challenge to maintain high crystalline quality while simultaneously realizing high electrical quality or UV transparency. We proposed the use of hydride vapor phase epitaxy (HVPE) as a cloning technique to replicate the high crystalline quality of existing solvothermally grown GaN or physical vapor transport (PVT) grown AlN substrates while maintaining high electrical and optical quality. In this talk, we report Kyma's recent results in the use of the HVPE replication technique for realizing both AlN and GaN substrates.

Electronic Materials and Photonics Room 102B - Session EM-MoM

Advances in Photonics

Moderators: Michael Filler, Georgia Institute of Technology, Daniel Wasserman, University of Texas at Austin

8:20am **EM-MoM1 Optical Materials for Far-IR Reststrahlen Optics**, *Daniel Wasserman*, University of Texas at Austin **INVITED**

The mid-infrared (mid-IR) spectral range (3-15 μ m) has become a burgeoning and dynamic field of research both for fundamental exploration as well as for more applied research in health and the environment, security and defense, communication, and sensing. New optoelectronic devices, in particular sources and detectors, have allowed for the rapid growth of the mid-IR, and the development of a range of optical systems for a variety of applications. At the same time, the areas of plasmonics and metamaterials have experienced explosive growth over the past decade, fueled in part by rapid developments in fabrication, characterization, computational science, and theory. These have become increasingly important in the mid-IR, where sub-wavelength confinement and manipulation of light offer the potential for new types of optical materials and structures for integration with the ever-improving mid-IR optoelectronic devices. Yet all of the above developments are, in some ways, spectrally limited to wavelengths <20 μ m, due largely to the strong absorption of light in semiconductors at, or near, to optical phonon energies. The strong absorption of optical phonons results in a far-IR wavelength band, which for simplicity sake we refer to as the Reststrahlen region, from 20-60 μ m where little to no optical and optoelectronic infrastructure exists.

In this talk, I will discuss our group's recent work developing novel optoelectronic, plasmonic, and phononic devices and structures for far-IR applications. I will present far-IR perfect absorber structures and discuss the potential and limitations of selective thermal emitters in the far-IR. In addition, I will demonstrate how phononic materials can behave similarly to plasmonic materials in a limited spectral band near the longitudinal optical (LO) phonon, showing coupling to both propagating and localized

surface phonon modes. I will also show how careful control of doping in semiconductor epilayers offers some wavelength flexibility in designing materials capable of supporting hybrid plasmonic/phononic modes. Finally, I will discuss the opportunities for development of far-IR optoelectronic devices capable of serving as light sources at far-IR wavelengths. In all, I hope to present a picture of the far-IR as a new optical frontier where we can not only apply the lessons from shorter wavelength photonic structures, but also explore exciting new approaches to the development of Reststrahlen band optical infrastructure.

9:00am **EM-MoM3 Mid-IR to THz Nanophotonics: Realizing Alternative Polaritonic Materials**, *Joshua Caldwell*, US Naval Research Laboratory **INVITED**

The field of nanophotonics is based on the ability to confine light to sub-diffractive dimensions. Up until recently, research in this field has been primarily focused on the use of plasmonic metals. However, the high optical losses inherent in such metal-based surface plasmon materials has led to an ever-expanding effort to identify, low-loss alternative materials capable of supporting sub-diffractive confinement. Beyond this, the limited availability of high efficiency optical sources, refractive and compact optics in the mid-infrared to THz spectral regions make nanophotonic advancements imperative. One highly promising alternative are polar dielectric crystals whereby sub-diffraction confinement of light can be achieved through the stimulation of surface *phonon* polaritons within an all-dielectric, and thus low loss material system. Due to the wide array of high quality crystalline species and varied crystal structures, a wealth of unanticipated optical properties have recently been reported. However, these materials also have some limitations, primarily in the limited spectral bandwidth of operation for any given material. This talk will discuss recent advancements to improve the material lifetime and to induce additional functionality through isotopic enrichment and hybridization of polaritonic modes for realizing low-loss, actively tunable/modulated nanophotonic materials.

9:40am **EM-MoM5 Time-Resolved Optical Studies on Reflection and Transmission of Niobium Dioxide Thin Films**, *Melissa Beebe**, College of William and Mary; *J.M. Klopff*, Helmholtz-Zentrum Dresden-Rossendorf, Germany; *D. Lahneman, Z. Xing, M.M. Qazilbash*, College of William and Mary; *Y. Wang, S. Kittiwatanakul, J. Lu, S.A. Wolf*, University of Virginia; *R.A. Lukaszew*, College of William and Mary

Niobium dioxide (NbO₂) is a highly correlated material that, like vanadium dioxide (VO₂), exhibits a first-order insulator-to-metal transition (IMT) at a material-dependent critical temperature, accompanied by a structural transformation from monoclinic to rutile. The nature of the IMT in VO₂ has been discussed at length, while fewer studies have been carried out on NbO₂. Here, we present ultrafast pump-probe studies comparing reflection measurements to the first ultrafast transient transmission measurements of this optically-induced transition in NbO₂ thin films, as well as compare these studies to similar ones carried out on VO₂ thin films.

10:00am **EM-MoM6 Fabrication of Nanosphere-Based Disordered Coatings for Radiative Cooling under Direct Sunlight**, *Sarun Atiganyanun, S.E. Han, S.M. Han*, University of New Mexico

In this study, we investigate a facile fabrication of coatings made of silica nanosphere-based disordered structures via evaporation coating and air atomization coating. In both methods, silica nanospheres with a diameter of ~900 nm are dispersed in a water or methanol solution, where the sphere size can be further tuned. The colloidal stability is then disrupted by dissolving salt in the solution. In the evaporation coating, the bulk solution is confined in a substrate and is let to evaporate. In the atomization coating, the solution is atomized by a spray nozzle, and resulting droplets are deposited onto a substrate. Scanning electron microscopy images and subsequent autocorrelation analyses show that the resulting structures are disordered without short- or long-range order. Transmission measurement also indicates that the structures have a short transport photon mean free path of approximately 4-8 μ m. These results suggest strong photon scattering properties in the visible region, while providing a strong emission window in 8 to 13 μ m range. Such films would enable potential applications in radiative cooling. To investigate this aspect, a computational model is used to calculate the cooling power of the coatings under direct sunlight. The model predicts that the disordered coating with 200 μ m thickness has a cooling power of ~250 W/m² at 27°C and could reduce the temperature of the sample under a direct sunlight by approximately 37°C

* TFD James Harper Award Finalist

below the ambient temperature. We will further discuss our experimental measurements in this presentation.

10:40am **EM-MoM8 Symmetry-Breaking Nanostructures for Light Trapping in Thin Crystalline Silicon Solar Cells**, *Seok Jun Han, S. Ghosh, O.K. Abudayyeh, B.R. Hoard, E.C. Culler, J.E. Bonilla, S.M. Han, S.E. Han*, University of New Mexico

While various materials have been investigated for photovoltaics, solar cells based on crystalline silicon (c-Si) dominate the current photovoltaics market. To reduce the cost of c-Si cells, wafer manufacturing companies have produced competitively priced thin c-Si films, ranging from a few microns to tens of microns, using a kerfless process. In such thin-film c-Si cells, light absorption becomes poorer than in thick films and light trapping is crucial to increase the photovoltaic efficiency. Han *et al.* have demonstrated that, among various light-trapping schemes, symmetry breaking in photonic nanostructures can approach the Lambertian light-trapping limit very closely. However, fabricating symmetry-breaking nanostructures in a scalable, cost-effective, manufacturable manner remains elusive. Here, we introduce a new approach to systematically break the symmetry in photonic nanostructures on c-Si surface. Using our approach, we fabricate low-symmetry inverted nanopillar structures. Our method makes use of low-cost, manufacturable wet etching steps on c-Si(100) wafers without relying on expensive off-cut wafers. Our experiment and computational modeling demonstrate that the symmetry breaking can increase the Shockley-Queisser efficiency from 27.0 to 27.9% for a 10-micron-thick c-Si film. Further, our computation reveals that this improvement would increase from 28.1 to 30.0% with over-etching for a 20-micron-thick c-Si film.

11:00am **EM-MoM9 Non-thermal Plasma Synthesis of In Situ Graphene Shells on Silicon Carbide Nanoparticles**, *Devin Coleman, L. Mangolini*, University of California - Riverside

The synthesis of beta-phase silicon carbide nanoparticles exhibiting a hollow core-shell morphology is demonstrated by means of a two-step non-thermal plasma method.[1] Crystalline silicon nanoparticles are nucleated from silane precursor gas in a non-thermal plasma reactor similar to the one described in [2] and injected into a secondary methane-containing plasma reactor, where they are carbonized to form beta-phase silicon carbide nanoshells. Furthermore, at sufficiently high input power in the second plasma, a single-layer graphene coating forms around the silicon carbide particles. These findings are consistent with XRD and Raman spectra. An analytical solution of the 1D diffusion equation in spherical coordinates, as well as the lattice volume expansion from silicon to silicon carbide are used to explain the formation of the interior void. This provides an alternative to previously reported results, which invoke the nanoscale Kirkendall effect to explain the void formation by means of fast out-diffusion of the core element.[3] Further consideration of the system kinetics indicates interactions with the ionized gas leads to particle superheating, allowing for the diffusion of carbon into the silicon matrix and nucleation of beta-phase silicon carbide to occur during the short residence time of the particles in the system. This work expands upon the materials achievable by non-thermal plasma synthesis and suggests that such systems offer the capability to engineer particle morphology, as well as grow conformal 2D materials on freestanding nanoparticles.

References:

[1] Hollow silicon carbide nanoparticles from a non-thermal plasma process. D. Coleman, T. Lopez, O. Yasar-Inceoglu, and L. Mangolini. *J. Appl. Phys.* In press (2015).

[2] Silicon nanocrystal production through non-thermal plasma synthesis: a comparative study between silicon tetrachloride and silane precursors. O. Yasar-Inceoglu, T. Lopez, E. Farshihagro, and L. Mangolini, *Nanotechnology* 23, 255604 (2012).

[3] Formation of Hollow Nanocrystals Through the Nanoscale Kirkendall Effect. Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, and A. P. Alivisatos, *Science* 304, 711 (2004).

11:20am **EM-MoM10 Size and Structure Dependence of Electronic Transport Properties at Nanosized Interfaces**, *Dawn Bonnell, J. Hou*, The University of Pennsylvania

It is an accepted truism that the behavior of surfaces and interfaces is dictated by the interactions of atoms. Consequently, understanding atomic interactions at surfaces and interfaces is the foundational basis for predicting, controlling, and designing devices and processes. This is particularly relevant to devices for memory storage, sensing, and photonics

in which electrical contacts must be made at very small scales. We use an ideal system to examine the size and structure dependence of interfaces.

We report that the size dependence of electronic properties at nanosized metal-semiconducting oxide (Au nanoparticle/SrTiO₃) interfaces is significantly affected by the interface atomic structure. The properties of interfaces with two orientations are compared over size range of 20–200 nm. Three different mechanisms of size dependence occur at various size regimes. The difference in interface atomic structure leads to electronic structure differences that alter electron transfer paths. Specifically, interfaces with a higher concentration of undercoordinated Ti result in enhanced tunneling due to the presence of defect states or locally reduced tunnel barrier widths.

In the case of materials which exhibit resistive switching the observed “eight-wise” bipolar resistive hysteresis loop is modulated by trap/detrapping process. The size-dependent high resistance state is consistent with changes in both the interfacial area and Schottky properties. The low resistance state exhibits size independent resistance through the dominant fast conductive path. Detrapping requires more work for smaller interfaces due to the associated larger built-in electric field.

11:40am **EM-MoM11 Metal Nanoparticles formed in Organic Molecular Crystals: HR-TEM and HR-PES Characterisation**, *Olga Molodtsova*, DESY, Hamburg, Germany; *I.M. Aristova*, ISSP RAS, Chernogolovka, Russia; *S.V. Babenkov*, DESY, Hamburg, Germany; *V.Y. Aristov*, ISSP RAS, Chernogolovka, Russia

The evolution of the morphology and the electronic properties of the hybrid organic-inorganic systems composed of metallic nanoparticles distributed in semiconductor organic matrix (FxCuPc, x=0,4,16), as a function of nominal metal content was studied by high-resolution transmission electron microscopy and by surface- and bulk sensitive high-resolution photoelectron spectroscopy performed at different Synchrotron Radiation facilities. Using HR-TEM the images of metal nanoparticles with direct resolving of atomic planes were obtained (see Figure). In particular, by this method for some coatings the coalescence processes of nanoparticles depending on the initial mutual orientation of the nanoparticles was observed. This work supported by the RFBR Grant No. 13-02-00818 and the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211

Electronic Materials and Photonics

Room 102A - Session EM-MoA

Surface and Interface Challenges in Wide Bandgap Materials

Moderators: Charles Eddy Jr., U.S. Naval Research Laboratory, Rachael Myers-Ward, Naval Research Laboratory

1:40pm **EM-MoA1 ALD Gate Dielectrics for GaN HEMTs, Andrea Corrion, HRL Laboratories, LLC** **INVITED**

While most reported GaN high-electron mobility transistors (HEMTs) to-date have utilized a Schottky barrier gate, there is a significant need for high-performance insulated-gate devices. Gate dielectrics play a critical role in reducing gate leakage as well as increasing the forward-bias gate voltage swing in normally-off devices. Atomic layer deposition (ALD) gate dielectrics have recently generated significant interest for GaN HEMTs due to the wide variety of high-k materials available, highly controlled deposition rates and film quality, and low-temperature process compatibility. ALD Al_2O_3 in particular has been widely investigated and initial promising performance has been reported for both high-frequency RF and high-voltage power switch devices. However, significant challenges remain for the interface trap density, device reliability, and stability of the gate dielectric. This talk will review the status of ALD gate dielectrics for GaN HEMTs and on-going materials challenges, and will describe processes and device results for HRL's insulating-gate RF and power switching device technologies.

2:20pm **EM-MoA3 Advances in High-k Dielectric Integration with Ga-polar and N-polar GaN, Charles Eddy, Jr., U.S. Naval Research Laboratory; C.R. English, University of Wisconsin; V.D. Wheeler, U.S. Naval Research Laboratory; D.I. Shahin, University of Maryland College Park; N.Y. Garces, U.S. Patent & Trade Office; A. Nath, J.K. Hite, M.A. Mastro, T.J. Anderson, U.S. Naval Research Laboratory**

Gallium- and nitrogen-polar GaN surfaces are subjected to a variety of pretreatments, including oxidation, before the application of high-k dielectrics by atomic layer deposition (ALD) in order to assess their ability to produce smooth, clean and electrically high-performing dielectric semiconductor interfaces. In terms of topographical and chemical cleanliness, a pretreatment with a wet chemical piranha etch ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$) was found to be optimum for both surfaces and, additionally, $(\text{NH}_4)_2\text{S}$ is effective for N-polar surfaces. Both thermal and plasma oxidations were employed for controlled growth of native oxides. For Ga-polar surfaces, all native oxides were as smooth as pretreated surfaces, while for N-polar surfaces all native oxides are much rougher except for very short, high temperature oxidations. Thermal ALD high-k dielectrics, including Al_2O_3 , HfO_2 and ZrO_2 , were deposited on "optimally" treated surfaces. ALD Al_2O_3 films on Ga-polar surfaces are smoother for pre-treated surfaces than for as-received surfaces, whereas for N-polar surfaces the opposite is true. In general, ALD HfO_2 films on Ga-polar surfaces are rougher (0.8 nm rms) than Al_2O_3 films (0.1 nm rms), whereas for piranha treated N-polar surfaces HfO_2 films are smoother than Al_2O_3 films. ZrO_2 films are smoother than HfO_2 but rougher than Al_2O_3 films. For Ga-polar surface, capacitance-voltage measurements of simple Al_2O_3 (measured $k = 9$) capacitors show the smallest hysteresis for unintentionally oxidized surfaces (0.37 V), whereas simple HfO_2 (measured $k = 14$) capacitors show the smallest hysteresis for a thermal GaO_x at the interface (0.1 V). In both cases, the thicker the GaO_x at the interface the larger the negative threshold voltage shift – suggesting an electron trap. Calculated total trapped charges associated with the dielectrics range from $3.2 \times 10^{11} \text{ cm}^{-2}$ (for HfO_2 on thermally oxidized GaN) to $1 \times 10^{12} \text{ cm}^{-2}$ for Al_2O_3 on thermally oxidized GaN and HfO_2 on plasma oxidized GaN. Finally, the leakage current density for nearly all capacitors is $< 10^{-5} \text{ A-cm}^{-2}$ for up to a +8V bias. Interestingly, without additional GaN oxidation, ZrO_2 films present a significant positive threshold shift which could be beneficial for enhancement-mode transistor operation. Further details of ZrO_2 performance on "optimally" treated Ga-polar surfaces will also be presented.

2:40pm **EM-MoA4 Effects of Surface Cleaning and Different Metals as Schottky Contacts to Bulk and Epitaxial $\beta\text{-Ga}_2\text{O}_3$, Yao Yao, R. Gangireddy, J. Kim, Carnegie Mellon University; T. Salagaj, N. Sbrockey, G.S. Tompa, Structured Materials Industries, Inc.; K.K. Das, JBP Materials; R.F. Davis, L.M. Porter, Carnegie Mellon University**

Beta-gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) has emerged over the past few years as a promising next-generation wide bandgap semiconductor. It has a bandgap

of $\sim 4.8 \text{ eV}$ and a breakdown electric field of $\sim 8 \text{ MV/cm}$, giving it a superior figure-of-merit compared to traditional wide bandgap semiconductors like SiC and GaN. Moreover, it can be produced from the melt, and single-crystal (2-in diameter) substrates have recently become commercially available. Devices based on $\beta\text{-Ga}_2\text{O}_3$ that have so far been demonstrated include Schottky diodes, metal-semiconductor field effect transistors (MESFETs), metal-oxide-semiconductor field-effect transistors (MOSFETs), and ultra-violet (UV) photodiodes. However, since research on $\beta\text{-Ga}_2\text{O}_3$ as a wide bandgap semiconductor is in its very early stages, there is little understanding on how to control device-relevant interfaces to this material. In this work, we have investigated Schottky diodes fabricated on Sn-doped ($5 \times 10^{18} \text{ cm}^{-3}$) single-crystal Ga_2O_3 (-201) substrates and lightly doped ($\sim 10^{17} \text{ cm}^{-3}$) Ga_2O_3 (010) homoepilayers. A surface study was first performed to evaluate the effect of different surface cleaning techniques on contact performance. The surface cleaning methods consisted of (1) an organic solvent clean only (acetone and isopropanol), and an organic clean followed with a (2) HCl, (3) BOE, (4) HCl and H_2O_2 or (5) BOE and H_2O_2 . The corresponding Schottky barrier heights (SBHs) were calculated from the I - V and C - V behaviour of Ni Schottky diodes fabricated on bulk Ga_2O_3 (-201). SBHs were lowest for the organically cleaned sample, and highest for the sample treated in HCl and H_2O_2 . The latter also had the lowest leakage current in reverse bias and showed the most stable performance even after a period of several weeks after deposition. We have therefore established that organic clean followed by HCl and H_2O_2 treatment is the most effective of the cleaning methods tested. We have also investigated Schottky diodes fabricated using different Schottky metals. On the bulk Ga_2O_3 (-201) substrates, we calculated SBHs from the I - V behavior of Ir, Ni, Au and Sn to vary from ~ 1.0 – 0.7 eV in approximate correspondence with the metal workfunctions. On the lightly doped $\beta\text{-Ga}_2\text{O}_3$ (010) epilayer, preliminary measurements indicate a SBH $> 1.0 \text{ eV}$ for Ni. Electrical behavior of other metals on the (010) epilayer will also be investigated and reported in the presentation.

3:00pm **EM-MoA5 Deep Traps in Wide Bandgap Semiconductors: From GaN to beta-Ga₂O₃, Steven Ringel, A. Arehart, E. Farzana, Z. Zhang, The Ohio State University; E. Ahmadi, Y. Oshima, J. Speck, University of California at Santa Barbara** **INVITED**

Deep level defects are pervasive in wide bandgap (WBG) semiconductors such as GaN. Over the years deep levels in GaN have been extensively studied. Several states have been directly linked with device degradation mechanisms in high electron mobility transistors and there is continued exploration of defect mitigation strategies to improve reliability. At the same time, there has been intense interest on the so-called ultra-wide bandgap (UWBG) semiconductors, whose bandgaps are $> 3.4 \text{ eV}$, driven by the desire to develop devices that can sustain even higher fields, operate at higher temperatures, while maintaining good high frequency performance. Of these UWBG materials, beta-phase gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) is attracting particular interest due to its large, direct bandgap of $\sim 4.8 \text{ eV}$, the availability of n doping, the ability to create heterostructures, and the availability of native substrates to support homoepitaxial growth. This latter point is unique amongst WBG and UWBG materials.

However, compared with incumbent technologies, $\beta\text{-Ga}_2\text{O}_3$ is in its infancy, with transistors recently announced that have created excitement regarding the future of this material.[1] This presentation will build from our work on GaN and focus on basic aspects of $\beta\text{-Ga}_2\text{O}_3$: (a) the application of deep level optical and transient spectroscopy (DLOS/DLTS) to reveal traps throughout the entire material bandgap, (b) comparative DLOS/DLTS studies made on substrates and epitaxial layers grown by molecular beam epitaxy, and (c) the influence of wafer orientation on the properties of $\beta\text{-Ga}_2\text{O}_3$ Schottky diodes using various metals. DLTS and DLOS measurements revealed a spectrum of distinct bandgap states at $E_c - 0.62 \text{ eV}$, 0.82 eV , 1 eV , 2.4 eV and 4.42 eV , with a total trap concentration of $\sim \text{mid } 10^{16} \text{ cm}^{-3}$ range, dominated by the traps at $E_c - 0.82 \text{ eV}$ and $E_c - 4.42 \text{ eV}$. [2] Several traps show strong lattice-coupling effects. Regarding Schottky contacts, Ni Schottky contacts were fabricated on (010) and (-201) surfaces, revealing a change in barrier height of almost 0.5 V , as measured by both internal photoemission and C - V methods, suggesting a surface orientation dependence of Schottky barrier formation. Comparing Ni, Au, Pt and Pd contacts on (010) $\beta\text{-Ga}_2\text{O}_3$, barrier heights appear partially unpinned with barriers ranging from $\sim 1.2 \text{ eV}$ for Pd, to $\sim 1.55 \text{ eV}$ for both Ni and Pt and as high as $\sim 1.8 \text{ eV}$ for Au. In all cases, nearly ideal Schottky barrier transport characteristics were observed. This presentation will focus on the extension of trap studies from GaN to $\beta\text{-Ga}_2\text{O}_3$.

[1] M. Higashiwaki, et al., Appl. Phys. Lett. **100**, 013504 (2012)

[2] Z. Zhang, et al., Appl. Phys. Lett. **108**, 052105 (2016)

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4:00pm **EM-MoA8 Study of Oxygen and Moisture Effect on Device Instability of Bottom-Gate ZnO Transistors with Sol-Gel Derived Channel Layers**, *Kosala Yapabandara, M. Park, M.C. Hamilton, D.-J. Kim, V. Mirkhani, S. Wang, M. Sultan, B. Ozden, M.P. Khanal, S. Uprety, Y. Chung*, Auburn University; *M.H. Sk*, Qatar University, Qatar

ZnO has been widely studied due to its promising material properties such as wide energy bandgap, optical transparency, and high carrier mobility for thin film transistor (TFT) technology. Solution-based ZnO can easily be deposited on large areas of substrates at low temperatures, which makes this material a good candidate for commercial device manufacturing. In the case of device reliability and performance, device stability under electrical stress is of imminent importance.

In this work, we report on the device instability of solution-based ZnO TFTs by studying the electrical characteristics during electrical stressing and subsequent relaxation. In order to elucidate the major source for device instability under electrical stress, the electrical characteristics of the transistors under the vacuum and ambient conditions were measured and compared. The positive shift of threshold voltage (V_T) of the device under gate stressing and negative shift under relaxation for both the vacuum and ambient conditions were observed, which suggest that the charge trapping near or at the semiconductor/dielectric interface and charge injection to dielectric layer may be main mechanisms for device instability. However, the continuous degradation of the field effect mobility with electrical bias-stressing in both environmental conditions and a full recovery of the device with a longer relaxation time provided evidence to disregard the assumption of charge injection to the dielectric layer.

Variation in sub-threshold swing (S) with biasing process indicates a new defect level creation. A negligible change in S during gate stressing and relaxation under the vacuum condition, compared to a significant change in S under ambient conditions confirmed that there is no new defect level creation in the absence of oxygen and moisture. Under ambient conditions, oxygen and moisture were adsorbed on the channel surface with the presence of a positive electric field. Upon adsorption, oxygen molecules can capture electrons from the conduction band and a depletion layer can be formed in the ZnO channel layer. Previously, it has been reported that oxygen molecules cannot diffuse into the channel layer at room temperature. However, we have suggested a plausible mechanism that oxygen can be located closer to semiconductor/dielectric interface in thin films upon acceptor-like reaction of H_2O that diffused into the channel *via* voids in grain boundaries. Further confirmation of charge trapping and new defect level creation was carried out by fitting the V_T shift vs. time curve with the power law and stretched exponential functions for the vacuum and ambient conditions, respectively.

4:20pm **EM-MoA9 Depth Dependent Modification of Optical Constants Arising from H^+ Implantation in n-type 4H-SiC Measured using Coherent Acoustic Phonons**, *Andrey Baydin, H. Krzyzanowska*, Vanderbilt University; *M. Dhanunjaya, S.V.S. Nageswara Rao*, University of Hyderabad, India; *J.L. Davidson*, Vanderbilt University; *L.C. Feldman*, Vanderbilt University, Rutgers University; *N.H. Tolk*, Vanderbilt University

Silicon carbide is a promising material for new generation electronics including high power/high temperature devices and advanced optical applications such as room temperature spintronics and quantum computing. Both types of applications require the control of defects particularly those created by ion bombardment. In this work, modification of optical constants of 4H-SiC due to hydrogen implantation at 180 keV and at fluences ranging from 10^{14} to 10^{16} cm^{-2} is reported. The depth dependence of the modified optical constants was extracted from coherent acoustic phonon spectra. Implanted spectra shows a strong dependence of the 4H-SiC complex refractive index depth profile on H^+ fluence. These studies provide basic insight into the dependence of optical properties of 4H silicon carbide on defect densities created by ion implantation, which is of relevance to the fabrication of SiC-based photonic and optoelectronic devices.

4:40pm **EM-MoA10 Electrical and Thermal Stability of ALD-TiN Schottky Gates for AlGaIn/GaN HEMTs**, *D.I. Shahin*, University of Maryland College Park; *Travis Anderson, V.D. Wheeler, M.J. Tadjer, A.D. Koehler, K. Hobart, C.R. Eddy, Jr., F. Kub*, U.S. Naval Research Laboratory; *A. Christou*, University of Maryland College Park

AlGaIn/GaN high electron mobility transistors (HEMTs) are useful devices for next-generation RF and power electronics systems^{1,2}. Traditional Ni-based Schottky gates in these devices have been shown to degrade when subjected to electrical stress, thermal stress, and radiation due to Ni migration into adjacent metal or semiconductor layers^{3,4}. The instability of

these Ni-based gates limits device reliability, rendering the search for replacement gate materials that are electrically- and thermally-stable a topic of tremendous importance. Of the transition metal nitrides, TiN is a particularly promising material, due to its near-metallic conductivity, suitable Schottky barrier heights and ideality factors on GaN and AlGaIn, and high temperature stability. This work investigates the performance of atomic layer deposited (ALD) TiN gates and directly compares them to traditional Ni/Au gates.

ALD TiN gates (75nm thick) were deposited on AlGaIn/GaN HEMTs in an Oxford FlexAL system at 350°C using Tetrakis(dimethylamido)titanium (TDMA-Ti) and an N_2/H_2 plasma as precursors. Devices with TiN gates exhibited improved static and dynamic on-state characteristics compared to the identical Ni/Au-gated HEMTs. Reverse bias gate stressing indicated a higher critical voltage ($V_{GS(TIN)} = -210V$, $V_{GS(Ni/Au)} = -120V$) and a higher breakdown voltage ($V_{GS(TIN)} = -270 \pm 10 V$, $V_{GS(Ni/Au)} = 240 \pm 30V$) for the TiN gates. Furthermore, the TiN gates exhibited a decrease in reverse leakage current after stressing indicating enhanced stability. Gate thermal stability was assessed through sequential device annealing from 400-800C in 100C increments. The TiN gated devices exhibited stable DC operation up to 800°C, while the Ni/Au gates showed significant degradation after annealing above 500°C and failed above 700°C. This suggests that ALD TiN gates are a strong candidate for reliable HEMT gate metallization and other applications where increased stability is required at higher temperatures.

¹ R.S. Pengelly, et al., *IEEE Trans. Microwave Theory Tech.* **60** [6], 1764 (2012).

² S.J. Pearton, et al., *J. Vac. Sci. Technol. A* **31** [5], 050801 (2013).

³ Y.H. Choi, et al., *Mater. Res. Soc. Symp. Proc.* **1167**, 1167-005-06 (2009).

⁴ A.D. Koehler, et al., *IEEE Elect. Dev. Lett.* **35** [12], 1194 (2014).

5:00pm **EM-MoA11 Spectroscopic Photo Current Voltage Measurements to Investigate Non-uniform Defect Distributions in AlGaIn/GaN HEMT Heterostructures**, *Burcu Ozden, M.P. Khanal, C. Yang, L. Shen, V. Mirkhani, K. Yapabandara, M. Park*, Auburn University

The nature and distributions of the electrically-active sub-bandgap point defects in the heterostructures of the AlGaIn/GaN high electron mobility transistors (HEMTs) layers have been analyzed by using spectroscopic photo current voltage (SPIV) measurement. Despite the great potential, device performance for the next generation of high power electronics is often limited by the presence of electronic traps in the AlGaIn/GaN HEMTs device structures. Therefore, the knowledge of defect distribution is critical in understanding the origin of the surface traps for mitigation in future device applications.

In this work, the AlGaIn/GaN HEMT epi-layers were grown on a 6" Si wafer by metal-organic chemical vapor deposition (MOCVD). Ni contacts with 600µm diameter and 20nm thickness were fabricated on the samples which are chosen from the three different locations of 6" wafer. The SPIV measurement was performed using a variable-wavelength light illumination from a Xe lamp. Vertical bias was applied between circular semi-transparent Ni Schottky contacts and the bottom ohmic contact.

Presence of sub-bandgap defects at different energy levels among the wafer were revealed by SPIV measurements indicating nonhomogeneous defect distribution among the wafer. It was concluded that observed defects are most probably due to either Ga vacancies in GaN or Al vacancies in AlGaIn by comparing the energy level of the defects with the formation energies of these vacancies. In conclusion, we have demonstrated the wafer quality in terms of the distribution of electrically active defects can be successfully assess by using SPIV measurements which will be useful for AlGaIn/GaN HEMT wafer vendors as a diagnostic tool.

Thin Film

Room 105A - Session TF+EM-MoA

ALD for Energy Conversion and Storage

Moderators: Virginia Wheeler, U.S. Naval Research Laboratory, Angel Yanguas-Gil, Argonne National Laboratory

1:40pm **TF+EM-MoA1 Fabrication of Nano-power Generators using Thin Atomic Layer Deposited Films**, *Giovanna Scarel, H.S. Mann, B.N. Lang*, James Madison University; *V.D. Wheeler*, Naval Research Laboratory; *B.C. Utter*, Bucknell University

Infrared power generation is emerging as a useful method to harvest infrared (IR) light and transform it into usable energy available day and

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night. So far, this method is implemented using bulk power generator (PG) devices, neglecting any effort to improve the materials employed as their active element. Here we initiate this effort by fabricating thin thermoelectric TiO_2/TiN multilayer films via atomic layer deposition (ALD) and focusing on the exploration of the effects of film resistance on the voltage produced by nano-PG devices with these films as their active elements. By changing the number and thickness of the TiO_2/TiN layers, we control the sheet resistance (W/\square) over three orders of magnitude. We observe that the voltage produced by nano-PG devices linearly increases with the thin multilayer films resistance, especially in the $k\text{-}W/\square$ range. On the contrary, we measure an almost constant voltage jump versus film resistance when we excite the nano-PG device through Joule heating. The observed behavior suggests that the nano-PG device works effectively when mimicking the mechanism of a capacitor, similar to the case of a bulk device. Our studies pave the way to improving the properties of nano-PG devices by improving the properties of the active materials in the form of thin films fabricated via ALD.

2:00pm TF+EM-MoA2 Ultrafast Triggered Transient Energy Storage by Atomic Layer Deposition Into Porous Silicon for Integrated Transient Electronics, Anna Douglas, N. Muralidharan, R.E. Carter, K. Share, C.L. Pint, Vanderbilt University

We demonstrate the first on-chip silicon-integrated rechargeable transient power source based on atomic layer deposition (ALD) coating of vanadium oxide (VO_x) into porous silicon. A stable specific capacitance above 20 F g^{-1} is achieved until the device is triggered with alkaline solutions. Due to the rational design of the active VO_x coating enabled by ALD, transience occurs through a rapid disabling step that occurs within seconds, followed by full dissolution of all active materials within 30 minutes of the initial trigger. This work demonstrates how engineered materials for energy storage can provide a basis for next-generation transient systems and highlights porous silicon as a versatile scaffold to integrate transient energy storage into transient electronics.

2:20pm TF+EM-MoA3 Refractory Solar Selective Coatings Synthesized by Atomic Layer Deposition, Jeffrey Elam, A. Mane, A. Yanguas-Gil, J.A. Libera, J.R. Avila, Argonne National Laboratory

One of the most economically viable methods for solar power uses an array of mirrors to concentrate sunlight onto a central receiver tower. The receiver surface heats up, and this heat is used to drive turbines that generate electricity. To improve the efficiency of these "power tower" facilities, the receiver must operate at higher temperatures and this requires developing high performance coatings. These coatings must be spectrally selective in order to absorb all of the visible light while emitting as little infrared radiation as possible (low emissivity). In addition, these coatings must be refractory to endure decades of high temperature operation under ambient conditions. We are pursuing a novel strategy to develop refractory solar selective coatings using ALD. Our strategy uses thin film nanocomposites composed of conducting metallic nanoparticles in a dielectric matrix. These films are prepared by combining the ALD processes for a metal (e.g. W using $\text{Si}_2\text{H}_6/\text{WF}_6$) with that of an oxide (e.g. Al_2O_3 using $\text{TMA}/\text{H}_2\text{O}$). The resulting nanocomposites have tunable optical properties that can be adjusted to achieve a high solar selectivity. In addition, we use these ALD coatings to infiltrate inverse opal scaffolds which serve as photonic crystals to further enhance the spectral selectivity. In this presentation I will discuss our ongoing work synthesizing and characterizing these refractory solar selective coatings. In particular, I will describe in situ quartz crystal microbalance, mass spectrometry, and infrared spectroscopy measurements performed to elucidate the unusual surface chemistry for these ALD nanocomposites, and discuss the relationships between the composition and the optical/electrical properties of these films. I will also describe the results of finite difference time domain modeling to understand how the photonic scaffold modulates the spectral selectivity, and finally I will report on the high temperature performance of these coatings.

2:40pm TF+EM-MoA4 Sequential Infiltration Synthesis of Doped Polymer Films with Tunable Electrical Properties for Efficient Triboelectric Nanogenerator Development, Yanhao Yu*, X.D. Wang, University of Wisconsin-Madison

Triboelectric nanogenerator (TEG) is rising as a promising technology for converting mechanical energy into electricity with merits of high output, simple design and low cost. The working principle of TEG is based on the combined effect triboelectrification and electrostatic induction. According

to this mechanism, controlling the charge density on the triboelectric surface is the most fundamental strategy for improving the performance of TENG. Nowadays, surface modification of triboelectric polymer is the predominate approach to regulate the charge density. However, operation of TENGs requires intimate contact and sometimes friction between triboelectric materials, which inevitably induces wearing of surface. In this regard, surface modification/engineering yields little contributions toward the performance gain in long-term operation. Therefore, one essential solution is to extend the property engineering from mere surface to the bulk of material.

Atomic layer deposition (ALD) is a powerful thin film growth technique on the basis of sequential self-limiting surface reactions. When implemented to certain polymers, the large permittivity of metalorganic precursors allows deep infiltration of inorganic compounds during ALD process, leading to inorganic/organic hybrid materials. This process is known as sequential infiltration synthesis (SIS). It has been successfully used to convert block co-polymer nanopatterns into more durable inorganic patterns and to improve the polymeric lithography resistance to subsequent etching. Inspired by these developments, we expect SIS could effectively tailor the internal composition and electrical properties of polymer films, which may provide an ultimate solution for triboelectric material design in the development of high-performance TENGs. Here, we report an internal AlO_x doping of several polymers via SIS, including polydimethylsiloxane (PDMS), polyimide (Kapton) and poly(methyl methacrylate) (PMMA).[1,2] We showed that SIS can introduce AlO_x molecules $\sim 3 \mu\text{m}$ deep into these polymers, which effectively tuned the bulk electrical property of the film. TENG devices using the modified polymer films exhibited enhanced power output; and this enhancement remained effective after the surface of polymer film was polished off for more than $2 \mu\text{m}$. This polymer doping approach opens a new route to bulk electrical property modification of polymer films, demonstrating a promising strategy for improving the performance of functional polymer based devices, such as TENGs.

Reference

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2. Y. Yu, X. Wang. *Extreme Mech. Lett.*, doi:10.1016/j.eml.2016.02.019, 2016.

3:00pm TF+EM-MoA5 ALD for Interfacial Engineering of Energy Conversion Devices, Neil P. Dasgupta†, University of Michigan, Ann Arbor
INVITED

Recently, there has been a dramatic increase in research of nanoscale materials for energy conversion and storage applications due to several advantageous features such as high surface areas, short transport distances, novel optical phenomena, and tunable material properties. However, with these benefits come challenges. In particular, the ability to precisely control the properties of surfaces and heterogeneous interfaces at the nanoscale limits the performance of many of these devices, and requires novel approaches. This problem becomes increasingly important as dimensions decrease, as the surface-to-volume ratios continually increase with decreasing feature size.

One technique that has been increasingly explored for surface and interfacial engineering of nanostructured energy conversion and storage devices is Atomic Layer Deposition (ALD). This gas-phase process allows for highly conformal deposition of a wide variety of materials with sub-nm precision in material thickness and tunable chemical composition. A wide range of materials, including oxides, sulfides, and metals can be deposited by ALD. The combination of conformality and thickness control of ALD facilitates precise tuning of the electronic, optical, thermal, and chemical properties to optimize their interfaces in energy conversion devices.

This talk will present several examples of using ALD to fabricate highly-controlled interfaces for energy conversion and storage devices. Examples include batteries [1], photovoltaics [2-3], and photoelectrochemical cells [4-5]. The key theme linking these studies is that through deterministic control of interfacial layer composition, thickness, crystallinity, and morphology, we can "program" properties such as charge transfer resistance, catalytic activity, and chemical stability. This control enables interfacial materials engineering to optimize both device efficiency and lifetime. The importance of fully understanding ALD surface chemistry will be discussed from a theoretical and experimental perspective. The talk will conclude with a perspective on future directions and challenges for widespread commercial adaption of these technologies.

* TFD James Harper Award Finalist

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† Paul Holloway Award Winner

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- [2] A. B. Wong, S. Brittman, Y. Yu, N. P. Dasgupta and P. Yang, *Nano Lett.***15**, 4096 (2015).
- [3] S. Brittman, Y. Yoo, N. P. Dasgupta, S.-I. Kim, B. Kim and P. Yang, *Nano Lett.***14**, 4665 (2014).
- [4] N. P. Dasgupta, C. Liu, S. Andrews, F. B. Prinz and P. Yang, *J. Am. Chem. Soc.***135**, 12932 (2013).
- [5] J. Resasco, N. P. Dasgupta, J. Rosell, J. Guo and P. Yang, *J. Am. Chem. Soc.***136**, 10521 (2014).

4:00pm **TF+EM-MoA8 Anchoring Down Soluble Polysulfides for Lithium and Sodium Sulfur Battery Cathodes using Atomic Layer Deposition**, Rachel Carter, A.P. Cohn, L. Oakes, N. Miralidharan, A.E. Douglas, K. Share, C.L. Pint, Vanderbilt University

Among the most significant challenges for practical lithium or sodium sulfur batteries is polysulfide shuttling, where intermediate discharge products (M_2S_8 , M_2S_6 and M_2S_4) dissolve into the electrolyte lowering active sulfur mass and fouling the metal anode. To overcome this, we demonstrate the use of atomic layer deposition (ALD) to produce thin oxide coatings on cathode materials to stabilize these soluble polysulfides and mitigate active material loss. We specifically focus on V_2O_5 (vanadium pentoxide) due to its demonstration in recent theoretical studies to exhibit strong polar interaction with soluble polysulfides that exceeds other oxide materials. With the application of the V_2O_5 binding interlayer the initial discharge capacity of the sulfur cathodes is enhanced by 20%, which is a direct result of anchoring the soluble species for optimal complete discharge of the sulfur. The capacity retention of the sulfur cathode is enhanced to 87% capacity retention over 100 cycles, in comparison to less than 50% retention without ALD binding layer. The binding effect was also probed using UV-Vis analysis, since there are distinct absorption peaks for the soluble S_6^{2-} state in the electrolyte. Solutions of Li_2S_6 and Na_2S_6 we studied before and after exposure to ALD binding layers with dramatic decrease in the S_6^{2-} signature in solution observed proving the binding interactions between the polysulfides and V_2O_5 binding interlayer. Overall, our work shows how ALD is a versatile tool to atomically engineer surfaces to sustain excellent performance without compromising the gravimetric performance needed for practical battery applications.

4:20pm **TF+EM-MoA9 Hybrid Inorganic-Organic Thin Films by ALD/MLD for Emerging Energy Technologies**, Maarit Karppinen, Aalto University, Finland **INVITED**

For hybrid inorganic-organic materials it is in principle possible to realize properties not seen for conventional materials. An elegant, yet industrially feasible way to link the inorganic and organic entities *via* strong chemical bonds to form coherent multi-layered hybrid materials is to combine the ALD (*Atomic Layer Deposition*) technique originally developed to deposit high-quality thin films of simple inorganic materials with MLD (*Molecular Layer Deposition*) cycles based on organic precursors. This enables the atomic/molecular layer-by-layer production of inorganic-organic hybrid thin films through sequential self-limiting gas-surface reactions with high precision for the film thickness and composition.

In this talk I will discuss our recent efforts towards synthesizing new functional materials by the combined ALD/MLD technique.¹ In particular, we have fabricated oxide-organic thin-film superlattices in which the periodically introduced single/thin organic layers between oxide layers are *e.g.* shown to hinder phonon transport and substantially enhance the thermoelectric properties of $(Zn,Al)O^{2,3}$ and $(Ti,Nb)O_2^4$ films. Other exciting application areas foreseen for the ALD/MLD hybrid thin films include the flexible and transparent Li-ion microbattery materials^{5,6} and so-called metal organic framework (MOF) materials.⁷

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Electronic Materials and Photonics Room 102A - Session EM+MN-TuM

New Materials and Devices for TFETs, Spintronics, and Extended CMOS

Moderator: Wilman Tsai, TSMC

8:40am **EM+MN-TuM3 Tunneling FET Technology using Ge and III-V Semiconductors**, *Shinichi Takagi, M. Takenaka*, The University of Tokyo, JST-CREST, Japan **INVITED**

Since TFETs based on band-to-band tunneling are expected as ultra-low power devices applicable to LSI for IoT, development of the optimum materials, structures and fabrication process have been strongly pursued for realizing both low sub-threshold swing (SS) of sub-60 mV/dec. and high drain Ion/Ioff ratio at the same time. For this purpose, the reduction in the effective band gap is important for enhancing tunneling current. Thus, we are currently focusing planar-type TFETs using Ge/III-V and their hetero-structures.

In this talk, we address two types of planar TFETs utilizing the Ge/strained Si (sSi) hetero-structure and the InGaAs channels. One of the key issues for TFETs is the formation of the steep and high quality source junctions, which provide both high tunneling current and low off current. For InGaAs TFETs, we have introduced solid-phase Zn diffusion through utilizing the inherent diffusion property of Zn in InGaAs creating defect-less extremely-steep profiles. The steepness of the Zn profiles less than 3.5 nm/dec. was obtained, thanks to the diffusion constant of Zn in InGaAs proportional to the square of the Zn concentration, leading to the automatic realization of the steep impurity profile. The small SS of 64 mV/dec and large Ion/Ioff ratio over 1E6 have been realized in the planar-type InGaAs TFETs at room temperature.

For tensile strain Si channel TFETs with Ge sources, in-situ doping p+ Ge/sSi source junctions are employed for realizing steep and defect-less tunneling junction formation. Here, the higher Ev edge of the Ge-source and the lower Ec edge of tensile-strained Si result in reduction in the effective band gap, leading to the increase the tunneling probability with maintaining the relatively large Eg of sSi in the drain regions, which can suppress the ambipolar leakage current. The fabricated Ge/sSOI (1.1 %) TFETs show high Ion/Ioff ratio over 1E7 and steep minimum SS of 28 mV/dec.

In conclusion, the enhancement of tunneling probability by utilizing III-V/Ge materials is quite effective in improving the performance of TFETs. Superior source junction formation and MOS interface control technologies are key factors to realize TFETs using III-V/Ge.

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9:20am **EM+MN-TuM5 Thin Film Materials in Novel Spintronic Devices**, *Gang Xiao*, Brown University **INVITED**

Tomorrow's spintronic MRAM (Magnetic Random Access Memory) and logic processors could exploit the physics of the giant spin Hall effect (GSHE) for switching bits, but the materials engineering is challenging. Solids with large atomic numbers and resistivities exhibit very large Spin Hall Angle (SHA), a key and characterizing parameter of GSHE. The origin of GSHE is the enhanced spin-orbit coupling (SOC), based on which the search on solids with even larger SHA continues. Some of these solids are difficult to fabricate due to their metastable structures. We have realized robust perpendicular magnetic anisotropy (PMA) in a layered structure combining the elusive, metastable β phase of tungsten and a ferromagnetic thin film. The large spin-orbit coupling in β -W yields, after suitable annealing, a very low critical current density for magnetization switching. Our structures furthermore are easily fabricated, making them even more technologically promising and compatible to modern semiconductor fabrication process.

11:00am **EM+MN-TuM10 Tunneling in Low-Dimensional Materials**, *Joerg Appenzeller*, Purdue University **INVITED**

Over the last years, two-dimensional (2D) materials are attracting an increasing amount of interest for various electronic applications owing in particular to the ideal electrostatics conditions that can be enabled in a

three-terminal field-effect transistor (FET) geometry. Transition metal dichalcogenides (TMDs) as MoS₂, WSe₂, or WS₂, to just name a few, or black phosphorus (BP) offer sizable bandgaps at mobilities that cannot be achieved in three-dimensional, bulk type materials that are scaled down to similar dimensions. The key is the absence of dangling bonds at the 2D semiconductor to substrate or gate dielectric interface that allows for highly conductive channels with sub-nm body thicknesses. In my presentation I will discuss the benefits of an ultra-thin body structure for scaled device applications with a particular emphasis on tunneling field-effect transistors (TFETs). I will also elucidate the critical impact of Schottky barrier (SB) contacts in the context of TMD and BP devices and will present an analytical approach that allows extracting materials and device information as the SB height and bandgap of single- and multi-layer FET structures. Moreover, I will present an analysis on the impact of strain in TMD FETs and discuss the potential relevance of strain for TMD TFETs to achieve ideal performance specs.

11:40am **EM+MN-TuM12 Controlled Phase Transition for Ultra Low Power Transistors**, *Sayef Salahuddin*, University of California, Berkeley **INVITED**

Phase transition materials have long been investigated for fundamental physics and also for potential application in electronics. In this presentation, I shall discuss how a controlled phase transition can lead to fundamentally new switching devices that has significantly less energy dissipation compared to the state of the art. In particular, I shall talk about the state of negative capacitance that can be achieved in certain material systems with stored energy of phase transition. Our recent experiments with ferroelectric materials have shown that such a state of negative capacitance can actually be achieved. I shall also describe our very recent results where such negative capacitance, when combined with conventional transistors, have demonstrated a reduction in supply voltage at a given ON current.

Electronic Materials and Photonics Room 102A - Session EM+MI+MN-TuA

New Materials and Devices for Emerging Memory Technologies

Moderators: Andy Antonelli, Nanometrics, Sean King, Intel Corporation

2:20pm EM+MI+MN-TuA1 Emerging Processing Challenges for Advanced Memory Technologies, *Bart Van Schravendijk*, Lam Research **INVITED**

The rapid scaling of semiconductor memory is radically changing the memory industry. Flash memory has switched from lateral scaling to vertical scaling while other new memory technologies are aggressively vying for new opportunities in the memory market. Their targets range from niche applications to replacing any one of the three big memory technologies : SRAM, DRAM or Flash.

For vertical NAND flash largely conventional materials are used in its fabrication at present. However, the unabated drive for higher density is driving aggressive vertical scaling, which poses new problems for stack design and processing. This drives improvements and maybe even changes in the materials.

Newer memory technologies, such as STT-RAM, ReRAM and PCRAM, bring with them different challenges to the processing arena. These new memories come with materials whose full scope of interactions with semiconductor processing are still poorly understood. These materials provide new challenges for the processing tools when scaling these memory technologies to dimensions that are economically attractive.

In this talk we will review some of the more challenging problems for advanced memories and some potential solutions.

4:20pm EM+MI+MN-TuA7 Resistance Change Memory and its Perspective toward 3D Integration, *Yoshio Nishi, B. Magyari-Kope*, Stanford University **INVITED**

As we face a situation in the next decade where further scaling of traditional CMOS based devices would not be cost effective from manufacturing issues such as superfine lithography/etching and device physics barriers. Thus non-traditional new materials and devices research have been instigated, which resulted in new principle based non-volatile memories. A short list of such newly emerging memory consists of resistance change memory ReRAM, phase change memory, PCRAM, spin based MRAM/STT RAM, depending upon desirable characteristics to implement.

Though resistance change phenomena in metal oxides have been recognized since early days, it is in the past few years when aggressive research for application as nonvolatile memory has taken off. Basic switching mechanism is formation and annihilation of conductive vacancy chain in the metal oxide sandwiched by two electrodes. Both atomistic and macroscopic models have been investigated. Role of electrode materials and switching oxide interfaces during memory operation have attracted strong attention, as it would imply not only memory characteristics but also device endurance and scalability. Further, development of this type of resistance change memory is toward vertical integration with multi-memory layers which could replace ultra-high density flash memory.

This talk will review progresses made for resistance change memories, covering fundamental physical mechanism, implementation of memory cells including scaling limit studies, and 3 dimensional integration of such devices.

5:00pm EM+MI+MN-TuA9 Atomic Disorder As an Intrinsic Source of Variability in Filamentary Rram Devices – Ab Initio Investigations, *Sergiu Clima*, IMEC, Belgium; *L. Goux, B. Govoreanu, M. Jurczak, G. Pourtois, A. Fantini*, IMEC **INVITED**

Resistive Random Access Memory concept is probably close to production in a new generation of non-volatile memories, but there are still some reliability issues to be fully understood. Resistive RAM devices can be scaled down below 10 nm [1], meaning that the discrete nature of atomic structure of the materials may already be observed in device operation properties. Material-wise, the transition metal oxides attracted the scientific interest due to their CMOS compatibility and their ability to operate on intrinsic defects (oxygen vacancies). For RRAM working with extrinsic defects like metallic inclusions called Conductive Bridge RAM (CBRAM), a larger spectrum of solid electrolytes can be used. Using Density Functional Theory simulations of RRAM materials, we evaluated the

kinetics of the defects migration of the conducting species to show that atomic disorder of amorphous state can exhibit large variability in terms of defect stability and kinetic barriers.[2] These have a great impact on filament resistance evolution in time, which can be observed during forming step of the resistive filament, but not only. In the short time immediately after filament formation, the atomic configuration can relax to a metastable state, therefore changing the resistivity of the filament. In a long time retention of the filament resistance we can still measure resistance change. All these observations can be explained with the computed statistical distributions of the defect stability and kinetic barriers in the RRAM materials.

[1] B. Govoreanu et al., Ext. Abstr. SSDM Conf., Nagoya, Japan, 1005 (2011)

[2] S. Clima et al., Electron Device Lett , 769 (2015)

5:40pm EM+MI+MN-TuA11 Reduction of Radiation Damage to HfOx-Based Resistive Random Access Memory using a Thin ALD HfOx Film, *Kaiwen Hsu, T. Chang*, University of Wisconsin-Madison; *L. Zhao, Z. Wang*, Stanford University; *R. Agasie, T. Betthausser, J. Nickles, Z. Ma, J. Chang*, University of Wisconsin-Madison; *Y. Nishi*, Stanford University; *J.L. Shohet*, University of Wisconsin-Madison

Resistive Random Access Memory (RRAM) [1], is considered to be a very promising memory technology for the next generation of computer memory. It has undergone intense research in both industry and academia in the last ten years. As RRAM technology matures and electronic devices using RRAM are likely to be built soon, a RRAM cell which is resistant to radiation will become an important topic in industry to prevent the malfunction of these devices. In this work, neutron and proton-induced effects on two types of RRAM cells are investigated. Type 1 HfOx RRAM cell is different from the Type 2 RRAM cell in two aspects, (1) the thickness of the HfOx film (Type 1 is thicker than Type 2) and (2) the fabrication process for depositing the HfOx within the RRAM cell. (Type 1 uses spin-on technology and Type 2 uses ALD technology)

Many Type 1 RRAM cells can be formed under neutron irradiation and end up in the LRS. On the other hand, unformed neutron-irradiated Type 1 RRAM cells only require a lower voltage to form. In addition, the resistance of the HRS increased on the Type 1 RRAM cell. The shift in values of the set voltage can be seen on the I-V characteristic of the neutron-irradiated Type 1 RRAM cell. A similar increase in the resistance of HRS is also observed in proton-irradiated Type 1 RRAM cells. The shift in values of the set voltage can be seen on the I-V characteristic of the proton-irradiated Type 1 RRAM cell.

There are no obvious changes to Type 2 RRAM cells after either neutron or proton irradiation. It is very likely that both the changes in thickness and fabrication are very important since these two modifications can cut down on the number of defects which affect the switching mechanism of the RRAM cell.

This work was supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359, by the National Science Foundation under Grant No. CBET-1066231.

[1] H.-S. Philip Wong, H-Y Lee, S. Yu, Y. S. Chen, Y. Wu, P-S Chen, B. Lee, F. T. Chen, and M-J Tsai, "Metal-oxide RRAM," Proceedings of the IEEE 100 1951 (2012).

6:00pm EM+MI+MN-TuA12 Potential Dependent Resistance of Doped TiO₂ Film Fabricated by Solgel Process: Perspective for Resistive Memory, *R.R. Pandey, Jyotirmay Sharma, C. Kant, K. Saini*, CSIR-National Physical Laboratory, India

Fastest growth has been registered in the field of electronics. It is the only field which has transformed every corner of the society and every age of the civic society, from youngest child to elderly persons. The growth was outcome of the miniaturization of the basic active device in electronics. The journey started from few millimeter size around 1965 and now reached to few tens of nanometers. At the beginning of this journey, the new smaller size devices not only performed better to its predecessor but were cost effective also. As we reached below ~300nm, the production was no longer economic. At around few tens of nanometer size the device performance also affected and at this junction the need was felt to explore alternate working principles for the device to maintain growth of the field and continue to benefit the society. New devices such as SET, RTD, resistive memory, magnetic memory, spintronic etc. were studied. Working device size of less than ten nanometers is expected from this new class of devices. Here we report fabrication of titanium oxide based resistive memory device by solgel technique. Thin films of high quality doped and undoped titanium oxide were applied on cleaned FTO or Pt-FTO glass substrates by

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solgel dip process. We doped titanium oxide with aliovalent cations by suitable choice of doped cation salt. Sequence of undoped and doped layers of titanium oxide was altered in different devices. Final structure was completed by thermal evaporation of metal electrode for electrical connection.

A resistance change of 2-3 orders of magnitude was observed up to the maximum applied potential of ± 3.0 volts. The resistance change has complex dependence on nature of the dopant, dopant concentration, electrode material and sequence of the doped and undoped layers. We tried to explore the resistance change behavior and remembrance of resistance on the basis of basic studies viz; XRD, XPS, SEM, etc. cyclic voltametric studies were also carried out to understand the contact between electrode and TiO_2 layer.

Electronic Materials and Photonics Room 102A - Session EM+NS-WeM

Nanoparticles for Electronics and Photonics

Moderators: Joseph Tischler, U.S. Naval Research Laboratory, Jessica Hilton, Mantis Deposition

8:00am **EM+NS-WeM1 Nanostructures on Surfaces: From Cluster Deposition to Low Energy Ion Bombardment, Luke Hanley, K. Steeves Lloyd, M.W. Majeski, I.L. Bolotin**, University of Illinois at Chicago; *M. Schmeling*, Loyola University Chicago; *I.V. Veryovkin*, University of Illinois at Chicago

INVITED

Two strategies are described for the preparation of unique nanostructures on surfaces or within thin films: cluster beam deposition and low energy ion beam irradiation. In cluster beam deposition, copper sulfide nanoparticles were prepared by magnetron sputtering under a flow of argon and hydrogen sulfide, then codeposited with evaporated pentacene to form a composite thin film (M.W. Majeski, *et al.*, ACS Appl. Mater. Interf., 2014, <http://dx.doi.org/10.1021/am5028428>). This all-gaseous method can prepare a variety of semiconductor nanoparticles without the surface ligand capping and oxidation effects often observed for colloidal prepared nanoparticles that can inhibit charge transfer or cause self-doping. X-ray photoelectron spectroscopy, transmission electron microscopy, and high-angle annular dark-field scanning transmission electron microscopy were used to determine that 2.3 ± 0.4 nm Cu_{2-x}S nanoparticles with copper in the +1 oxidation state were deposited into pentacene films. In low energy ion beam irradiation, nanocone and nanoripple arrays were prepared on Si surfaces by grazing incidence irradiation with 1 keV Ar⁺ ion beams that simultaneously sputtered away surface atoms and sputter-deposited metal impurity atoms from adjacent targets (K. Steeves Lloyd, *et al.* Surf. Sci., 2016, <http://dx.doi.org/10.1016/j.susc.2016.03.016>). Scanning electron microscopy and atomic force microscopy observed that when Si, Cu, or stainless steel was employed as a co-sputtering target, only stainless steel was found to assist the growth of dense arrays of nanocones. The structural characterization of samples further correlated the role of incident ion fluences on the formation of nanoripples vs. nanocones. Characterization of sample chemical composition by total reflection X-ray fluorescence and X-ray photoelectron spectroscopy revealed that the concentration of metal impurities originating from stainless steel (Fe, Cr and Ni) was relatively high in the regions with high density of nanocones and much lower in the region of nanoripples. Overall, these two strategies open up multiple possibilities for the preparation of complex nanostructures on surfaces and in thin films that are compatible with more common lithographic strategies.

8:40am **EM+NS-WeM3 Designer Nanocrystal Electronic and Optoelectronic Materials through Controlled Coupling and Doping, Cherie Kagan**, University of Pennsylvania

INVITED

Semiconductor nanocrystals (NCs) are prized for their size- and shape-dependent electronic and optical properties and as building blocks in the assembly of NC solids. However, the long, insulating ligands commonly employed in the synthesis of colloidal NCs inhibit strong interparticle coupling and charge transport once NCs are assembled into the solids state as NC arrays. In this talk, I will describe methods to introduce atoms, ions, and more compact molecules at the NC surface that allows us to increase interparticle coupling and dope NC solids. NC coupling and doping provide control over the density of states, the carrier statistics and the Fermi energy. I will also describe the importance of engineering device interfaces to study the fundamental physics of NC solid transport and to design device architectures for applications. Examples of strong coupling and doping in II-VI and IV-VI semiconductor NC solids will be given that yield high-mobility, high-conductivity NC solids. Temperature-dependent transport measurements of these materials are consistent with a transition from localized to extended-state charge transport. These high mobility n- and p-type materials are used as the semiconductors to construct large-area, flexible, field-effect transistors and integrated circuits and for solar photovoltaics.

9:20am **EM+NS-WeM5 Au Nanoparticle Modified Indium Tin Oxide Ultramicroelectrode for Single Particle Spectro-electrochemistry Study and Ultrasensitive Electrochemistry Sensing, Yanxiao Ma**, The University of Alabama; *S. Pan*, The University of Alabama

Plasmonic active metal NPs are broadly used in electrochemical and optical sensing of molecular recognition events. However, it is extremely challenging to resolve chemical and physical transformation at single NP level using conventional optical and electrochemical methods for resolving their local structure-function relationship. We are developing an optical and electrochemical technique to resolve electrocatalytic property of single NPs. Combined methods of photolithography and electrodeposition are used for fabricating Au NP modified indium tin oxide ultramicroelectrode (ITO UME). Dark field scattering (DFS) microscopy and scanning electron microscopy (SEM) were used to characterize NPs on the surface of ITO UME. The electrochemistry voltammetric study shows that Au and Pt NPs are ideal catalytic materials for hydrazine oxidation reaction. Dark field spectroelectrochemical study of hydrazine oxidation at planer ITO and ITO UME confirmed the formation of nanobubbles on NPs surface. Relationship between DFS light intensity and hydrazine oxidation current profile was obtained.

9:40am **EM+NS-WeM6 Band Gap-Control of Spray Pyrolysis Synthesized CZTS Nanoparticles, Stephen Exarhos, E. Palmes, A. Alvarez-Barragan, L. Mangolini**, University of California, Riverside

An innovative and scalable synthesis approach to the formation of phase-pure Cu₂ZnSnS₄ (CZTS) nanoparticles has been developed using aerosol spray pyrolysis. CZTS material is an inherent direct-band gap p-type semiconductor with a band gap of ~1.5 eV and absorption coefficient of >10⁴ cm⁻¹, making it suitable for solar absorption applications. As an earth-abundant absorber material, it has been well-studied for application in thin film photovoltaics [1]. Little experimental work has been done to test the viability of the material as a photocatalyst, though the material shows low activity in driving water splitting or pollutant degradation unless synthesized in a noble metal heterostructure [2]. By its nature, CZTS is a very adaptable material system. It is relatively straightforward to alloy into the material primarily as a method of band gap control. By optimizing the band gap and band alignment of alloyed CZTS-like nanoparticles, we intend to improve the catalytic quality of CZTS-based heterostructures. We have previously shown that aerosol spray pyrolysis is an effective inexpensive and scalable technique for the synthesis of CZTS [3]. By processing a solution with copper-, tin-, and zinc-diethylthiocarbamate precursors dissolved in a toluene solvent, we can form phase-pure, surface-ligand-free, kesterite CZTS nanoparticles with a size distribution average of ~20 nm. Using the same process, by adding hydrogen-terminated silicon nanoparticles — synthesized in-house by a non-thermal plasma process — to the precursor solution, we can alloy silicon into the material (making CZTSiS), and in turn increase the band gap of the material from the 1.5 eV for pure CZTS. We also have the ability to decrease the band gap by alloying different transition metals in place of zinc in the crystal lattice. We present preliminary studies characterizing CZTS and CZTSiS nanoparticles for potential use as a photocatalytic heterostructure material.

[1] Liu, Xiaolei, Yu Feng, Hongtao Cui, Fangyang Liu, Xiaojing Hao, Gavin Conibeer, David B. Mitzi, and Martin Green. Progress in Photovoltaics: Research and Applications, January 1, 2016.

[2] Yu, Xuelian, Alexey Shavel, Xiaoqiang An, Zhishan Luo, Maria Ibáñez, and Andreu Cabot. Journal of the American Chemical Society 136, no. 26 (July 2, 2014): 9236–39.

[3] Exarhos, Stephen. eScholarship, January 1, 2015. <http://escholarship.org/uc/item/1pw1t81k>.

11:00am **EM+NS-WeM10 Designer Nanomaterials by Magnetron Sputtering and Ion Soft Landing, Grant Johnson, V. Prabhakaran**, Pacific Northwest National Laboratory; *T. Moser*, Michigan Technological University; *M.H. Engelhard*, *N. Browning*, *J. Laskin*, Pacific Northwest National Laboratory

Clusters and nanoparticles comprised of controlled amounts of different atoms are of interest for applications in optics, magnetism, catalysis, sensors, and biotherapeutics. Alloy nanoparticles, in particular, may possess enhanced properties compared to single-metal species due to the additional interplay between their different elemental components. By reducing the quantity of precious metals in alloys by substitution with cheaper base metals, it is possible to achieve equivalent or superior performance to noble metal nanoparticles at reduced material cost. In addition, alloying of elements that are immiscible in the bulk is possible at

the nanoscale because the enthalpy of mixing decreases and becomes negative at small particle sizes. As a result, a broad array of alloy species may be generated in the form of clusters and nanoparticles. Magnetron sputtering of multiple targets in the same region of gas aggregation is demonstrated to produce ionic alloy clusters and nanoparticles with defined composition and morphology that are not obtainable through solution synthesis. Introduction of reactive gases into the sputtering and aggregation region is shown to result in the formation of complex morphologies. A suite of characterization techniques including atomic force microscopy, scanning and transmission electron microscopy, and x-ray photoelectron spectroscopy is utilized to determine how the size, shape, and elemental composition of soft landed particles may be tuned through variations in source parameters. The electrochemical activity of the soft landed nanomaterials toward the oxygen reduction reaction, a critical process occurring in proton exchange membrane fuel cells, is evaluated ex-situ using cyclic voltammetry in solution and in-situ using an ionic liquid membrane in vacuum.

11:20am EM+NS-WeM11 A Facile Electrodeposition Method for Vertically Standing Plasmonic Nanorods for Surface Enhanced Photoelectrochemical Catalysis, *Jue Wang, S. Pan*, The University of Alabama

A facile template-free electrodeposition technique is developed for large-scale fabrication of vertically standing plasmonically active silver nanorods (NRs). The diameter, length, and surface coverage of Ag NRs are dependent on the electrodeposition time. The growth mechanism of the vertically standing Ag NRs is investigated by tracking their morphology evolution as a function of deposition time. Because of their large specific surface area, oriented alignment, broad range light scattering, and light absorption tunability, these NRs are ideal substrates for thin layer photocatalysts for enhancing light absorption and charge collection. The Preliminary tests on plasmon-induced photocurrent of bare Ag NRs, Ag NR converted to Ag₂S NRs, and coated with CdS nanoparticles (NPs) are presented to demonstrate surface enhancement characteristics. This simple NR fabrication method can be extended to other conductive substrates and other materials for obtaining vertically standing NR structures.

11:40am EM+NS-WeM12 Influence of Surface Reaction on the Infrared Localized Surface Plasmon Resonance of Indium Tin Oxide Nanocrystals, *Weize Hu, M.A. Filler*, Georgia Institute of Technology

Heavily doped oxide nanocrystals exhibit a tunable plasmonic response in the infrared, a capability that is promising for future photonic, spectroscopic, and energy harvesting/transport technologies. Nanocrystal carrier density, and thus spectral response, is adjustable via chemical reaction; however, the fundamental processes governing this behavior are poorly understood. Here, we study the oxidation and reduction of indium tin oxide (ITO) nanocrystals with O₂ and H₂, respectively, with in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). We show that the main absorption feature redshifts upon oxidation more than 1000 cm⁻¹ and blueshifts to its original position upon reduction. The same magnitude spectral shift is observed over many cycles of oxidation and reduction. A kinetic model, which includes surface reaction and bulk diffusion, allows us to quantitatively rationalize the process, revealing that surface reaction is rate limiting under the conditions studied. Our experiments provide a deeper understanding of the connection between surface reaction and carrier density in oxide nanocrystals, and open the door to a priori control of plasmonic response.

12:00pm EM+NS-WeM13 Electrochemical Synthesis of Nanostructured Cu and Cu_xO Electrodes for the Reduction of CO₂ to Usable Fuels, *Nelly Kaneza, S. Pan*, The University of Alabama

In effort to controlling carbon dioxide (CO₂) levels in the atmosphere, the conversion of CO₂ into useful products, although very challenging, has emerged as a very attractive area of research. In this work, a series of Cu based nanostructures are synthesized and characterized to demonstrate a low cost approach to reduce CO₂ electrochemically to specific fuel products at low overpotential. The synthesized Cu and Cu_xO nanostructures are characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) and their performance evaluated in terms of their activity, selectivity and stability using cyclic voltammetry (CV), gas chromatography (GC) equipped with a mass spectrometry (MS).

Electronic Materials and Photonics Room 102A - Session EM+NS+SP+SS-WeA

Nanoscale Imaging of Metals and Compound Semiconductor based Nanostructures, Surfaces and Interfaces

Moderators: Yohannes Abate, Georgia State University, Andy Antonelli, Nanometrics

2:20pm EM+NS+SP+SS-WeA1 The Importance of Contact Engineering for 2D Devices, *Saptarshi Das*, Pennsylvania State University **INVITED**

Contact resistance is one of the most important factors which could potentially limit the performance of novel electronic and optoelectronic devices based on two-dimensional (2D) materials like graphene, black phosphorus, various transition metal dichalcogenides (TMDs) like MoS₂, WSe₂ and beyond [1-3]. It is now widely accepted that metal-2D contacts are mostly Schottky barriers type [1-3]. Hence, various contact engineering strategies have been adopted to minimize the Schottky barrier height at the metal-2D interface and thereby reduce the contact resistance. In this talk I will provide a comprehensive overview of different contact engineering schemes metal work function engineering, interface engineering and phase engineering [4-6]. Additionally, I will also talk about the scalability of the contact resistance since an aggressively scaled 2D device will also have aggressively scaled contacts.

1. Das S, Chen H-Y, Penumatcha AV, Appenzeller J: **High performance multilayer MoS₂ transistors with scandium contacts.** *Nano letters* 2012, **13**(1):100-105
2. Das S, Appenzeller J: **WSe₂ field effect transistors with enhanced ambipolar characteristics.** *Applied Physics Letters* 2013, **103**(10):103501
3. Das S, Demarteau M, Roelofs A: **Ambipolar phosphorene field effect transistor.** *ACS nano* 2014, **8**(11):11730-11738.
4. Das S, Appenzeller J: **Where does the current flow in two-dimensional layered systems?** *Nano letters* 2013, **13**(7):3396-3402
5. Das S, Gulotty R, Sumant AV, Roelofs A: **All two-dimensional, flexible, transparent, and thinnest thin film transistor.** *Nano letters* 2014, **14**(5):2861-2866.
6. Kappera R, Voiry D, Yalcin SE, Branch B, Gupta G, Mohite AD, Chhowalla M: **Phase-engineered low-resistance contacts for ultrathin MoS₂ transistors.** *Nature materials* 2014, **13**(12):1128-1134.

3:00pm EM+NS+SP+SS-WeA3 Imaging Stress-Directed Compositional Patterning in Silicon Germanium with μ -Raman Spectroscopy, *Brian Rummel, S.M. Han*, University of New Mexico

We have previously demonstrated that a patterned elastic stress field can be used to change the near-surface atomic composition in an epitaxial compound semiconductor film.¹ This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner. In this example, an array of silicon pillars is pressed against a relaxed Si_{0.8}Ge_{0.2} substrate in a mechanical press, and the entire assembly is heated to high temperatures. This serves to promote a diffusive separation of the germanium into highly localized regions. Here, the difficulty in analyzing these structures is due to the lack of surface detail on the stress-annealed substrate as there is only elastic deformation observed during the fabrication process. To visualize the regions compressively stressed by the pillars and therefore compositionally altered regions, we report the use of μ -Raman spectroscopy to produce a 2D compositional map of a substrate. The substrate is patterned with feature sizes on the order of 1 to 3 microns to remain within the spatial resolution of μ -Raman spectroscopy for the purpose of demonstration. The first-order Raman spectrum for pure silicon and germanium produces peaks at 520.2 and 300.7 cm⁻¹, respectively. The deviations from these relaxed silicon and germanium peaks have been attributed to residual tensile stress in the Ge-depleted regions. Lateral line scans are performed to map the compositions of the stressed and annealed substrate, which provides a clear image of the resulting diffusion process. This imaging also allows the quantum structures to be addressable.

¹ S. Ghosh, D. Kaiser, J. Bonilla, T. Sinno, and S. M. Han, "Stress-Directed Compositional Patterning of SiGe Substrates for Lateral Quantum Barrier Manipulation," *Applied Physic Letters* **107**, 072106-1:5 (2015).

3:20pm EM+NS+SP+SS-WeA4 Atomic-scale Characterization of III-V Nanowire Heterostructures and Devices, *J. Knutsson, S. McKibbin, M. Hjort, J. Colvin, S. Yngman, A. Troian, O. Persson, A. Mikkelsen, Rainer Timm*, Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1]. With their flexibility in creating heterostructures, by radial and axial stacking during epitaxial growth, comes an increasing complexity of device structure. Furthermore, due to their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. It is therefore essential to study the structural and electronic properties of NW surfaces down to the atomic level and across interfaces regarding doping, material composition, or crystal phase.

We recently obtained atomically resolved scanning tunneling microscopy (STM) images of various GaAs, InAs, and InP NW surfaces [2,3]. By combining STM imaging with scanning tunneling spectroscopy (STS) measurements, we correlate the surface structure and local electronic properties [3]. Here, we will present examples from InAs NWs with interfaces between different crystal phase. Our low-temperature STM/S results show that even the smallest possible insertion of zincblende phase within a wurtzite segment, a single bilayer stacking fault, shows a clear zincblende signature. We observe transitions in the local density of states with sub-nm lateral resolution. Furthermore, we map the interface band alignment and measure quantum confinement energies of single and double bilayer stacking faults.

Beyond traditional steady-state surface characterization, it is desirable to even investigate nanostructure devices *in-situ*, meaning while they are operating under an applied bias. We are now using simultaneous STM, AFM, and electrical transport measurements for studying individually contacted NWs during device operation [4], complemented by Kelvin probe force microscopy and scanning photoemission microscopy. We will present initial results of such combined *in-situ* studies on axial *pn*-junctions in InP and GaInP NWs, where we also investigate the influence of NW surface modification (e.g. removal of native oxide by atomic hydrogen) on photovoltaic properties.

- [1] E. Lind *et al.*, IEEE J. El. Dev. Soc. **3**, 96 (2015); J. Wallentin *et al.*, Science **339**, 1057 (2013).
- [2] M. Hjort *et al.*, ACS Nano **6**, 9679 (2012); J. Knutsson *et al.*, ACS Appl. Mat. & Interf. **7**, 5748 (2015).
- [3] M. Hjort *et al.*, Nano Lett. **13**, 4492 (2013); M. Hjort *et al.*, ACS Nano **8**, 12346 (2014).
- [4] O. Persson *et al.*, Nano Lett. **15**, 3684 (2015); J. L. Webb *et al.*, Nano Res. **7**, 877 (2014).

4:20pm EM+NS+SP+SS-WeA7 Revealing Optical Properties of Reduced-Dimensionality Materials at Relevant Length Scales using Nanospectroscopic Imaging, *P. James Schuck*, The Molecular Foundry, Berkeley Lab **INVITED**

Reduced-dimensionality materials for photonic and optoelectronic applications including energy conversion, solid-state lighting, sensing, and information technology are undergoing rapid development. The search for novel materials based on reduced-dimensionality is driven by new physics. Understanding and optimizing material properties requires characterization at the relevant length scale, which is often below the diffraction limit. The nano-optical imaging community has now crossed the boundary from insufficient to sufficient resolution, mapping critical optoelectronic properties in these exciting materials at their native length scales. Here, I will describe the recent near-field imaging advances that lay groundwork for generally-applicable nano-optical studies of these low-D materials, and will show recent results on 0, 1, and 2D systems. I will spend time discussing the importance of near-field polarization in probing these materials, and will also highlight recent applications in 2-D semiconductor transition metal dichalcogenides (TMDCs), where we and others have uncovered new optoelectronic regions and spatially-varying features that were hidden in prior optical studies. These findings have broad implications for the development of atomically thin transistors, quantum optical components, photodetectors and light-emitting devices.

5:00pm EM+NS+SP+SS-WeA9 Polarizability Mapping of Nanolayers Based on Near-Field Edge Fringes, *Viktorii Babicheva, V.S. Yakovlev, S. Gamage, M.I. Stockman, Y. Abate*, Georgia State University

Scattering-type scanning near-field optical (s-SNOM) microscopy enable spectroscopic imaging with nanoscale resolution and provide chemical and structural information of surfaces [1]. In this work, we investigate

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identification of material type using an approach based on analyzing near fields at the sample edge [2]. We develop theoretical approach that includes full-wave numerical simulations and calculations of s-SNOM signal in different demodulation orders. This model allow characterization of structures of any shape and material, as well as different tips, and does not include any fitting parameters. In this way, we defined that metallic edge has bright and dark fringes in near-field characterization, whereas a bright edge of dielectric material has no outside fringe. Similar behavior is observed for anisotropic material with hyperbolic dispersion (boron nitride in mid-IR range): depending on the wavelength, it shows either metallic or dielectric properties.

1. Y. Abate, R.E. Marvel, J.I. Ziegler, S. Gamage, M.H. Javani, M.I. Stockman, and R.F. Haglund "Control of plasmonic nanoantennas by reversible metal-insulator transition" *Sci. Rep.* 5, 13997 (2015).

2. Y. Abate, S. Gamage, L. Zhen, S.B. Cronin, H. Wang, V. Babicheva, M.H. Javani, M.I. Stockman, "Nanoscopy reveals metallic black phosphorus," *Light: Science & Applications*, accepted (2016). <http://arxiv.org/abs/1506.05431>

5:20pm **EM+NS+SP+SS-WeA10 Wedding Cake Growth Mechanism in One-Dimensional and Two-Dimensional Nanostructure Evolution, *Xin Yin****, University of Wisconsin-Madison; *J. Shi*, Rensselaer Polytechnic Institute; *X. Niu*, Northeastern University; *D. Geng*, University of Wisconsin-Madison; *H. Huang*, Northeastern University; *X.D. Wang*, University of Wisconsin-Madison

Morphology is one essential element that gives rise to extraordinary physical, chemical, and mechanical properties in nanomaterials. Precise morphology control of nanomaterials is a notorious task, which heavily relies on fundamental understanding of the governing atomistic mechanisms and kinetics at the nanoscale. Despite numerous studies on the growth and application of nanostructures, current understanding of kinetics that governs the nanocrystal evolution is yet limited.

By programming deposition conditions at time domain, we observed the wedding cake growth mechanism in the formation of 2D ZnO nanostructures. Within a narrow growth window, the surfaces of 2D structures were covered with a unique concentric terrace feature. This mechanism was further validated by comparing the characteristic growth rates to the screw dislocation-driven model. An interesting 1D to 2D morphology transition was also found during the wedding cake growth, when the adatoms overcome the Ehrlich-Schwoebel (ES) barrier along the edge of the top crystal facet triggered by lowering the supersaturation. The evolution of 2D plate structure from 1D pillars represents a dynamic crystal growth behavior transition when the local deposition conditions were tuned in-situ. It lively recorded the wedding cake growth model in nanostructure formation from vapor phase, which was rare to be observed when the deposition conditions were remained constant. The terrace feature on these nanostructures provided a valuable platform for understanding the wedding cake growth kinetics that could be an important mechanism to design and predict the nanocrystal morphology formation from the bottom-up. Analyzing the supersaturation and temperature-related growth behavior provides a new insight into nanostructure growth mechanisms and morphology control.

Wedding cake growth is a layer-by-layer growth model commonly observed in epitaxial growth of metal films, featured by repeated nucleation of new atomic layers on the topmost surface owing to the confinement of the Ehrlich-Schwoebel (ES) barrier. This study expands the application of the wedding cake growth mechanism to the nanostructure growth. It enriches our understanding on the fundamental kinetics of nanostructured crystal growth and provides a transformative strategy to achieve rational design and control of nanoscale geometry.

5:40pm **EM+NS+SP+SS-WeA11 Detecting the Invisible - The Atomic Structure of Radiation Sensitive Nano-Materials, *Christian Kisielowski***, Molecular Foundry, Lawrence Berkeley National Laboratory; *P. Specht*, University of California Berkeley **INVITED**

As heterogeneous materials scale below 10 nm, a suitable combination of single digit nanocrystals with their rich variety of tunable surfaces and interfaces allows tailoring unprecedented materials with novel structure-function relationships. The design of new catalysts [1], investigations of polymers at atomic resolution [2] or analyses of deviations from a random doping distributions at atomic resolution [3] may serve as examples. This contribution describes research that aims at exploiting the emerging ability to analyze and understand such materials by directly determining their

atom arrangement in three-dimensions using aberration-corrected transmission electron microscopy [4]. Attempts to unravel the atomic structure of such nanoscale composites in this manner must explicitly address their pronounced sensitivity to the probing radiation that can unintentionally alter their pristine structure, often beyond recognition. We address this challenge by applying low dose-rate in-line holography [5], which allows operating electron microscopes with dose rates as low as 5-10 e/Å²s that help maintaining structural integrity at atomic resolution to an unexplored end. The approach mimics best practices in biological research but achieves atomic resolution with single atom sensitivity by the acquisition of large image series. We observe a variety of previously unknown atom configurations in surface proximity of CoO_x nanocrystals and coatings that are hidden behind unusually broadened diffraction patterns but become visible in real space images because the phase problem is solved. The observed structures are drastically altered by an exposure of the material to water vapor or other gases, which is investigated at atomic resolution in environmental electron microscopy. It is shown for Rh/W catalysts that electron beam-induced atom dynamics can be entirely suppressed even for atom clusters made from less than 10 atoms. Resultantly, chemical compositions can be determined by contrast measurements alone and functional processes can be triggered and tracked in real time at atomic resolution.[6]

[1] J. A. Haber et al., *Advanced Energy Materials* 5 (2015) 1402307

[2] D. Lolla et al., *Nanoscale* 8 (2016) 120 - 128

[3] P. Specht, C. Kisielowski, On the chemical homogeneity of In_xGa_{1-x}N alloys - Electron microscopy at the edge of technical limits, submitted (2016)

[4] F.R. Chen et al., *Nature Commun.* 7:10603 doi: 10.1038/ncomms10603 (2016)

[5] C. Kisielowski, *Advanced Materials* 27 (2015) 5838-5844

[6] The Molecular Foundry, which is supported by the Office of Science, the Office of Basic Energy Sciences, the U.S. Department of Energy under Contract No. DE-AC02-05CH11231

Advanced Surface Engineering Room 101D - Session SE+2D+EM-WeA

Multifunctional Thin Films and Coatings

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Michael Stueber, Karlsruhe Institute of Technology, Germany

2:20pm **SE+2D+EM-WeA1 Investigation of H₂S Poisoning Process on Composite Material Made of Metal Oxides and Carbon Nanotubes, *Yichen Duan, A.V. Teplyakov***, University of Delaware

The composite material based on a combination of SnO₂, CuO and acid-treated carbon nanotubes is considered to be promising for H₂S sensing applications. By applying large dosage of H₂S (1% in volume) to the composite and evaluating the chemical changes spectroscopically via XPS, SEM and EDS, the poisoning mechanism of this type of sensing material is revealed. Specifically, metal sulfides (CuS and SnS₂), metal sulfate (Sn(SO₄)₂) and thiols are formed as the products following the introduction of H₂S. In fact, all the three components of the material are affected by H₂S. Moreover, when oxygen is present, metal sulfides can be reoxidized back into metal oxides while metal sulfate and thiols remain unchanged. The measurements of the model sensor response also support the assessment of the poisoning process.

2:40pm **SE+2D+EM-WeA2 Graphene-family Nanomaterials Co-assembled with Nanostructured Cobalt Oxide Polymorphs as Hybrid Supercapacitive Electrodes and Enzymeless Glucose Detection Platforms, *Sara Carrizosa, B. McDonald, S. Gupta***, Western Kentucky University

Graphene-family Nanomaterials Assembled with Cobalt oxides and Cobalt Nanoparticles As Hybrid Supercapacitive Electrodes and Enzymeless Glucose Detection Platforms We developed graphene/cobalt oxides and graphene/cobalt nanoparticles hybrid assembly highlighting the impacts of nanoscale surface morphology and microstructure producing tailored interfaces for improved electrochemical and electroanalytical properties. Molecular electrodeposition and facile hydrothermal synthesis techniques followed by thermal treatment are demonstrated to be effective approaches for nanoengineered electrochemical electrodes. Hybrid electrodes consisting of supercapacitive graphene nanosheets and pseudocapacitive nanostructured cobalt oxide polymorphs (CoO and Co₃O₄) as well as cobalt nanoparticles (CoNP) synthesized on two- and

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three-dimensional graphene nanosheets facilitate chemically bridged (covalently and electrostatically anchored) yet tunable graphene-cobalt interfaces. The intrinsic microstructure and surface of these hybrids were characterized by electron microscopy combined with elemental mapping, X-ray diffraction and Raman spectroscopy. The graphene/cobalt hybrid composites were investigated as asymmetric supercapacitor cathodes and as electroanalytical platforms for enzymeless detection of glucose. We demonstrate that Co₃O₄/ErGO and Co₃O₄/multilayer graphene hybrids are capable of delivering high specific capacitance of > 600 F g⁻¹ at a current density of 10 A g⁻¹ is achieved when the mass ratio of Co₃O₄ to ErGO is equal to 80:20 as compared with other hybrids with excellent cycling stability in voltage range 0–1.2 V. It can also detect glucose with ultrahigh sensitivity of 4.57 mA mM⁻¹ cm⁻² and a remarkable lower detection limit of < 50 nM in the following order Co₃O₄/rGO_{HT} < CoO/ErGO < CoNP/MLGNiFoam < Co₃O₄/MLGNiFoam. We attribute all of these remarkable findings due to interplay of (a) open pore system beneficial to ion diffusion and transport kinetics owing to larger accessible geometric surface area, (b) three-dimensional topologically multiplexed and highly conductive pathways provided by MLG, ErGO and rGO_{HT} nanoscaffold architectures to ensure rapid charge transfer and electron/ion conduction (< 10 ms), and (c) synergistic integration of functional nanomaterials devoid of graphene sheets agglomeration with optimal transition metal (oxides) nanoparticles loading.

3:00pm **SE+2D+EM-WeA3 Cross-Bonding between Silicon, Silica and III-V Surfaces at the Nano-Scale Using Energy Analysis via Three Liquid Contact Angle Analysis (3LCAA) to achieve Hermetic Wet NanoBonding™**, *Ashley Mascareno*, SiO₂ NanoTech LLC/Arizona State University Physics Dpt; *N.X. Herbots*, SiO₂ NanoTech LLC; *C.F. Watson*, SiO₂ NanoTech LLC/Arizona State University Physics Dpt

Mobile ions such as Na, percolate from saline environments into marine and atmospheric sensors and limit their reliability to less than a week. Implantable glucose monitors for diabetics require replacement about every 3-7 days, with finger blood samples re-calibration daily. Hermetic bonding can yield economic, medical, and human benefits by extending lifetime of such integrated sensors from days to years. Si-based surfaces such as thermally-grown amorphous a-SiO₂ on Si(100), and on III-V surfaces can be hermetically bonded with Wet NanoBonding™ to yield dense, hermetic cross-bonding. In Wet Nonbonding™, planarization is first accomplished at the nano-scale, then a-SiO₂ is etched with HF, while a 2 nm precursor β-cSi₂O₄H₄ phase is grown on Si(100) to initiate cross-bonding. Next, both surfaces are put into mechanical contact in a class 10 clean-room and nano-bonded under low temperature (T<180° C) steam pressurization.

Modifying the surface energy components of 2 surfaces can help optimize hermeticity by increasing the density of cross-bonding. Surface energy γ^T can be measured via 3 Liquid Contact Angle Analysis (3LCAA) using the Van-Oss theory, which models γ^T for semiconductor and insulators in 3 interactions: (1) Lifschitz-Van der Waals molecular dipole interactions γ^{LW}, (2) electron donor interactions γ⁺, and (3) electron acceptor interactions γ⁻. Successful NanoBonding™ can occur between one surface with high γ⁺ and one with high γ⁻. 3LCAA extracts these from contact angles between several liquids with known surface energies and the surface. Sessile drop analysis with water, glycerin, and α-bromonaphthalene is conducted in a Class 100 hood using 4-8 drops per liquid for statistical accuracy. RCA cleaned Si(100) and Si(100) terminated with 2-nm β-cSi₂O₄H₄ via the Herbots-Atluri (H-A) process are used, in combination with Rapid Thermal Anneal and Oxidation (RTA and RTO), to grow a-SiO₂ [3]. The γ^T of hydrophilic RCA-cleaned Si(100) is 47.3±0.5 mJ/m², 25% higher than the γ^T of ordered, hydrophobic β-cSi₂O₄H₄ Si(100), 37.3±1.5mJ/m², and 30% higher than RTO oxides 34.5±0.5 mJ/m². Interactions from γ^{LW} account for 90-98±2% of γ^T in ordered oxides, but only 76.5±2.0% of those in hydrophilic surfaces. Thus, 3LCAA detects changes in surface reactivity from defects, impurities, and dangling bonds. While γ⁺ accounts for little to none of γ^T for all but one surface, 180° C annealing during Wet NanoBonding significantly increases γ⁺ in β-cSiO₂. Conversely, HF etching significantly increases γ⁻ for a-SiO₂. When matching acceptor with donor interactions between surfaces via 3LCAA, cross-bonding density appears to increase, and NanoBonding™

3:20pm **SE+2D+EM-WeA4 Porous Materials for Solid Phase Microextraction by Sputtering and Chemical Vapor Deposition**, *Tuhin Roychowdhury*, *A. Diwan*, *B. Singh*, *M. Kaykhai*, *M.R. Linford*, Brigham Young University

Solid phase microextraction (SPME) is an important sampling tool. It consists of placing a coated fiber above a sample (headspace mode) or immersing it in a liquid such that molecules (analytes) of interest can be selectively extracted and concentrated. The captured species are then released by heating into a chromatograph for separation and identification. It is a 'green' method because no additional solvent is used in this process. We have developed a new class of SPME fibers that offer extraordinary capacity and speed. They are prepared by sputtering a material under conditions that lead to a nanoporous coating on the fiber. When silicon is sputtered under these conditions, its outermost surface can be additionally oxidized, leading to a high density of silanol groups than can be subsequently silanized. For example, the fibers can be derivatized with octadecyldimethylmethoxysilane by chemical vapor deposition (CVD), which creates a hydrophobic extraction medium. The performance of our 2 micron sputtered coatings has been compared to that of thicker (7 micron) commercial coatings. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for alcohols, amines, aldehydes, and esters. Real world samples, e.g., hops and PAH from water, have also been analyzed. Different coating thicknesses have been prepared and evaluated. Sputtered coatings have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and wetting.

4:20pm **SE+2D+EM-WeA7 Ferroelectric Thin Films for Memory Applications**, *Joyprakash Chakrabarty*, Institut national de la recherche scientifique (INRS), Canada

Ferroelectric (FE) oxides draw attention in science community because of its spontaneous switchable polarization often used in electronic devices. FEs are earth abundant, easy to synthesis and low degradation of electronic properties while exposed to room atmosphere. One of its promising applications is in computer memory devices. FEs function as memory by storing data in its two polarization states normally defined as up and down state. However the challenges lie in enhancing data bit density at room temperature. Here we show four step ferroelectric polarization switching in BiFeO₃(BFO)/SrRuO₃(SRO)/BiMnO₃(BMO) heterostructure thin films which act as FE memory devices. All crystalline films are grown on (100) oriented Niobium doped SrTiO₃ (NSTO) single crystal substrates by pulsed laser deposition. Our experimental results show a promising device concept, unique in FE memories that can enhance the data storage capacity in heterostructure capacitor devices at room temperature.

4:40pm **SE+2D+EM-WeA8 Thermoelectric and Optical Properties of Advanced Thermoelectric Devices from Ni/Bi₂Te₃/Ni and Ni/Sb₂Te₃/Ni Thin Films**, *Satilmis Budak*, *Z. Xiao*, *J. Cole*, *A. Kassu*, *D. Price*, *T. Davis*, *T. Strang*, *J. Gray*, Alabama A&M University

Thermoelectric devices were prepared from Ni/Bi₂Te₃/Ni and Ni/Sb₂Te₃/Ni thin films using DC/RF magnetron sputtering and E-beam deposition systems. Thermoelectric devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thin film devices were characterized using Seebeck coefficient measurement systems; four probe van der Pauw measurement system to measure resistivity, sheet resistance, density, mobility and type of the charge carrier concentration. In addition to the Seebeck coefficient and van der Pauw measurements, the laser thermal conductivity system was used for the thermal conductivity measurements. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM). Raman Spectroscopic technique is used for identification of inherent molecular specificity and analysis of chemical compositions of the films. The resonant features of the scattering spectra measured under the 532 nm and 785 nm wavelength excitation lasers are analyzed.

Acknowledgement

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5:00pm **SE+2D+EM-WeA9 Effects of Composition and Strain on Band Gaps of Pseudomorphic Ge_{1-x}Si_xSn_y on Ge**, *Nalin Fernando*, New Mexico State University; *R. Hickey, J. Hart, R. Hazbun, D. Zhang, J. Kolodzey*, University of Delaware; *S. Zollner*, New Mexico State University

Ge-Si-Sn alloys are interesting for CMOS applications for a variety of reasons. For example, adding Sn to Si-Ge lowers the band gap, which reduces parasitic contact resistance. Also, the lattice constant of Ge-Sn alloys increases when adding Sn. Therefore, such alloys could be used to impart strain on PMOS devices with Ge channels. We used deformation potential theory to determine the compositional dependence of the direct, indirect, E₁, and E₁+ Δ₁ band gaps of pseudomorphic Ge_{1-x}Si_xSn_y on Ge and theoretical predictions are validated through spectroscopic ellipsometry measurements of the band gaps of pseudomorphic Ge_{1-y}Sn_y on Ge grown by MBE.

The band structure of Ge is a strong function of strain and alloy composition, and a transition from an indirect to a direct band gap has been observed for ~6-10% for relaxed Ge_{1-y}Sn_y, indicating the possibility of widespread applications of Ge-based photonic devices. The pseudomorphic nature of the Ge-based alloy layer on a substrate is important to keep dislocation densities low at the interface to improve the performance of the device. Band gap engineering of Ge by controlling strain and alloying with Si and Sn has attracted great interest since a Ge_{1-x}Si_xSn_y ternary alloy with two compositional degrees of freedom allows decoupling of the lattice constant and electronic structures.

The pseudomorphically grown Ge_{1-x}Si_xSn_y layer on Ge experiences a biaxial stress due to the lattice mismatch between the alloy layer and the Ge. The strain resulting from the stress affects the band structure of the alloy. Deformation potential theory is used to determine the compositional dependence of the band gaps of pseudomorphic Ge_{1-x}Si_xSn_y on Ge as a function of Si (x) and Sn (y) compositions. The predictions of the deformation potential theory are validated for pseudomorphic Ge_{1-y}Sn_y (for Si=0) on Ge through measurements of the optical properties. The complex pseudodielectric functions of pseudomorphic Ge_{1-y}Sn_y alloys grown on Ge by MBE were measured using ellipsometry in the 0.1-6.6 eV energy range for Sn contents up to 11%, to investigate the compositional dependence of the band gaps. Critical point energies (CP) and related parameters were obtained by analyzing the second derivative spectrum of the dielectric function. Our experimental results for E_g^{dir}, E₁ and E₁+ Δ₁ gaps are in good agreement with the theoretically predicted CP energies. We will discuss the strain and compositional dependence of the band gaps and the effects of the growth temperature of the Ge buffer layer on Si to the band gaps.

This work was supported by AFOSR (FA9550-13-1-00222). FTIR measurements were performed at CINT.

5:20pm **SE+2D+EM-WeA10 MBE Growth of Hexagonal Boron Nitride for use in Novel Electronic Devices**, *Adam Barton, R. Yue, C.M. Smyth, R. Addou, L. Cheng, R.M. Wallace, J. Kim, M. Kim, J. Hsu, K.J. Cho*, The University of Texas at Dallas; *L. Colombo*, Texas Instruments; *C.L. Hinkle*, The University of Texas at Dallas

2D materials offer unique opportunities in device fabrication due to the weak van der Waals interaction between crystalline layers that allows for the growth of high-quality heterostructures with significantly less impact from lattice mismatch with the substrate. Hexagonal boron nitride (hBN) has a honeycomb structure similar to graphene except with alternating boron and nitrogen atoms. The hexagonal rings are composed of six sp²-hybridized atoms (three boron atoms and three nitrogen atoms). The electronic structure results in a bandgap of 5-7eV, a low-κ dielectric constant of 2-4ε₀, and an electron affinity of roughly 2 eV. These electronic properties make hBN an exciting material for a wide range of applications in electronic devices. In particular, we are interested in coupling hBN with transition metal dichalcogenides (TMDs) for low-power tunnel FET applications. Previous publications have primarily utilized chemical vapor deposition (CVD) to grow hBN on catalyzing transition metal substrates (Co, Ni, Cu, etc.) at growth temperatures ranging from 800-1200°C. However, these substrates and growth temperatures are not practical for the majority of device applications. Chalcogen loss in TMDs, for example occurs well below those temperatures.

In this work we report on our recent findings on the growth and characterization of hBN thin films grown by molecular beam epitaxy (MBE). This will include a detailed discussion of the growth mechanism on a variety of substrates (MoS₂, HOPG, WSe₂, Bi₂Se₃, and sapphire) using substrate growth temperatures ranging from 300-800°C. The impact of the source fluxes, substrate temperatures, and in particular, the presence of atomic hydrogen during growth will be presented. The hexagonal phase of

BN is achieved as determined by diffraction, Raman, and XPS. AFM, TEM, and RHEED are also used to assess film quality and the experimentally determined bandgap and band alignment will be presented. We will also present our recent work on coupling hBN with ALD-deposited Al₂O₃ to enable higher-k gate dielectrics on top of 2D materials heterostructures.

This work is supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST. This work was also supported in part by the Texas Higher Education Coordinating Board's Norman Hackerman Advanced Research Program.

5:40pm **SE+2D+EM-WeA11 Passivation of Interfaces Between High-k Dielectrics and SiGe: Ex Situ Wet Sulfur Clean vs. In Situ Plasma Nitridation**, *Kasra Sardashti*, *M.S. Clemons*, UC San Diego; *M. Yakimov*, SUNY College of Nanoscale Science and Engineering; *K. Tang*, Stanford University; *S. Oktyabrsky*, SUNY College of Nanoscale Science and Engineering; *P.C. McIntyre*, Stanford University; *L. Dong, N. Yoshida*, Applied Materials, Inc.; *A.C. Kummel*, UC San Diego

Silicon-Germanium is a promising channel material to be used in novel CMOS device architectures such as FinFET and Nanowire FET, due to its high hole mobility. Moreover, it enables control of carrier mobility by mechanical stress and band gap by variation in Si/Ge content in multilayer design. One of the important issues to address in the integration of SiGe in the MOS devices is formation of low-defect interfaces with very thin high-k gate dielectrics such as Al₂O₃, HfO₂ and ZrO₂. Due to adverse effect of Ge sub-oxide (GeO_x) formation and subsequent Ge out-diffusion on the performance of the devices, robust strategies to control the Ge reactions during and after oxide deposition are essential to further the development of SiGe FETs. This study determines the effects of two passivation methods on the quality of the interfaces between SiGe and high-k dielectrics: 1) Ex-situ wet sulfur passivation using (NH₄)₂S solution; 2) In-situ NH₃ plasma nitridation. Al₂O₃ and HfO₂ were deposited on SiGe surfaces by atomic layer deposition (ALD). Electrical and chemical properties of the interfaces were evaluated by capacitance-voltage (C-V) spectroscopy, angle-resolved photoelectron spectroscopy (AR-XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Both sulfur passivation and plasma nitridation resulted in smaller density of interface traps with a large majority of the trap energy levels adjacent to the valence band edge. Ex-situ sulfur passivation was found to improve the interface quality by reducing the extent of GeO_x formation at the high-k/SiGe interface, therefore constraining the extent of Ge out-diffusion within the oxide. The mechanism is distinct; sulfur forms much stronger bonds to Ge than to Si due to the d-orbitals on the Ge; this promotes selective oxidation of the Si and prevents formation of GeO_x. Using plasma nitridation, a thin layer of SiON forms selectively at the high-k/SiGe interfaces, preventing the presence of thermally-unstable species such as GeO_x and GeON. In addition, SiON can act as a physical diffusion barrier to Ge out-diffusion. The nitridation is selective due to the higher enthalpy of formation for Si vs Ge oxynitrides. Both ex-situ sulfur passivation and in-situ NH₃ plasma nitridation were found to be effective approaches in preparing low-defect Al₂O₃/SiGe and HfO₂/SiGe interfaces; the different chemical mechanisms show there are multiple paths to selective bond formation to SiGe which can be utilized to engineer low-defect stable interfaces.

6:00pm **SE+2D+EM-WeA12 Enhanced Voltage Control of Perpendicular Magnetic Anisotropy in Magnetic Tunnel Junctions Using Ultrathin PZT Composite Oxide Tunneling Barriers**, *Kevin Fitzell, X. Li, K. Wong, G. Yu, S. Robbenolt, S.H. Tolbert, P.K. Amiri, K.L. Wang, J.P. Chang*, University of California at Los Angeles

In contrast to manipulating magnetization with applied current, using an applied electric field can significantly reduce the required energy and result in less heat generation, leading to increased energy density. This can be accomplished using the voltage-controlled magnetic anisotropy (VCMA) effect, which forms the basis of next-generation magnetoelectric MRAM devices. Specifically, applying an electric field across a CoFeB/MgO interface can decrease the perpendicular magnetic anisotropy field as a result of the altered electron density at the interface, thus destabilizing the magnetization state and allowing for its efficient and deterministic reorientation with a small applied magnetic field. This operation principle stands in contrast to that of STT-RAM, which uses upwards of 100 fJ to write a single bit (300,000 times more energy than the actual energy barrier to switching).

Previous research on CoFeB/oxide interfaces has shown that increasing the dielectric constant of the oxide layer also increases the sensitivity of the

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interfacial magnetic anisotropy energy to an applied electric field. Lead zirconate titanate (PZT), having excellent ferroelectric properties including a large dielectric constant, is therefore a prime candidate for integration into such oxide layers in an attempt to maximize the VCMA effect. Using atomic layer deposition (ALD), PZT was thus incorporated into magnetic tunnel junctions having MgO/PZT/MgO multilayer composite tunneling barriers. Our group has shown that MRAM devices fabricated using these MgO/PZT/MgO tunneling barriers resulted in a 40% increase in the VCMA coefficient (and thus substantial energy savings) over magnetic tunnel junctions simply employing MgO tunneling barriers, despite the PZT layer being amorphous. Our most recent work has focused on the crystallization of these ultrathin PZT layers, which would cause an even larger dielectric response (even greater energy savings) and open an avenue toward four-state memory devices relying on the ferroelectric polarization of the PZT.

Surface Science

Room 104D - Session SS+AS+EM-WeA

Semiconductor Surfaces and Interfaces

Moderator: Andrew Gellman, Carnegie Mellon University

2:20pm **SS+AS+EM-WeA1 Adsorption of Triethylenediamine on Si(100)-2x1 Surface via N-Si Dative Bonding and C-N Dissociation, Jing Zhao, M. Madachik, University of Delaware; K. O'Donnell, Curtin University, Australia; O. Warschkow, University of Sydney, Australia; L. Thomsen, Australian Synchrotron, Australia; G. Moore, S. Schofield, University College London; A.V. Teplyakov, University of Delaware**

The functionalization of silicon surfaces with thin layers of organic materials is an important area of studies with current and potential applications in microelectronics, catalysis, and bio-sensing. Triethylenediamine (also known as 1,4-diazabicyclo[2.2.2]octane, or DABCO) presents an interesting case study for silicon functionalization because of its symmetric structure with two x nitrogen atoms in tertiary amine configuration. Each of these atoms could potentially form a dative bond with a clean Si(100)-2x1 surface while the other may remain accessible for further modification. We applied infrared spectroscopy (MIR-FTIR), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD) supported by density functional theory calculations (DFT) to investigate the reaction mechanism of triethylenediamine with a clean Si(100)-2x1 surface, focusing specifically on dative bond formation and C-N dissociation.

2:40pm **SS+AS+EM-WeA2 Chemoselective Adsorption of Functionalized Cyclooctynes on Silicon, M. Reutzel, N. Munster, M.A. Lipponer, Philipps-Universität Marburg, Germany; C. Langer, Justus Liebig University Giessen, Germany; U. Hofer, U. Koert, Philipps-Universität Marburg, Germany; Michael Durr, Justus Liebig University Giessen, Germany**

The adsorption of organic molecules on silicon surfaces has been subject of intense research due to the potential applications of organic functionalization of silicon surfaces in semiconductor technology. The high reactivity of the silicon dangling bonds, however, presents a major hindrance for the first basic reaction step of such a functionalization, i.e., chemoselective attachment of bifunctional organic molecules on the pristine silicon surface. Due to the high reactivity of the dangling bonds, each functional group of a bifunctional molecule adsorbs with an initial sticking coefficient close to unity and thus the final adsorption product will typically consist of a mixture of molecules adsorbed via different functional groups.

We overcome this problem employing cyclooctyne as the major building block of our strategy. Using scanning tunneling microscopy and X-ray photoelectron spectroscopy, cyclooctyne derivatives with different functional side groups are shown to react on Si(001) selectively via the strained cyclooctyne triple bond while leaving the side groups intact. The origin of this chemoselectivity is traced back to the different adsorption dynamics of the functional groups involved. We show that cyclooctyne's strained triple bond is associated with a direct adsorption channel on the Si(001) surface, in contrast to most other organic molecules which adsorb via weakly bound intermediates. In these intermediate states, the molecules have a finite lifetime and are often mobile and free to rotate on the surface. This allows the bifunctional molecule to sample the surface with the strained triple bond during its finite lifetime in the trapped state and in consequence, bifunctional molecules with a strained triple bond as one functional group will end up with this group attached to Si(001) even if the initial interaction proceeds via the second functional group.

Chemoselectivity can thus be achieved even on the highly reactive Si(001) surface when exploiting the adsorption dynamics of the respective reaction channels.

3:00pm **SS+AS+EM-WeA3 Compositions, Structures, and Electronic Properties of Grain Boundaries of Cu(InGa)Se₂, Xudong Xiao, Chinese University of Hong Kong**

INVITED

Polycrystalline semiconductors are important energy materials and the grain boundaries play crucial role in their electrical transport property. While in general grain boundary is detrimental, for Cu(InGa)Se₂ (CIGS), it was found that the grain boundary is benign to the electrical transport and a record solar cell energy conversion efficiency of 22.3%, the best among all thin film solar cells, has been achieved with a polycrystalline film. This peculiar benign behavior has attracted great attention in the materials science community, unfortunately, even with tremendous effort, the mechanism of the benignity of CIGS grain boundary remains as an outstanding problem, mostly due to the lack of convincing experimental evidences.

We performed our study by design and prepare well controlled CIGS samples with two different Cu content. By careful treatment of the samples to remove artifacts, we used a combination of techniques, namely AFM, STM, and TEM, to probe at nanoscales the composition, structure, and electrical properties of the individual grain boundary in direct comparison to those of the individual grain interior. We discovered that the grain boundary in fact consists of a boundary layer of finite thickness in addition to the grain boundary surface/interface for the non $\Sigma 3$ grain boundaries. This boundary layer has a definitive composition, structure, and electronic band, independent of the overall Cu content in the CIGS films. The observation of similar grain interior and similar grain boundary except the boundary layer thickness for the two samples with very different overall Cu content is indeed a surprising finding that has never been reported before. The band alignment between grain boundary and grain interior was discovered to be of type II with downward offset for both conduction and valence bands at grain boundary, well correlating to the local copper deficiency and structure. Our findings expressively support the type inversion and large hole barrier in this grain boundary layer, and establish a comprehensive mechanism for the suppression of carrier recombination therein.

4:20pm **SS+AS+EM-WeA7 Thermal Self-limiting CVD Silicon and ALD Silicon Nitride Containing Control Layers on In_{0.53}Ga_{0.47}As(001)-(2x4), Si_{0.5}Ge_{0.5}(110), and Si_{0.7}Ge_{0.3}(001), Steven Wolf, M. Edmonds, T. Kent, K. Sardashti, University of California at San Diego; M. Chang, J. Kachian, Applied Materials; R. Droopad, Texas State University; E. Chagarov, A.C. Kummel, University of California at San Diego**

Compound semiconductors with high mobilities such as InGaAs and SiGe are being employed in metal oxide semiconductor field effect transistors (MOSFETs) to increase transistor performance. However, these surfaces contain dangling bonds that can affect the surface Fermi level; thus, depositing a control layer via ALD or self-limiting CVD on multiple materials and crystallographic faces is required. Silicon uniquely bonds strongly to all crystallographic faces of InGa_{1-x}As, In_xGa_{1-x}Sb, In_xGa_{1-x}N, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which can then be passivated by atomic hydrogen. Subsequently, the surface may be functionalized with an oxidant such as HOOH in order to create a terminating Si-OH layer, or a nitriding agent such as N₂H₄ in order to create an Si-N_x diffusion barrier and surface protection layer. This study focuses on depositing saturated Si-H_x and Si-OH seed layers via a self-limiting CVD process on InGaAs(001)-(2x4), and depositing a Si-N_x seed layer on Si_{0.5}Ge_{0.5}(110) and Si_{0.7}Ge_{0.3}(001) via an ALD process. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of these control layers on the various surfaces. A thin Si-H_x capping layer (2.5 monolayers) was deposited in a self-limiting CVD fashion on InGaAs(001)-(2x4) by exposing to Si₂Cl₆ at 350°C. This layer allows for multilayer silicon or Si-O_x growth by ALD through cyclically dosing Si₂Cl₆ with either atomic H or anhydrous HOOH. STM and STS measurements show the Si₂Cl₆ exposed InGaAs(001)-(2x4) surface is atomically locally ordered and has an unpinned surface Fermi level. Exposure to anhydrous HOOH at 350°C terminates the surface with Si-O bonds and does not lead to oxidation of substrate peaks. The HOOH treated surface then nucleates TMA at 250°C and ultimately further high-k gate oxide growth. MOSCAP device fabrication was performed on n-type InGaAs(001) substrates with and without a Si-H_x passivation control layer deposited by self-limiting CVD in order to determine the effects on C_{max}, frequency dispersion, and midgap trap states. Deposition of a SiO_xN_y diffusion barrier and surface protection

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layer was achieved on the Si_{0.5}Ge_{0.5}(110) and Si_{0.7}Ge_{0.3}(001) surfaces via an ALD process at 275°C through cyclically dosing Si₂Cl₆ and anhydrous N₂H₄. MOSCAP device fabrication was performed on Si_{0.7}Ge_{0.3}(001) with and without a SiO_xN_y passivation control layer to compare device performance. Ultimately, the Si-H_x passivation layer gave less frequency dispersion at flat band and a lower D_{it}, and the SiO_xN_y passivation layer yielded lower gate leakage and D_{it} when compared to the respective wet clean only devices.

4:40pm **SS+AS+EM-WeA8 Formation of Atomically Ordered and Chemically Selective Si-O-Ti Monolayer on Si_{0.5}Ge_{0.5}(110) for a MIS Structure via H₂O₂(g) Functionalization, SangWook Park, J.Y. Choi, University of California, San Diego; E. Chagarov, University of California, San Diego; B. Sahu, S. Siddiqui, GLOBALFOUNDRIES; N. Yoshida, J. Kachian, Applied Materials; A.C. Kummel, University of California, San Diego**

To overcome challenges when scaling down silicon-based complementary metal-oxide semiconductor (CMOS) devices, SiGe has received much attention due to its high carrier mobility and applications in strain engineering. Extremely thin oxides with appropriate band offsets can be utilized to form unpinned contacts on SiGe for a metal-insulator-semiconductor (MIS) structure. The TiO₂ interfacial layer on Ge is known to form a MIS structure which reduces the tunneling resistance due to the nearly zero conduction band offset (CBO) between TiO₂ and Ge. In this study, formation of TiO_x monolayer on SiGe(110) via H₂O₂(g) functionalization was investigated using *in-situ* scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS). H₂O₂(g) was employed instead of the conventional H₂O(g) oxidant since H₂O₂(g) can form a uniform monolayer of -OH ligands on the surface without subsurface oxidation which should be ideal for forming the most stable possible interface which is a layer of Si-O-Ti bonds. STM verified that clean Si_{0.5}Ge_{0.5}(110) surfaces were terminated with both Si and Ge adatoms. STS measurements indicated that the Fermi level of clean Si_{0.5}Ge_{0.5}(110) surfaces was pinned near midgap between the valence and conduction band edges due to the half-filled dangling bonds of the adatoms. In order to passivate the dangling bonds, atomic H was dosed onto clean Si_{0.5}Ge_{0.5}(110) at 300°C which unpinned the Fermi level as demonstrated by STS. XPS analysis showed a saturation dose of H₂O₂(g) at 25°C left the Si_{0.5}Ge_{0.5}(110) surfaces terminated with a monolayer of both Ge-OH and Si-OH sites. STS indicated that the Fermi level on H₂O₂(g) dosed Si_{0.5}Ge_{0.5}(110) was shifted to near the valence band edge due to the formation of surface dipoles induced by hydroxyl bonds. Tetrakis(dimethylamido)titanium (TDMAT) or titanium tetrachloride (TiCl₄) was subsequently dosed onto hydroxyl-terminated Si_{0.5}Ge_{0.5}(110) at 25°C forming Ti bonds on surface. Both TDMAT and TiCl₄ dosed Si_{0.5}Ge_{0.5}(110) surfaces were annealed at 300°C and XPS verified that the Ti-O bonds were totally transferred from Ge atoms to Si atoms forming exclusively Ti-O-Si bonds on Si_{0.5}Ge_{0.5}(110) surfaces consistent with the strong bonding between Si and oxygen pulling Si atoms toward the surface to bond with oxygen while pushing Ge atoms into the subsurface during the annealing. STM demonstrated an ordered TiO_x monolayer was formed with a row spacing which doubles the spacing of adatoms on clean Si_{0.5}Ge_{0.5}(110). In addition, STS indicated a TiO_x monolayer on SiGe(110) was unpinned and therefore can serve as an ultra-thin insulating layer for a MIS structure.

5:00pm **SS+AS+EM-WeA9 The Effect of Ultrasonic Treatment (UST) on the Defect Structure of the Si-SiO₂ System, Daniel Kropman, T. Laas, Tallinn University, Estonia**

The effect of ultrasonic treatment (UST) on the defect structure of the Si-SiO₂ system by means of electron spin resonance (ESR), selective etching, MOS capacitance technique and secondary ions mass-spectroscopy is presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. In the ESR spectra of Si samples a signal with g=1.9996 (Pa centres) connected with vacancy complexes is observed. After UST appears another signal with g=2.0055 (broken bonds of Si atoms). The influence of the US frequency and sample orientation on the ESR signal intensity varies for different centres. The frequency and orientation dependence of the ESR signal with g=1.9996 and the lack of this dependence for the centres with g=2.0055 show that vibration energy dissipation depends on the type of defect centers. Defect density at the interface grows with an increase of US wave intensity or changes nonmonotonously depending on the oxide thickness and crystallographic orientation. In the samples with thick oxide/0,6 mkm there is a maximum in the dependence of the charge carriers lifetime on the US wave amplitude and in the samples with thin oxides /0,3 mkm/ there is a

minimum. This shows that the structural defects form electrically active centres and their density can be varied by US. The density of point defects and absorbed impurities at the Si-SiO₂ interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. US is widely used not only for materials treatment but in medicine as well (cancer treatment).

References:

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5:20pm **SS+AS+EM-WeA10 Adsorption of C₆₀ Buckminster Fullerenes on a Carbon-free Hydrazine-modified Silicon Surface, Fei Gao*, A.V. Teplyakov, University of Delaware**

Buckminster fullerene C₆₀ was used as a model to understand the attachment chemistry of large molecules on amine-terminated semiconductor surfaces. The resulting interface may serve as a foundation for devices in such fields as solar energy conversion, biosensing, catalysis, and molecular electronics. In this work, a monolayer of buckminster fullerenes C₆₀ was covalently attached to silicon surfaces using an efficient wet chemistry method. The starting chlorine-terminated Si(111) surface was initially modified with hydrazine to produce NH-NH functionality. Then the C₆₀ fullerenes were reacted directly with this surface. The chemical state and surface topography of the C₆₀-modified surface were characterized by surface analytical spectroscopic and microscopic methods, including X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and atomic-force microscopy (AFM). The experimental results were also supported by computational investigation, density functional theory (DFT) calculations, that were performed to predict core-level energies of surface species formed and to propose the possible mechanism of surface reactions.

5:40pm **SS+AS+EM-WeA11 Passivation of SiGe Surfaces with Aqueous Ammonium Sulfide, Stacy Heslop, A.J. Muscat, University of Arizona**

Ge and SiGe are promising materials for future p-type metal-oxide semiconductor field effect transistors (MOSFETs) due to their higher hole mobilities and narrower bandgap compared to Si. In contrast to silicon, Ge and SiGe readily oxidize in ambient air forming nonstoichiometric Ge oxides that are detrimental to the electrical performance of the device. One approach is to remove these oxides and passivate the surface. SiGe with molar ratios of 25 and 75% Ge were treated with aqueous ammonium sulfide, (NH₄)₂S, to deposit sulfur. The composition of the surface was measured using x-ray photoelectron spectroscopy (XPS) as a function of concentration and pH. The (NH₄)₂S concentration was varied from 3 mM to 3 M, and the pH was varied from 10 to 8 using HCl and HF. Film thicknesses were measured with spectroscopic ellipsometry.

A fresh SiGe starting surface was produced by immersing in SC-1 (1:1:500 v/v) to form oxides and stripping the oxides using HF:HCl:H₂O (1:3:300 v/v). In the case of SiGe 25%, sulfides were not detected based on the S 2p XPS state for surfaces treated with (NH₄)₂S (Figure 1a). The oxygen coverage increased with increasing (NH₄)₂S concentration, forming primarily SiO₂ and a small coverage of GeO. The surface was enriched in Si and oxidized, and there was not enough Ge atoms exposed for S to bond to. HCl and HF were added to remove the Si and Ge oxides that formed. The addition of HCl and HF resulted in the deposition of sulfides on SiGe 25% (Figure 1b). The Si/Ge peak area ratio after oxide removal was 1.7. After immersion in 30 mM (NH₄)₂S at a pH of 10 the surface composition was unchanged (Si/Ge=1.7). For the same (NH₄)₂S concentration at a pH of 8 the surface was only slightly enriched with Si (Si/Ge=2.4). Overall, (NH₄)₂S is not an effective passivation reagent for Si-rich SiGe surfaces due to the lack of S deposited and the undesirable oxides which form during processing. By dropping the pH to 8, less than a monolayer of S is deposited but oxides still remain. In contrast, SiGe 75% did not oxidize as a function of the (NH₄)₂S concentration. Sulfur was detected based on the S 2p XPS state and the S coverage was independent of (NH₄)₂S concentration. The sulfur thickness increased from about 2.3 Å for (NH₄)₂S (30 mM or 1:100 v/v) at a pH of 10 to 3.4 Å for the same (NH₄)₂S dilution at a pH of 8 (Figure 1c and d). These film thicknesses were approximated from XPS peak areas based on a single layer model for S on Ge. The deposition of the S layer did not affect the surface stoichiometry between oxide removal steps (Si/Ge=0.19) and 30 mM passivation (Si/Ge=0.20).

* Morton S. Traum Award Finalist

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6:00pm **SS+AS+EM-WeA12 Novel Electrical Circuit Model for the Design of InGaAs/GaAs (001) Strained-Layer-Super-Lattice**, *Tedi Kujofsa, J.E. Ayers*, University of Connecticut

Understanding lattice relaxation and dislocation dynamics has important implications in the design of highly functional and reliable semiconductor device heterostructures. Strain-layer-superlattices (SLSs) have been commonly used as dislocation filters whereby threading dislocations (TDs) can be removed by the insertion of a series of mismatched interfaces. The reduction of the threading dislocation in SLSs can be explained by the bending over of TDs associated with misfit segments of one sense by misfit dislocations having the opposite sense. Furthermore, the use of multilayered metamorphic buffer layers (MBLs) with intentionally mismatched interfaces may be used to take advantage of the strain compensation mechanism.

Previously, we developed a generalized energy minimization model, which determines the equilibrium configuration of an arbitrary compositionally-graded or multilayered heterostructure. The present work focuses on the development of a *novel electrical circuit* model for understanding equilibrium lattice relaxation in InGaAs/GaAs (001) strained-layer-superlattice heterostructures. This work focuses on the design of the SLS buffer layer of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited on a GaAs (001) substrate. The SL contains a set of 10 uniform layers with alternating mismatch. In other words, the SSL contains alternating uniform layers of $\text{In}_x\text{Ga}_{1-x}\text{As}$ with indium compositions x and $x + \Delta x$ respectively. For each structure, we present minimum energy calculations and show that for a given SLS total layer thickness h_{SLS} , it is possible to find the combination x and Δx such that it provides tight control of the in-plane strain of the strained-layer-superlattice. In addition, for each structure type we present minimum energy calculations by studying the (i) depth profile of strain and (ii) the misfit dislocation density profile. Most importantly, the use of the electrical circuit model allows the analysis of semiconductor heterostructures using a standard SPICE circuit simulator and provides an intuitive understanding of the relaxation process in these multilayered heterostructures.

Thin Film

Room 105A - Session TF+EM+MI-WeA

Thin Films for Microelectronics

Moderators: Paul Poedt, Holst Centre / TNO, Netherlands, Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France

2:20pm **TF+EM+MI-WeA1 Impact of ALD VO_2 Film Thickness on the Electrical and Optical Properties of the Metal-Insulator Phase Transition**, *Virginia Wheeler, B.P. Downey, J. Roussos, M. Currie, A. Giles, C. Ellis, J. Tischler, J. Caldwell, D.J. Meyer, C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

VO_2 films are known to undergo a metal-insulator phase transition (MIT) at a critical temperature ($T_c = 68^\circ\text{C}$) near room temperature which results in significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties; thus attracting interest in a variety of new electronic, optoelectronic, and photonic applications. Atomic layer deposition (ALD) provides a way to obtain large area film uniformity, abrupt interfaces and angstrom-scale control of thickness conformally across planar, as well as three-dimensional, high surface area nanostructures, which could be used to integrate VO_2 films into complex electronic and optical devices for additional functionality. In this work, VO_2 electrical devices and VO_2 coated SiC-based nanoresonators are used to investigate the impact of film thickness on electrical and optical properties.

The influence of VO_2 thickness on electrical performance was investigated using a simple two-terminal device structure. Sheet resistance measurements as a function of temperature revealed that the $R_{\text{off}}/R_{\text{on}}$ ratio increased with increasing VO_2 thickness, up to $R_{\text{off}}/R_{\text{on}}$ of ~ 7000 for a 92 nm film. Similarly, the T_c increased slightly with increasing thickness ($T_c = 66^\circ\text{C}$ for 35nm, 73°C for 92nm), while all films show relatively low hysteresis ($\Delta T < 8^\circ\text{C}$). Initial small-signal rf measurements using the 92 nm ALD VO_2 film demonstrated a cut-off frequency of greater than 1 THz, indicating the potential for rf-switch applications into millimeter wavelength frequencies using these ultra-thin ALD films, and the potential of these films to be conformally integrated into complex circuits with an ALD process.

For applications in the infrared, surface phonon-polariton-based SiC nanoresonators exhibiting strong, narrowband absorption features within the 10-12.5 μm range were coated with different thickness ALD VO_2 films. Since these films are transparent to infrared light below the T_c and

reflective above the T_c , conformally coating these SiC nanostructures provides a way to add functionality to these structures by modulating the amplitude of the resonances with temperature. Initial results show that the magnitude of the resonance suppression increases with increasing VO_2 thickness and a VO_2 film thickness greater than 16nm is required to fully inhibit the signal. It was also determined that the SiC resonances become increasingly shifted and broadened with increasing thickness of the VO_2 coating. These results suggest that VO_2 can add active tunability and integrated switching to optical structures.

2:40pm **TF+EM+MI-WeA2 Study of Ru Silicidation with and without Sub-nm ALD TiN and TaN Barrier/nucleation Layers for Ru Interconnect Applications**, *Sonal Dey*, SUNY College of Nanoscale Science and Engineering; *K.-H. Yu, S. Consiglio, K. Tapily, C.S. Wajda, G.J. Leusink*, TEL Technology Center, America, LLC; *J. Jordan-Sweet, C. Lavoie*, IBM T.J. Watson Research Center; *A.C. Diebold*, SUNY College of Nanoscale Science and Engineering

With continual shrinkage of the feature size in devices, contribution of the Cu interconnects, liners, and barrier layers to the RC time-delay is becoming a significant obstacle at the 10 nm technology node and below. Ru is a potential candidate to replace Cu as an interconnect material for ultra-scaled line widths where scaling effects on Cu line resistance become increasingly problematic. Ru has already been demonstrated to be useful as the seed layer for Cu electroplating but has been shown to be an inadequate barrier to prevent Cu diffusion into surrounding BEOL dielectrics and requires the use of an additional barrier layer such as a Ta-based nitride. In addition, TaN deposited by PVD is reaching a limit in its ability to conformally coat aggressively scaled structures in the sub 10 nm node. Accordingly, in this study we evaluated the thermal stability of thin Ru films (3 nm) with and without ultra-thin (~ 0.5 nm) highly conformal ALD TiN and TaN films as nucleation and/or barrier layers for Ru interconnect applications in advanced technology nodes. Si (100) substrates were chemically cleaned to remove the native oxides followed by deposition of ultra-thin ALD TiN and TaN barrier films. TiCl_4 and $\text{Ta}(\text{NCMe}_3)(\text{NETMe}_3)_3$ precursors, along with NH_3 , were used for deposition of the TiN and TaN layers, respectively. Using $\text{Ru}_3(\text{CO})_{12}$, 3 nm of Ru was deposited by CVD on top of these refractory metal nitride films and also directly on Si. We also used PVD Cu (25nm)/Si as a control stack for our experiments. The diffusion kinetics of metal-silicide formation was evaluated using in-situ rapid thermal anneal (RTA) synchrotron x-ray diffraction (XRD) measurements and a Kissinger-like analysis to determine the transition temperatures of the metal-silicidation in these stacks and the effective activation energy (E_a) using three different ramp rates (0.3, 3, and 10°C/s). The Ru/Si stack showed higher $E_a = 2.48$ eV as compared to the Cu/Si stack ($E_a = 1.88$ eV). A 0.5 nm thick TaN ($E_a = 2.88$ eV) was found to act as a more effective barrier as compared to 0.5 nm thick TiN ($E_a = 2.64$ eV). Scanning electron microscopy (SEM) data shows that both TaN and TiN act as nucleation layers for the growth of Ru microstructure on top. A fewer number of pin holes was observed for Ru films deposited on TaN although there was not significant change on the wettability properties of the Ru film with either TiN and TaN nucleation layers underneath. Additional physical and chemical characterization with XPS and TOF SIMS were also performed to gain understanding of the film stack properties before and after silicide formation.

3:00pm **TF+EM+MI-WeA3 2D - Material and Process Challenges of the Ultimate Thin Films in Nanoelectronics**, *Stefan de Gendt*, KU Leuven, IMEC, Belgium; *S. Brems, D. Chiappe*, IMEC, Belgium; *M. Heyne, K. Verguts*, KU Leuven, IMEC, Belgium; *R. Philipson*, KU Leuven, Belgium; *C. Lockhart de la Rosa, A. Delabie*, KU Leuven, IMEC, Belgium; *S. De Feyter*, KU Leuven, Belgium; *C. Huyghebaert*, IMEC, Belgium

INVITED

Graphene has emerged as one of the promising candidates for post-Si electronics, both for channel (Logic, RF, sensors) and interconnect applications. Further, other two-dimensional (2D) materials such as transition metal dichalcogenides (MX₂, with M a transition metal of group 4-7 and X a chalcogen) have versatile properties that complement or even supersede those of graphene. Both categories however share similar problems, related to the absence of good quality synthesis processes, subsequent layer transfer processes and doping and contacting challenges. To tackle the **first challenge** – growth – chemical vapor deposition (CVD) is widely considered to be the most economically viable method to produce both graphene and MX₂ materials for high-end applications. However, in most cases, this deposition technique typically yields undesired grain boundaries in the 2D crystals, which drastically increases the sheet resistance of the layer. Strategies w.r.t. template and process development will be presented. Further, given growth temperature and template, direct

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growth on devices is often unfeasible, thus a **second challenge** relates to the requirement for a transfer process. For graphene, several transfer process possibilities have been evaluated, but up to now, the graphene transfer suffers from contamination often coming from the temporary support layer and/or etching products, wrinkle formation during bonding, crack formation during graphene handling, ... Moreover, with improvement in 2D quality the release from the growth template is hindered due to increased adhesion forces. At least for MX2 materials, the transfer challenge can be avoided through area selective growth. A process based on a reductive two step CVD process will be presented, whereby in a first step the metal precursor (WF6) is reduced to a lower oxidation state through sacrificial reaction with Si. Subsequently, the metallic film is allowed to react with a sulphur precursor (H2S). Challenges are again related to the (poly)crystallinity of the films and the control of lateral 2D versus crystal 3D growth. Last but not least, a **third challenge** related to 2D materials resides in the contacting and doping of these materials. Different strategies have been proposed to achieve doping, but in this presentation we will demonstrate the self-assembly of organic molecules physisorbed on top bulk and thin 2D layers as a means to achieve controlled doping.

4:40pm TF+EM+MI-WeA8 Atomic Layer Deposition of Stoichiometric TaSi₂ on Si(001), JongYoun Choi, S.W. Park, University of California San Diego; R. Hung, Applied Materials Inc.

Transition metal disilicides are of great interest in Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs) due to their ability to tune the work function at the metal contact in the source/drain regions. Various kinds of transition metal silicides such as TiSi₂, NiSi₂ and WSi₂ have been studied in previous decades, however, nanoscale studies of TaSi₂ are relatively scarce. Previously, Lemonds *et al.* successfully demonstrated atomic layer deposition (ALD) of tantalum silicide (TaSi_x) on SiO₂ using TaF₅ and Si₂H₆. In this work, it is demonstrated that using similar reaction conditions TaSi₂ can be grown by ALD process on oxide-free clean Si(001). The growth rate of TaSi₂ on Si(001) was monitored *in-situ* using a Quartz Crystal Microbalance (QCM) during the deposition. This enabled optimization of the TaF₅ and Si₂H₆ dosing to avoid chemical vapor deposition (CVD) components. Scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), scanning tunneling spectroscopy (STS) and atomic force microscopy (AFM) have been used to investigate the atomic and electronic structure of Si(001) surface after TaSi₂ thin film deposition. HF cleaned Si(001) was used for the substrate. The chemical composition was determined by XPS after ALD to be that of a stoichiometric TaSi₂ film formed on the Si substrate. The key variables in forming stoichiometric TaSi₂ are the ratio of the precursors and the surface temperatures. In the ALD process, a 100x fold excess of Si₂H₆ is required to prevent formation of TaOx; in addition, the surface temperature must be above 240C. These requirements for excess Si₂H₆ and a high surface temperature are likely due to high activation barrier to break the residual Ta-F bonds on the surface after the TaF₅ half pulse since the Ta-F bonds are stronger than the Si-H bonds.

5:00pm TF+EM+MI-WeA9 Different Approaches for Enhancing the Thermal Stability of Ge₂Sb₂Te₅ Thin Films by Carbon Addition, David Adams, K. Childs, T. Gurrieri, W. Rice, Sandia National Laboratories

Different forms of carbon-doped Ge₂Sb₂Te₅ chalcogenide thin films have been evaluated for potential use in phase change memory and thermal sensor applications. This includes films sputter deposited from single, carbon-doped targets and refined multilayers made by sequential deposition of chalcogenide and C layers. In both forms, the crystallization temperature (T_{cryst}) and the resistance change through crystallization vary with carbon content. Doped chalcogenide films sputter deposited from single targets exhibit increased T_{cryst} as the concentration of C is made larger. For example, films having ~7 at.% C exhibit a T_{cryst} that is approximately one hundred and fifteen degrees above that of undoped Ge₂Sb₂Te₅. Films with reduced C content, in the range 1-6 at.%, show intermediate crystallization temperatures. Multilayers fabricated by the sequential deposition of thin chalcogenide and C layers behave much like films grown from single targets, provided that multilayer periodicity is made small, < 3 nm. The crystallization temperature of multilayers also increases with C concentration and a prompt transition to a crystalline phase is observed when the carbon content is low. Interestingly, multilayers made with ≥ 9 at.% C do not transition abruptly to a crystalline state. Instead, a transformation occurs over a broad range of elevated temperature. Each form of chalcogenide thin film exhibits a decreased resistivity upon crystallization. In most cases, resistivity is reduced by 5 decades upon transforming to a face centered cubic structure or a subsequent hexagonal close packed lattice at higher temperature. The

changes to microstructure and thickness associated with phase change will also be described. These film properties are investigated by cross-section and plan view electron microscopy.

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

5:20pm TF+EM+MI-WeA10 Comparison of Electromigration and Resistivity in On-chip Co and Cu Damascene Nanowires, C.-K. Hu, J. Kelly, J.H.-C. Chen, H. Huang, Y. Ostrovski, R. Patlolla, B. Peethala, P. Adusumilli, T. Spooner, IBM Research Division, Albany; L. Gignac, S. Cohen, IBM Research Division, T.J. Watson Research Center; R. Long, G. Hornicek, T. Kane, G. Lian, M. Ali, IBM Systems; V.M. Kamineni, F. Mont, S. Siddiqui, GLOBALFOUNDRIES

Cu metallization has been used for back end of the line (BEOL) on-chip interconnections since 1997. However, scaling Cu BEOL dimensions has increased Cu resistivity and degraded electromigration (EM) reliability. The Cu effective resistance has increased rapidly as the interconnect size has reduced and the ratio of liner area to total interconnect cross sectional area has increased. This size effect was caused primarily by increasing the probability of electron scattering with interfaces and grain boundaries. The EM lifetime degradation was caused by an increase in the volume fractions of diffusing atoms at interfaces and grain boundaries and a decrease in the void volume required to cause EM failure. It is estimated that ~ 70% of interconnect metal area could be occupied by the liner in the 5 nm technology node for reliable Cu metallization. To this end, an alternate metal, Co, was investigated. Multi-level Co BEOL was fabricated using typical 10 nm node technology wafer processing steps. A Co dual damascene process was used to fill the interconnect trenches and holes. The present Co resistivity study showed a similar size effect in Co as in Cu. This can be explained by the fact that the slope of resistivity vs. interconnect size is proportional to the product of the electron mean free path and resistivity, with the two slopes being about the same for Cu and Co. The effective resistivity difference between Co and Cu becomes small when no liner is used in Co lines. EM in 22 nm to 88 nm wide Co lines was tested using sample temperatures from 376°C to 425°C. Two-level EM structures consisted of either Co M1 to Co V1 to Co M2 or W CA to Co V0 to Co M1. The EM stress conditions for Co were far more severe than those for Cu. For comparison, EM in 24 nm wide Cu lines with a Co cap was also included. These data showed that both Co and Cu BEOL were highly reliable EM.

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

5:40pm TF+EM+MI-WeA11 UV/VUV Curing Process for Low-k Organosilicate Dielectrics, Huifeng Zheng, X. Guo, D. Pei, W. Li, J. Blatz, K. Hsu, D. Benjamin, University of Wisconsin-Madison; Y. Lin, H. Fung, C. Chen, National Synchrotron Radiation Research Center, Taiwan, Republic of China; Y. Nishi, Stanford University; J.L. Shohet, University of Wisconsin-Madison

Porous SiCOH films are of great interest in semiconductor fabrication due to their low-k properties. Post-deposition treatments of SiCOH thin films are required to decompose labile pore generators (porogens) and to ensure optimum network formation to improve the electrical and mechanical properties of low-k dielectrics. The goal of this work is to optimize the vacuum-ultraviolet spectrum to identify those wavelengths that will have the most beneficial effect on improving dielectric properties and minimizing damage without the need for thermal heating of the dielectric. Vacuum ultraviolet (VUV) irradiation between 8.3-8.9 eV was found to increase the hardness and elastic modulus of low-k dielectrics at room temperature. Combined with UV exposure of 6.2 eV, it was found that this UV/VUV curing process compares favorably with current UV curing. The results also show that UV/VUV curing can overcome many of the drawbacks of UV curing and improve properties of dielectrics more efficiently without the need for high-temperature heating of the dielectric.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359

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6:00pm TF+EM+MI-WeA12 Effects of Cesium Ion Implantation on the Mechanical and Electrical Properties of Organosilicate Low-k Films, *Weiji Li, D. Pei, X. Guo, M.-K. Cheng, S. Lee*, University of Wisconsin-Madison; *Q. Lin*, IBM Research Division, T.J. Watson Research Center; *S.W. King*, Intel Corporation; *J.L. Shohet*, University of Wisconsin-Madison

The effects of cesium (Cs) ion-implantation on uncured plasma-enhanced chemical-vapor-deposited (PECVD) organosilicate low dielectric constant (low-k) (SiCOH) films have been investigated and compared with the effects of ultraviolet (UV) curing. The mechanical properties, including the elastic modulus and hardness, of the films were improved by up to 30% with Cs implantation, and further up to 52% after annealing at 400°C in a N₂ ambient for one hour. These improvements in mechanical properties are either comparable with or better than the effects of UV-curing. These improvements are attributed to an enhancement of the Si-O-Si network structure. The k-value of the SiCOH films increased slightly after Cs implantation, and increased further after annealing. These increases are attributed to two carbon-loss mechanisms, i.e. the carbon loss due to Si-CH₃ bond breakage from implanted Cs ions, and the carbon loss due to oxidation during the annealing. The time-zero dielectric breakdown strength was improved after the Cs implantation and the subsequent annealing, and were shown to be better compared with the UV-cured SiCOH films. Within the investigated range of implantation dose, an optimal dose can be found to achieve the best effects. These results indicate that Cs ion implantation has the potential to be a supplement to or a substitution for the incumbent UV curing method for processing SiCOH low-k films.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359.

[1] Y. Kayaba, K. Kohmura, H. Tanaka, Y. Seino, T. Odaira, F. Nishiyama, et al., "Electrical reliabilities of highly cross-linked porous silica film with cesium doping," *Journal of the Electrochemical Society*, **155**, G258 (2008)

Electronic Materials and Photonics

Room 102A - Session EM+AC+SS+TF-ThM

Radiation Detection Materials and Devices

Moderators: Sean King, Intel Corporation, Michelle Paquette, University of Missouri-Kansas City

8:00am **EM+AC+SS+TF-ThM1 Novel High Energy Resolution Scintillator Detectors**, **Arnold Burger**, E. Rowe, L. Matei, P. Bhattacharya, M. Groza, Fisk University; K. Stassun, Vanderbilt University; A. Stowe, Consolidated Nuclear Security Y-12; N. Cherepy, S. Payne, Lawrence Livermore National Laboratory

INVITED

This presentation will review the status of bright scintillators for gamma and thermal neutrons applications. The scintillators are based on single crystals of halides or selenides that are activated by rare earth ions or are self activated. The main features that make them attractive for biological, medical, space and national security applications are: (i) high stopping power of radiation, (ii) high energy resolution, (iii) fast decay time, (iv) crystal growability at low cost, (v) good gamma/neutron discrimination via pulse shape analysis, and (vi) good spectral matching with silicon photodetectors for compact and low power devices and instrumentation.

8:40am **EM+AC+SS+TF-ThM3 Improved p-n Heterojunction Device Performance Induced by Irradiation in Amorphous Boron Carbide Films**, **George Peterson**, Q. Su, University of Nebraska - Lincoln; Y. Wang, Los Alamos National Laboratory; P.A. Dowben, M. Nastasi, University of Nebraska - Lincoln

Amorphous hydrogenated boron carbide films ($a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$) on Si p-n heterojunctions were fabricated utilizing plasma enhanced chemical vapor deposition (PECVD). These devices were found to be robust when irradiated with 200 keV He^+ ions. For low doses of irradiation, contrary to most other electrical devices, the electrical performance improved. On the heterojunction I(V) curve, reverse bias leakage current decreased by 3 orders of magnitude, series resistance across the device decreased by 64%, and saturation current due to generation of electron-hole pairs in the depletion region also decreased by an order of magnitude. It is believed that the improvements in the electrical properties of the devices are due to an initial passivation of defects in the $a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$ film resulting from electronic energy deposition, breaking bonds and allowing them to reform in a lower energy state, or resolving distorted icosahedron anion states.

9:00am **EM+AC+SS+TF-ThM4 Amorphous Hydrogenated Boron Carbide for Direct-Conversion Solid-State Neutron Detection**, **Gyanendra Bhattarai**, T.D. Nguyen, S. Dhungana, A.N. Caruso, M.M. Paquette, University of Missouri-Kansas City

The trade-off between conversion layer thickness and penetration depth of primary reaction products inherently limits the efficiency of conversion-layer solid-state neutron detectors, motivating the need for direct-conversion solutions. Direct-conversion devices, in principle, offer nearly unity detection efficiency, a minimum of fabrication steps, large-area scalability, and high efficiency density, all of which are essential for small-sized neutron spectrometers as well as for large-area detectors. However, to date, there is a lack of well-developed semiconductor materials with high thermal neutron absorption that also lead to energetic reaction products amenable to detection. Amorphous hydrogenated boron carbide ($a\text{-B}_x\text{C:H}_y$), a complex disordered semi-insulating material, is a promising candidate because of its high neutron absorption and high resistivity. Additionally, excellent mechanical, chemical, and thermal stability make it suitable for harsh detection environments. The main challenges, however, in the study of $a\text{-B}_x\text{C:H}_y$, are its low charge carrier mobility, the difficulties associated with making proper electrical contacts for accurate charge transport measurements, and the inefficacy of traditional experimental techniques and interpretations to address the complex nature of the material (i.e., it is a high-resistivity, disordered, molecular solid). This contribution will present an overview of how $a\text{-B}_x\text{C:H}_y$ may lead to high-efficiency neutron detectors based on theoretical simulations, the study of its charge transport metrics focusing mainly on charge carrier mobility and lifetime, and the development of proper electrical contacts on PECVD grown thin films of this material.

9:20am **EM+AC+SS+TF-ThM5 Radiation Damage of Low- κ Interlayer Dielectrics Studied with Electrically Detected Magnetic Resonance**, **Michael Mutch**, P.M. Lenahan, Pennsylvania State University; S.W. King, Intel Corporation

Radiation effects of MOS devices have been extensively studied due to the demand for electronic devices in space applications.[1] The scaling of these MOS devices will lead to an eventual need for low-dielectric constant (i.e., low- κ) dielectrics to reduce parasitic capacitances associated with scaling of back-end-of-line interlayer dielectrics (ILDs). However, little is known about radiation effects of low- κ ILDs. We utilize electrically detected magnetic resonance (EDMR) via spin-dependent trap-assisted tunneling (SDTAT) to study point defects in porous low- κ a-SiOC:H systems before and after exposing samples to radiation damage. SDTAT/EDMR has the sensitivity and analytical power to specifically identify only those defects which are involved in electronic transport. Due to the inherent complexity of the a-SiOC:H systems, multiple frequency EDMR is utilized to better understand defect structure when featureless spectra are present.

The a-SiOC:H films are grown via PECVD, and exhibit carbon dangling bonds prior to porogen removal via UV-annealing.[2] After porogen removal via UV treatment, it has been shown, via multiple frequency EDMR, that silicon dangling bonds are the dominating defect center responsible for SDTAT in these films.[2] The porous a-SiOC:H systems were subjected to a 15 Mrad total dose via a cobalt-60 dry cell gamma-ray source while simultaneously applying either positive, negative, or no bias. We find that the post-radiation IV curves are a strong function of the biasing conditions which were applied during radiation. This likely indicates that electron and hole traps will both play a role in radiation damage effects in these systems. We find that the EDMR response amplitude is greatly increased (by a factor of 4 or greater) after irradiation for all biasing conditions. This result indicates a substantial increase in the density of defects involved in electronic transport. Multiple frequency EDMR measurements suggest that the generated defects are primarily silicon dangling bonds.

[1] J. R. Schwank et al., IEEE Trans. Nuc. Sci. **55**, 1833 (2008).

[2] M. J. Mutch et al., J. Appl. Phys. **119**, 094102 (2016).

9:40am **EM+AC+SS+TF-ThM6 Modeling Unit Displacement Damage in Amorphous Silicon Oxycarbides**, **Hepeng Ding**, M. Demkowicz, MIT

Amorphous silicon oxycarbide (SiOC) is of great technological interest. To study its potential application as a radiation-resistant material, we present *ab initio* modeling investigations of unit displacement damage processes in it using density functional theory. We model 0.1 keV primary knock-on atoms (PKA) in SiO_2 , SiOC, and hydrogenated SiOC (SiOCH) with different hydrogen levels. We find that PKAs affect the carbon-clustering tendency in both SiOC and SiOCH. Our results also suggest that SiOCH is irradiation indifferent, i.e., upon PKA, the potential energy does not increase and there is no major structural change.

This work was funded by the DOE Office of Nuclear Energy, Nuclear Energy Enabling Technologies, Reactor Materials program, under contract No. DE-NE0000533. Computational support was provided by DOE-NERSC and DOE-OLCF.

11:00am **EM+AC+SS+TF-ThM10 Position-Sensitive 3D CZT Gamma-Ray Detectors with Thickness Up to 50 mm**, **Ralph James**, A.E. Bolotnikov, G.S. Camarda, Y. Cui, G. De Geronimo, J. Fried, A. Hossain, G. Mahler, U. Roy, E. Vernon, G. Yang, Brookhaven National Laboratory

INVITED

High-granularity position-sensitive detectors allow for accurate charge-signal corrections to overcome non-uniformities in the devices' responses caused by crystal defects. The operational principle of position-sensitive detectors is analogous to the well-known drift ionization chambers used for tracking charged particles and detecting the interaction events generated by gamma rays. Advantages of the position-sensitive designs were realized in a number CZT detectors, including CAPture™, hemispherical, Frisch-ring, capacitive Frisch-grid and even pixel detectors in which pixel contacts act like shielding electrodes. In our virtual Frisch-grid (VFG) devices, the sensing strips are separated from the crystal surfaces by a thin insulating layer, as it was originally done in other Frisch-grid designs. The amplitudes of the signals readout from the strips are used to measure the coordinates of the interaction points and correct the response non-uniformities. The drift time and the cathode-to-anode ratio were used to independently evaluate the location of the interaction points in Z directions, correct for electron loss, and identify and reject the events for which the charge losses caused by defects are so great that they cannot be corrected accurately. Combining these two techniques allows us to significantly enhance the spectral responses of position-sensitive VFG detectors, and to significantly

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improve their performance. Such high-granularity position-sensitive detectors open up the opportunity for using thicker, less expensive crystals. We demonstrated that today's CZT material is suitable for detectors with up to 40-50-mm drift distances, provided that the detectors have the ability to correct their response non-uniformities on a scale comparable to the sizes of electron clouds, which is ~ 100 m m. We employed an ASIC and data-acquisition system developed by BNL's Instrumentation Division for arrays of VFG detectors. For each detector we used 6 ASIC channels to read the negative signals from the cathode and from four position-sensing pads, and the positive signals from the anode. For each interaction event, the anode signal correlates with the X and Y values converted from the 4 strip signals and Z coordinate evaluated from the cathode signal. This relationship allows us to correct each anode signal in accordance with the location of the interaction point. We selected the voxel sizes to achieve the best performance, typically $\sim 30 \times 30$ pixels in XY -space and ~ 100 segments in the Z -direction. The performance of thick position-sensitive VFG detectors fabricated from CZT crystals will be reported for a variety of radioactive sources and testing conditions.

11:40am **EM+AC+SS+TF-ThM12 Understanding the Electrical Properties of U_3O_8 for Direct Conversion Neutron Detectors**, *Brandon Shaver, S. Lawson, B. Musicó*, The University of Tennessee Knoxville; *S. Dhungana, G. Bhattarai, M.M. Paquette, A.N. Caruso*, University of Missouri-Kansas City; *T. Meek*, The University of Tennessee Knoxville

With a high neutron fission cross section for ^{238}U , U_3O_8 is one of a series of uranium oxide semiconductors that may be suitable for direct-conversion neutron detectors. However, the electrical transport properties of U_3O_8 are not well-characterized: the literature that does exist reports largely inconsistent resistivity values, and similarly contradictory values for work function. One of the reasons for these wide ranges is that slight changes in stoichiometry in urania-based systems, UO_2 for example, can have a tremendous influence on electrical properties; however, the details of these effects are not well-understood. We seek to rigorously characterize the electrical transport properties in U_3O_8 to understand the range of values that can be achieved and—importantly—their relationship to fabrication method as well as composition/microstructure. Samples of U_3O_8 pellets have been made by uniaxial pressing of U_3O_8 powder and subsequent sintering under various conditions. These samples have then been characterized to determine their microstructure, exact stoichiometric composition, and electrical properties. By carefully studying the relationship between sample preparation and electrical properties, we aim to establish the ability to control and optimize the electrical transport metrics of U_3O_8 critical for detection applications.

12:00pm **EM+AC+SS+TF-ThM13 Radiation Damage in 4H SiC nMOSFETs Detected by Electrically Detected Magnetic Resonance**, *Ryan Waskiewicz, M.A. Anders, P.M. Lenahan*, Pennsylvania State University; *A.J. Lelis*, U.S. Army Research Laboratory

Metal oxide semiconductor field effect transistors (MOSFETs) based upon 4H-SiC have great promise in high power and high temperature applications. An area of substantial interest is in outer space, where the devices will be subjected to ionizing radiation. The effects of ionizing radiation have been well studied in Si-based MOS devices, where E' and Pb centers play dominating roles as oxide and interface traps respectively. Very little is known about the types of defects created in radiation damage in SiC MOSFETs. In order to develop a fundamental understanding of ionizing radiation effects, we have performed a study utilizing electrically detected magnetic resonance (EDMR) via the bipolar amplification effect (BAE) [1]. We observe several changes between the pre- and post-irradiation EDMR results, which strongly indicate change in the structure of the SiC/SiO₂ interface region but relatively little change in the number of observed interface defects.

The devices used in this study had 50 nm thick thermally grown gate oxides in N₂O. After oxidation, the devices were subjected to the standard post-oxidation NO anneal at 1175°C. The n-channel 4H-SiC MOSFETs have been subjected to 6MRads of gamma radiation from a ⁶⁰Co gamma source while a 10V bias applied to the gates. Standard transistor characteristic measurements made on the devices before and after irradiation indicate a threshold voltage shift of approximately -4V. We observed several significant changes in the EDMR response, the most obvious EDMR differences are in the amplitude of the BAE EDMR measurements as a function of applied gate voltage. The maximum EDMR amplitude increased by a factor of 7 as a result of the irradiation, and the gate bias at which the peak occurred shifted by approximately -4V, consistent with the approximate -4V shift in threshold voltage. BAE measurements measure

spin dependent recombination due to deep level defects at and very close to the SiC/SiO₂ interface. We find significant change in the EDMR line shapes, observing significant post-irradiation broadening of the spectra. Surprisingly, we are unable to observe either silicon or carbon dangling bond defects in these preliminary measurements. It is clear from the measurements that both the pre-irradiation and post-irradiation measurements are dominated by silicon vacancies on the SiC side of the interface. EDMR measurements as a function of microwave power show quite significant changes in the saturation behavior of the magnetic resonance. These results suggest significant structural changes in the interface region.

[1] Thomas Aichinger and Patrick M. Lenahan, Appl. Phys. Lett. **101**, (2012)

Spectroscopic Ellipsometry Focus Topic Room 104C - Session EL+AS+BI+EM+TF-ThA

Optical Characterization of Nanostructures and Metamaterials (2:20-3:40 pm)/Application of Spectroscopic Ellipsometry for the Characterization of Thin Films (4:00-6:00 pm) and Biological Materials Interfaces

Moderators: Tino Hofmann, University of North Carolina at Charlotte, Stefan Zollner, New Mexico State University, Heidemarie Schmidt, Technische Universität Chemnitz, Germany

2:20pm EL+AS+BI+EM+TF-ThA1 Optical Properties of (Self-assembled) Nanostructured Surfaces Studied by Spectroscopic Mueller Matrix Ellipsometry and Local Direct Imaging Techniques, *Morten Kildemo*, Norwegian University of Science and Technology, Norway **INVITED**

This paper covers several applications of ex-situ and in-situ Spectroscopic Mueller Matrix Ellipsometry (SMME) for the study of self-assembled nanostructured surfaces, with applications ranging from antireflection coatings, PV-absorbers, nanoimprinting masks, plasmonic polarizers, plasmonic meta-materials and in particular hyperbolic metamaterials and meta-surfaces. The optical analysis is systematically supported by AFM, SEM and TEM. As nanostructured surfaces are often inherently anisotropic, SMME with variable angle of incidence and full azimuthal rotation of the sample is shown to be a powerful optical technique to fully characterize such anisotropic and sometimes bi-anisotropic materials. The first part of the presentation briefly reviews an uniaxial effective medium approach to model the kinetics of the optical response of self-assembled straight and tilted GaSb nanopillars [Le Roy et al., Phys. Rev. B 2010, Nerbo et al. Appl. Phys. Lett. 2009], and SiO₂-nanopillars containing plasmonic Cu [Ghadyani et al., Opt. Exp. 2013]. The second part of the presentation discusses the experimentally extracted uniaxial and biaxial optical properties of self-assembled plasmonic hyperbolic meta-materials [X. Wang et al., *Block-copolymer based self-assembled hyperbolic metamaterials in the visible range*. (manuscript in preparation), 2016] and metasurfaces [Aas et al., Opt. Expr. 2013]. Hyperbolic metamaterials use the concept of controlling the propagative modes through the engineering of the dispersion relation, and are considered highly promising to reach different meta-properties. The presentation is closed by the discussion of the fascinating Mueller matrix response of a highly organized array of hemispherical Au nanoparticles produced by Focused-Ion-Beam milling, and the response is discussed in the context of highly organized meta-surfaces and plasmonic photonic crystals [Brakstad et al. Opt. Express 2015]

3:00pm EL+AS+BI+EM+TF-ThA3 Optical Properties of Nanocrystalline Si₃N₄:TiN Thin Films, *Neil Murphy*, Air Force Research Laboratory; *L. Sun*, General Dynamics Information Technology; *J.G. Jones*, Air Force Research Laboratory; *J.T. Grant*, Azimuth Corporation

Nanocomposite films comprised of mixed nitrides, especially Si-Me-N (Me=Ti, Zr, Hf), have generated significant attention due to their robust thermal and mechanical properties. In addition to their desirable structural characteristics, the mixing of dielectric Si₃N₄ with various metallic nitrides has the potential for the deposition of hybrid thin films with controllable optical absorption based on the fraction of metallic nitrides present within the Si₃N₄ matrix. In this work, nanocrystalline Si₃N₄ thin films, doped with varying amounts of TiN (1-20 at.%), are deposited using reactive magnetron co-deposition. Note that the Berg model for reactive sputtering is utilized to select the initial conditions for the deposition of the films, which are sputtered from elemental targets within a mixed nitrogen-argon environment and characterized *in-situ* using spectroscopic ellipsometry. The TiN content is varied through systematic adjustment of the current applied to the Ti cathode concurrent with pulsed DC deposition of Si₃N₄ at a constant current of 0.4 A. The use of *in-situ* ellipsometry, interrogating wavelengths from 381-1700 nm, allows for the real-time measurement of the refractive index, extinction coefficient, and thickness of the growing films. Additionally, *in-situ* ellipsometry data is used to observe the behavior of the films at the onset of growth, indicating the onset of Volmer-weber type nucleation. All ellipsometric data are fit using a Bruggeman effective medium approximation, varying the amount of TiN present within the films. Optical characterization of the Si₃N₄:TiN thin films indicates that the refractive index at 550 nm decreases gradually from 2.05 to 1.99 as the TiN content is increased from 0-20 at%, while the extinction coefficient rises from 0 to 0.35. These films demonstrate strong absorption features starting from 550 nm out to 1500 nm, allowing for efficient absorption of

visible and near-infrared wavelengths. Variation of the TiN content within Si₃N₄:TiN films allows for the user to select the magnitude of extinction coefficient and refractive index, leading to potential applications as mechanically robust layers in interference filters, or as alternatives to lossy metallic configurations in plasmonic devices.

3:20pm EL+AS+BI+EM+TF-ThA4 The Effect of Aluminum Content on Properties of Al-doped Zinc Oxide Thin Films Grown at Room Temperature, *Lirong Sun*, General Dynamics Information Technology; *N.R. Murphy*, Air Force Research Laboratory; *J.T. Grant*, Azimuth Corporation; *J.G. Jones*, Air Force Research Laboratory

Transparent conductive Al-doped zinc oxide (AZO) thin films have shown excellent structural, optical and electrical properties for applications in photovoltaic and optoelectronic devices, transparent conducting electrodes, solar cells, liquid crystal displays, touchscreens, energy efficient window coatings and heat reflective coatings. In this work, the AZO thin films were deposited at room temperature by multi-target reactive magnetron sputtering using metallic Zn and Al targets simultaneously. The Al doping content of the AZO films by x-ray photoelectron spectroscopy (XPS) had great impacts on optical properties in the near infrared (NIR) and in the UV regions and were strongly correlated to their electrical properties. The spectroscopic ellipsometry data in three incident angles and transmission intensity data were measured and fitted simultaneously with a Tauc-Lorentz oscillator and a Drude model in the wavelength of 270 -2500 nm. The transmittance and reflectance spectra, the derived refractive index and extinction coefficient, were tailored in the NIR region by Al content and correlated to the electrical resistivity. The blue shift of the absorption edge in the UV region and the widening of the optical band gap were associated with the increase of the Al content. Structural, optical and electrical properties were characterized using x-ray diffraction, scanning electronic microscopy, UV-Vis-NIR spectra and four-point probe methods.

4:00pm EL+AS+BI+EM+TF-ThA6 Optical Monitoring of Growth (and Death) of Thin Film Materials for Solar Cells, *Nikolas Podraza*, *K. Ghimire*, *M.M. Junda*, *A.A. Ibdah*, *P. Koirala*, University of Toledo; *S. Marsillac*, Old Dominion University; *R.W. Collins*, *Y. Yan*, University of Toledo **INVITED**

Performance of thin film solar cells depends on (i) electronic quality of the components (doped and undoped semiconductors, metallic and transparent conducting contact layers), (ii) component optical response, and (iii) full opto-electronic response of the photovoltaic (PV) device structure dictated by layer properties and thickness. Spectroscopic ellipsometry probes (ii) and (iii) through measurement of both thickness and optical response ($N = n + ik$, $\epsilon = \epsilon_1 + i\epsilon_2$, $\alpha = 4\pi k/\lambda$) of multiple layers in thin film device structures. Assessing (i) electronic quality of materials or devices optically relies on understanding other property information deduced from the optical response, such as connecting variations in film structure (crystallinity, degree of disorder) or growth evolution to device performance. In situ, real time spectroscopic ellipsometry (RTSE) monitors growth evolution and post-deposition processes to better understand property changes with thickness, phase transitions and separation, and process kinetics. RTSE of hydrogenated silicon (Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS) absorbers have been used to understand growth and its relationship to the respective device performance. All of these are relatively mature PV technologies, where knowledge gained from RTSE during growth can potentially improve metrology and manufacturing. The potential impact of RTSE is equally strong when applied to developing technologies. Organometal lead halide perovskite semiconductors (CH₃NH₃PbI₃) are used in >20% initial efficiency solar cells but suffer from degradation with temperature, bias, moisture, and ultraviolet light exposure. The time scale of device performance degradation is much shorter than that of other polycrystalline PV (CdTe, CIGS). RTSE has been applied during co-evaporation of CH₃NH₃I and PbI₂ to produce the perovskite, but also during decomposition of the perovskite. Significant fractions of CH₃NH₃I and PbI₂ at the substrate / perovskite and perovskite / ambient interfaces after deposition even under simple atmospheric exposure begin to appear in a matter of minutes. The ability to track the degradation – or death of this material – in addition to growth may be equally important to assessing the ultimate stability and manufacturability of these next generation PV materials.

4:40pm EL+AS+BI+EM+TF-ThA8 Monitoring Nanometer-Thin Film Formation using Ellipsometry, *Bert Müller*, *F.M. Weiss*, *T. Töpfer*, *B. Osmari*, University of Basel, Switzerland

Elastomers can transform electrical energy into mechanical one. They have a wide variety of applications including powering wipers, sound

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generation, and operating camera lenses. Sandwiched between electrodes the deformable but incompressible elastomer laterally expands when applying a voltage. To provide the necessary strain of at least 10 %, micrometer-thick silicone membranes need an operation voltage of several hundred volts, which is inappropriate for the human body. Nanometer-thin membranes, however, require only a few volts. To generate forces as necessary for artificial sphincters, i.e. muscles to treat incontinence, several ten thousand membranes have to be sandwiched. Currently, the manufacturing methods such as organic molecular deposition only reach deposition rates of about one micrometer per hour, which does not allow fabricating the sandwiched nanostructures in an efficient way. We have developed an alternative deposition method to prepare extremely flat silicone membranes that are below one micrometer thick. The root-mean-square-roughness is smaller than one nanometer. For this purpose, silicone polymers in solution are sprayed by electrospray deposition [1,2]. Usually electrospraying is based on direct current mode. Here, we have employed, however, an alternating current to avoid charge accumulation on the substrate. Spectroscopic ellipsometry has been used to monitor the formation of confluent organic films and electrodes as well as the changes of the organic thin films during ultra-violet radiation treatments. This in situ technique enabled us to derive the refractive index, the porosity, the surface roughness, and the film thickness. The derived quantities on surface roughness and film thickness were validated using atomic force microscopy. The combination of electrospraying, ultra-violet light curing, and in situ ellipsometry has a huge potential to efficiently create and monitor nanometer-thin, ultra-flat elastomeric membranes, which may become part of artificial muscles for medical applications and beyond.

[1] F.M. Weiss, T. Töpfer, B. Osmani, S. Peters, G. Kovacs, and B. Müller *Electrospraying Nanometer-Thin Elastomer Films for Low-Voltage Dielectric Actuators Advanced Electronic Materials* (2016) 1500476; DOI: 10.1002/aelm.201500476

[2] F.M. Weiss, T. Töpfer, B. Osmani, H. Deyhle, G. Kovacs, and B. Müller *Thin Film Formation and Morphology of Electro-sprayed Polydimethylsiloxane* *Langmuir* 32 (2016) 3276-3283

5:00pm **EL+AS+BI+EM+TF-ThA9 Optical Determination of Electrical Response for Thin Film Transparent Conductors: Spectral Range Dependence**, *Prakash Uprety, M.M. Junda, K. Lambright, R. Khanal, A. Phillips, M. Heben, D. Giolando, N.J. Podraza*, University of Toledo

Thin films with simultaneous high transparency and electrical conductivity have applications in photovoltaics, displays, and other opto-electronic devices. Accurate characterization of electrical transport properties along with optical properties in these transparent conductors, particularly when in the device structure, is of critical importance to their use. Spectroscopic ellipsometry (SE) provides a widely applicable method for determining such properties without many of the complications and limitations that accompany other methods that make use of physical contact to the film. As is described by the Drude model, free carrier optical absorption has increasing effect on the complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) with decreasing photon energies. Thus, extracting ϵ from SE measurements spanning the visible to terahertz (THz) frequency ranges provides sensitivity to film thickness and morphology at higher energies and free carrier absorption dominating the optical response at low energies. In this work fluorine doped tin oxide (SnO₂:F), aluminum doped zinc oxide (ZnO:Al), and sprayed single walled carbon nanotube (CNT) thin films are measured with ex situ SE over a spectral range of 0.035 to 5.9 eV using a single rotating compensator multichannel ellipsometer (0.75 - 5.9 eV) and a single rotating compensator Fourier transform infrared ellipsometer (0.035 - 0.75 eV). Additionally, the ZnO:Al and CNT films are measured using a single rotating compensator THz ellipsometer (0.4 - 5.8 meV) to further extend the measured spectral range to lower energies. Due to the wide spectral range measured, a single model describing ϵ and layer thicknesses has sufficient sensitivity to simultaneously determine electronic transitions, vibrational phonon modes, and free carrier absorption. The electrical properties in the Drude model are described by the bulk material resistivity ρ and scattering time τ . Optically extracted ρ has increasing correspondence to ρ deduced from four point probe electrical measurements as increasing low photon energies are included in the fitting (< 5% variation in ρ for ZnO:Al analyzing the full measured range); a behavior that demonstrates the benefit of extending the measurement spectrum to very low energies. The analyzed spectral range dependence of optically determined transport properties in these examples is considered to illustrate how narrower spectral range measurements impact deduced ρ and τ .

5:20pm **EL+AS+BI+EM+TF-ThA10 Spectroscopic Ellipsometry Studies of CdS-CdSe-CdTe Alloys: Applications in Thin Film Solar Cells**, *Maxwell Junda, C.R. Grice, Y. Yan, N.J. Podraza*, University of Toledo

Recent studies have demonstrated that photovoltaic (PV) device performance of thin film cadmium telluride (CdTe) solar cells is improved when a thin cadmium selenide (CdSe) layer is added at the cadmium sulfide (CdS) / CdTe interface and when oxygen is added to the CdS window layer (CdS:O). Specifically, devices fabricated with this configuration show increased short circuit current density without a corresponding degradation in open circuit voltage. The high temperature close spaced sublimation (CSS) deposition of the CdTe layers in these devices effectively anneals the existing CdS:O / CdSe window layer creating alloyed regions between these three materials as opposed to distinct, separate layers at the front side of the device. To better understand the sources of performance gain, we begin by using ex situ spectroscopic ellipsometry (SE) from the near infrared to the ultraviolet (0.74 – 5.9 eV) to study the optical and structural properties of these alloys. Films of CdS:O, CdS_{1-x}Se_x, and CdSe_yTe_{1-y} are fabricated on soda lime glass substrates by radio frequency sputtering a stack of layered combinations of CdS, CdSe, and/or CdTe followed either by annealing at the CdTe CSS deposition temperature or actual CSS of CdTe. A parameterized model describing the critical point transitions in the optical response ($\epsilon = \epsilon_1 + i\epsilon_2$) is developed, allowing for tracking of the changes in ϵ as a result of film composition and processing for each alloy. Additionally, structural and compositional variations introduced by the alloying of materials is considered and supported by complementary x-ray diffraction and energy dispersive x-ray spectroscopy measurements. The database of ϵ developed for these materials can be used to assess how the oxygen introduced in the CdS:O layer and diffusion of CdSe into both CdTe and CdS:O modify that interface and impact PV device performance.

5:40pm **EL+AS+BI+EM+TF-ThA11 Development of Growth Evolution Diagrams for RF Sputtered Nanocrystalline Hydrogenated Silicon Thin Films via Real Time Spectroscopic Ellipsometry**, *Dipendra Adhikari, M. M. Junda, N. J. Podraza*, University of Toledo

As a result of its increased visible light absorption and increased stability in comparison to hydrogenated amorphous silicon (a-Si:H), hydrogenated nanocrystalline silicon (nc-Si:H) thin films are of considerable interest for a variety of opto-electronic applications, including photovoltaic (PV) devices. Radio frequency (RF) sputtering in an Ar + H₂ ambient provides a cost effective deposition technique for Si:H films and has advantages over conventional plasma enhanced chemical vapor deposition as a result of the potential to improve deposition rates and the elimination of hazardous precursor gasses. In this work we investigate how pressure, RF power, and Ar/H₂ ambient gas composition ratio influence film structure (thicknesses; amorphous, nanocrystalline, mixed phase composition) and optical response of Si:H films deposited by RF sputtering onto native oxide covered crystalline silicon wafer substrates using in situ real time spectroscopic ellipsometry (RTSE) over the near infrared to ultraviolet spectral range. Through analysis of RTSE measurements and application of virtual interface analysis where appropriate, the time evolution of bulk layer thickness, surface roughness, and complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) spectra are extracted. Variations in nucleation and evolution of crystallites forming from the amorphous phase as a function of pressure, power, or Ar/H₂ ratio can be deduced from the growth evolution and used to create growth evolution diagrams. Overall film quality, crystallinity, and hydrogen incorporation (assessed using infrared extended measurements), are also determined from ϵ . X-ray diffraction measurements provide complementary information about how deposition conditions influence the density, size, and preferred orientation of crystallites. In addition to controlling film phase and structure, improvement of the deposition rate is also of practical interest and is explored here.

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Electronic Materials and Photonics

Room 102A - Session EM+SS+TF-ThA

Materials and Interfaces for Energy Storage

Moderators: Michelle Paquette, University of Missouri-Kansas City, Lee Walsh, University of Texas at Dallas

2:20pm EM+SS+TF-ThA1 Strain Engineering of Ultrathin Metal Oxide Coatings Deposited using Atomic Layer Deposition for Controlled Electrochemical Energy Storage, Nitin Muralidharan, R.E. Carter, A.P. Cohn, L. Oakes, C.L. Pint, Vanderbilt University

Strain engineering has transformed applications in the semiconductor electronics industry, but has not been widely explored as a tool for electrochemical applications. Here we study the role of strain on the electrochemistry of metal oxide coatings deposited using atomic layer deposition onto super-elastic NiTi alloy surfaces. Specifically, we focus on vanadium pentoxide (V_2O_5) due to its well-known capability to function as a cathode for the intercalation of lithium ions. Exploiting the capability of NiTi to "lock-in" strain in the elastic regime, which extends up to $\sim 15\%$ strain, we study the correlation between strain transferred to the V_2O_5 active material and the electrochemical performance during lithium intercalation. Overall, our results indicate that pre-straining the material changes both the kinetics and energetics for intercalation properties. Furthermore, the diffusion coefficient of lithium ions in the V_2O_5 lattice can be effectively doubled through the application of elastic strains as low as $\sim 0.25\%$. These results provide a route to controllably engineer bulk materials using principles of mechanics to improve battery or other electrochemical application performance.

2:40pm EM+SS+TF-ThA2 Probing Li-Ion Transport in All-Solid-State Batteries through Electron Transparent Electrodes, Alexander Yulaev, Center for Nanoscale Science and Technology, NIST, Gaithersburg, MD, USA; A.A. Talin, Sandia National Laboratories; M.S. Leite, University of Maryland; A. Kolmakov, NIST/CNST

All-solid-state batteries demonstrate a high power-to-weight ratio and high energy density, offering prospective opportunities for miniaturized micro-electronics and medical devices. Moreover, solid state batteries reduce the safety risk of thermal runaway that may occur in electrochemical cells with liquid electrolytes. In spite of growing interests, the details of lithium transport in solid electrolytes and their interfaces are not yet well understood due to a scarcity of experimental methods to probe electrochemical processes at the nanoscale. For instance, the factors controlling the rate and reversibility of Li ion intercalation are still an active area of research. Here we apply a combination of optical and scanning electron microscopies to resolve spatially Li-ion transport across a thin LiPON electrolyte. Using lithographically patterned electrodes, we monitor Li-ion transport through optically and electron transparent ultrathin anodes made either of high capacity silicon or carbon. The variation of the probing depth is achieved by altering the energy of the primary electron beam from 1 keV to 15 keV. Analogous to SEM tomography, the sequence of depth dependent 2D images can be employed to reconstruct the 3D diffusion pathways of Li ions in the electrolyte. In addition, we investigate Li plating/intercalation reactions, which occur at the anode-electrolyte interface during charge/discharge cycles. We foresee that this approach will help elucidate the effects of chemical and ion transport inhomogeneity inside the electrolyte and electrodes on the overall performance of the battery.

3:00pm EM+SS+TF-ThA3 Thin Film Battery Materials for Fundamental Studies and Applications, Nancy Dudney, K. Kercher, M. Veith, Oak Ridge National Laboratory

INVITED

Although most commercial rechargeable batteries are prepared by bulk and powder processing methods, vapor deposition of materials has led to important advances for fundamental research, modification of battery materials and interfaces, and also for commercialization of thin film batteries. Each of these areas will be illustrated with our studies of thin film materials for electrolyte, anode, and cathode components of rechargeable lithium and lithium-ion batteries with both planar and 3-dimensional architectures.

Acknowledgement: This work was supported by the U. S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

4:00pm EM+SS+TF-ThA6 Silicon Compatible Pseudocapacitors Based on Nickel Hydroxide Functionalization of Carbonized Porous Silicon, Joshua Fain, J.W. Mares, S.M. Weiss, Vanderbilt University

We report on silicon (Si) compatible energy-storage supercapacitors (SCs) that incorporate pseudocapacitive nickel hydroxide $[Ni(OH)_2]$ coupled with an electric double layer capacitance (EDLC) contributed by constituent $Ni(OH)_2$ and carbon layers. SCs can charge and discharge their energy much more rapidly than conventional batteries (within a few seconds to minutes), while possessing a higher energy storage capability than traditional capacitors (specific capacitances can reach thousands of F/g). Although SCs have made a commercial impact in regenerative braking, there remains untapped potential for this technology in on-chip energy storage that could lead to reduced size and weight of microelectronic devices. However, advancements in Si-based on-chip energy storage has been hindered due to the rapid corrosion of Si by most electrolytes necessary for energy storage. Recently, it has been shown that conformal carbonization of high surface area porous silicon (PSi) electrodes protects the Si matrix from corrosion while also contributing to energy-storage EDLC behavior. Here, we show that functionalization of carbonized PSi with pseudocapacitive $Ni(OH)_2$ leads to significantly improved energy-storage capabilities of the SC electrode from a few to over 100F/g (with respect to the mass of the entire electrode), and up to 1400 F/g (with respect to the mass of only the $Ni(OH)_2$ - corrected for EDL contribution of the carbon). The electrodes were fabricated by electrochemical etching of PSi, followed by carbonization using chemical vapor deposition, and finally inclusion of $Ni(OH)_2$ into the matrix via a sol-gel process or electrochemical deposition. Cyclic voltammetry (CV) and charge/discharge experiments were carried out to investigate the energy storage capabilities of composite pseudocapacitive electrodes prepared with varying sol-gel concentrations and different electrochemical deposition parameters. Scan rates of 1-50 mV/s were used. Clear oxidation and reduction peaks were evident in the CV curves along with the EDLC contribution. We observed a tradeoff between specific surface area and $Ni(OH)_2$ quantity: the higher the $Ni(OH)_2$ coverage in the PSi matrix, the lower the accessible surface area. The highest specific capacitance of 1400 F/g was measured on an electrode with a modest concentration of $Ni(OH)_2$ (5 mg/mL nickel acetate tetrahydrate:2-methoxyethanol) at 50 mV/s. The results of these studies suggest that PSi is an excellent high surface area host template for $Ni(OH)_2$ that enables high specific capacitance to be achieved on a Si-compatible platform that could be directly integrated into microelectronic devices.

4:20pm EM+SS+TF-ThA7 In-situ Raman of Sodium Ion Cointercalation into Highly Crystalline Few-Layered Graphene, Adam Cohn, C.L. Pint, Vanderbilt University

A maximum sodium capacity of ~ 35 mAh/g has restricted the use of crystalline carbon for sodium ion battery anodes. We demonstrate that a diglyme solvent shell encapsulating a sodium ion acts as a "non-stick" coating to facilitate rapid ion insertion into crystalline few-layer graphene and bypass slow desolvation kinetics. This yields storage capacities above 150 mAh/g, cycling performance with negligible capacity fade over 8000 cycles, and ~ 100 mAh/g capacities maintained at currents of 30 A/g (~ 12 second charge). Raman spectroscopy elucidates the ordered, but non-destructive cointercalation mechanism that differs from desolvated ion intercalation processes. In-situ Raman measurements identify the Na^+ staging sequence and isolates Fermi energies for the first and second stage ternary intercalation compounds at ~ 0.8 eV and ~ 1.2 eV.

4:40pm EM+SS+TF-ThA8 Using X-ray Reflectivity to Measure the Vacuum Ultraviolet Absorption Spectrum in Low-k Dielectrics, Faraz Choudhury, H.M. Nguyen, W. Li, University of Wisconsin-Madison; Y. Nishi, Stanford University; J.L. Shohet, University of Wisconsin-Madison

During plasma processing, low-k dielectrics are exposed to high levels of vacuum ultraviolet (VUV) radiation that can cause severe damage to the dielectric material. The degree and nature of VUV-induced damage depends on the VUV photon energies.[1] In this work, we determine the VUV absorption spectrum of low-k organosilicate glass (OSG) using specular X-ray reflectivity (XRR). Low-k SiCOH films were exposed to synchrotron VUV radiation with energies ranging from 7 to 25 eV and the electron density depth profile of the VUV irradiated films were extracted from the fitting of the XRR experimental data using the Parratt method. The results show that the depth of the VUV induced damage layer is sensitive to the photon energy. Between 7 to 11 eV, the depth of the damaged layer decreases sharply from 110 nm to 60 nm and then gradually increases to 85 nm at 21 eV. The maximum VUV absorption in low-k films occurs between 11 and 15 eV. This method is also utilized to investigate the penetration depth of 5 to 25 eV photons in porous SiCOH films with

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porosities ranging from 15 to 50%. It is seen that the penetration depth of photons increases with porosity. This work shows that XRR electron density depth profiling can be a very effective, non-destructive tool to determine the penetration depth and absorption coefficients of photons and other reactive species from a plasma in various kinds of dielectric films.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359

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5:00pm **EM+SS+TF-ThA9 On-chip [¹⁸F]fluoride Concentration for Microfluidic PET Tracer Synthesis**, *Xin Zhang, J. Buck, M. Nickels, C. Manning, L. Bellan*, Vanderbilt University

Positron emission tomography (PET) is a valuable medical imaging method that relies on radioactive tracers that target specific sites in the body. Development of these tracers is currently hindered by the enormous infrastructure requirements to perform the necessary radioisotope production and subsequent reactions. To overcome this hurdle and facilitate PET tracer development, we are designing simple, modular microfluidic systems that support on-chip radiosynthesis reactions with small volumes of reagents. In this work, [¹⁸F]fluoride (a positron emitter widely used in PET imaging due to its convenient half-life of 110 minutes) is concentrated with a miniaturized anion exchange column located in a microfluidic device fabricated in polydimethylsiloxane (PDMS). By employing a microfluidic device, we aim to achieve more controlled diffusion and reactive kinetics. Instead of relying on complicated flow control elements (e.g. valves), in this microfluidic system, a channel containing pillars with a spacing less than the average diameter of the anion exchange beads is used to trap relatively monodispersed, rigid polystyrene/divinyl benzene beads. We characterized the ability of this miniaturized on-chip exchange column to capture and release quantities of [¹⁸F]fluoride appropriate for human imaging (a typical dose is 10 mCi).

Our device is composed of a main chamber with larger microchannels (9 mm long) connected to an inlet and outlet. A laser writer (Heidelberg μ PG 101) was used to create patterns on a silicon wafer using a 60 μ m thick layer of mr-DWL resist; this template was subsequently used to pattern a microfluidic structure in PDMS. The desired quantity (2.9 mL) of anion exchange beads was trapped by a double row of square pillars near the outlet of the chamber, and the beads subsequently activated with 1.0 M of KHCO₃. Diluted [¹⁸F]fluoride (100 mCi/mL) sourced from a nearby cyclotron was introduced into the system using a syringe pump, flowing at 0.05 mL/min for 10 minutes.

By quantifying the radioactivity of the [¹⁸F]fluoride introduced, the radioactivity of the chip, and the radioactivity of the outflow, we could determine trapping and release efficiency. We observed near complete capture of [¹⁸F]fluoride (50 mCi) on our chips in a relatively short time. Moreover, elution with a small volume (less than 200 mL) of Kryptofix (K₂₂₂)/K₂CO₃ was able to release nearly all the [¹⁸F]fluoride (49 mCi). Thus, this device is capable of simply and efficiently trapping [¹⁸F]fluoride and controllably releasing the concentrated radiolabel in small volumes for downstream reaction with desired molecules.

5:40pm **EM+SS+TF-ThA11 The Role of Electron-Beam Deposition Rate in Controlling Properties of the Titanium/Semiconductor Interface**, *Keren Freedy, A. Giri, B.M. Foley*, University of Virginia; *J. Bogan, R. O'Conner*, Dublin City University, Ireland; *P.E. Hopkins, S. McDonnell*, University of Virginia

Electron beam evaporation under high vacuum is very widely used for contact deposition in electronic device fabrication. Ti has a low work function and is commonly deposited as a contact or adhesion layer for other metals in silicon-based devices and more recently in 2D semiconductors. Previous work on Ti/MoS₂ contacts suggests that electron beam evaporation of Ti under high vacuum results in the formation of TiO₂ at the interface while UHV deposition results in unintentional reactions between metallic Ti and the MoS₂ substrate (McDonnell et al., 10.1021/acsami.6b00275). Since the majority of reports using Ti as a contact metal utilize HV rather than UHV e-beam processes, understanding the role of process conditions on the properties of this contact/semiconductor interface is of the utmost importance. To avoid the large variability observed in metal/MoS₂ contacts, we focus on Si as a case study to investigate the thermal and electronic properties of the Ti/semiconductor interface. The present study examines the effect of deposition rate on the properties of the Ti/Si interface. Electron beam evaporation of Ti onto both hydrogen-terminated and native oxide (001) Si surfaces is performed at varied deposition rates ranging from 0.1 to 5 Å/s at pressures of $\sim 10^{-6}$ Torr. Prior to ex-situ characterization, the samples are

capped with Au in the evaporator to prevent further oxidation in air. Photoelectron spectroscopy measurements reveal that oxide composition is inversely proportional to the deposition rate. X-ray diffraction data shows no evidence of metallic Ti at slower deposition rates. Due to an appreciable partial pressure of O₂ at high vacuum, the composition of the deposited material is sensitive to the impingement rate of Ti on the surface. It follows that higher deposition rates should result in a smaller fraction of oxide phases. Electron and phonon transport across the interface will be studied as a function of deposition rate.

6:00pm **EM+SS+TF-ThA12 Single Crystal Study of Layered U₂RhIn₃₊₂ Materials: Case of the Novel U₂RhIn₈ Compound**, *Attila Bartha, M. Kratochvílová*, Charles University, Czech Republic; *M. Dušek*, Institute of Physics ASCR, Czech Republic; *M. Diviš, J. Custers, V. Sechovský*, Charles University, Czech Republic

Materials of reduced dimensionality appear in many contemporary fields of research and technology, because they encompass a wide variety of interesting electronic phenomena. For instance carbon can be prepared in 3D (diamond), quasi-2D (graphite), 2D (graphene) or 1D (carbon nanotubes). All of these structures have distinct electronics. Diamond is an insulator. Graphene is semimetal. However, when the dimensionality is increased by putting several graphene layers together (eventually making graphite), the resulting band structure moves to that of a more trivalent metal. Another example is high temperature superconductors being quasi-2D materials as well.

The role of dimensionality in *f*-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series Ce_nT_mIn_{3n+2m} ($n = 1, 2$; $m = 0, 1, 2$; $T =$ transition metal) of layered compounds has been extensively investigated. CeIn₃ is cubic (3D) and orders antiferromagnetically (AFM) at $T_N = 10.2$ K. Under hydrostatic pressure superconductivity appears with highest $T_c = 0.3$ K at $p = 2.5$ GPa. In CeRhIn₅, the anisotropic crystal structure leads to a quasi-2D electronic and magnetic structure. The AFM order is reduced ($T_N = 3.8$ K) while superconductivity is supported, T_c increases to 1.9 K at $p = 1.77$ GPa.

We report on the properties of the novel U₂RhIn₈ compound studied the single crystal form in the context of parent URhIn₅ and UIn₃ systems [1]. The compounds were prepared by In self-flux method. U₂RhIn₈ adopts the Ho₂CoGa₈-type structure with lattice parameters $a = 4.6056(6)$ Å and $c = 11.9911(15)$ Å. The behavior of U₂RhIn₈ strongly resembles features of related URhIn₅ and UIn₃ with respect to magnetization, specific heat, and resistivity, except for magnetocrystalline anisotropy developing with lowering dimensionality in the series UIn₃ vs. U₂RhIn₈ and URhIn₅. U₂RhIn₈ orders AFM below $T_N = 117$ K and exhibits slightly enhanced Sommerfeld coefficient $\gamma = 47$ mJ.mol⁻¹.K⁻². Magnetic field leaves the value of Néel temperature for both URhIn₅ and U₂RhIn₈ unaffected up to 9 T. On the other hand, T_N increases with applying hydrostatic pressure up to 3.2 GPa. Results of thermal expansion measurement will be discussed in the framework of Ehrenfest relations. The character of uranium 5*f* electron states of U₂RhIn₈ was studied by first principles calculations based on the density functional theory combined with the Hubbard model. The overall phase diagram of U₂RhIn₈ is discussed in the context of magnetism in related UTX₅ and UX₃ ($T =$ transition metal, $X =$ In, Ga) compounds.

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Thursday Afternoon Poster Sessions, November 10, 2016

Spectroscopic Ellipsometry Focus Topic Room Hall D - Session EL+AS+EM+TF-ThP

Spectroscopic Ellipsometry Poster Session

EL+AS+EM+TF-ThP1 FTIR Ellipsometry Studies of Thermally Grown GeO₂ on Ge, Jaime Moya, T.N. Nunley, N.S. Fernando, N. Samarasingha, S. Zollner, New Mexico State University

To study the vibrational modes of GeO₂, we produced a set of thermal GeO₂ oxides ranging from 45 to 136 nm in thickness. Receiving a set of Ge Bulk wafers, we cleaved and roughened the back sides via an aluminum abrasive to avoid backside reflections. To remove carbon-containing surface contaminants and leave a stable oxide on the wafer, we performed a hybrid dry/wet clean. The dry clean was done by subjecting the wafer to an ozone clean in an ultrapure oxygen environment while heating the sample to 150°C for 1 hour, followed by a 30 minute incubation period. The samples were then cleaned ultrasonically for 20 minutes in deionized water followed by 20 minutes in isopropanol. No harsh chemicals were used. The samples were then dried with nitrogen and annealed at 270 kPa and 550°C in ultrapure oxygen for a few hours to achieve different oxide thicknesses.

Using Fourier-transform infrared ellipsometry, the ellipsometric angles ψ and Δ were measured from 250 to 6000cm⁻¹ at several angles of incidence (60° to 75°). The infrared lattice absorption peak of the amorphous GeO₂ was fit with a Lorentz oscillator.

When comparing our results to Lippincott's *et al.* [1] transmission measurements of vitreous GeO₂ formed by quenching hexagonal GeO₂, we see a negative shift in vibrational frequency. The difference can be attributed to the different Ge-O bond length comparing the vitreous GeO₂ and our amorphous thermal oxide. Our amorphous thermal oxide GeO₂ samples have a longer bond length, corresponding to a weaker bond and a lower vibrational frequency. This shift also shows a lower density of our samples compared to Lippincott *et al* [1].

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EL+AS+EM+TF-ThP2 Anisotropic Bruggeman Effective Medium Approach for Modeling Spectroscopic Ellipsometry Data of Porous Samples, Stefan Schöeche, J. VanDerslice, J.A. Woollam, J.A. Woollam Co., Inc.

Porous materials are widely used with applications including filtration devices, low-k dielectrics, catalysts, optical coatings, and more. The porous medium is described by its total porosity, pore diameter and specific surface area. The overall properties of the porous material are a result of the combined constituents and can often be approximated using effective medium theories. Due to complicated microstructure, these effective properties may vary along different directions or within the material resulting in anisotropic optical properties or gradients in pore size and total porosity.

Spectroscopic ellipsometry (SE) based porosimetry monitors the optical and structural changes of a porous sample during an adsorption and desorption cycle, i.e., insitu monitoring while the sample is exposed to an atmosphere with solvent partial pressure P varied between zero and the saturation vapor pressure of the solvent over flat surface P_0 . Ellipsometric porosimetry based on the Lorentz-Lorenz equation is widely used to characterize thin porous films since it is simple (only requires refractive index at one wavelength) and the skeletal material refractive index is not needed for the calculation. However, the theory is based on invalid assumptions on the microscopic nature of the film, the choice of refractive index is random, it is applicable only to isotropic and homogeneous samples, makes assumptions on the filling of pores at relative pressures $P/P_0=0$ and $P/P_0=1$, ignores potential inaccessible pores, and does not provide access to the skeletal refractive index.

We present an alternative approach to analyze porous samples based on the anisotropic Bruggeman effective medium approximation (ABEMA). The model uses well established theory to best match the SE data over a wide spectral range, is easily extendable to more constituents, accounts for optical anisotropy due to the shape of the pores or the pore network, allows determination of the skeletal refractive index in unknown materials, is sensitive to inaccessible pores, and allows grading of relevant sample properties such as the total porosity. A comparison of the two model approaches for data obtained on a porous SiO₂ film on Si substrate will be shown.

EL+AS+EM+TF-ThP3 Optical Constants of M2-phase VO₂ Measured by Spectroscopic Ellipsometry, Samuel T. White, R.F. Haglund, K. Hallman, Vanderbilt University

Vanadium dioxide (VO₂) is a highly interesting material due to changes in its electronic and optical properties associated with the reversible phase transition from a monoclinic (M1) to a rutile (R) crystal structure. This transition makes VO₂ a promising candidate for many applications, including ultrafast electrical switching and optical modulation. There exists another, distinct monoclinic phase (M2) which also can undergo the transition to R, and which is structurally similar to a possible transient phase appearing in the M1-R phase transition. Thus, M2 is important to understanding the M1-R transition, besides being potentially useful for application in its own right; however, M2 and its phase transition are not as well-characterized as M1. Establishing the optical constants for M2-phase vanadium dioxide is an important step in characterizing this phase and will help provide understanding of its relationship to the other phases.

Here, variable-temperature spectroscopic ellipsometry is used to measure the optical constants of thin-film M2-phase VO₂ below and above the phase-transition temperature, for wavelengths ranging from 370 to 1690 nm. Samples were prepared by electron-beam deposition onto a silicon substrate, with Cr doping to prepare the M2-phase. Experiments were performed both at room temperature and at 95°C with a JA Woollam M-2000 Spectroscopic Ellipsometer equipped with a heated sample stage. VO₂ layer thickness was established by profilometry measurements, and the optical constants were extracted by fitting data to a sum of three Lorentz oscillators. The results are compared to those obtained for thin-film M1-phase VO₂.

The optical constants for M2 and M1 are found to have similar wavelength-dependence, and to agree generally with results obtained for M1 by other researchers. The extinction coefficient, k , is very close for both samples over all wavelengths measured. The index of refraction, n , on the other hand, is larger for M2 than for M1 by ~5-10% for almost all wavelengths measured, with the greatest difference occurring at wavelengths near the peak value, ~430 nm. At elevated temperatures, both samples show optical constants typical of R-phase VO₂, though the index of refraction again appears to be higher for the M2 sample than for the M1 sample. Repeating this experiment with samples prepared by another method may help to distinguish effects due to phase difference due to those due to other sample differences.

Electronic Materials and Photonics Room Hall D - Session EM-ThP

EMPD Poster Session

EM-ThP1 The Effects of VUV Radiation on Low-k Organosilicate Glass (SiCOH) as Measured with Electron-Spin Resonance, Panpan Xue, W. Li, University of Wisconsin-Madison; J. de Marneffe, M. Baklanov, IMEC, KU Leuven Belgium; V. Afanas'ev, Catholic University of Leuven, Belgium; Y. Nishi, Stanford University; J.L. Shohet, University of Wisconsin-Madison

The effects of VUV radiation on defect concentrations in SiCOH are investigated. Electron-spin resonance (ESR) spectroscopy is a very effective tool to detect defects in dielectrics. ESR has been used on various high-k dielectrics, such as HfO₂. Here, in order to obtain a clear spectroscopic signal, 60-nm thick SiCOH ($k=2.4$) was deposited on high-resistivity (3000 Ω -cm) wafers. There are at least two kinds of detectable defects in SiCOH: Si dangling bonds ($g=2.0054$) and Oxygen vacancies ($g=2.0020$). In this work, we concentrate on the silicon dangling-bond defects. In order to eliminate dangling bonds from the silicon substrate as well as its edges, CP4 and HF treatments were used. To investigate the influence of VUV radiation, the samples were exposed to synchrotron radiation with a range of photon energies from 7.3 to 21 eV. The ESR measurements showed that the defect concentration of the silicon dangling bonds increased after VUV exposure with photon energies higher than 8eV. In addition, when the photon energy was less than 15 eV, the defect concentration increased with higher photon energy, but did not increase further for VUV exposures with higher photon energies. This is likely caused by electron depletion by photoemission from defects during VUV irradiation. That is, before VUV irradiation, the silicon dangling bonds are filled with electrons. The electrons are then depleted by photoemission during irradiation. Since the band gap for SiCOH is approximately 8 eV, this is also consistent with the fact that the energy threshold for Si-H bond photolysis at the surface of H-passivated Si is ~7.9 eV. Moreover, VUV exposure can cause a loss of

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methylated species.^{3,4} It is possible that the loss of $-CH_3$ groups results in additional Si dangling bonds near the surface of the SiCOH films. The ESR signals have a Lorentzian shape and the Bloch model fits these well. We conclude that silicon dangling bond defects in SiCOH and its interface with silicon can be detected using ESR and that VUV exposure increases the defect concentration.

Work supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and the National Science Foundation under Grant No. CBET-1066231.

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EM-ThP2 Effect of Initial Substrate Conditioning on Structural and Optoelectronic Properties of $In_{1-x}Ga_xN$ Grown by MEPA-MOCVD, Indika Senevirathna, D. Seidlitz, A. Fali, Y. Abate, N. Dietz, Georgia State University
Fabrication of high quality Indium rich- $In_{1-x}Ga_xN$ layers is still a challenge due to the immiscibility between the binaries InN and GaN. The lack of lattice-matched substrate is an additional challenge for the growth of $In_{1-x}Ga_xN$ layers. The lattice mismatch between the substrate template and the $In_{1-x}Ga_xN$ layer generate residual strains and threading dislocations at the interface that propagate into the $In_{1-x}Ga_xN$ layers, and consequently, degrade the quality of the $In_{1-x}Ga_xN$ epilayer. To mitigate these effects, different approaches such as the use of buffer layers (e.g. GaN, InN, AlN) between the $In_{1-x}Ga_xN$ layers are explored.

In this contribution, we present our findings on the effects of substrate treatments on the structural and optoelectronic properties of $In_{1-x}Ga_xN$ layers grown by Migration-Enhanced, Plasma-Assisted MOCVD (MEPA-MOCVD). Furthermore, the analysis consist the data for $In_{1-x}Ga_xN$ layers grown on different nitrided sapphire substrates as well as layers grown on sapphire substrates templates, containing InN, GaN or AlN interlayers.

The optoelectronic properties – e.g. free carrier concentration, the mobility of the carriers, high-frequency dielectric constant ϵ_∞ , and layer thickness in the $In_{1-x}Ga_xN$ layers have been analyzed by simulating the reflectance spectra, obtained via Fourier Transform Infra-red (FTIR) spectroscopy, using a multilayer stack model and a dielectric function based on Lorentz-Drude model. AFM topography has been used to study the surface morphology of the layers. Raman spectroscopy has been utilized to analyze the local crystallinity (E_2 (high) mode) of the $In_{1-x}Ga_xN$ layers as well as the composition via the shift of the A_1 (LO) mode and its broadening with $In_{1-x}Ga_xN$ target composition.

EM-ThP3 An In-Depth Study of Cu_2ZnSnS_4 Films Synthesized by Sulfurization of Stacked Metallic Layers, A. Alvarez Barragan, S.A. Exarhos, Lorenzo Mangolini, University of California Riverside

The quaternary chalcogenide Cu_2ZnSnS_4 (CZTS) is composed of earth-abundant elements and has interesting optoelectronic properties that project it as an important candidate for thin-film photovoltaics. Among several synthesis methods, sulfurization of metallic stacked layers has been heavily used because it does not rely on toxic compounds and provides good control over the final stoichiometry of the sample [1-3]. We present an in-depth structural and compositional analysis of CZTS synthesized by this technique. A first study exhibits preferential segregation of hexagonal SnS_2 when increasing the sulfurization pressure in a closed annealing chamber. Variations in film morphology suggest that different reaction pathways take place as the pressure is raised. Formation of gaseous SnS is favored at lower pressure, while nucleation of solid SnS_2 preferentially occurs at higher pressure. In addition to this investigation, an individual grain study sheds light on the complexity of this material system. Elemental analysis shows significant grain-to-grain variations in composition despite dealing with an overall close-to-ideal stoichiometry. High resolution Raman spectroscopy indicates that this is accompanied by grain-to-grain structural variations as well. The intensity from the 337 cm^{-1} Raman peak, generally assigned to the kesterite phase of CZTS, remains constant over a large area of the sample. On the other hand, signals from secondary phases at 376 cm^{-1} (copper-tin-sulfide) and 351 cm^{-1} (zinc-sulfide) show significant variation over the same area. These results demonstrate how a seemingly homogeneous CZTS thin film can actually have considerable structural and compositional variations that are often overlooked.

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EM-ThP4 Optical and Magneto-Optical Properties of $ZnO/Zn_{1-x}Co_xO$ Thin Films Grown by Pulsed Laser Deposition, Da-Ren Liu, C.J. Weng, Instrument Technology Research Center, National Applied Research Laboratories

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. $ZnCoO$ is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the Si substrates by atomic layer deposition (ALD). Then the $Zn_{1-x}Co_xO$ ($0.01 < x < 0.10$) coatings were grown on ZnO layer by Nd:YAG pulsed laser deposition (PLD). The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR). According to the results of high-resolution x-ray diffraction, the $ZnO/Zn_{1-x}Co_xO$ thin films are polycrystalline with a preferential growth direction of (002). Photoluminescence spectra demonstrate ultraviolet emission peaks which have shift with the increase of Co ion concentration. The temperature-dependent magnetization (M-T) curves of the $ZnO/Zn_{1-x}Co_xO$ thin films were measured by a superconducting quantum interference device (SQUID) magnetometer and the magneto-optical properties were measured by micro-MOKE spectroscopy. The results show the room temperature ferromagnetism of the $ZnO/Zn_{1-x}Co_xO$ thin films suggested that the possibility for the application to diluted magnetic semiconductors.

EM-ThP5 A bi-functional Bolometer with Sensitivity to IR Radiation and Hot Air Induced Temperature Variation, Evgenia Vaganova, The Hebrew University of Jerusalem, Israel

ABSTRACT We have shown previously that doping a poly(4-vinyl pyridine)/pyridine gel with an ester group-containing polymer (e.g. poly(butyl methacrylate)) (polymer acids as additives) expands the wavelength range of the gel photoelectrical sensitivity from the uv into the infra-red. Here we characterize the temporal response of the gel resistivity and demonstrate its ability to operate as a bi-functional bolometer. At constant room temperature, the bolometer can function as a rapidly responding IR detector. It can also respond to temperature variation produced by hot air, but with a much longer time constant. Measurements are shown in the figure below.

b)

Figure. a) Time dependence of the resistance changes of the polymer gel due to IR irradiation at $1\ \mu\text{m}$. The down pointing arrows indicate switch-on of the radiation source while the up pointing arrows indicate switch-off. b) Time dependence of the resistance changes of the polymer gel in response to temperature variation produced by hot air. The maximum temperature change was 4C ($26\text{C} - 30\text{C}$).

The fractional change in resistance caused by IR irradiation at 1mm is $\Delta R/R_0 = 0.13$; the fractional change caused by hot air induced temperature variation - $\Delta R/R_0 = 0.06/1^\circ\text{C}$. The relaxation rate of the IR response following switch-off is $260\%/s$. The temperature-induced relaxation curve could be fit to an exponential function with two time constants - $t_1=0.148\text{s}$ and $t_2=17.11\text{s}$. Analysis of the relaxation of the photo-response was limited by the time resolution of the resistance measurements, i.e. 0.02s .

Polymer/liquid pyridine interactions² are considered to be responsible for this interesting functionality of the polymer blend and they will be discussed.

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EM-ThP6 Proton-Induced Effects on HfO_x-Based Resistive Random Access Memory, *K. Hsu, T. Chang*, University of Wisconsin-Madison; *L. Zhao, Z. Wang*, Stanford University; *R. Agasie, T. Betthausser, J. Nickles, J. Chang*, University of Wisconsin-Madison; *Y. Nishi*, Stanford University; *Z. Ma, J. Leon Shohet*, University of Wisconsin-Madison

Resistive Random Access Memory (RRAM) [1], is considered to be a very promising memory technology. As RRAM technology matures and electronic devices using RRAM are likely to be built soon, malfunctions of RRAM caused by radiation will become an important problem in industry since the size of these devices will continue to decrease. The goal of this work is the measurement of proton-induced effects on HfO_x RRAM cells. Proton irradiation in the MeV range of energies were initially chosen since most cosmic-ray protons are in this range. However, protons lose energy when they pass through matter and thus, lower-energy protons were also investigated. According to TRIM code calculations, there is more interaction between protons and HfO_x films when the proton energy decreased to several keV.

Two proton fluences were chosen ($\sim 2 \times 10^{15}$ cm⁻² and $\sim 2 \times 10^{14}$ cm⁻²). The proton-induced effects on HfO_x RRAM cell include forming rate, modification to forming voltage, resistance of high resistance state (HRS) and shifts in set/reset voltage. After proton irradiation, no RRAM cells were formed and ended up in the low resistance state (LRS) and no changes were observed in the forming voltage of irradiated RRAM cells even when exposed to very high fluence ($\sim 2 \times 10^{15}$ cm⁻²).

An increase in the resistance of HRS was observed in proton-irradiated RRAM cells. RRAM cells irradiated with 60 keV protons have a higher increase in their HRS state than RRAM cells irradiated with 5 MeV protons. The shift in values of the set voltage can be seen on the I-V characteristic of the proton-irradiated RRAM cell. It is very likely that there is an annealing process occurs and it might be a result of defect reordering after proton irradiation.

The shift in set voltage after 5 MeV proton irradiation (fluence $\sim 2 \times 10^{15}$ cm⁻²) is from 3.5 V to 7 V. The shift in set voltage after 60 keV proton irradiation (fluence $\sim 2 \times 10^{14}$ cm⁻²) is from 3.5 to 11 V. Such shifts of set voltages may create problems in real device applications. These shifts are likely to be attributed to atomic-structure changes in HfO_x caused by proton irradiation.

This work was supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359, by the National Science Foundation under Grant No. CBET-1066231.

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EM-ThP7 SiGe_x (100) (x=0.25, 0.5, 0.75) and Ge (100) MOSCaps with Aqueous Ammonium Sulfide Passivation, *Lauren Peckler, S.L. Heslop, A.J. Muscat*, University of Arizona

SiGe_x is a potential semiconductor for next generation transistors because it could be incorporated into current, silicon-based semiconductor manufacturing processes and it would improve transistor performance due to the high carrier mobility of Ge. Despite these advantages, one major challenge is to reduce the number of Ge defects at the SiGe_x/dielectric interface because they degrade electrical performance of the transistor. While a relatively stable SiO₂ layer can be grown on Si with relatively few defects, the same is not true for Ge. One approach to forming a high quality interface is to remove Ge oxides by passivating the Ge atoms on the surface. SiGe and Ge metal oxide semiconductor capacitors (MOSCaps) were fabricated (10 nm Al₂O₃) and tested to evaluate the effect of sulfur-based chemical passivation on electrical performance. The (100) faces of three SiGe_x substrates – x = 0.25, 0.5, 0.75 – and one Ge substrate were cleaned and treated with one of two ammonium sulfide, (NH₄)₂S, wet chemistries: (NH₄)₂S/H₂O (1:100 v/v) or (NH₄)₂S/HCl/HF/H₂O (1:0.15:0.15:100 v/v). The surfaces of control MOSCaps were cleaned only. The contact area on each device was 12.6 μm².

Average capacitance in accumulation for SiGe_x MOSCaps (x = 0.25, 0.5) was 199 ± 5.4 and 205 ± 22 pF, with a DC bias sweep from -2 to +2 V at 1 MHz. The same capacitance was 42 ± 1.3 pF for SiGe_x (x = 0.75) and 457 ± 12 pF for the Ge MOSCaps. Both (NH₄)₂S treatments increased the accumulation

capacitance by 6% and 34%, on average, for SiGe_x (x = 0.25, 0.5), 8% for SiGe_x (x = 0.75), and 8% for Ge MOSCaps. Similarly, V_{FB} shifted -2 V (SiGe_x (x = 0.25, 0.5)) and -14 V (SiGe_x (x = 0.75) and Ge) with respect to the controls. While flatband shifting is at least due to reduction of oxide defects in the Al₂O₃ layer, the low magnitude of accumulation capacitance (according to oxide thickness calculations) suggests that there are other oxide layers present.

Half of the SiGe_x MOSCaps (x = 0.25, 0.75) were annealed in forming gas. V_{FB} shifted +3 V for SiGe_x MOSCaps (x = 0.25) with respect to non-annealed results, which is indicative of a reduction in negatively charged bulk oxide defects. SiGe_x (x = 0.75), and Ge MOSCaps possibly had less bulk oxide defects because their V_{FB} were within ± 0.5 V before and after annealing. Less bulk oxide defects in these MOSCaps suggest that nucleation and growth of the Al₂O₃ layer on these surfaces may differ from that of the SiGe_x (x = 0.25) surface. Among all three SiGe_x (x = 0.25) MOSCaps, the one treated with (NH₄)₂S and acid and annealed resulted in the flatband voltage closest to 0 V, as well as the lowest capacitance.

EM-ThP8 Investigating U₃O₈ for Solid-State Direct-Conversion Neutron Detection Applications, *Shailesh Dhungana, G. Bhattarai*, University of Missouri-Kansas City; *B.C. Shaver, S. Lawson, B. Musićó, T. Meek*, The University of Tennessee Knoxville; *M.M. Paquette, A.N. Caruso*, University of Missouri-Kansas City

Solid-state direct-conversion neutron detectors, wherein a semiconductor detector heterostructure is made up of a neutron absorbing material, are capable in principle of very high neutron detection efficiencies. High-efficiency direct-conversion detectors have not yet been achieved in practice, however, because of challenges in finding suitable materials that simultaneously meet the necessary criteria, including high neutron absorption, high mobility–lifetime product, and low leakage current. Uranium-oxide-based semiconductors make up a promising class of neutron detection materials as uranium undergoes neutron-induced fission to yield very high energy primary reaction products, which can in turn create a large number of electron–hole pairs—two-to-four orders of magnitude higher than in the case of boron and lithium, the materials commonly studied for direct-conversion detectors. This additional charge can help to overcome limitations in charge transport properties, such as high leakage current and low charge carrier mobility, typically seen in candidate neutron-absorbing semiconductor materials. Of the uranium oxides, UO₂ has been studied the most, and literature reports show that its resistivity and charge carrier mobility vary widely with stoichiometry and microstructure. Very few studies on the electrical transport properties of U₃O₈ exist, with one reporting values of 10⁴ Ω cm for resistivity and 1 cm²/V s for mobility (George & Karkhanavala, 1963). Like for UO₂ and other semiconductors, however, these properties would be expected to vary widely. To determine the range of the possible charge transport properties in U₃O₈, as well as how they vary with material composition and microstructure, a rigorous study is necessary. We report the results of charge transport measurements using a range of techniques, including four-point van der Pauw resistivity and DC Hall, on sintered U₃O₈ pellets of varying stoichiometry and grain size. Additionally, we report results from ultraviolet and x-ray photoelectron spectroscopy toward probing the electronic structure of the U₃O₈ surface toward the development of suitable electrical contacts for this material.

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EM-ThP9 Investigation of Electro-Optical and Chemical properties InN epilayer grown on Ga-face GaN by RF-MOMBE, *W.-C. Chen, Chien-Nan Hsiao*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China

Epitaxial indium nitride layers were grown on gallium nitride/c-sapphire by radio frequency metal-organic molecular beam epitaxy. We discussed the effect of V/III flow ratios on the Electro-Optical and Chemical properties of epitaxial indium nitride. The chemical properties of the indium nitride films were characterized in detail using Secondary ion mass spectrometry and X-ray photoelectron spectroscopy, and the electrical and optical properties were studied by Hall Effect and photoluminescence measurements. Secondary ion mass spectrometry and X-ray photoelectron spectroscopy results showed that carbon and hydrogen of average concentration were

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measured about 10^{20} cm^{-3} in InN films and O concentration in the InN film is about 10^{19} cm^{-3} . Also, the C and O concentrations decrease with increasing trimethylindium flow rate. A relatively high C, H and O concentration exists near the surface of the InN film. After etching, the etched InN film exhibited a decreased carrier concentration of $3.31 \times 10^{19} \text{ cm}^{-3}$, increased electron mobility of $335 \text{ cm}^2/\text{V}\cdot\text{s}$. Optical properties showed that the PL spectra exhibited NBE peak in the range of $0.692 \sim 0.735 \text{ eV}$. Also, the peaks showed blue-shift with increasing V/III flow ratio.

EM-ThP12 Temperature-Resistance Effect of Carbon Black / Polydimethylsiloxane Composite, *Jing Xu, L.Z. Ouyang*, Tennessee State University

In the present work, temperature-resistance effect is found in carbon black/Polydimethylsiloxane composites. The composites were made by mixing the carbon black, aluminium oxide power and polydimethylsiloxane (PDMS). Interdigitated copper electrodes were obtained using chemical etching method on the flexible polyimide substrate in order to determine the resistance change of the composites at different temperatures. The resistances of as-fabricated composites at different temperatures are measured using multimeter. From the results, we found out that the resistance increases dramatically with temperature increasing, and the fitting result shows that it's an exponential increase. This composite has the potential to fabricate the flexible and high-precision temperature sensor.

EM-ThP13 Dependence of Electrical Conductivity on Observed Microstructure of Sintered U_3O_8 , *Seth Lawson, B.C. Shaver, B. Musicó*, The University of Tennessee Knoxville; *S. Dhungana, G. Bhattarai, M.M. Paquette, A.N. Caruso*, University of Missouri-Kansas City; *T. Meek*, The University of Tennessee Knoxville

Actinide compounds, such as uranium oxides, have been shown to have band gaps similar to conventional semiconducting materials such as Si, Ge, and GaAs but with significantly higher operating temperatures as well as higher resistance to radiation damage, allowing for possible use as a detector material in environments and conditions that would otherwise be impractical. Under standard atmosphere and pressure, U_3O_8 is the most stable form of uranium oxide. This work will focus on the stoichiometric composition and will detail the methods used to develop green pellets of U_3O_8 from natural uranium in the form of uranyl acetate. Understanding the microstructure morphology of these pellets as a function of sintering conditions is an important step toward elucidating the activation energy of sintering and grain growth kinetics of this material. The morphology and grain size can then be correlated to changes of measured electrical properties. Optical microscopy was used to determine the grain characteristics for each sintering condition in order to evaluate the influence on sintering on grain growth. Electrical property studies were conducted with measurements including four-point van der Pauw resistivity and DC Hall measurements. These studies will contribute to a larger effort aimed at exploring the electrical properties of uranium oxides to determine whether the properties of U_3O_8 can be optimized to fabricate a competitive direct conversion solid-state neutron detector.

Spectroscopic Ellipsometry Focus Topic Room 104C - Session EL+AS+EM+MI+TF-FrM

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Morten Kildemo, Norwegian University of Science and Technology, Nikolas Podraza, University of Toledo

8:20am **EL+AS+EM+MI+TF-FrM1 Magneto-optical properties of Metals, Half-Metals, and Garnets Probed by Vector-Magneto-Optical Generalized Ellipsometry, Heidemarie Schmidt**, Technische Universität Chemnitz, Nano-Spintronics Group, Germany **INVITED**

Magnetotransport measurements are a standard technique for the electrical characterization of single layers on insulating substrates. However, magnetotransport measurements require electrical contacts and known current paths, which excludes application to multilayer stacks. Motivated by the recent development of fast Mueller matrix ellipsometers, we have set-up a vector magneto-optical generalized ellipsometer (VMOGE) with an 0.4 T octupole magnet [1] and have investigated magneto-optical response of a single layers and multilayer stacks in a magnetic field of arbitrary orientation and magnitude up to 0.4 T at room temperature. We assume that the off-diagonal element of the magneto-optical dielectric tensor of every magnetizable layer in the multilayer stack is a product of the magnetic field independent and wavelength dependent complex magneto-optical coupling constant and the magnetic field dependent and wavelength independent magnetization of the layer. As an example, the complex magneto-optical coupling constant of nominally 10, 20, and 30 nm thick ferromagnetic Ni films obtained from modelling corresponding VMOGE data is discussed. It was challenging to identify the magnetization direction of Ni films from different sets of magnetic field dependent Mueller matrix elements [2]. In the future knowledge of complex magneto-optical coupling constant of all magnetizable materials in a multilayer stack will allow for modelling and optimizing the magneto-optical response of given stack. As a second example, the modelled complex magneto-optical coupling constant of capped, ferromagnetic Fe, Ni₂₀Fe₈₀, Co, Ni₈₀Fe₂₀, and Ni thin films on ZnO substrates is discussed and related with the spin-dependent electronic bandstructure of given weakly correlated, magnetizable materials [3]. For this comparison the experimental complex off-diagonal elements of the magneto-optical dielectric tensor have been converted into theoretical complex off-diagonal elements of magneto-optical conductivity tensor. Finally, the experimental magneto-optical response of strongly correlated, magnetizable materials [4], e.g. half-metals and garnets, is presented and as an outlook development of new theoretical frameworks for calculating the bandstructure of such strongly correlated, magnetizable materials for a comparison with experiment is motivated. [1] K. M. Mok, N. Du, H. Schmidt, Rev. Sci. Instrum. 82 (2011) 033112; [2] K.M. Mok, C. Scarlat, G. J. Kovács, L. Li, V. Zviagin, J. McCord, M. Helm, H. Schmidt, J. Appl. Phys. 110 (2011) 123110; [3] K.M. Mok, G. J. Kovács, J. McCord, L. Li, M. Helm, H. Schmidt, Phys. Rev. B 84 (2011) 094413; [4] G. Kotliar and D. Vollhardt, Physics Today 57 (2004) 53

9:00am **EL+AS+EM+MI+TF-FrM3 In Situ Terahertz Optical Hall Effect Measurements of Ambient Doping Effects in Epitaxial Graphene, S. Knight**, University of Nebraska-Lincoln; **C. Bouhafs**, N. Armakavicius, P. Kühne, V. Stanishev, R. Yakimova, Linköping University, Sweden; **S. Wimer**, M. Schubert, University of Nebraska-Lincoln; **V. Darakchieva**, Linköping University, Sweden; **Tino Hofmann**, University of North Carolina at Charlotte

Recently, the cavity-enhanced THz optical Hall effect (THz-OHE) has been demonstrated as non-contact method to obtain free charge carrier properties using low-field permanent magnets [1,2]. A tunable, externally-coupled cavity is used to enhance the THz-OHE signal which allows the accurate determination of a sample's free charge carrier properties even at low magnetic fields. In this work we take advantage of this approach by integrating the permanent magnet into a gas flow cell. We demonstrate for the first time the application of the cavity-enhanced THz-OHE for the *in-situ* characterization of free charge carrier properties of monolayer graphene on Si-face 4H-SiC as a function of ambient conditions. The experiments were performed using a new rotating-analyzer THz ellipsometer at Linköping University. Upon changing the CO₂, H₂O, and O₂ concentration in the cell, large variations in both free charge carrier sheet density N_s and mobility μ are observed for the *n*-type graphene. The lowest N_s was found

for the as-grown sample with $N_s = 5.9(1) \times 10^{11} \text{ cm}^{-2}$ where $\mu = 2507(57) \text{ cm}^2/\text{Vs}$. The highest N_s was found after purging the sample with nitrogen for 6 hours with $N_s = 2.43(4) \times 10^{12} \text{ cm}^{-2}$ where $\mu = 1604(23) \text{ cm}^2/\text{Vs}$. These significant changes are attributed to a redox-reaction of oxygen and water at the graphene surface which results in the extraction of electrons from graphene [3]. This will be discussed in detail in our presentation. We further observe that this doping mechanism is only partially reversible at room temperature upon removal of oxygen, carbon dioxide, and water by purging the cell with nitrogen. In conclusion, we demonstrate *in-situ* THz-OHE as a new and powerful technique to determine ambient-dependent doping mechanisms which is illustrated here using monolayer epitaxial graphene on Si-face 4H-SiC.

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9:20am **EL+AS+EM+MI+TF-FrM4 Excitons at Interfaces in Ellipsometric Spectra, Nuwanjula Samarasingha, C. Rodriguez, J.M. Moya, N.S. Fernando, S. Zollner**, New Mexico State University; **P. Ponath, K. Karmondy, A. Demkov**, University of Texas at Austin; **D. Pal, A. Mathur, A. Singh, S. Dutta, J. Singhal, S. Chattopadhyay**, Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants and ellipsometry spectra of bulk semiconductors and insulators has been known for many years. In Si, Ge, and GaAs, the E_1 critical points are strongly enhanced by two-dimensional excitons, even at room temperature. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. Excitons also influence the dielectric function of SrTiO₃. An exciton is an electron-hole pair bound by the Coulomb interaction, with properties similar to a hydrogen atom. The influence of excitonic absorption on the dielectric function was described by Tanguy.

In a thin epitaxial layer (with a thickness below or near the Bohr radius) on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In a thin type-I quantum well, consisting of a narrow-gap semiconductor grown on a large-gap substrate, both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the dominant absorption peak at 4.2 eV is larger in a 20 nm thick SrTiO₃ layer on a LaAlO₃ substrate than in bulk SrTiO₃. (The band gap of LaAlO₃ is larger than that of SrTiO₃.)

On the other hand, in a staggered type-II quantum well, either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element (and thus the excitonic absorption) is strongly reduced, because one quasiparticle resides in the quantum well and the other one in the substrate. If a SrTiO₃ layer is grown on Si or Ge, the valence band maximum occurs in the substrate, while the conduction band offset is very small. Therefore, the exciton wave function is delocalized (deconfined), which reduces the dipole overlap matrix element. Therefore, the real and imaginary part of ϵ of thin SrTiO₃ layers on Si or Ge are much smaller than in the bulk and decrease monotonically with decreasing thickness. A similar effect can be seen for thin ZnO layers on Si as a function of thickness.

The dielectric function of SrTiO₃ is not only affected by layer thickness. A very thick polycrystalline SrTiO₃ layer on Si has a much lower dielectric function than a single-crystalline SrTiO₃ substrate. In this case, we speculate that the magnitude of the dielectric function is related to other Tanguy parameters, perhaps the excitonic binding energy or the exciton decay rate (broadening). To investigate this further, we will perform temperature-dependent ellipsometry measurements on bulk zinc blende GaP, which has a much simpler band structure than wurtzite ZnO or the correlated metal oxide SrTiO₃, but shows similar excitonic effects.

9:40am **EL+AS+EM+MI+TF-FrM5 Infrared and Visible Dielectric Properties of (LaAlO₃)_{0.3}(Sr₂AlTaO₆)_{0.35}, Jacqueline Cooke, N.T. Nunley, T. Willett-Gies, S. Zollner**, New Mexico State University

Using spectroscopic ellipsometry, we determined the dielectric function of LSAT, from the mid-IR to the deep UV (0.03 to 6.5 eV). LSAT is an acronym for the chemical formula (LaAlO₃)_{0.3}(Sr₂AlTaO₆)_{0.35}, equivalent to (La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O₃. LSAT is a common substrate for epitaxial growth of complex metal oxides. Precise knowledge of the optical constants is useful to investigate the properties of epitaxial films grown on LSAT. We also

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investigated the band gap and the infrared-active phonons. Czochralski-grown LSAT wafers with (001) surface orientation were obtained commercially (MTI Corp., Richmond, CA). Single-side polished wafers were used for spectroscopic ellipsometry and two-side polished wafers with 0.5 mm thickness for transmission. Between 0.8 and 6.5 eV, we measured the normal-incidence transmission and the ellipsometric angles from 60° to 80° incidence in 2° steps on a J.A. Woollam variable angle of incidence ellipsometer with a computer-controlled Berek waveplate compensator. We also measured in the mid-IR on a rotating compensator FTIR ellipsometer. Transmission measurements show a steep rise of the absorption coefficient (α) between 4.6 and 4.8 eV, where LSAT becomes opaque. Fitting the ellipsometry data with a model containing two Tauc-Lorentz oscillators and 19 Å surface roughness thickness yields an excellent fit to the data. The Tauc gap is 4.9 eV and the high-frequency dielectric constant ϵ_{∞} = 4.0. Plotting α^2 versus photon energy yields a direct band gap of 5.8 eV. An Urbach tail extends towards lower energies. The resulting dielectric function is in agreement with previous ellipsometry and minimum-deviation prism measurements. The mid-IR dielectric function shows four ϵ_2 peaks due to TO phonon absorption. The loss function shows four LO peaks. A fifth TO phonon was seen at 155 cm⁻¹ in far-IR ellipsometry. An ideal ABO₃ perovskite has only three IR-active TO phonons. FCC ordering on the B-site as in (Sr₂AlTaO₃) adds a fourth phonon. We argue that the TO phonons at 155 and 283 cm⁻¹ are vibrations of the tetrahedra against the La/Sr sublattices, respectively (mode splitting due to disorder). On the other hand, the 397 and 442 cm⁻¹ modes are B-O bending modes due ordering in the Al/Ta sublattice. Finally, a B-O stretch mode at 664 cm⁻¹ and broad two-phonon absorption at 765 cm⁻¹ are also found. Fitting the spectra with a factorized TO/LO model yields better results than a sum of Lorentzians, because the individual TO/LO pairs are not well separated. The presence of FCC ordering was also confirmed with x-ray diffraction. We will also discuss temperature dependent ellipsometry and transmission measurements.

10:00am EL+AS+EM+MI+TF-FrM6 A New Constant of Product of Electronic Scattering Time and Resistivity in Thin Silver Refractive Index Calculation from Ellipsometry and Resistivity Measurements, Guowen Ding, C. Clavero, D. Schweigert, M. Le, Intermolecular, Inc.

The optical and electrical response of metal thin films is highly affected by electronic scattering with the interfaces and defects. We are able to successfully model the electrical resistivity and near infrared (IR) optical response using a thickness dependent electronic scattering time. We investigated Ag films thickness in the range of 3 nm to 74 nm and determined that the product of electronic scattering time (τ) and resistivity (ρ) remains constant regardless of the thickness ($\tau \times \rho = C$), with a value of $59 \pm 2 \mu\Omega \text{ cm-fs}$ for Ag films. As a result, determining the constant C for a given thin film will allow to calculate the properties of the film over a large range of wavelengths while limiting the number of measurements. Our findings enable us to develop a theoretical framework to determine the optical response of metal thin films in the near IR by using single wavelength ellipsometer measurements. An excellent agreement is found between experimental measurements and predicted values. We first reported this constant $\tau \times \rho = C$ for silver, and we posit that such constant concept could be applied for other conducting films. Application of the model presented here will allow rapid characterization of the IR optical response of metal thin films, with important application in a broad spectrum of fundamental and industrial applications, including optical coatings, low-emissivity windows and semiconductor industry.

10:20am EL+AS+EM+MI+TF-FrM7 Realization of an In Situ Mueller-matrix Imaging Ellipsometer for the Real Time Observation of Surface Properties in an Ultra-high Vacuum EUV Facility, Pim Mulwijk, N.B. Koster, F.T. Malkenboer, E. Sligte, te, A.F. Deutz, P. Walle, van der, TNO Technical Sciences, Netherlands

TNO is realizing EUV Beamline 2 (EBL2), a facility to investigate the effects of Extreme Ultra-Violet (EUV) radiation on surfaces to enable future EUV High Volume Manufacturing (HVM) production. In this facility, samples with sizes up to 152x152x20 mm (6" EUV reticles) can be exposed to EUV radiation of up to 500W equivalent at intermediate focus (IF) under realistic environmental conditions and analyzed by in-situ ellipsometry and XPS. EBL2 consists of EUV source, automated handling system, beam line and an exposure chamber with an in-situ dual wavelength Mueller-matrix imaging ellipsometer.

Light from the dual wavelength light source (405 & 640nm) enters the exposure chamber through a polarizer, configurable retarder and a vacuum window producing a defined polarization state. After reflecting off of the

sample, the light exits the exposure chamber through a vacuum window, configurable retarder and polarizer. The sample position is imaged on two camera's, one for each wavelength. By combining all combinations of 4 polarization illumination states with 4 analyser states the full Mueller matrix of the sample can be recovered.

Calibration is performed in-situ with two insertable polarizers and two different calibration samples. The calibration procedure does not require prior knowledge of the polarizer orientation nor of the calibration samples.

This presentation will focus on the design and realization of the ellipsometer and will also touch upon the process of interpreting the data.

EBL2 will be publicly accessible as a test facility for EUV lithography related research after qualification, which is expected to be finished end of Q1 2017.

10:40am EL+AS+EM+MI+TF-FrM8 Conducting, Semi-Conducting and Insulating 2D-Materials Characterized by Spectroscopic Imaging Ellipsometry, Matthias Duwe, S. Funke, Accurion GmbH, Germany; U. Wurstbauer, Technical University of Munich, Germany; A. Matkovic, University of Belgrade, Serbia; A. Green, SUNY College of Nanoscale Science and Engineering; A. Molina-Mendoza, Universidad Autonoma de Madrid, Spain; A. Castellanos-Gomez, IMDEA Nanoscience, Spain; P.H. Thiesen, Accurion GmbH, Germany

Finding thin-film flakes of 2D-materials after the fabrication and identifying their layer thicknesses often is a challenging and time-consuming task. Here, we present various applications of spectroscopic imaging ellipsometry (SIE) to a variety of conducting, semi-conducting, and insulating 2D-Materials such as graphene, molybdenum disulfide (MoS₂), hexagonal boron nitride, and black phosphorus. As a combination of polarization-contrast microscopy and spectroscopic ellipsometry, SIE measurements localize microscopic flakes of the 2D-materials, yield the samples' optical dispersion functions, and determine the layer thicknesses.

Matkovic et al. [1] characterized monolayers of graphene by SIE, and they obtained the optical dispersion by Fano-resonance modelling. Using this dispersion, SIE offers a straightforward search for and identification of few-layer graphene flakes on various opaque or transparent substrates. As this flake search uses ellipsometric measurements, it depends far less on the used substrate compared to e.g. conventional light-microscopy. In a similar procedure, SIE identified monolayers of insulating hexagonal boron nitride, and it yielded the material's optical properties.

SIE measurements on MoS₂ revealed the repercussion of the used substrate [2]. Ellipsometric contrast micrographs showed the lateral variation of the optical parameters for a structured flake. Spectroscopic measurements of the ellipsometric values (Ψ & Δ) obtained from selected regions of interest on the flake yielded the optical dispersion for the in-plane and out-of-plane components of the dielectric function in the visible spectral range.

Finally, we will present imaging Mueller-matrix ellipsometry (IMME) for the characterization of thin-film flakes of the semi-conducting 2D-material black phosphorus. In contrast to MoS₂, black phosphorus also features an optical in-plane anisotropy. IMME-micrographs easily reveal this anisotropy as the Mueller matrix's off-diagonal blocks deviate from zero. By performing spectroscopic Mueller-Matrix mapping and rotational Mueller-matrix measurements combined with atomic force microscopy, we obtained the flake's layer thickness, the orientations of the optical axes, and the material's optical properties in the visible spectral range.

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Electronic Materials and Photonics

Room 102A - Session EM-FrM

Late Breaking News on Electronic Materials and Devices

Moderator: Nikolaus Dietz, Georgia State University

8:40am **EM-FrM2 Pulsed Laser Deposition of $\text{In}_2\text{O}_3\text{-SnO}_2$: From Films to Nanowires**, *Davide Del Gaudio, C. Reese, C. Boone, S. Yarlagadda, J.T. Heron*, University of Michigan, Ann Arbor; *I. Shalish*, Ben-Gurion University of the Negev, Beersheba, Israel; *R.S. Goldman*, University of Michigan, Ann Arbor

As micrometer sized device structures approach their limits in performance, nano-structures, such as nano-wires (NW) are being considered for next-generation high efficiency energy conversion and storage devices.^[1] For example, metal oxides have been identified as promising materials for lithium ion batteries^[2] and UV lasers.^[3] Furthermore, metal-oxide NWs have been embedded in field-effect transistors, lasers, solar cells, and various chemical sensors.^[4] Typically, metal-oxide NW are prepared by vapor deposition^[4] or thermal evaporation.^[5] Recently, pulsed-laser deposition (PLD)^{[6][7][8]} has emerged as a promising approach for the fabrication of tin-doped indium oxide (ITO), with film or NW growth often determined by the choice of a reactive (O_2) or inert (N_2) atmosphere.^[6] To date, cubic NW with up to 5 atomic % Sn incorporated into In_2O_3 have been reported. However, a mechanistic understanding of the influence of growth parameters and substrates on the morphology, composition, and crystal structure of the deposited film is needed. Additionally, PLD of various $\text{In}_2\text{O}_3\text{-SnO}_2$ mixtures has yet to be considered. Therefore, we report on PLD of various $\text{In}_2\text{O}_3\text{-SnO}_2$ mixtures, onto c-plane sapphire and Inconel substrates. Using an inert atmosphere, we have identified parameters to obtain smooth films; pyramid-shaped nano-scale clusters; sparse, tapered nano-rods; and high density, vertically oriented NWs, with and without catalyst spheres. We will present high-resolution transmission electron microscopy (HRTEM) images and selective-area electron diffraction (SAED) patterns illustrating the structure and composition of the films, nanowires, and catalyst spheres. The photoluminescence emission from NWs and films, as well as the electronic transport properties of individual NWs will also be discussed.

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9:00am **EM-FrM3 ZnSnN_2 : Band Gap Engineering Through Cation Disorder**, *R. Makin*, Western Michigan University; *N. Senabulya, J.P. Mathis, R. Clarke*, University of Michigan; *T. Veal*, University of Liverpool; *Steven Durbin*, Western Michigan University

Chalcopyrite heterovalent ternary compounds can undergo an order-disorder transition between an ordered chalcopyrite structure and a disordered zinc-blende-like phase. Unlike in adamantane alloys, the disorder results in a band gap reduction in the disordered phase relative to the band gap of the ordered lattice. ZnSnN_2 represents an interesting member of the chalcopyrite family of materials, due to its earth abundant element constituents and a band gap of use for solar cells. It is also part of the Zn-IV-N₂ family of materials, whose band gaps span from the infrared to the UV. Density functional theory (DFT) calculations predict the ordered ZnSnN_2 phase to have an orthorhombic lattice and a direct band gap of 2.0 eV. Using special quasirandom structures (SQS) to model the disordered Zn and Sn cation sub-lattice, DFT simulations predict that the band gap for the disordered ZnSnN_2 phase will be close to 1.0 eV and will have a hexagonal lattice. This almost 1.0 eV reduction of the band gap of ZnSnN_2 presents an opportunity for band gap engineering by controlling the disorder on the

cation sublattice. Recently, however, an alternative theory of disorder for ZnSnN_2 has been proposed that does not depend on cation lattice disorder. This alternate disorder, unlike the cation disorder model, does not violate the octet rule locally and results in a band gap that is independent of the order. If either model is accurate is presently unknown.

A series of films has been grown by plasma assisted molecular beam epitaxy in order to investigate the possibility of controlled cation disorder as well as its effects on physical and electronic properties of the material. By varying the growth conditions, specifically either the metal flux to the nitrogen pressure or the substrate, we have confirmed the existence of both the hexagonal and orthorhombic phases of the crystal via synchrotron x-ray diffraction (performed at Argonne National Laboratory). All of the films at present have a high free carrier concentration (in excess of 10^{19} cm^{-3}). Taking into account the Burstein-Moss shift caused by the high carrier concentration and calculating the effective masses of the carriers from parabolic fits to the density results, the optically measured band gaps appear to be consistent with the DFT calculations; the band gap shows a clear dependence on cation disorder.

9:20am **EM-FrM4 Role of Single Dopants in Inter-Band Current Enhancement of Nano-*pn* Tunnel Diodes: An Atomistic Study**, *Manoharan Muruganathan*, Japan Advanced Institute of Science and Technology, Japan; *D. Moraru, M. Tabe*, Research Institute of Electronics, Shizuoka University; *H. Mizuta*, Japan Advanced Institute of Science and Technology, Japan

As the Tunnelling Field Effect Transistor (TFET) overcomes the subthreshold slope thermal limitation of MOSFETs, they are a potential successor of MOSFETs [1]. Moreover silicon-based TFETs are the most attractive because of the well-established silicon technology. However, a large bandgap in silicon results in a small band-to-band-tunnelling efficiency, hence low on-current. In order to improve the on-current, fundamental study of atomistic *pn* tunnel diode is an imperative step. Here, we report that inter-band tunnelling current can be enhanced by the resonance of deepened energy levels of discrete dopants. Number and position of dopants at the *pn* junction interface play a crucial role in enhancing the inter-band tunnelling current. These results are based on the first-principles simulations in comparison with our experimental results for nano-*pn* tunnel diodes [2].

Our simulated atomistic structure consists of *p*- and *n*-type electrodes, which are highly doped with doping concentration similar to the experimental levels and a thin central intrinsic Si channel that corresponds to the depletion region. As realized in the fabricated devices, single P and B dopants are placed in the intrinsic Si channel the depletion region. The uniform bulk doping in the regions away from the depletion region was realized by using the atomic compensation technique [3-4]. We noticed a remarkable current increase by four orders of magnitude for the device with a P-B pair placed 1.3 nm apart as compared to no discrete dopants in the depletion region. This is due to the energy levels created by the P-B pair in the depletion region and their matching to the electrode energy levels when the bias voltage is changed. Moreover, these devices exhibit typical Esaki-diode negative differential conductance (NDC) behaviours as well. When the single dopants were placed nearer to the uniformly doped bulk regions then well aligned energy levels were formed in the depletion region. This leads to an increase in the inter-band tunnelling current. If the number of single dopants in the depletion region is increased then we have more induced states in the depletion region, which also helps to increase the inter-band tunnelling current. These results illustrate the impact of individual dopants in the depletion region and provide pathways to increase the inter-band tunnelling in nano-*pn* tunnel diodes.

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9:40am **EM-FrM5 CVD growth of Hexagonal Boron Nitride Films on Cu-Ni Alloys**, *Karthik Sridhara*, Texas A&M University; *B.N. Feigelson, J.K. Hite, V. Anderson, A. Nath, F. Kub*, US Naval Research Laboratory; *L.O. Nyakiti*, Texas A&M University Galveston

Chemical vapor deposition (CVD) method of growth of hexagonal boron nitride (h-BN) has been demonstrated on various transition metal substrates such as Ni, Pt, Au and Ag. Of these metals, polycrystalline Cu is

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by far the most frequently used substrate for CVD growth of h-BN. Despite being extensively studied, issues still persist with Cu, including a high density of nucleation sites where the imperfections in surface morphology act as potential nucleation sites. Recently, Cu-Ni alloys have been reported for the growth of controllable monolayer h-BN with fewer nucleation sites [1]. Despite the promise, there are still questions of optimal Ni concentration and the morphology of Cu-Ni alloys.

In this work, we prepare Cu-Ni alloys by electroplating Ni on high purity (99.98%) polycrystalline Cu foils (25 μm thickness). Four different weight percents of Ni (10, 15, 20 and 25 wt%) are electroplated onto Cu. The electroplated foils are then thermally annealed at 1030°C for 3 hours in an H_2 environment, during which time the Ni diffuses into the Cu foils. We then grow h-BN on these Cu-Ni alloys, with high purity (~99.98%) Cu foils acting as our control samples. The growth uses borazane as the precursor at 1030°C with H_2 and N_2 as carrier gases. FTIR and scanning electron microscope (SEM) are used to confirm and assess the growth of h-BN on the samples. Energy dispersive spectroscopy (EDS) mapping is employed to cross-check the Ni percentage in Cu. From the preliminary results, we observe that with increasing Ni concentration there is an increase in surface roughness with the existence of atomic step edges and various morphological irregularities. Initial FTIR results show that with increasing amount of Ni in the Cu foil, we see a gradual increase in the amount (proportional to the FTIR peak intensity) of h-BN grown where the amount is proportional to the h-BN film effective thickness on the substrate [2]. We see the lowest amount of h-BN is on Cu, while the highest is on $\text{Cu}_{0.75}\text{Ni}_{0.25}$ foils. The growth kinetics of h-BN on Cu-Ni alloys will be discussed.

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10:00am **EM-FrM6 p-GaAs/AlGaAs Heterostructures with a Current Blocking Barrier for Mid-infrared Detection**, *Dilip Chauhan, A.G.U. Perera*, Georgia State University; *L.H. Li, L. Chen, E.H. Linfield*, University of Leeds, United Kingdom

p-GaAs/Al_xGa_{1-x}As heterojunction is an attractive material system due to its mature III-V material growth and processing technology. Infrared detection in the mid-infrared range is possible by exploiting the intra-valance band hole transitions in the light hole/heavy hole and spin-orbit split-off bands. The wavelength threshold can be tuned by varying the Al mole fraction (x), while graded Al_xGa_{1-x}As potential barriers create an asymmetry to allow a photovoltaic operation. The operation under photovoltaic mode is advantageous due to thermal noise limited performance. In a preliminary study in a 2 – 6 μm photovoltaic detector, we implemented a current blocking barrier, which improved the specific detectivity by two orders of magnitude, to 1.9×10^{11} Jones at 2.7 μm , at 77K. At zero bias, the resistance-area product (R_0A) had a value of $\sim 7.2 \times 10^8 \Omega \text{ cm}^2$, which is five orders higher in magnitude compared to the R_0A value without the blocking barrier. A photoresponse was observed up to 130K. Further work is in progress to optimize the detector at a higher operating temperature.

Acknowledgement: This work was supported in part by the U.S. Army Research Office under Grant No. W911 NF-15-1-0018, and in part by National Science Foundation (NSF) under Grant No. ECCS-1232184.

10:20am **EM-FrM7 SSI-LEDs - 20,000 Hrs of Lifetime and Failure Mechanism Study**, *Yue Kuo, S. Zhang*, Texas A&M University

Recently, a new type of solid state incandescent LED (SSI-LED) that emitted the broad band warm white light upon the application of a voltage was reported by our group [1-4]. This kind of device also has unique antifuse- and diode-like characteristics in the low voltage operation range [5,6]. The operation of this new device is based on the passing of current through nano-sized conductive paths after the breakdown of an amorphous high-k thin film stack deposited on top of a silicon wafer. The principle of light emission of the SSI-LED is the black body effect, which is different from the electron-hole or exciton-exciton recombination in the conventional crystalline compound semiconductor structure. A lifetime of over 12,000 hours was obtained previously [4].

In this talk, authors will present the new result on the lifetime study of the SSI-LED. Without a passivation layer, the device has been successfully operated continuously for over 20,000 hours in air. Changes of electrical

and optical characteristics of the device over the whole operation period have been monitored. In order to understand the failure mechanism within a short period of time, we further carried out accelerated voltage stress tests. The change of the surface morphology with the applied voltage has been systematically investigated. Based on these results, authors review the mechanisms of the device operation and failure.

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 Splawn, H.: EM+NS+PS+SS+TF-MoM8, 2
 Spooner, T.: TF+EM+MI-WeA10, 20
 Sridhara, K.: EM-FrM5, 34
 Stanishev, V.: EL+AS+EM+MI+TF-FrM3, 32
 Stassun, K.: EM+AC+SS+TF-ThM1, 22
 Steeves Lloyd, K.: EM+NS-WeM1, 11
 Stockman, M.I.: EM+NS+SP+SS-WeA9, 13
 Stowe, A.: EM+AC+SS+TF-ThM1, 22
 Strong, T.: SE+2D+EM-WeA8, 15
 Su, Q.: EM+AC+SS+TF-ThM3, 22
 Sultan, M.: EM-MoA8, 5
 Sun, L.: EL+AS+BI+EM+TF-ThA3, 24; EL+AS+BI+EM+TF-ThA4, 24
 — T —
 Tabe, M.: EM-FrM4, 34
 Tadjer, M.J.: EM-MoA10, 5
 Takagi, S.: EM+MN-TuM3, 8
 Takenaka, M.: EM+MN-TuM3, 8
 Talin, A.A.: EM+SS+TF-ThA2, 26
 Tang, K.: SE+2D+EM-WeA11, 16
 Tapiy, K.: TF+EM+MI-WeA2, 19
 Teplyakov, A.V.: SE+2D+EM-WeA1, 14; SS+AS+EM-WeA1, 17; SS+AS+EM-WeA10, 18
 Thiesen, P.H.: EL+AS+EM+MI+TF-FrM8, 33
 Thomsen, L.: SS+AS+EM-WeA1, 17
 Timm, R.: EM+NS+SP+SS-WeA4, 13
 Tischler, J.: TF+EM+MI-WeA1, 19
 Tolbert, S.H.: SE+2D+EM-WeA12, 16
 Tolk, N.H.: EM-MoA9, 5
 Tompa, G.S.: EM-MoA4, 4
 Töpfer, T.: EL+AS+BI+EM+TF-ThA8, 24
 Troian, A.: EM+NS+SP+SS-WeA4, 13
 Tweedie, J.: EM+NS+PS+SS+TF-MoM1, 1
 — U —
 Udworthy, K.: EM+NS+PS+SS+TF-MoM8, 2
 Uprety, P.: EL+AS+BI+EM+TF-ThA9, 25
 Uprety, S.: EM+NS+PS+SS+TF-MoM6, 1; EM-MoA8, 5
 Utter, B.C.: TF+EM-MoA1, 5
 Uyar, T.: EM+NS+PS+SS+TF-MoM3, 1
 — V —
 Vaganova, E.: EM-ThP5, 29
 Van Schravendijk, B.: EM+MI+MN-TuA1, 9
 VanDerSlieck, J.: EL+AS+EM+TF-ThP2, 28
 Veal, T.: EM-FrM3, 34
 Veith, M.: EM+SS+TF-ThA3, 26
 Verguts, K.: TF+EM+MI-WeA3, 19
 Vernon, E.: EM+AC+SS+TF-ThM10, 22
 Veryovkin, I.V.: EM+NS-WeM1, 11
 — W —
 Wajda, C.S.: TF+EM+MI-WeA2, 19
 Wallace, R.M.: SE+2D+EM-WeA10, 16
 Walle, van der, P.: EL+AS+EM+MI+TF-FrM7, 33
 Wang, J.: EM+NS-WeM11, 12
 Wang, K.L.: SE+2D+EM-WeA12, 16
 Wang, S.: EM-MoA8, 5
 Wang, X.D.: EM+NS+SP+SS-WeA10, 14; TF+EM-MoA4, 6
 Wang, Y.: EM+AC+SS+TF-ThM3, 22; EM-MoM5, 2
 Wang, Z.: EM+MI+MN-TuA11, 9; EM-ThP6, 30
 Warschkow, O.: SS+AS+EM-WeA1, 17
 Waskiewicz, R.J.: EM+AC+SS+TF-ThM13, 23
 Wasserman, D.: EM-MoM1, 2
 Watson, C.F.: SE+2D+EM-WeA3, 15
 Weiss, F.M.: EL+AS+BI+EM+TF-ThA8, 24
 Weiss, S.M.: EM+SS+TF-ThA6, 26
 Weng, C.J.: EM-ThP4, 29
 Wheeler, V.D.: EM-MoA10, 5; EM-MoA3, 4; TF+EM+MI-WeA1, 19; TF+EM-MoA1, 5
 White, S.T.: EL+AS+EM+TF-ThP3, 28
 Willett-Gies, T.: EL+AS+EM+MI+TF-FrM5, 32
 Wimer, S.: EL+AS+EM+MI+TF-FrM3, 32
 Wolf, S.: SS+AS+EM-WeA7, 17
 Wolf, S.A.: EM-MoM5, 2
 Wong, K.: SE+2D+EM-WeA12, 16
 Woollam, J.A.: EL+AS+EM+TF-ThP2, 28
 Wurstbauer, U.: EL+AS+EM+MI+TF-FrM8, 33
 — X —
 Xiao, G.: EM+MN-TuM5, 8
 Xiao, X.D.: SS+AS+EM-WeA3, 17
 Xiao, Z.: SE+2D+EM-WeA8, 15
 Xing, Z.: EM-MoM5, 2
 Xu, J.: EM-ThP12, 31
 Xue, P.: EM-ThP1, 28
 — Y —
 Yakimov, M.: SE+2D+EM-WeA11, 16
 Yakimova, R.: EL+AS+EM+MI+TF-FrM3, 32
 Yakovlev, V.S.: EM+NS+SP+SS-WeA9, 13
 Yan, Y.: EL+AS+BI+EM+TF-ThA10, 25; EL+AS+BI+EM+TF-ThA6, 24
 Yang, C.: EM-MoA11, 5
 Yang, G.: EM+AC+SS+TF-ThM10, 22
 Yanguas-Gil, A.: TF+EM-MoA3, 6
 Yao, Y.: EM-MoA4, 4
 Yapabandara, K.: EM+NS+PS+SS+TF-MoM6, 1; EM-MoA11, 5; EM-MoA8, 5
 Yarlagadda, S.: EM-FrM2, 34
 Yilmaz, I.: EM+NS+PS+SS+TF-MoM3, 1
 Yilmaz, M.: EM+NS+PS+SS+TF-MoM3, 1
 Yin, X.: EM+NS+SP+SS-WeA10, 14
 Yngman, S.: EM+NS+SP+SS-WeA4, 13
 Yoshida, N.: SE+2D+EM-WeA11, 16; SS+AS+EM-WeA8, 18
 Yu, G.: SE+2D+EM-WeA12, 16
 Yu, K.-H.: TF+EM+MI-WeA2, 19
 Yu, Y.Y.: TF+EM-MoA4, 6
 Yue, R.: SE+2D+EM-WeA10, 16
 Yulaev, A.: EM+SS+TF-ThA2, 26
 — Z —
 Zhang, D.: SE+2D+EM-WeA9, 16
 Zhang, S.: EM-FrM7, 35
 Zhang, X.: EM+SS+TF-ThA9, 27
 Zhang, Z.: EM-MoA5, 4
 Zhao, J.: SS+AS+EM-WeA1, 17
 Zhao, L.: EM+MI+MN-TuA11, 9; EM-ThP6, 30
 Zheng, H.: TF+EM+MI-WeA11, 20
 Zollner, S.: EL+AS+EM+MI+TF-FrM4, 32; EL+AS+EM+MI+TF-FrM5, 32;

