

## Electronic Materials and Processing

Room: 612 - Session EM-MoM

## Organic Materials and Devices

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

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

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

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

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

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

Considerable interest has developed in the potential of macro-electronics enabled by low-cost manufacturing techniques such as roll-to-roll printing. Solution-processable small molecule based semiconductor films are emerging as a viable candidate for the active layer in thin film transistors (TFTs). The performance of TFTs fabricated from fluorinated 5,11-Bis(triethylsilylethynyl)anthradithiophene (diF-TESADT) are strongly dependent on processing conditions and the chemical treatment of the contacts. High performance devices can be fabricated with Au contacts treated with perfluorinated-benzenethiol PFBT. We report on the structure of thin films of diF-TESADT, formed on both Au and SiO<sub>2</sub> substrates, as a function of substrate treatment and film thickness. Both spectroscopic ellipsometry and infrared absorption are used to assess the molecular orientation in the films. In films formed on PFBT treated Au, the orientation is found to be consistent with the bulk crystal structure, with a near optimal orientation of the pi-stacked conjugated cores in the channel of the transistor, consistent with the observed good device performance.

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

The cesium-derivatives (Cs<sub>2</sub>CO<sub>3</sub>, CsF and CsNO<sub>3</sub>) have been investigated as a dopant in tris-(8-hydroxyquinoline)-aluminum (Alq<sub>3</sub>) or a thin electron injection layer in organic light emitting devices. Unlike low work function metal which would be evaporated from a complex deposition process, the cesium-derivatives have a very simple deposition process and are easy to

handle. By using ultraviolet and x-ray photoemission spectroscopy, the properties of electronic structures and the interface chemistry are studied. The paper presents the investigation of interfacial interactions and electron-injection between cesium-derivatives and Alq<sub>3</sub>. According to our results, the Fermi level of Alq<sub>3</sub> after doped with cesium-derivatives shifts inside the gap toward the lowest unoccupied molecular orbital (LUMO) as a result of the charge transfer from cesium atom to Alq<sub>3</sub>, showing that electron-injection ability would be improved as a result of strong n-type doping effect. It is noteworthy to emphasize that through the ultraviolet and x-ray photoemission spectroscopy measurement, Cs<sub>2</sub>CO<sub>3</sub> does not decompose during evaporation with various evaporation rates and pressures. The relatively abrupt decreasing in vacuum level is found via UPS, which can be explained by charge exchanges and a strong dipole field at the interface with deposition of cesium-derivatives. Moreover, doping cesium-derivatives into Alq<sub>3</sub> not only reduces the electron-injection barrier height, but also increases the carrier concentration for current conduction. We also demonstrate that the interfacial chemical reaction leads to the excellent electron injection efficiency.

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

Pentacene thin-film transistors (TFTs) have attracted much attention due to their unique potentials. Nevertheless, there are still several issues to be considered before the TFTs are launched into real applications. Among these issues, the ultraviolet (UV)-induced degradation of pentacene is probably the most immediate and serious. However, in the present study we unexpectedly found that a lower energy UV radiation could rather be advantageous. Since this finding is quite surprising and may be applicable to the improvement of the performance of pentacene TFTs, we report on the contrasting effects of deep and shallow UV on the device performance of pentacene-based TFTs. Furthermore, we also fabricated the low-voltage high-gain pentacene-based inverter using a thin polymer/high-k dielectric through UV treatments. A substrate of 200 nm-thick SiO<sub>2</sub> or 450 nm-thick poly-4-vinylphenol (PVP) on p<sup>+</sup>-Si (-0.01 Ωcm) was adopted for the gate dielectric and gate electrode in the present TFTs. The pentacene channel layers of 50 nm thickness were then patterned on the substrate by the thermal evaporation at RT. Subsequently, Au was evaporated onto the pentacene channels through a source/drain mask at RT (top-contact mode). Under the illumination of 254 nm-UV the TFTs showed degraded mobility and lowered saturation current. It is because the high energy UV degraded the crystalline quality of the pentacene channel as confirmed by optical absorption technique. However, under 352 nm UV the pentacene devices rather exhibited the enhancement of saturation current and also a positive shift of the threshold voltage (V<sub>T</sub>), maintaining their mobilities. We also found that these UV-induced advantages were more clearly obtainable from the TFTs with polymer dielectric where extra negative charges are generated to exist as permanent form at the pentacene/polymer interface while those charges are not necessarily fixed at the pentacene/SiO<sub>2</sub> interface. Through inverters fabricated by illuminating 352nm-UV onto the load-TFT to selectively adjust its V<sub>T</sub>, we also could achieve a stable high-gain low-voltage inverting within the input voltage (V<sub>in</sub>) range of 0 ~ -6 V. We thus conclude that illuminating a low energy UV on the TFT with pentacene/polymer dielectric interface is a simple promising way of enhancing the general performance of pentacene TFTs and controlling their V<sub>T</sub> that enables to achieve stable pentacene-based inverters as well.

9:40am **EM-MoM6 High Efficient Organic Light-Emitting Device with MoO<sub>3</sub>.** *C.-T. Lin, G.-R. Lee, C.-I. Wu, T.-Y. Cho, C.-C. Wu*, National Taiwan University, *T.-W. Pi*, National Synchrotron Radiation Research Center, Taiwan

Two high efficient devices will be discussed in this paper. The first is ITO/MoO<sub>3</sub>/N,N-diphenyl-N,N-bis(1-naphthyl)-1,1-biphenyl-4,4-diamine (NPB) based organic light emitting diodes (OLEDs). Current-voltage characteristics (I-V) and quantum-efficiency (η-J) measurements show the improvement of device performance with insertion of thin MoO<sub>3</sub> between ITO and NPB. Ultraviolet photoemission spectra (UPS) and core-level x-ray photoemission spectra (XPS) data show that MoO<sub>3</sub> would catch electrons from NPB and results in p-type doping in NPB. In addition, there is a significant structure transition from insulating MoO<sub>3</sub> to metallic MoO<sub>2</sub>. As a result of high work function MoO<sub>2</sub> in anode structure and p-type doping NPB, holes can easily be injected from ITO to NPB. The second efficient devices relate to MoO<sub>3</sub>/metal structures in tandem OLEDs. Non-stoichiometric MoO<sub>3</sub> films consist of defect states due to O defects which pins the Fermi level in the forbidden gap. I-V characteristics show that with the MoO<sub>3</sub> hole injection layer between anode and NPB, the current efficiency is almost identical, regardless the choice of anodes. We further

investigation the interaction between low work function metals and MoO<sub>3</sub>. According to UPS and XPS results, low work function metals would easily get O atoms from MoO<sub>3</sub>, resulting in the transition to MoO<sub>2</sub> and the increase in conductivity at the same time. The high work function of MoO<sub>3</sub> can be tuned to relatively low work function of MoO<sub>3</sub>/Al, Mg anode. These results show that MoO<sub>3</sub> can act as a effective hole injection layer in OLEDs, a charge generation layer in tandem OLEDs, and a high ohmic contact of metal/MoO<sub>3</sub> in top-emitting OLEDs.

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

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

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

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

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

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

<sup>3</sup> B. H. Hamadani and D. Natelson, Appl. Phys. Lett. 84[3], 443(2004).

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

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

<sup>1</sup> Pei et al. Science (1995)

<sup>2</sup> deMello et al. Phys. Rev. B (1999)

<sup>3</sup> Leger et al. J. Appl. Phys. (2005).

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

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

<sup>1</sup> D. Käfer and G. Witte, Phys. Chem. Chem. Phys. 7, 2850 (2005).

<sup>2</sup> S. Seo, B. Park, and P. G. Evans, Appl. Phys. Lett. 88, 232114 (2006).

<sup>3</sup> N. Stingelin-Stutzmann, E. Smits, H. Wondergem, C. Tanase, P. Blom, P. Smith and D. Deleuw, Nature. Mater. 4, 601 (2005).

<sup>4</sup> S. Park, J. Whang, J. Choi, D. Whang, M. Oh, J. Kim, S. Im, Appl. Phys. Lett. 90, 153512 (2007).

# Monday Afternoon, October 15, 2007

## Electronic Materials and Processing

Room: 612 - Session EM+NS-MoA

### Semiconductor Nanostructures for Electronics and Optoelectronics I

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

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

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

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

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

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

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

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

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

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

<sup>1</sup>S. Kobayashi et al Jpn. J. Appl. Phys. 46 (2007) L392.

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

The formation of atomically sharp interfaces during the epitaxial growth of heterojunctions is a challenging task since atomic intermixing between the different materials is often unavoidable due to the relatively high growth temperatures involved. This effect has been found to be particularly important during the growth of self-assembled quantum dots (QDs) for which evidence of highly alloyed structures have been reported by several authors for a wide variety of semiconductor systems.<sup>1</sup> In the present work, we investigate intermixing during the growth of self-assembled InAs/InP QDs by chemical beam epitaxy. Using a careful combination of photoluminescence (PL) and transmission electron microscopy (TEM) measurements as well as tight-binding (TB) calculations, we have devised a procedure that enables an unambiguous assignment of QD heights ( $h_{\text{QD}}$ ) and composition to the observed PL transitions. PL spectra from ensembles of QDs are characterized by distinctive peaks which can be attributed to the ground state emission of QD families having the same thickness in terms of an integer number of monolayers (ML).<sup>2</sup> Consequently, QDs electronic

transitions are analogous to those of quantum wells and can be analyzed accordingly. TB calculations were performed by assuming (i) InP/InAs<sub>1-x</sub>P<sub>x</sub>/InP structures of varying P concentration ([P]) with abrupt interfaces and (ii) InP/InAs/InP structures with P diffusion concentration profiles described by the diffusion length L<sub>D</sub>. Both calculation frameworks lead to similar, realistic descriptions of the as-grown material. However, the above procedure yielded two solutions sets of (h<sub>OD</sub> : [P] or L<sub>D</sub>) compatible with experimental results. In order to determine which solution set is the most suitable, they were used as input data in a Bloch-wave simulation of TEM image contrast providing a sequence of contrasts versus h<sub>OD</sub>. A unique solution set was compatible with observed TEM data, therefore allowing an unambiguous assignment of h<sub>OD</sub> and [P] to the observed PL transitions. For the samples under investigation, it was concluded that the electronic transitions can be best attributed to a 3 ML-thick wetting layer and 4 to 13 ML-thick QDs with a relatively constant [P] of 10 ± 1 %.

<sup>1</sup> N. Liu, et al., Phys. Rev. Lett. 84, 334 (2000).

<sup>2</sup> S. Raymond, et al., Semicond. Sci. Technol. 18, 385 (2003).

**4:00pm EM+NS-MoA7 Improved Long-Term Thermal Stability of InGaN/GaN Multiple Quantum Well Light-Emitting Diodes using TiB<sub>2</sub>- and Ir-based p-Ohmic Contacts.** *L. Stafford, L.F. Voss, S.J. Pearton, H.T. Wang, F. Ren*, University of Florida

InGaN/GaN multiple quantum well light-emitting diodes (MQW-LEDs) are commercially available in a broad range of wavelengths for use in applications such as full color displays, traffic signals, and exterior lighting. There is also interest in shorter wavelength LEDs with AlGaIn active regions which can be used in conjunction with down conversion phosphors to produce white light, and hold significant promise for next generation lighting technology. Nevertheless, to compete with fluorescent and other high-efficiency lighting sources, it is essential to drive GaN-based LEDs at very high current densities to maximize light output. One drawback of the high current densities is self-heating of the heterostructure. This can produce either indiffusion of the Ohmic contact elements, leading to an electrical short of the pn junction, or intermixing of the contact scheme, producing very rough surface morphology. One possible way to prevent excessive Ohmic contact degradation is to use a high-melting-point diffusion barrier in the contact stack. TiB<sub>2</sub>, with a melting temperature of ~3000°C, reasonable electrical resistivity (28 μΩ.cm) and thermal conductivity (26 W.m<sup>-1</sup>.K<sup>-1</sup>), and heat of formation comparable to those for silicides or nitrides, shows promise as a diffusion barrier. In this work, we report on the long-term annealing characteristics at 200-350°C of InGaN/GaN MQW-LEDs with TiB<sub>2</sub>- and Ir-based p-Ohmic contacts. This high-temperature stress stimulates accelerated aging of GaN-based LEDs and gives an idea of the expected reliability of the Ohmic contacts. By comparison with companion devices with conventional Ni/Au Ohmic contacts fabricated on the same wafer, MQW-LEDs with TiB<sub>2</sub>- and Ir-based Ohmic metallization schemes showed superior long-term thermal stability after 45 days at 200°C and 350°C, as judged by the change in turn-on voltage, leakage current, and output power. This is a promising result for applications where high-temperature operation is required.

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

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

suggesting the dominant scattering mechanism is long-range ionized impurity scattering. For the nitride samples (GaAsN channel), α is 0.2~0.3, and the mobility saturates for n>1.5x10<sup>11</sup>cm<sup>-2</sup>, suggesting that N atoms act as short-range neutral scattering centers. The effects of rapid thermal annealing on the substitutional and interstitial N concentrations and the resulting transport properties of GaAsN films will also be discussed.

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

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

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

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

# Tuesday Morning, October 16, 2007

## Electronic Materials and Processing

Room: 612 - Session EM-TuM

## Molecular Electronics

Moderator: I. Hill, Dalhousie University

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

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

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

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

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

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

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

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

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

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

<sup>1</sup> A. K. Mahapatro, S. Ghosh, and D. B. Janes, IEEE Trans. Nanotech., 5, 232 (2006).

<sup>2</sup> B. Muralidharan and S. Datta, Preprint, arXiv:cond-mat/0702161 (2007).

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

<sup>4</sup> T. Ren et al., J. Organ. Chem., 690, 4734 (2005).

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

It is important for the advancement of the field of molecular electronics to develop an improved understanding the electron transport through molecular junctions, specifically silicon-based junctions that may enable the integration of molecular devices with traditional semiconducting technologies. In this work we examine the effects of molecular length and dipole on the electrical behavior of a metal-molecule-silicon, planar, enclosed devices. Devices with alkanethiol molecules of different lengths, with semi-fluorinated and non-fluorinated molecules, and with differently

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

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

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

<sup>1</sup> P. Allongue, C. H. de Villeneuve, J. Pinson, F. Ozanam, J. N. Chazalviel, and X. Wallart, *Electrochim. Acta* 43, 2791 (1998).

<sup>2</sup> A. Scott, C. Risko, M. A. Ratner, D. B. Janes, *Appl. Phys. Lett.*, to be published.

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

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

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

We have investigated the deposition of metals on alkanethiolate self-assembled monolayers (SAMs) adsorbed on Au using chemical vapor deposition (CVD) and electroless deposition. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. Chemical vapor deposition (CVD) is a widely employed technique for the deposition of metals on semiconductor substrates. CVD has not been widely employed to deposit films on organic materials because high temperatures ( $T_{\text{substrate}} > 200\text{ }^{\circ}\text{C}$ ) are often required that are not compatible with most organic thin films. However, by exploiting the chemical reactivity of functional groups at the SAM surface it is possible to deposit thin metallic films at room temperature. We demonstrate this method using trimethyl aluminum (TMA). TMA reacts at room temperature with a -COOH terminated SAM to form an Al overlayer, whereas TMA does not react with a -CH<sub>3</sub> terminated SAM. We have also investigated the mechanism of electroless deposition of copper on functionalized SAMs using a copper sulphate/formaldehyde reaction. Copper is deposited on -CH<sub>3</sub> and -COOH terminated SAMs but not on -OH terminated SAMs. For -CH<sub>3</sub> and -COOH SAMs, the deposited Cu is weakly stabilized at the SAM/vacuum interface and so slowly penetrates through the SAMs to the Au/S interface. Further, Cu does not deposit on -OH terminated SAMs because the formaldehyde reacts with the -OH terminal groups rather than reducing the copper.

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

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

# Tuesday Afternoon, October 16, 2007

## Electronic Materials and Processing

Room: 612 - Session EM+NS-TuA

## Semiconductor Nanostructures for Electronics and Optoelectronics II

**Moderator:** S.E. Mohney, The Pennsylvania State University

1:40pm **EM+NS-TuA1 Epitaxial NiFe Contacts on GaAs via Electrodeposition.** *Z.L. Bao, K.L. Kavanagh, A.S. Arrott*, Simon Fraser University, Canada, *A.A. Talin*, Sandia National Laboratories

We report the electrodeposition of epitaxial  $\text{Fe}_x\text{Ni}_{(1-x)}$  films on n-GaAs (001) substrates from aqueous metal ammonium sulphate solutions. Structural measurements using x ray diffraction show that the films have single crystalline BCC or FCC structure at Fe and Ni-rich compositions, respectively. The ratio of Fe concentration in the FCC films to that in the electrolyte is surprisingly close to unity (1.1). BCC  $\text{Fe}_x\text{Ni}_{(1-x)}/\text{GaAs}$  diodes have constant Schottky barrier heights independent of Fe composition consistent with a constant interfacial composition while the FCC Ni-rich alloys barriers increase with increasing Ni composition consistent with room temperature reactions.

2:00pm **EM+NS-TuA2 Medard W. Welch Award Lecture - Growth of Semiconductor Nanostructures: Simple Models for Complex Behavior.** *J. Tersoff\**, IBM T.J. Watson Center **INVITED**

Epitaxial islands and wires can "self assemble" during growth, producing quantum dots and nanowires with sub-lithographic dimensions. Such growth exhibits many remarkable and puzzling features, which must be understood in order to grow well controlled nanostructures. I will describe simple models that can explain many of the phenomena observed during growth of quantum dots in strained-layer heteroepitaxy, and also some recently discovered phenomena in growth of nanowires via the vapor-liquid-solid mechanism.

2:40pm **EM+NS-TuA4 Fast Synthesis Method for Binary and Ternary alloy Quantum Dots.** *N. Shukla, M.M. Nigra, A.J. Gellman*, Carnegie Mellon University

We have developed a one step synthesis process for binary and ternary alloy quantum dots with photoluminescence ranging from the red through to the violet region of the solar spectrum. This synthesis method allows us to control particle size and composition of quantum dots. We have also studied the effect of solvent boiling point and the addition of various chemical precursors on the synthesis and the photoluminescence properties of quantum dots. The photoluminescence peak in this synthesis method can be controlled by using different reaction time to produce quantum dots of different sizes. Photoluminescence peaks can also be controlled through varying composition of the chemical precursors. In addition, we have also studied the effect of solvent boiling point and the type of solvent on the physical and photoluminescence properties of these quantum dots. The type of solvent plays an important role in the photoluminescence properties of quantum dots. High boiling point non-polar solvents shift the photoluminescence peak to higher wavelength and low boiling point polar solvents shift the photoluminescence peak to lower wavelength.

3:00pm **EM+NS-TuA5 Zinc Oxide Nanowalls and its Optical and Field Emission Properties.** *D. Pradhan, K.T. Leung*, University of Waterloo, Canada

Vertically grown ZnO nanowalls, with typical dimensions of 40-80 nm thick and several micrometers wide, were electrodeposited on an ITO-glass substrate at 70 °C. XRD study shows that these nanowalls have the wurtzite structure and are highly crystalline. The corresponding Raman and photoluminescence spectra further indicate the presence of oxygen deficiency. These ZnO nanowalls exhibit excellent field emission performance, with not only a considerably lower turn-on field of 3.6 V/ $\mu\text{m}$  (at 0.1  $\mu\text{A}/\text{cm}^2$ ) but also a higher current density of 0.34 mA/ $\text{cm}^2$  at 6.6 V/ $\mu\text{m}$  than most of ZnO nanowires and other one-dimensional nanostructures reported to date. We will also discuss a plausible growth mechanism for these nanowalls, and our recent work on the growth of these and other novel ZnO two-dimensional nanostructures on ITO-plastics.

\* Medard W. Welch Award Winner

4:00pm **EM+NS-TuA8 Bright and Color-Saturated Light Emitting Devices Based on Colloidal Nanocrystal Quantum Dots.** *J. Xu*, Pennsylvania State University, *Q. Sun*, University of Dayton, *T. Zhu*, Pennsylvania State University, *A. Wang*, Ocean NanoTech LLC., *Y. Li*, Chinese Academy of Science, China **INVITED**

Recently, the development of low cost, solution-based synthesis of monodisperse, well characterized colloidal quantum dots (QDs) has generated a new class of material for the next generation-light emitting devices. Electroluminescent (EL) devices have been fabricated from thin films of colloidal QDs and exhibit saturated colors and broad wavelength coverage. Emission of EL devices can be easily tuned by varying the size and/or the material composition of nanoparticles during the synthesis process, while their chemical properties remain largely the same. Therefore, one device fabricating procedure can be adopted for different nanocrystals to produce emissions over a broad wavelength, covering the visible (0.4 $\mu\text{m}$  – 0.8 $\mu\text{m}$ ) and NIR (0.8 $\mu\text{m}$  - 2.5 $\mu\text{m}$ ) regions of the spectrum. In addition to the broad wavelength tunability, high fluorescence quantum yield and photochemical stability can be achieved by careful modification of the nanocrystal surface, and this may favor the efficiency of the EL device. All these unique properties have made semiconductor NQDs promising candidates for a broad range of applications, including flat panel display (FPD), light illumination, lightwave communication, and bio/chemical sensing. In this talk we present our work on the design and optimization of colloidal quantum dot (QD)-based light emitting diodes (LEDs) by tailoring the structure and layer thickness of the emissive QDs in the LED active region, the device configuration, as well as the electrode composition. The maximum brightness of red (?peak=619nm), orange (?peak=595nm), yellow (?peak=575nm), and green (?peak=526nm) QD-LEDs were measured to be 9064 cd/m<sup>2</sup>, 3200 cd/m<sup>2</sup>, 4470 cd/m<sup>2</sup>, and 3700 cd/m<sup>2</sup>, respectively, representing the highest brightness reported for QD-based EL devices. These devices were characterized with low turn-on voltages (3-4 V), high efficiency (1.1-2.7 Cd/A), and longer operation time at high brightness (t50%=300hrs at 1100 cd/m<sup>2</sup>), indicative of the superior radiative properties and adequately-tailored carrier-injection and transport functions of the QD-active region in the LEDs.

4:40pm **EM+NS-TuA10 Ligand Quenching of CdSe Quantum Dot Photoluminescence Investigated by Single Molecule Spectroscopy.** *A.M. Munro, I. Jen-La Plante, D.S. Ginger*, University of Washington

Colloidal quantum dots are a unique class of solution processable chromophores with high photoluminescence quantum yields, good photostability, and narrow, size-tunable emission spectra that make them potentially useful for many optoelectronic and photonic applications. Surface chemistry strongly affects the optical and electrical properties, as well as the solubility and stability of the quantum dots. However, many properties of ligand-quantum dot interactions remain unresolved. For instance, it is not known exactly how different ligands alter quantum dot photoluminescence and a better understanding of ligand effects is necessary in order to tailor quantum dot surface chemistry for specific applications. We investigate changes in the photoluminescence of colloidal CdSe quantum dots as we bind different ligands to quantum dot surfaces using both single-molecule and ensemble averaged spectroscopy. Using single-molecule spectroscopy, we monitor the photoluminescence of single CdSe quantum dots over time in the presence of varying concentrations of octadecanethiol and determine the average quantum dot intensity, the average number of emissive quantum dots, and the blinking statistics of the quantum dots. This allows us to determine that the binding of a single thiol molecule to the surface of a CdSe quantum dot creates a trap state that decreases the photoluminescence intensity of the individual quantum dot by a significant amount, but that there is no change in the quantum dot blinking rate. We use this single-molecule data to refine our previously reported Langmuir isotherm quenching fits to ensemble solution photoluminescence spectra. By modeling the effects of octadecanethiol on CdSe quantum dots, we develop a better general understanding of ligand exchange and ligand binding to quantum dots.

5:00pm **EM+NS-TuA11 Controlling the Electronic Structure of Graphene Layers.** *T. Ohta*, LBNL; Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *A. Bostwick*, LBNL, *J.L. McChesney*, LBNL; Montana State University, *T. Seyller*, Univ. Erlangen-Nürnberg, Germany, *K. Horn*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *E. Rotenberg*, LBNL

Much recent attention has been given to the electronic structure of graphene, the honeycomb carbon sheet which is the building block of graphite, carbon nanotubes, C<sub>60</sub>, and other mesoscopic forms of carbon. Following recent developments in synthesizing or isolating graphene films,

experiments have revealed many interesting and physical properties, including an anomalous quantum Hall effect, ballistic electron transport at room temperature, and micron-scale coherence lengths. These unconventional properties are the direct consequence of graphene's peculiar and structure, with massless "Dirac Fermions" as charge carriers at the Fermi level. We have determined the layer-dependent electronic properties of graphene sheets prepared on silicon carbide, using angle-resolved photoemission spectroscopy. We examine this unique two-dimensional system in its development from single layers to multilayers in the  $\pi$  band, the highest occupied state, and the dispersion relation in the out-of-plane electron wave vector in particular.<sup>1</sup> By exploiting the sensitivity of graphene's electronic states to the charge carrier concentration, changes in the on-site Coulomb potential leading to a change of  $\pi$  and  $\pi^*$  bands can be examined. We demonstrate that, in a graphene bilayer, the gap between  $\pi$  and  $\pi^*$  bands can be controlled by selectively adjusting relative carrier concentrations, suggesting a potential application in switching functions in electronic devices.<sup>2</sup>

<sup>1</sup>T. Ohta, A. Bostwick, J. L. McChesney, T. Seyller, K. Horn, E. Rotenberg, Phys. Rev. Lett., 2007, in press.

<sup>2</sup>T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, Science 313, 951, 2006.

# Wednesday Morning, October 17, 2007

## Electronic Materials and Processing

Room: 612 - Session EM-WeM

## Contacts, Interfaces and Defects in Semiconductors

Moderator: L.M. Porter, Carnegie Mellon University

8:00am **EM-WeM1 Role of Hydrogen Bonding Environment in Amorphous Silicon Films for Passivation of Crystalline Silicon Based Photovoltaic Devices**, *M.Z. Burrows, U.K. Das, R.L. Opila, R.W. Birkmire*, University of Delaware

The search for an ideal surface passivation layer of crystalline silicon (c-Si) to be employed in the silicon heterojunction photovoltaic device has garnered much attention. The leading candidate is a few nanometers thick amorphous silicon (a-Si:H) film. This is due to the fact high open circuit voltages above 700mV, key to 20% power conversion efficiencies, are only possible with low surface recombination velocities at the passivated c-Si / a-Si interface. Our approach involves a concentrated effort to link the deposition parameters to the thin a-Si:H material properties as revealed with Fourier transform infrared spectroscopy (FTIR) and match observed changes in H bonding to passivation quality as determined by effective minority carrier lifetime measurements. Reported dependencies of film surface passivation quality on substrate preparation, orientation, and deposition temperature have been extended in this work to include H to SiH<sub>4</sub> dilution ratio and post-deposition annealing. Marked differences have been observed with carrier lifetimes ranging from few microseconds to few milliseconds. A simple yet extremely sensitive FTIR procedure based on Brewster angle transmission measurements enables the probing of films of just 5-10nm thickness. By cataloguing the changes in H content and bonding environment as hydrogen dilution or annealing conditions were varied a comprehensive picture of material quality as related to passivation quality has emerged. Simple avoidance of the growth regimes that lead to epitaxial growth of Si on the c-Si substrate produces decent lifetimes on the order of 500μsec can be achieved. However this often entails harsh deposition conditions that lead to defective films of primarily bulk SiH<sub>2</sub> bonding. Subsequent low temperature anneals, presumed to only relax the amorphous lattice, are shown to not only cause unexpected bulk hydrogen evolution but also involve various complex reactions. Annealing in atmosphere changes surface SiH<sub>2</sub> to chainlike (SiH<sub>2</sub>)<sub>n</sub> as well as oxygen back-bonding to create surface oxides like SiH(O<sub>2</sub>). Annealing in vacuum causes minimal surface SiH<sub>2</sub> disturbance but rather surface SiH and SiH<sub>3</sub> evolution. Finally it is concluded that the best passivation layer consists of primarily well ordered mono-hydride bonding in purely amorphous phase. Sub-optimal amorphous phase films can be improved by post-deposition anneal.

8:20am **EM-WeM2 Impact of Intrinsic Vacancies on Phase Change and Epitaxial Growth of In<sub>2</sub>Se<sub>3</sub> on Si(111)**, *C.Y. Lu, E.N. Yitamben, T.C. Lovejoy*, University of Washington, *K.M. Beck, A.G. Joly*, Pacific Northwest National Laboratory, *M.A. Olmstead, F.S. Ohuchi*, University of Washington

The strong change in optical reflectivity during the amorphous-crystalline phase transition in ternary chalcogenides is the basis of re-writable compact disc and digital video disk technology. The binary, group-III-chalcogenide semiconductor, In<sub>2</sub>Se<sub>3</sub> has recently been proposed as a resistance-based phase-change random access memory (PRAM) material due to its large (10<sup>2</sup>) resistance change between the crystalline and amorphous phases.<sup>1</sup> The intrinsic vacancies and structural variability characterizing crystalline In<sub>2</sub>Se<sub>3</sub> likely play an important role in controlling phase-change characteristics. We have investigated growth of amorphous and epitaxial In<sub>2</sub>Se<sub>3</sub> films on Si(111), as well as the crystallization of amorphous In<sub>2</sub>Se<sub>3</sub> films through resistive annealing using a combination of scanning tunneling microscopy, photoemission spectroscopy, and X-ray diffraction. Amorphization of crystalline In<sub>2</sub>Se<sub>3</sub> films by laser annealing was studied using photo electron microscopy. Despite the 7.3% lattice mismatch, we are able to grow laminar, epitaxial films of γ-In<sub>2</sub>Se<sub>3</sub> (0001) up to at least 3 nm in thickness that exhibit a surface reconstruction associated with the ordered vacancy structure; we attribute this ability to grow laminar films to the flexibility provided by the intrinsic vacancy structure. A minimum thickness of 2 bilayers (0.64 nm) is required to undergo the phase change and a minimum thickness of 3 bilayers (0.96 nm) is required for the ordered-vacancy reconstruction characteristic of the epitaxially grown material during phase change. Annealing room-temperature-deposited films can transform amorphous In<sub>2</sub>Se<sub>3</sub> to be highly

textured γ-In<sub>2</sub>Se<sub>3</sub> with the (0001) plane parallel the substrate surface. A buffer layer of epitaxial In<sub>2</sub>Se<sub>3</sub> before deposition of the amorphous film lowers the crystallization temperature and improves the uniformity of the crystalline In<sub>2</sub>Se<sub>3</sub> phase. This work was supported by NSF grant DMR 0605601. TCL acknowledges support from NSF/NCI IGERT DGE-0504573. Some of the research was pursued at the Advanced Light Source, which is supported by the DOE under contract DE-AC02-05CH11231. KMB acknowledges the support from U.S. Department of Energy by Battelle Corporation.

<sup>1</sup> H. Lee, D-H. Kang, and L. Tran, *Mat. Sci. Eng. B* 119 (2004) 196.

8:40am **EM-WeM3 Reliability of Electrical Contacts to Single Crystal SiC**, *R.S. Okojie*, NASA Glenn Research Center **INVITED**

The utilization of Silicon Carbide (SiC) semiconductor-based microsystems targeted for extreme applications (i.e., high temperature, high power, extreme vibration, and aggressive chemical environments) has largely been hindered by intrinsic material defects and the reliability issues that are associated with the stability of the contact metallization.<sup>1</sup> In this talk, the research efforts at NASA Glenn to resolve the reliability problems of the contact metallization will be presented, which includes the in-depth reliability studies to identify the multilayer metallization that provides stable long-term performance of ohmic contact to SiC. The observation of process-induced stacking faults (SFs) has also been determined to present a reliability problem to 4H-SiC polytype devices. The formation of single and multiple stacking faults that sometimes give rise to 3C-SiC was observed in several doped n-type 4H-SiC epilayer following thermal oxidation. Transmission electron microscopy following oxidation revealed double stacking faults and bands of 3C-SiC in the 4H-SiC epilayer. Depth-resolved cathodoluminescence spectroscopy at 25 oC based on low energy-excited electron nanoscale luminescence revealed a spectral peak at 2.5 eV photon energy that was not present in the sample prior to oxidation. This is in addition to the 3.22 eV photon energy peak corresponding to 4H-SiC.<sup>2</sup> The polytypic transformation is attributed to the motion of Shockley partial dislocations on the (0001) slip planes.<sup>3</sup> Auger electron spectroscopy, Scanning Electron Microscopy, Transmission electron microscopy, and current-voltage measurements that were used to develop an in-depth knowledge of these failure mechanisms will be discussed.

<sup>1</sup> P. G. Neudeck, R. S. Okojie, Liang-Yu Chen, *Proceedings of the IEEE*, Vol: 90 , Issue: 6 , pp.1065 - 1076. 2004

<sup>2</sup> R.S. Okojie, D. Lukko, L. J. Brillson S. Tumakha, G. Jessen, M. Xhang and P. Pirouz., *Appl. Phys. Lett.* 79, 3056 (2001).

<sup>3</sup> Robert. S. Okojie and Ming Zhang, in *Silicon Carbide 2004-Materials Processing and Devices*, edited by Michael Dudley, Perena Gouma, Tsunenobu Kimoto, Philip G. Neudeck, and Stephen E. Saddow (Mater. Res. Soc. Symp. Proc. 815, Warrendale, PA , 2004).

9:20am **EM-WeM5 Epitaxial CVD of Metallic HfB<sub>2</sub> on SiC Substrates**, *Y. Yang*, University of Illinois at Urbana-Champaign, *V.M. Torres*, Dow Corning Compound Semiconductor, *J.R. Abelson*, University of Illinois at Urbana-Champaign

HfB<sub>2</sub> is an attractive candidate for many technological applications owing to its refractory melting temperature (3250°C), high mechanical hardness (29 GPa), low electrical resistivity (15 μΩ-cm), high optical reflectivity, and chemical inertness at high temperatures. The epitaxial growth of HfB<sub>2</sub> is particularly interesting because the (0001) plane has a small lattice mismatch with the compound semiconductors GaN (1.5%) and SiC (-2%) and the coefficients of thermal expansion are reasonably close for these three materials. In principle, epitaxial HfB<sub>2</sub> could be used as a growth template and/or as an electrical contact in a multilayer compound semiconductor device while maintaining crystallographic continuity. We report that high quality HfB<sub>2</sub> thin films can be deposited on SiC(0001) substrates by chemical vapor deposition using the single source precursor Hf(BH<sub>4</sub>)<sub>4</sub>. This precursor is a solid which sublimates at room temperature with a vapor pressure of 15 Torr, such that no carrier gas or heated delivery lines are needed; and it contains no organic or halogen groups. The HfB<sub>2</sub> microstructure is strongly dependent on temperature. Films deposited at low substrate temperature are (0001) textured and polycrystalline, as indicated by SEM and XRD analysis. An increase of deposition temperature increases the grain size and reduces the mosaic spread. Films deposited under optimal deposition conditions are extremely flat. The (0001) rocking curve has a FWHM of only 0.26°, indicating a very high epitaxial quality. The room temperature resistivity is < 20 μΩ-cm, close to the bulk value. The surface morphology of the epitaxial film is sensitive to the surface finish of the SiC substrate: film coalescence can be delayed by substrate surface imperfections.

9:40am **EM-WeM6 Surface and Grain Boundary Electron Scattering in Encapsulated Cu Thin Films**, *T. Sun, B. Yao*, University of Central Florida, *V. Kumar*, Carnegie Mellon University, *A.P. Warren, K.R. Coffey*, University of Central Florida, *K. Barmak*, Carnegie Mellon University

Surface and grain boundary electron scattering contribute greatly to resistivity as the dimensions of polycrystalline metal thin films and interconnects are reduced to and below the length of the electron mean free path. A quantitative measurement of the relative contributions of surface and grain boundary scattering to the resistivity is very challenging, requiring not only the preparation of suitably small conductors having independent variation of the two relevant length scales, namely, the sample critical dimension and the grain size, but also independent, experimental quantification of these two length scales. Since for most work to date the sample grain size has been either assumed equal to conductor dimension or measured for only a small number of grains, the quantification of the classical size effect still suffers from an uncertainty in the relative contributions of surface and grain boundary scattering. A methodology is reported to independently evaluate surface and grain boundary scattering in dielectric encapsulated polycrystalline Cu thin films. The film resistivity measured at both room temperature and at 4K is compared for samples having different grain sizes (determined from 400 to 1,500 grains per sample) and film thicknesses. The experimental data is compared to existing and empirical models of surface and grain boundary scattering in thin films. The resistivity measured at room temperature and 4K is observed to follow similar trends. We find that the resistivity contribution from grain boundary scattering to be significantly greater than that of surface scattering for Cu thin films having Cu/SiO<sub>2</sub> surfaces and grain sizes similar to their thickness. We also find that the resistivity at room temperature is not equal to the simple sum of the low temperature resistivity and the room temperature phonon resistivity contribution, suggesting that either Matthiessen's rule can not be applied, or that the grain boundary and/or surface scattering has a temperature dependence.

10:40am **EM-WeM9 Microstructural Evolution of Nickel Germanides in the Ni<sub>1-x</sub>Ta<sub>x</sub>/Ge Systems during In-situ Annealing**, *J.W. Lee, J.H. Bae, M.H. Park, H.B. Kang, H. Kim, C.W. Yang*, Sungkyunkwan University, Korea

It is becoming increasingly difficult to further improve the performance of Si-based complementary metal-oxide-semiconductor (CMOS) using traditional device scaling. Ge-based devices have attracted considerable attention for high-performance logic applications on account their its lower effective mass and high carrier mobility (double for electrons and four times higher for holes compared with those in Si).<sup>1</sup> However, the NiGe shows a poorer thermal stability than NiSi. The limited thermal stability of NiGe may deteriorate the performance improvement of Ge metal-oxide-semiconductor field-effect transistors (MOSFETs). These features of Ge substrate motivated us to investigate the mechanism of the formation and thermal stability of NiGe and the effect of alloying elements, i.e. the tantalum which is the refractory metal. In this study, the formation and morphological evolution of the germanides formed from the Ni<sub>1-x</sub>Ta<sub>x</sub> (~30nm)/Ge (x=0 and 0.1) systems as a function of temperature was investigated by in-situ annealing in the transmission electron microscope (TEM, JEM-3011, JEOL Co. Ltd) with a specimen heating holder. The sheet resistance of the germanides formed in the Ni<sub>0.9</sub>Ta<sub>0.1</sub>/Ge system was lower at temperatures above 550°C than the Ni/Ge system. Through the addition of Ta atoms, Ni germanide grain growth was retarded and the surface morphology of the Ni germanide layer improved. An approximately 10nm thick Ta-rich layer formed on the top of the germanide layer. Eventually, the agglomeration of Ni germanide was retarded and the thermal stability of the Ni germanide formed from the Ni-Ta alloy became superior to that formed from the pure Ni.

<sup>1</sup> C. O. Chui, S. Ramanathan, B. B. Triplett, P. C. McIntyre, and K. C. Saraswat, IEEE Electron Dev. Lett. 23, 473 (2002).

11:00am **EM-WeM10 Probing the Effect of Interaction and Thermal Expansion Mismatch between Ge and Templated Mask on Defects during Selective Molecular Beam Epitaxy of Ge on Si**, *D. Leonhardt, Q. Li, S.M. Han*, University of New Mexico

We have previously demonstrated that high-quality, single-crystalline Ge can be grown on Si by epitaxial lateral overgrowth (ELO) as well as by touchdown where nanoscale windows (~7 nm in diameter) are created through a thin chemical SiO<sub>2</sub> layer. These techniques have been successfully used to reduce threading dislocations in the Ge-Si lattice mismatched system. Despite the improvement, dislocations are generated in the epilayer above the templated mask. To test the hypothesis that these defects occur due to varying level of epilayer-template interaction energy (e.g., bond strength and diffusion activation barrier) and thermal expansion differences between the epilayer and template, in addition to coalescence events, we have created masks of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Ta having thermal expansion coefficients smaller, larger, and equal to Ge epilayers selectively

grown on Si in the mask openings. The windows in the masks are created by spin-coating a disperse layer of polystyrene spheres on the Si substrate followed by mask deposition and lift-off. Ge islands are selectively grown in the mask openings using molecular beam epitaxy (MBE), and further grown laterally over the mask until coalescence occurs. The Ge layers are then characterized by x-ray diffraction, transmission electron microscopy, and etch pit density after chemical-mechanical polishing to determine the effect of interaction energy and thermal expansion differences on the resulting film quality. Furthermore, we quantitatively measure the desorption activation energy of Ge adspecies from the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Ta masks to determine the characteristic diffusion lengths of Ge adspecies on the mask surfaces. We will then present the impact of inter-distance of windows in the masks on dislocation density in the Ge epilayer.

11:20am **EM-WeM11 Silver-Bearing Ohmic Contacts for AlGaIn/GaN Heterostructures**, *M.A. Miller, S.E. Mohney*, The Pennsylvania State University

We have investigated the use of Ag in place of Au in V- and Ti-based ohmic contacts to Al<sub>0.27</sub>Ga<sub>0.73</sub>N/GaN heterostructures for high electron mobility transistors. An optimized V/Al/V/Ag contact provided a specific contact resistance of 1.7x10<sup>-6</sup> Ohm-cm<sup>2</sup> when annealed at 825°C for 60s in N<sub>2</sub>. As measured by atomic force microscopy, the contacts had a root-mean-square roughness of 4.5 nm over a 10 x 10 micron area, which was much smoother than the analogous Au-bearing metallizations. An optimized Ti/Al/Ti/Ag contact provided a higher minimum specific contact resistance of 7.4x10<sup>-6</sup> Ohm-cm<sup>2</sup>, and the Ti/Al/Ti/Ag contacts were not as smooth as the V/Al/V/Ag contacts, perhaps due to the higher annealing temperatures necessary to minimize the resistance of the Ti-based contacts. The specific contact resistance and morphology of the V/Al/V/Ag contacts were also superior to those of the more conventional Ti/Al/Ti/Au and V/Al/V/Au contacts tested. Transmission electron microscopy revealed a very limited reaction of the annealed V/Al/V/Ag metallization with the semiconductor, leaving the AlGaIn layer intact. The majority of the AlGaIn interface is contacted by Ag-bearing phases. Silver has a lower work function than Au and may facilitate the formation of a low-resistance ohmic contact.

11:40am **EM-WeM12 Schottky Barrier Characteristics and Interfacial Reactions of Ir and Ti Gate Metallizations on In<sub>0.52</sub>Al<sub>0.48</sub>As/In<sub>0.53</sub>Ga<sub>0.47</sub>As High Electron Mobility Transistors**, *L. Wang, I. Adesida*, University of Illinois at Urbana-Champaign

InAlAs/InGaAs HEMTs are promising devices for high speed circuits, millimeter-, and sub-millimeter-wave applications. Selection of gate metallizations plays a significant role in the performance, operation mode, stability, and manufacturability of these devices. Two factors need to be considered in choosing gate metals, namely, work function and reactivity with InAlAs during fabrication and operation. Electrically, metal work function determines Schottky barrier height ( $\phi_B$ ) which in turn decides key device operation parameters such as threshold voltage, transconductance, gate capacitance, etc. Structurally, reactivities or diffusivities of metals/InAlAs control the final gate-channel distance and thermal stability of the transistors. However, a thorough correlation of electrical and structural characterizations of metal/InAlAs contacts at various annealing conditions is still lacking. In this study, we examined the relationship between the  $\phi_B$  characteristics and interfacial reactions of Ti/InAlAs and Ir/InAlAs. I-V characteristics of Schottky diodes were used for  $\phi_B$  and ideality factors characterizations. Cross-sectional transmission electron microscopy is utilized to elucidate the microstructural evolution occurred at the metal/semiconductor interfaces. For Ir/InAlAs,  $\phi_B$  decreased slightly compared to the as-deposited value when annealed at 250 °C. Beyond that  $\phi_B$  increased monotonically until it reached the peak value of 825 meV at 400 - 425 °C. Further increasing the temperature led to  $\phi_B$  degradation. Over a wide temperature range from ~375 to 450 °C,  $\phi_B$  of over 800 meV could be achieved. XTEM studies showed that enhancement in  $\phi_B$  is due to the formation of amorphous layer at the interface. Annealing above 455 °C led to the nucleation of IrAs<sub>2</sub> crystals. For Ti/InAlAs, as-deposited diodes had a typical  $\phi_B$  of 668 meV and an ideality factor of 1.0. Two maxima in  $\phi_B$  were observed for samples annealed at temperatures above 300 °C. The first set of maxima had values between 748 and 726 meV. The second set of maxima had higher  $\phi_B$  of over 760 meV after prolonged annealing. Similar to Ir/InAlAs, an amorphous mixture between Ti and InAlAs formed for samples annealed at short durations. Prolonged thermal treatment resulted in aggressive reaction leading to Kirkendall voids formation, deformation of InAlAs, and TiAs crystal growth. Such aggressive reaction and thus defects formation led to higher diode ideality factors.

12:00pm **EM-WeM13 Improvement of AlGaIn/GaN HEMT and GaN Schottky Contact Device Performance by Reduction of Epitaxial Film Dislocation Density**, *D.J. Ewing, M.A. Derenge, P.B. Shah, U. Lee, T.S. Zheleva, K.A. Jones*, Army Research Lab

The electrical characteristics of AlGaIn/GaN high electron mobility transistors (HEMTs) and GaN Schottky contacts were correlated with dislocations and other material defects. AlGaIn/GaN heterostructures and GaN epitaxial films were grown using conventional MOCVD and pendeo-epitaxy (PE), a lateral growth technique that reduces the dislocation density of the epitaxial films by 2-3 orders of magnitude. Current-voltage (I-V) and capacitance-voltage (C-V) measurements were conducted to determine the quality of the Ni gate (Schottky) contacts to both the conventional and PE films. The Schottky contacts to the PE material all displayed a single, homogeneous Schottky barrier height evidenced by the linearity of the log I-vs-V plot over 4-5 orders of magnitude. Conversely, the Schottky contacts to the conventional material displayed an inhomogeneous Schottky barrier height, with a characteristic "knee" at low voltage indicating the presence of a low Schottky barrier height. The average ideality factor increased from 1.71 for the PE material to 2.29 for the conventionally grown GaN. The average reverse leakage current increased from  $7.5 \times 10^{-4}$  A for the PE GaN to  $4.0 \times 10^{-3}$  A for the conventionally grown GaN. The electrical properties were then correlated with improved material quality as determined by several microscopy techniques. The conventional GaN epitaxial films were found to have an RMS surface roughness twice as large as that of the PE film. Similarly, cathodoluminescence revealed that the near band edge intensity of the PE films was almost an order of magnitude higher than the conventionally grown material, indicating the presence of fewer defects in the PE material. Devices fabricated on the AlGaIn/GaN heterostructure also displayed variations in electrical properties. Variations in the ideality factor, Schottky barrier height, and reverse leakage current density were 1.60-2.60,  $\Phi_B=0.60-0.95$  eV, and  $J=1 \times 10^{-4}-1 \times 10^1$  A/cm<sup>2</sup>, respectively. These variations correlated with a variation in local etch pit density directly under the gate contact as determined by SEM. For devices with high leakage-current density, the etch-pit density was found to be twice as high as that of devices with low leakage current density. Determining the relationship between the electrical characteristics and materials defects will facilitate the fabrication of high-power and high-frequency devices with improved performance and reliability.

## Nanometer-scale Science and Technology

**Room: 616 - Session NS+EM-WeM**

### Nanoscale Devices and Nanowires I

**Moderator:** S. Pang, University of Michigan, C. Eddy, Naval Research Laboratory

8:00am **NS+EM-WeM1 Self-Organization of SiGe Quantum Dots Grown on Ultrathin Si Nanomembranes**, *F.S. Flack, C.S. Ritz, M.G. Lagally, H.J. Kim, K. Turner*, University of Wisconsin-Madison, *M. Huang, F. Liu*, University of Utah

Self-assembly in nanostructures is a linchpin of the bottom-up design technique essential to the advance of nanoscale fabrication. In particular, the self-assembly demonstrated by quantum dots (QDs) in strain-mismatched systems has potential for applications in lasers, high-density memory, and thermoelectric devices. Self-assembled arrays of QDs have been fabricated by several techniques with varying degrees of success and usability. We demonstrate an entirely new route for investigating the nucleation and ordering of QDs: growth on ultrathin semiconductor nanomembranes, substrates that are so thin, usually on the order of tens of nm, that they allow the strain created by a QD to penetrate the entire structure. Such freestanding thin films are truly compliant and, when thin enough, regions of high strain will bend. Thus, we must address the effects of both strain and bending on the preferential nucleation of SiGe QDs. Tethered Si nanomembranes (cantilevers, ledges, wires, and ribbons) with thicknesses ranging from 20 nm to 60 nm are fabricated from silicon-on-insulator (SOI) substrates. SiGe QDs are then grown epitaxially by ultrahigh vacuum chemical vapor deposition. To ensure appropriate strain, the QDs are grown to have dimensions of the same order as the membrane thickness - roughly 8 nm in height. CVD allows for QD nucleation simultaneously on both sides of the membrane, so that nucleation of a QD on one side influences nucleation on the other. In addition, the nanomembranes are thin enough to be semi-transparent in an SEM, granting us a direct view of the alignment of QDs on the top surface to those on the bottom. We model this growth system with finite element analysis and see that a SiGe island nucleated on the top creates regions of high strain on the bottom along preferential

crystallographic directions. These strained regions act as sites for preferential nucleation for QDs on the bottom, which will then seed the next QDs on the top layer and so on to create highly ordered, anticorrelated, arrays on both the top and bottom of the membrane. We discuss the simulations and observations in the limits of QD nucleation due to substrate bending and strain modulation. Research supported by DOE and AFOSR.

8:20am **NS+EM-WeM2 Synthesis of Si<sub>x</sub>Ge<sub>y</sub> Nanowire Alloys by Chemical Vapor Deposition**, *S.G. Choi*, Los Alamos National Laboratory, *P. Allea*, Arizona State University, *S.B. Chikkannavar, E. Akhadov, S.T. Picraux*, Los Alamos National Laboratory

There is an increasing interest in semiconductor nanowires (NWs) as a result of their unique physical properties which have resulted in new conceptual devices at the "nano" scale. Among a large number of NWs explored so far, Si and its related NWs have received much attention, in part due to their potential for easy integration into the well-developed Si microelectronics. Recently, attention has been given to SiGe alloy NWs which offer bandgap tuning from 0.7 to 1.1 eV and possible applications in various devices. In order to synthesize these SiGe alloy NWs in a controlled manner and to realize nanoscale devices with optimum performance, it is important to understand the nature of alloy NWs growth. Although the two binary endpoints - Si and Ge NWs - have been well investigated, studies of SiGe alloy NWs are still in a formative stage. In this work, we studied effects of growth conditions on the structural characteristics of SiGe alloy NWs. SiGe alloy NWs were grown by chemical vapor deposition (CVD) on Si(111) substrates by the vapor-liquid-solid (VLS) mechanism. Au nanoparticles were used as the catalysts, and SiH<sub>4</sub> and GeH<sub>4</sub> were used as the source gases. Partial pressures were controlled precisely by mass-flow controllers for the flow rate of individual gases and a pressure controller for the total process pressure. NWs were grown at temperatures between 450 and 600°C. Morphology and composition of the grown NWs were investigated by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS), respectively. The NWs are observed to become more tapered as growth temperature or Ge composition is increased. Also for the same Au nanodot seeding conditions, the epitaxial Ge-rich alloy NWs grow primarily in the four <111> directions with a substantial fraction of these being vertical [111]-directed NWs, whereas the Si-rich alloy NWs exhibit a noticeable amount of the smaller diameter <110> oriented NWs as well as the four <111> NW orientations. In this work, we examined possible dependences of composition on: (1) diameter of NWs, (2) growth orientations, (3) growth temperature, (4) ratio of GeH<sub>4</sub> to the total partial pressure (i.e.,  $P[\text{GeH}_4]/(P[\text{SiH}_4] + P[\text{GeH}_4])$ ). In this presentation, we will contrast alloy growth with Si and Ge end point growth, and discuss possible mechanisms for explaining the observed effects of growth parameters on composition, morphology, and structure of SiGe alloy NWs.

8:40am **NS+EM-WeM3 In Situ Kinetic Measurements during the Nucleation and Growth of Si and Ge Nanowires**, *F.M. Ross*, IBM T. J. Watson Research Center **INVITED**

In this presentation we will discuss the growth of epitaxial nanowires in Si and Ge using Au as the catalyst, focusing on the kinetic processes that influence nucleation and wire shape. We grow wires in an environmental TEM, which has capabilities for evaporating Au onto a clean Si substrate and for introducing the precursor gases while the sample remains under observation. In situ video rate imaging allows us to measure nucleation events and growth kinetics and to observe structures during growth. We will start by showing the nucleation of Si nanowires within the catalyst particles, and will discuss the buildup of supersaturation that leads to nucleation. After nucleation, the variation of growth rate with pressure, temperature and droplet size allows us to determine the rate limiting step and evaluate the relevance of curvature-driven effects to wire growth. For Si wires, the simple picture that results is complicated by some interesting phenomena caused by the high mobility of Au on the wire surface. And for Ge wires, we show that the growth-driven supersaturation can stabilize the droplets and allow growth far below the eutectic temperature. We finally discuss the growth of hybrid nanowires composed of group IV and group III-V components, showing how the balance of interface energies determines the overall structure. Thus we find that nanowires provide a unique window into fundamental crystal growth processes, as well as an opportunity to fabricate precisely controlled structures for novel applications.

9:20am **NS+EM-WeM5 Self-Catalyzed Growth of Defect-Free Indium Phosphide Nanowires on Silicon**, *R.L. Woo*, University of California, Los Angeles, *Y. Kobayashi, T. Mallouk*, Penn State University, *R.F. Hicks*, University of California, Los Angeles

Compound semiconductor nanowires exhibit promising properties for high-speed nanoelectronic devices. However, in order to realize their full potential, growth processes must be developed for the precise control of the nanowire shape, density, uniformity, and crystalline quality. In this study, we report on the fabrication of indium phosphide nanowires on silicon (100)

and (111) by metalorganic vapor-phase epitaxy. Nanoscale indium droplets were used instead of gold catalyst to nucleate wire deposition. High-resolution transmission electron microscopy with selected area electron diffraction has revealed that the InP nanowires are free of crystal defects and grow along either the <110> or the <113> axis. This may be contrasted to gold catalyze growth, where the preferential orientation is <111>, and there is a relatively high density of stacking faults. Through careful control of the substrate preparation and the MOVPE process conditions, it has been possible to grow vertical InP nanowires of uniform diameter and lengths over 1.0 micron. At the meeting, we will present data on the novel electrical and optical properties of the indium phosphide nanowires.

9:40am **NS+EM-WeM6 Plasma-stimulated Control of Silicon Nanowire Nucleation, Orientation and Growth Kinetics**, *P. Aella, W.T. Petuskey*, Arizona State University, *S.T. Picraux*, Los Alamos National Laboratory

Plasma-enhanced chemical vapor deposition is shown to significantly alter the nucleation rate and activation energy for vapor-liquid-solid (VLS) growth of silicon nanowires compared to thermal growth, providing new control over nanowire morphologies and new insight into the rate-limiting mechanisms of VLS growth. Initially, catalytic gold films (0.5 - 2 nm thick) were thermally evaporated onto hydrogen terminated Si (100) substrates at room temperature in a UHV deposition system. Subsequently, Si nanowires were grown in a cold wall reactor at 0.5 Torr in atmospheres of 10% SiH<sub>4</sub> in H<sub>2</sub> between 350 to 510°C and RF plasma powers of 2.5 to 10 W. SEM images show that thermally grown nanowires on Si (100) substrates nucleate and grow predominantly in <111> directions. In contrast, plasma stimulation significantly enhances the nucleation rate of smaller diameter <110> Si nanowires and also reduces coarsening of Au dots. A two step growth process is demonstrated whereby initial plasma excitation nucleates <110> nanowires followed by thermal growth to preferentially form a high density of small diameter <110> nanowires on Si (100) surfaces, greatly limiting the large diameter <111> nanowire formation found under thermal growth conditions with identical Au seeding. This demonstrates the overall effect of the plasma on shortening nucleation times, favoring thinner wires, and thereby dominating the rest of the growth process. A comparison of the growth rate vs. temperature for both <111> and <110> nanowires shows a large reduction in the activation energy (from 0.74 to 0.26 eV) due to the plasma. The overall growth rate is also greatly enhanced at low temperatures by plasma excitation, with growth rates at 350°C an order of magnitude greater than for thermal growth. Under our low temperature thermal conditions the predominant source gas is silane, while in the case of plasma stimulation SiH<sub>3</sub> radicals are also present. Our results unequivocally demonstrate that the rate limiting step for Si nanowire growth under these conditions is due to the kinetics of silicon incorporation at the vapor-liquid interface and not at the liquid-solid interface as has also been previously proposed in some cases. Based on our measured incorporation coefficients and activation energies under thermal and plasma-enhanced growth we suggest the first model for the rate-limiting kinetic steps for Si nanowire growth by the VLS mechanism.

10:40am **NS+EM-WeM9 Nanowires in Nanoelectronics: Problems and Promise**, *D.K. Ferry*, Arizona State University **INVITED**

Progress in microelectronics has generally followed the well known scaling rules known as Moore's Law. By the end of this decade, we will approach some well recognized limits in traditional semiconductor devices. Nanowires have been put forward as a new technology with new promise to extend nanoelectronics. For this to be the case, the nanowires must fit into the scaling rules and must offer important new options, primarily in circuit cleverness. In this talk, I will review the scaling rules, and where they have led us, then discuss how the constraints of these rules, particularly Si area cost, dictate how new technologies can be used. These suggest that the impact of nanowires will likely be in providing new options for architectural revolutions, as opposed to merely clever new devices.

11:20am **NS+EM-WeM11 Electrical and Mechanical Characterization of Nanowire Properties using In-Situ SEM**, *D.F. Ogletree*, Lawrence Berkeley National Laboratory

Nanowires have unique electrical and mechanical properties with a wide range of potential applications in electronics, opto-electronics and nano-mechanics. Local measurements of the electrical and mechanical properties of individual nanowires in controlled environments are required to develop these applications and to optimize nanowire growth conditions. A flexible system for nanowire characterization based on a high-resolution environmental scanning electron microscope (SEM) has been developed combining sample heating in controlled gas environments with nano-positioning of local probes. This system has been used to investigate the evolution of size-dependent nanowire mechanical properties between room temperature and the melting point of the nanowires.

11:40am **NS+EM-WeM12 Four Independent STM Navigated by High Resolution UHV SEM: Transport Measurements on In-Situ Grown Titanium Silicide Nanowires on Si(111)**, *J. Koeble, M. Maier*, Omicron NanoTechnology, Germany, *B. Grandider*, IEMN, Lille, France

A major challenge in Nanotechnology is the incorporation of single nano-devices into larger integrated circuits. Traditional instrumentation suffers from one fundamental issue: How to cover the dimensional range of a fully integrated circuit down to the nanometer range (or even atomic scale) of single devices and have an adequate integrated navigation system. To meet these requirements, we have established and being advancing a new approach to integrating state-of-the-art SPM technology via high resolution electron microscopy and spectroscopy: (1) Bridging dimensions and rapid navigation; (2) Combining different surface analysis methods at the very same sample area to gain complementary information; (3) Integrated position-readout of sample and probe positioning; (4) Pushing each single technology to its inherent limits. The system facilitates four independent Scanning Tunneling Microscopes and the UHV version of the Zeiss Gemini SEM column with ultimate resolution below 4nm for probe navigation and rapid localisation of sample features or devices. STM imaging is used to pro-actively position and contact the probe(s) on nano-devices. Using STM probe approach technology, a controlled electrical contact is ensured to finally perform a four-point measurement on the nano-scale. We report on electrical measurements on self-assembled titanium silicide nanowires (NWs) in-situ grown on a Si(111) surface. Transport measurements have been taken in 2-point and 4-point configuration. The transport measurements indicate metallic behavior for the silicide nanowires and that the NWs are electronically decoupled from the Si surface and reveal a Schottky barrier between the NWs and the Si surface.

12:00pm **NS+EM-WeM13 Anisotropic Plasmon and Electronic Structure of Ag Nanowires on Cu(110)**, *P.T. Sprunger, I. Senevirathne, W. Zhao, B.M. Watson, O. Kizilkaya, A.K. Sekharan, R.L. Kurtz*, Louisiana State University

Epitaxial Ag nanowires have been found to self-assemble on Cu(110) for Ag coverages exceeding 1.2 ML. The electronic and plasmon loss structure of the nanowires have been characterized by ARPES and EELS. STM images reveal that Ag nanowires grown on Cu(110) are approximately 2 nm high and ~12 nm wide. The nanowires grow oriented with the long axis parallel to the [110] substrate direction and they have aspect ratios up to 20:1. The ARPES results show that the valence bands within the Ag nanowire are strongly anisotropic with clear band dispersion in the along-wire direction, but no dispersion in the across-wire direction. This strongly suggests that the valence electrons of Ag behave as quasi-one-D conductors along the wire yet confined with atomic-like states perpendicular. Fermi surface crossings have been observed, confirming that metallic behavior is realized along the wire axis. In accord with the ARPES measurements, EELS reveals that the plasmon excitation is red-shifted at the zone-center and is nearly dispersionless perpendicular to the nanowire direction. These results will be discussed in light of recent band-structure calculations of Ag nanowires and models for plasmon behavior in quasi-1D structures. We would like to acknowledge the support of the LSU CAMD synchrotron light source and the support of and LA-R&D and NSF through DMR-0504654.

## Surface Science

**Room: 611 - Session SS2+EM+TF-WeM**

## SAMs and Organic Films I

**Moderator:** H. Fairbrother, Johns Hopkins University

8:00am **SS2+EM+TF-WeM1 Scanning Tunneling Microscopy Growth Study of a Columnar Liquid Crystalline Hexaazatriphenylene Derivative on Au(111)**, *S.D. Ha*, Princeton University, *Q. Zhang, S. Barlow, S.R. Marder*, Georgia Institute of Technology, *A. Kahn*, Princeton University

The growth of a discotic liquid crystal derivative of tris(thieno)hexaazatriphenylene (THAP) is studied with scanning tunneling microscopy (STM). An electron transport material with relatively high electron affinity (4.59eV), THAP is expected to form columnar stacks in a thick bulk film. It is shown with STM that on Au(111), the first four monolayers of THAP molecules order in such columnar mesophases. The first monolayer forms a square 10.1Å x 10.1Å unit cell with one molecule per cell. However, this is much smaller than expected, and it may be due to buckling caused by the substrate interaction or in-plane molecule-molecule interaction. The second monolayer, at partial coverage, grows commensurate to the first monolayer in a rectangular herringbone with two

molecules per  $15.7\text{\AA} \times 14.0\text{\AA}$  unit cell. The molecules tilt in order to conform to the packing of the first layer and the interlayer interaction controls the molecular orientation. Yet upon full coverage of the second monolayer, the intralayer interaction prevails and the molecules reorganize into a hexagonal close-packed (HCP) structure without obvious tilt. The unit cell is rhomboidal with dimensions  $21.0\text{\AA} \times 22.2\text{\AA}$  and one molecule per cell. Moreover, the rotational orientation of the molecules forms a herringbone pattern, with alternating rows of the HCP structure switching between two opposite orientations. As for the third and fourth monolayers, STM images indicate that they have HCP geometry with the same dimensions as the second layer. Given the tendency of molecules similar to THAP to stack into columns, it is likely that because the third and fourth layers have the same in-plane structure as the second layer, they are commensurate to the latter. Thus, on Au(111), THAP readily grows in the expected columnar liquid crystal fashion directly from the interface layer, and the columns are hexagonal close-packed with negligible molecular tilt.

8:20am **SS2+EM+TF-WeM2 UHV-STM Studies of DNA Bases on Au(111)**, *W. Xu, R. Otero, M. Schock*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark, *R. Kelly, L. Kantorovich*, King's College London, UK, *F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

The self-assembly of Nucleic Acid (NA) base molecules on solid surfaces has recently attracted much attention as on one hand, such studies provide invaluable insight into fundamental interactions between these molecules. On the other hand, NA base molecules and DNA molecules are particularly interesting as promising building blocks for the bottom-up fabrication of functional supramolecular nanostructures on surfaces within the emerging area of nanotechnology. From a biological point of view, the self-assembly processes in DNA and RNA molecules are controlled by i) cross-strand interactions between NA base molecules, which are dominated by hydrogen bonds (H-bonds), ii) stacking interactions between NA base molecules along the strand, and iii) the interactions of NA base molecules with water molecules and metal ions, such as  $\text{Na}^+$ ,  $\text{K}^+$ . Among these interactions, the hydrogen bonding between NA base molecules plays a crucial role in determining the conformation and biochemical properties of DNA and RNA molecules. Hence, it is important and interesting to study the fundamental interactions between NA base molecules at the single molecule level to reveal the exact physicochemical nature of the biological systems. Here we will show our recent experimental progress on four individual NA base molecules (guanine, adenine, cytosine, thymine) that are adsorbed on Au(111) surface under Ultrahigh Vacuum (UHV) conditions. We demonstrate by variable-temperature scanning tunnelling microscopy (VT-STM) experiments that guanine and adenine form 2D island with well-ordered structures through hydrogen bonds, and the so-called guanine quartet structure is found to be stabilized by the cooperative hydrogen bonds. Interestingly, cytosine only forms disordered 1D filamentary structure by fast cooling the sample, whose behavior could be described as a 2D organic glass. Thymine in the first stage (low surface coverage) also forms 1D filamentary structure steered by hydrogen bonds. However, when the surface coverage is increased, the filaments could merge into 2D well-ordered islands by van der Waals (vdW) interactions. Moreover, we have also investigated that the thymine 2D island can be broken back into the 1D hydrogen bonded filaments by STM manipulation, which further confirm that we are able to directly probe the hierarchy of bond-strengths involved in the surface self-assembly of multifunctional organic molecules with highly anisotropic interactions.

8:40am **SS2+EM+TF-WeM3 Understanding Molecular Exchange on Surfaces: Controlling and Elucidating the Mechanism of 1-Adamantathiolate Monolayer Displacement**, *H.M. Saavedra, T.J. Mullen, C.M. Barbu*, The Pennsylvania State University, *A.A. Dameron*, University of Colorado, *V.H. Crespi, P.S. Weiss*, The Pennsylvania State University

We have investigated the solution-phase displacement kinetics of 1-adamantanethiolate self-assembled monolayers on Au{111} by n-dodecanethiol molecules using infrared spectroscopy, scanning tunneling microscopy, x-ray photoelectron spectroscopy and electrochemical desorption. The displacement reaction can be described by the fast insertion of n-dodecanethiolate at defects in the original 1-adamantanethiolate monolayer, which nucleates island growth and is followed by eventual slow ordering of the n-dodecanethiolate domains. Langmuir-based kinetics, which describe alkanethiolate adsorption on bare Au{111}, fail to describe this displacement reaction. Instead, a Johnson-Mehl-Avrami-Kolmogorov model of perimeter-dependent island growth yields good agreement with kinetic data obtained over a hundred-fold variation in n-dodecanethiol concentration. Analysis on a model-free basis suggests that displacement is a scale-free process within this concentration regime. The crucial role of the adsorbate lattice, along with the thermodynamic driving forces, rationalizes the rapid and complete displacement of 1-adamantanethiolate monolayers

and explains why other monolayers reach kinetic traps that result in slow and incomplete displacement.

9:00am **SS2+EM+TF-WeM4 Thermal Treatment of Glutamic Acid Etched Ni Nanoclusters on Au{111} Leads to the Formation of 1-D Metal Organic Co-Ordination Networks**, *A.G. Trant, T.E. Jones, C.J. Baddeley*, University of St Andrews, UK

The adsorption of glutamic acid onto 2-D Ni clusters on Au{111} has been investigated using reflection absorption infrared spectroscopy (RAIRS) and scanning tunnelling microscopy (STM). Adsorption at 300 K leads to two distinct adsorbate species which we conclude are zwitterionic species adsorbed either at Ni-like sites in the centre of the clusters or at interfacial sites at the edges of clusters. Adsorption of (S)-glutamic acid causes the complete destruction of clusters of initial diameter  $<3$  nm. We conclude that the Ni islands have been corroded resulting in the formation of a Ni salt - presumably nickel (II) glutamate. On annealing to 350 K, chains of 1-D molecular features are observed in STM experiments. We discuss the possible composition and structure of this salt and conclude that the chains most likely consist of nickel (II) pyroglutamate. Metal pyroglutamate salts are known to be produced by heating glutamate salts. The intermolecular bonding and azimuthal alignment of the 1-D chains are discussed. We also report the formation of analogous networks from Ni + (R)-glutamic acid and discuss the influence of stereochemistry on the structure of the networks.

9:20am **SS2+EM+TF-WeM5 Crossover from Site-Sensitive to Site-Insensitive Adsorption of the Fullerene Derivative PCBM on Au(111) due to Hydrogen-Bond Formation**, *D. Ecija, R. Otero*, Univ. Autonoma de Madrid, Spain, *L. Sanchez*, Univ. Complutense de Madrid, Spain, *J.M. Gallego*, Inst. de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *Y. Wang, M. Alcamí, F. Martín*, Univ. Autonoma de Madrid, Spain, *N. Martín*, Univ. Complutense de Madrid, Spain, *R. Miranda*, Univ. Autonoma de Madrid, Spain

The 2D arrangement of organic adsorbates at solid surfaces results from a combination of non-covalent intermolecular forces with molecule-substrate interactions. It is generally thought that molecule-substrate interactions determine adsorption geometry and conformation in first place, while intermolecular interactions affect the subsequent self-assembly of the adsorbates. Only when the molecules can form strong directional bonds, like hydrogen bonds or coordination bonds, and the corrugation of the adsorption potential energy is small, the supramolecular structure is dominated by intermolecular interactions. On the other end of the spectrum, vicinal or heterogeneous surfaces show a strong selectivity in the adsorption site of the adsorbates, leading to a final morphology which is almost exclusively substrate-controlled (templated growth). Usually, the role of molecule-substrate interactions on self-assembly is discussed at the single-molecule level, but this is strictly speaking just an approximation, since the formation of intermolecular bonds might modify the adsorption geometry and thus molecule-substrate interactions. For systems showing site-selective adsorption, the modification of the adsorption geometry upon intermolecular bond formation might result in the removal of the site-selectivity. By means of variable-temperature Scanning Tunneling Microscopy (STM) experiments and Density Functional Theory (DFT) calculations, here we investigate the crossover from site-selective to site-insensitive adsorption of PCBM, a C<sub>60</sub> derivative, on the herringbone-reconstructed Au(111) surface as a function of the coverage. Whereas at low coverages PCBM self-assembly is dictated almost exclusively by the substrate-related preference for nucleating at the fcc sites of the reconstruction, with a selectivity close to 100%, at higher coverages intermolecular interactions take over the substrate influence, giving rise to PCBM islands that extend through fcc, hcp and dislocations of the herringbone reconstruction. Comparison with theoretical calculations offers the following picture of this crossover: at high-enough coverages hydrogen bonds between double rows are formed that modify the adsorption geometry of PCBM molecules, which in turn removes site-selectivity. The phenomenon of intermolecular interaction-driven modification of the adsorption geometry might thus be crucial to optimize the templating effect of surface nano-scale patterns on adsorbed organic overlayers.

9:40am **SS2+EM+TF-WeM6 Nanostructured Binary Molecular Films: Lessons from ACA:C<sub>60</sub> Mixtures**, *J.E. Reutt-Robey*, University of Maryland, *B. Xu*, Yanshan University, China, *C.G. Tao*, University of Maryland, *D.B. Dougherty*, National Institute of Standards and Technology, *W. Jin*, University of Maryland

Multi-component aromatic molecular films are of increasing interest in photovoltaic technologies and other organic electronic applications. Binary organic films offer the potential to tailor film structure on the nanoscale to optimize device performance through phase selection, domain size, distribution and orientation. A basic understanding of the factors that control structure in binary molecular films is thus important to advance

these materials technologies. We report STM-studies of structure evolution in model donor-acceptor systems, such as ACA:C<sub>60</sub> and Pentacene:C<sub>60</sub>. Films prepared by sequential physical vapor deposition onto Ag(111) substrates under UHV are monitored directly with an integrated UHV-STM. We demonstrate how ACA:C<sub>60</sub> film growth conditions can be adjusted to selectively fabricate films that range from phase-separated hexagonal -C<sub>60</sub> and chain-phase [4 0, 2]-ACA domains to intermixed co-crystalline chiral domains comprised of C<sub>60</sub>-terminated ACA pinwheels. Films produced with arbitrary composition generally lead to complex multi-phase structures. Predeposited ACA films with single phase structures provide the most effective pathway to single phases of intermixed structures. For example, the intermixed chiral phase is only accessible from the 2-D ACA molecular gas, whereas extended C<sub>60</sub> chain structures may be accessed only from the dimer-phase [12 2, 6 5]-ACA domains. We apply lessons from the ACA:C<sub>60</sub> system to Pentacene:C<sub>60</sub> mixtures, utilizing the 2-D pentacene gas to access an intermixed honeycomb Pentacene:C<sub>60</sub> phase.

10:40am **SS2+EM+TF-WeM9 Detection of Gaseous Nitric Oxide Using X-ray Photoelectron Spectroscopy**, *M. Dubey, J. Schwartz, S.L. Bernasek*, Princeton University

Detection of gaseous nitric oxide (NO) in biological systems has attracted significant attention since the identification of NO as the endothelial-derived relaxing factor (EDRF).<sup>1</sup> NO also acts as a signal molecule in the nervous system, and is associated with the presence of infection and Alzheimer's and other diseases. Apart from biological systems, NO is a main product released on the pyrolysis of nitro-organic explosives. For these reasons, much work has been done in the field of NO detection, and the need for a sensitive detector is evident. In this study, we report a direct and a highly sensitive technique to detect gaseous NO using X-ray Photoelectron Spectroscopy (XPS). The binding of NO by heme proteins is well understood,<sup>2</sup> and we have utilized it for detection. We have developed a reliable method to grow Self-Assembled Monolayers (SAMs) of alkylphosphonic acids on oxide surfaces.<sup>3</sup> This platform is used to covalently attach a uniform layer of an iron heme-like molecule, which was synthesized separately. Differential charging in XPS has been used to ascertain the uniformity of the organic film.<sup>4</sup> The N1s signal from the heme ligand was measured by XPS before and after exposure to NO. Before NO binds to the iron, a single nitrogen peak is present, attributed to the nitrogens of the porphyrin ring. After reaction with NO, a new, distinct peak was observed in the high resolution N1s spectrum. This peak is at a higher binding energy (approx 5.5 eV), and is attributed to the NO bound to the iron. An estimate of the bound NO was calculated using XPS and QCM to be about 40 picomoles.

<sup>1</sup> R. M. J. Palmer, A.G. Ferrige, S. Moncada, *Nature*, 1987, 327, 524.

<sup>2</sup> K. R. Rodgers, *Curr Opin Chem Biol*, 1999, 3, 158.

<sup>3</sup> E. L. Hanson, J. Schwartz, B. Nickel, M. Koch, M. F. Danisman, *J. Am. Chem. Soc.*, 2003, 125, 16074.

<sup>4</sup> M. Dubey, I. Gouzman, S. L. Bernasek, J. Schwartz, *Langmuir*, 2006, 10, 4649.

11:00am **SS2+EM+TF-WeM10 An In Situ EC-STM Study of the Restructuring of Self-Assembled Monolayers upon Metal Deposition**, *C. Silien, M. Buck*, University of St Andrews, UK

The combination of electrochemistry and self-assembled monolayers offers interesting opportunities for nanotechnology due to high resolution defined by patterned SAMs and simplicity and scalability afforded by electrochemistry. However, control of processes such as electrochemical metal deposition on the nanometer length scale requires exact knowledge of the mutual influence of a SAM structure and electrochemical processes. Aiming for an understanding at the molecular level we report an investigation of the underpotential deposition of copper on Au(111) electrodes modified by  $\omega$ -(4'-methyl-biphenyl-4-yl)-alkanethiols (H<sub>3</sub>C-(C<sub>6</sub>H<sub>4</sub>)-(C<sub>6</sub>H<sub>4</sub>)-(CH<sub>2</sub>)<sub>n</sub>SH, BPn). As reported recently, this class of molecules gives rise to pronounced structural variations with length n of the alkane spacer and, for n = even, exhibits polymorphism.<sup>1,2</sup> Furthermore they can be prepared to an exceptionally high structural perfection. These properties make SAMs of BPn thiols an attractive basis for further tailoring of properties of functionalized electrodes and the electrochemical generation of nanometer-scaled structures. A decisive step in SAM controlled electrometallisation is the deposition of the first layer of metal which takes place in the underpotential region. Its understanding is of crucial importance as this layer forms at the SAM-substrate interface and, therefore, affects the properties of the system. Our in situ STM investigations of the underpotential deposition reveal, firstly, pronounced differences between BPn SAMs and alkane thiols and, secondly, a pronounced influence of the length of the alkane spacer in the BPn SAMs, i.e., whether n = odd or even. The molecular resolution achieved in this study combined with time resolved monitoring of the events occurring in the course of the copper deposition allows us to highlight the relationship between the SAM structure and its influence on the generation of nanometer scaled structures by electrochemical metal deposition.

<sup>1</sup> Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Wilton-Ely, J. D. E. T.; Zharnikov, M.; Wöll, C. *J. Am. Chem. Soc.* 2006, 128, 13868.

<sup>2</sup> Cyganik, P.; Buck, M.; Azzam, W.; Wöll, C. *J. Phys. Chem. B* 2004, 108, 4989.

11:20am **SS2+EM+TF-WeM11 Irradiation-Promoted Exchange Reaction: A New Approach to the Fabrication of Heterogeneous Self-Assembled Monolayers and Chemical Lithography**, *N. Ballav, T. Weidner, M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can undergo an exchange reaction with the molecules capable of building a SAM on the same substrate upon the immersion into the respective solution. However, for most systems, the exchange reaction is very slow and incomplete at normal conditions, taking from days to weeks and occurring to a limited extent only. Using several different model systems, we show that the rate and extent of the exchange reaction can be significantly enhanced and even precisely tuned by either electron irradiation with a small dose or exposure to UV light. We assume that both electron and UV irradiation result in the appearance of structural and chemical defects in the target SAM, which promote the molecular exchange. The effect of irradiation and the parameters of the exchange reaction were monitored in detail and correlated with each other using several complementary experimental techniques. The developed approach, irradiation-promoted exchange reaction, can be considered as a platform for the preparation of heterogeneous mixed SAMs. Also, in combination with e-beam or UV-lithography, this method can be used for the fabrication of chemical patterns, including gradient ones. In this regard, the approach is similar to conventional photography: a desired pattern is initially written by electron or UV beam and later "developed" upon its immersion into the solution of a molecular substituent. There are no principal limitations for the form of the fabricated features while the characteristic length scale can be varied in a broad range from centimetres to several tens of nanometers.

11:40am **SS2+EM+TF-WeM12 Calcium Adsorption on Regioregular Poly(3-hexylthiophene): Synchrotron Radiation Photoemission and Microcalorimetric Studies**, *J.F. Zhu, W. Zhao, W.H. Zhang*, University of Science and Technology of China, *J. Farmer, C.T. Campbell*, University of Washington

The adsorption of Ca on the regioregular poly(3-hexylthiophene) (rr-P3HT) thin film surfaces at 300 K has been studied using synchrotron radiation photoemission spectroscopy, adsorption microcalorimetry and atomic beam/surface scattering. The polymer films were spin-coated on the Si wafers with typical thickness of > 100 nm and were free of oxygen contamination as clarified by both X-ray photoelectron spectroscopy and Auger electron spectroscopy. Synchrotron radiation photoemission spectroscopy provides precise experimental information on the alteration of the Ca/polymer interfacial energy level line-up and the chemical nature at this interface. The deposition of calcium on the rr-P3HT film at room temperature induced a decrease of the work function, indicating Ca donates electron density to the polymer substrate. Moreover, Ca adsorption led to the depression of the bands of the rr-P3HT. The strength of interaction between Ca and the rr-P3HT is probed by both microcalorimetric heats of adsorption and sticking probability measurements.

12:00pm **SS2+EM+TF-WeM13 Supramolecular Coordination Networks at Surfaces: Self-selection and Error Correction in Multi-ligand Nanopore Arrays**, *S.L. Tait, A. Langner, N. Lin*, Max Planck Institute for Solid State Research, Germany, *C. Rajadurai, M. Ruben*, Research Center Karlsruhe, Germany, *K. Kern*, Max Planck Institute for Solid State Research, Germany and Ecole Polytechnique Fédérale de Lausanne, Switzerland

Supramolecular self-assembly of organic ligands and metal centers is a topic of growing interest for efficient molecular-scale patterning of surfaces. Molecular networks can be designed to self-organize in regular, 2D nanopore lattices, whose dimensions and properties can be controlled by selection of the organic ligands. This approach offers a natural alternative to current nano-fabrication methods, allowing atomic and molecular building blocks to organize themselves into useful nanostructures, and is a model system for supramolecular and biomolecular assembly in general. We present recent results of self-assembled supramolecular networks on the Cu(100) surface, which demonstrate multi-ligand construction of 2D arrays of compartments with tunable shape and size. These binary combinations of complementary ligands represent a significant step in complexity over previous studies. Of technological interest is the capability for modular replacement of either of the two ligands to produce a range of nanopore lattice sizes and shapes in a very predictable and programmable way. Of more fundamental interest in these systems is molecular level resolution imaging using scanning tunneling microscopy, which allows an unprecedented perspective of fundamental steps to supramolecular assembly, such as structural error correction achieved by efficient molecule self-selection. Non-covalent metal-organic coordination provides room temperature stability and high structural ordering through directional and selective

interactions, but also allows for bonding reversibility, enabling error correction during assembly. By selection of molecular building blocks with specific properties, we can "program" these systems to pattern a surface with homogenous networks of specific size, structure, and physical and chemical properties. The ability to tailor the size and functionality of nanometer-scale arrays produced by molecular self-assembly represents a unique opportunity for molecular recognition, heterogeneous catalysis, thin film growth, and other fields.

# Wednesday Afternoon, October 17, 2007

## Electronic Materials and Processing

Room: 612 - Session EM-WeA

### Growth and Characterization of Complex Oxides

**Moderator:** C.H. Swartz, University of Canterbury, New Zealand

1:40pm **EM-WeA1 Spatially and Energy Resolved Imaging of Nucleation Centers in Ferroelectrics**, *S.V. Kalinin, S. Jesse, B.J. Rodriguez*, Oak Ridge National Laboratory, *I. Vrejoiu, D. Hesse, M. Alexe*, Max Planck Institute of Microstructure Physics, Germany, *Y.H. Chu, R. Ramesh*, University of California, Berkeley, *S. Choudhury, L.Q. Chen*, Pennsylvania State University, *E.A. Eliseev, A.N. Morozovska*, National Academy of Science of Ukraine

Ferroelectric polarization switching in non-volatile memory and high density data storage devices is governed by a number of nucleation centers that account for the experimentally observed low values of coercive fields. Despite 50 years of research, the microstructural origins of the Landauer paradox (switching fields corresponding to implausibly large nucleation activation energies) are still a mystery. Here, Switching Spectroscopy Piezoresponse Force Microscopy (SS-PFM) is developed as a quantitative tool for real-space mapping of polarization dynamics in ferroelectrics. SS-PFM is an extension of PFM spectroscopy that involves the acquisition and analysis of multiple hysteresis curves at every point in an image to extract maps of parameters describing the local switching properties. In nanodots, the non-uniform work of switching was imaged with ~10 nm resolution within 50 nm ferroelectric nanoparticles. In epitaxial lead zirconate-titanate thin film, the spatial distribution of the switching centers is obtained and the components of thermal (variation in depolarization energy of domain wall energy) and field (built-in polarization) disorder are extracted independently. Phase-field modeling of PFM switching yields nearly quantitative agreement between experimentally measured and calculated nucleation biases on the free surfaces and in the vicinity of the in-plane domains. This indicates that switching in PFM is close to the intrinsic thermodynamic limit. Further prospects of SS-PFM studies of ferroelectric devices and nanostructures for information technology are discussed. Research supported by the Division of Materials Science and Engineering, Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, which is managed by UT-Battelle, LLC.

2:00pm **EM-WeA2 Strain-Enhanced Ferroelectrics and Multiferroics Grown by MBE\***, *D.G. Schlom*, Penn State University **INVITED**

Aided by theoretical predictions, we have used epitaxy and the misfit strain imposed by an underlying substrate to enhance the ferroelectric properties of SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, and BaTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices grown by MBE. The enhancements include shifting the paraelectric-to-ferroelectric transition temperature by hundreds of degrees and maintaining ferroelectricity in BaTiO<sub>3</sub> layers as thin as one unit cell in BaTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices. The effect of strain on EuTiO<sub>3</sub> will also be presented.

\*Additional Authors: Biegalski, M.D., Oak Ridge National Laboratory; Soukiasian, A., Haeni, J.H., Lee, J.H., Ulbricht, R.W., Brooks, C.M., Jia, Y., Vaithyanathan, V., Tian, W., Ke, X., Tenne, D.A., Vasudevarao, A., Kumar, A., Tian, L., Sharan, A., Choudhury, S., Schiffer, P., Trolrier-McKinstry, S., Xi, X.X., Gopalan, V., Chen, L.Q., Penn State University; Choi, K.J., Kim, D.M., Eom, C.B., University of Wisconsin-Madison; Chen, Y.B., Sun, H.P., Pan, X.Q., University of Michigan; Fong, D.D., Zurbuchen, M.A., Eastman, J.A., Fuoss, P.H., Streiffer, S.K., Argonne National Laboratory; Irvin, P., Levy, J., University of Pittsburgh; Chang, W., Kirchoefer, S.W., Naval Research Laboratory; Heeg, T., Schubert, J., Forschungszentrum Jülich GmbH, Germany; Bruchhausen, A., Lanzillotti-Kimura, N.D., Fainstein, A., Centro Atómico Bariloche & Instituto Balseiro, Argentina; Katiyar, R.S., University of Puerto Rico; Cantarero, A., University of Valencia, Spain; Li, Y.L., Hawley, M.E., Jia, Q.X., Los Alamos National Laboratory; Fennie, C.J., Nakhmanson, S.M., Rabe, K.M., Rutgers University; Tagantsev, A.K., Ecole Polytechnique Fédérale de Lausanne, Switzerland; Velickov, B., Uecker, R., Reiche, P., Institute for Crystal Growth, Germany

2:40pm **EM-WeA4 Molten Salt Synthesis and Luminescence Properties of Rare-Earth Doped Yttrium Oxide and Rare-Earth Zirconate/Hafnate**, *Y. Mao, J. Dorman, J.P. Chang*, University of California at Los Angeles

A molten salt synthetic method is described in this work for synthesizing rare-earth doped yttrium oxide (RE:Y<sub>2</sub>O<sub>3</sub>) and rare-earth zirconate/hafnate (RE<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub>) (0 ≤ x ≤ 1), since it is one of the simplest, most versatile, and cost-effective approaches available for obtaining crystalline, chemically purified, single-phase powders at lower temperatures and often in overall shorter reaction times with little residual impurities as compared with conventional solid-state reactions. RE:Y<sub>2</sub>O<sub>3</sub> are promising rare-earth-ion-activated phosphor materials with wide applications including amplifiers,

lasers, waveguides, X-ray imaging, bioimaging, and field emission or electroluminescent displays due to their luminescent characteristics and stability in high vacuum. RE<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> are of great interest in recent years for their possible applications as high-temperature heating elements, oxidation catalysts, thermal barrier coatings, nuclear waste hosts, and host materials for luminescence centers. The as-prepared nanoparticles have sizes around 100 nm for RE:Y<sub>2</sub>O<sub>3</sub> and around 30 nm for RE<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub>. They are thoroughly characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and UV-vis spectroscopy to delineate the structure and composition of these nanoparticles. Their room temperature luminescent properties (photoluminescence and cathodoluminescence) are measured as a function of the particle size and distribution. In order to process these materials for device fabrication, they are made water soluble by surface modification of these nanoparticles with DMSA (2,3-dimercaptosuccinic acid). We will discuss the effect of these nano-coatings on the optical properties of the nanoparticles.

3:00pm **EM-WeA5 Thermoelectric Properties of Concentration Graded Bulk Co-Doped TiO<sub>2</sub>**, *N. Nguyen*, University of Washington, *A. Yamamoto*, Advanced Institute for Science and Technology, Japan, *D. Kukuruzyak, T. Chikyow*, National Institute of Materials Science, Japan

There has been a recent increased interest in using segmented thermoelectric elements to improve the performance of the thermoelectric devices. Concentration graded of dopants in the oxides can be regarded as a segmented component composed of a single parent based material. In terms of material processing and operating temperature, concentration graded oxides is more advantageous, and may result in higher efficiency at elevated operating temperature, especially for bulk thermoelectric devices. In this work, concentration graded n-typed Co-doped TiO<sub>2</sub> synthesized by solid state reaction method by mixing the powder of Ti and Co oxides, followed by hot-pressed under vacuum of 3x10<sup>-5</sup> torr and temperature of 1473 K. The distribution of the Co doping concentration in the graded samples was mapped out by using Energy Dispersive X-ray Fluorescence Spectrometer scanning technique. The 2D X-ray diffraction measurements indicate polycrystalline Co-doped TiO<sub>2</sub> rutile were fabricated. The Current-Voltage characteristics under the presence of the temperature gradient were generated for selected samples by applying a current source in such a way that the thermopower current was suppressed by applied current in the opposite direction. Power factors (S<sup>2</sup>Σ) were then evaluated over a temperature range from 300 K – 800 K. Surprisingly, uniformed Co doping shows parallel declined in both conductivity and thermopower magnitude, whereas graded Co doping enhanced the power factor. This implies the enhancement of the power factor could be related to electron spin entropy effect induced by Co doping to TiO<sub>2</sub>

4:00pm **EM-WeA8 Growth and Characterization of Vanadium Dioxide (VO<sub>2</sub>) Thin Films Prepared by Reactive Biased Target Deposition (RBTd)**, *K.G. West, J. Lu, W. Chen, J. Yu, Y. Pei, S.A. Wolf*, University of Virginia

Vanadium dioxide (VO<sub>2</sub>) undergoes a well known first order metal to semiconductor structural phase transformation just above room temperature at 341K. The abruptness of the phase transformation from its high temperature tetragonal phase to its low temperature monoclinic phase is accompanied by large changes in its electrical conductivity and infrared transmission characteristics, making it an excellent candidate for sensor and switching applications. Also recently it has been observed that an electric field can induce an abrupt transition and change in electrical conductivity below the phase transition temperature, owing even greater potential for its use in practical devices. The growth of high quality VO<sub>2</sub> thin films can be problematic since several distinct oxide states exist. Growth conditions, such as O<sub>2</sub> flow rate, process pressure, and substrate temperature can highly influence the phase of the growing film. Using a novel growth technique called reactive bias target deposition (RBTd), we have prepared highly oriented VO<sub>2</sub> thin films on Al<sub>2</sub>O<sub>3</sub> (0001) substrates at various growth temperatures ranging from 250C-550C. The influence of the growth parameters on the microstructure, and transport properties of VO<sub>2</sub> thin films was systematically investigated. A change in electrical conductivity of 10<sup>3</sup> was measured at 341K associated with the well known structural phase transition (SPT). It was observed that the SPT temperature can be tuned to higher temperatures by mixing VO<sub>2</sub> and other vanadium oxide phases. In addition a current/electric-field induced metal-insulator transition (MIT) was observed at room temperature with a change in electrical conductivity of 8x. The current densities required to induce the MIT in VO<sub>2</sub> are on order of 6x10<sup>4</sup> A/cm<sup>2</sup>. The switching time of the MIT, as measured by high frequency current pulsed measurements, was determined to be roughly

10ns. RBTU utilizes a low energy broad beam ion source that reliably produces a very high density of low energy (5-50eV) inert gas ions. A large negative potential bias is applied to the metal sputtering target. The high density of low energy inert gas ions in front of the sputtering target, seeing a very large potential difference, are accelerated to the target surface at a near normal incidence angle at high enough energies to induce sputtering. A pulsed DC bias is used to avoid target poisoning during reactive processing.

**4:20pm EM-WeA9 Elaboration, Chemical and Electrical Analyses of Intermixed and Nanolaminate HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> MIM Capacitor Structures.** *M. Bonvalot, M. Kahn, C. Vallee, C. Dubourdieu, O. Joubert, CNRS, France*

High quality MIM capacitors are seeing increased use in CMOS, BICMOS and bipolar chips. The economic demand for smaller devices directly leads to the request for higher MIM charge storage densities. Therefore new high  $\epsilon$  dielectric materials, such as Al<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub> and HfO<sub>2</sub>, are being evaluated as MIM dielectrics and are or will be used in future applications. Among those materials, it is generally admitted that Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> show good potentials for this purpose. Al<sub>2</sub>O<sub>3</sub> exhibits a lower  $k$  value but has a larger breakdown field than HfO<sub>2</sub>, and thus the simultaneous use of these two materials in a MIM structure may lead to some improved electrical properties. In this work, we investigated the behaviour of nanolaminate and intermixed HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> MIM capacitor structures. HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have both been deposited by Atomic Layer Deposition (ALD) on WSi<sub>x</sub> ( $x=2.3$ ) substrates. Numerous materials stackings have been realised, such as simple HfO<sub>2</sub>/WSi<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, bilayered HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, sandwiched Al<sub>2</sub>O<sub>3</sub>/ HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, and nanolaminate Al<sub>2</sub>O<sub>3</sub>/ HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/ HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, as well as intermixed (HfO<sub>2</sub>)<sub>x</sub>( Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub>/WSi<sub>x</sub> compounds. All these structures were carefully analysed by UV ellipsometry up to 8 eV, and show an overall thickness of 13 nm. ATR and variable angle XPS analyses have been performed for interface analysis. C(V) and I(V) electrical characterizations were also carried out after metallic deposition of top electrodes (Au, Al, Ni, Pt). Comparisons of these measurements are useful for identification of individual contributions to the overall electrical behaviour of the MIM structures. In particular, we studied the gain obtained in the linearity of the C(V) curves and the overall capacitance value of these numerous MIM structures. A detailed discussion will be presented on the multiple advantages of using nanolaminate and intermixed compound structures.

**4:40pm EM-WeA10 Suppression of Metal-Insulator-Metal (MIM) Capacitor Leakage Current in BaSrTiO<sub>3</sub> (BST) Dielectrics by Ni Doping : Spectroscopic Studies Changes in Conduction Band Edge Defect States with Ni Doping.** *H. Seo, North Carolina State University, Y.B. Kim, Hanyang University, Korea, G. Lucovsky, North Carolina State University*

A significant reduction of leakage current in MIM capacitors in Ni-doped BST dielectrics is reported. Ni-doping increases the breakdown voltage from ~10-12 V to >35 V, and reduces the leakage current by several orders of magnitude,  $10^2$ - $10^3$ , as compared to un-doped BST. The conduction mechanism is changed from i) tunneling injection plus Poole-Frenkel transport in un-doped BST to ii) Fowler-Nordheim tunneling in the Ni-doped BST. These decreases are explained by a spectroscopic study of changes in conduction band, and band edge defect states. The large changes in breakdown voltage and leakage current between doped and un-doped BST have been correlated with changes in band edge oxygen vacancy defects detected by spectroscopic ellipsometry (SE). The  $\epsilon_2$  spectrum from the SE measurements on Ni-doped BST is qualitatively different than that from un-doped BST. Changes in conduction band states from 3.5 to 6 eV are assigned to Ni<sup>2+</sup>/Ni<sup>3+</sup> transitions, and changes in band edge defect state features between 2.5 and 3 eV due to reduction of Ti<sup>3+</sup> bonding at O-atom vacancies. In particular, the defect state difference is attributed to charge transfer between Ni<sup>2+</sup> states, and Ti<sup>4+</sup> band states, as well as Ti<sup>3+</sup> pre-existing defect states of the BST host. The band edge vacancy defect is ~0.2 eV shallower in Ni-doped BST and this leads to the significant changes in transport and trapping, accounting for reductions in leakage current, and improved resistance to breakdown in the Ni-doped BST. The study demonstrates that addition of transition metal doping atoms with different valence states than Ti in BST, and/or Zr in other insulating perovskites, can have a significant effect on transport by providing a way to reduce/control leakage current and breakdown. These doping effects will be important in transition metal/rare earth atom complex oxides that have been identified for device applications, not only as high- $k$  capacitors or gate dielectrics, but for ferro-electric devices as well.

**5:00pm EM-WeA11 Comparison Between Film Characteristics and Gas-Phase Diagnostics in Magnetron Sputtering Deposition of Superconducting YBaCuO.** *K. Fukaya, K. Sasaki, J. Gao, T. Kimura, M. Watanabe, M. Inoue, A. Fujimaki, Nagoya University, Japan, H. Sugai, Chubu University, Japan*

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub> (YBaCuO) thin films are promising materials for high-temperature superconducting integrated-circuit devices. Magnetron sputtering deposition is a useful method for preparing YBaCuO thin films because of the cheaper process cost than pulsed laser deposition and metal organic chemical vapor deposition. This work reports gas-phase diagnostics of magnetron sputtering deposition of YBaCuO thin films. Because of the lack in detailed plasma diagnostics, the precursors for the deposition of YBaCuO films have not been identified yet. In this work, we measured two-dimensional distributions of the densities of Y, Ba, Cu, YO, BaO, and CuO by laser-induced fluorescence imaging spectroscopy. In addition, we adopted two-photon absorption laser-induced fluorescence for measuring one-dimensional distribution of the O atom density. By comparing the results of the gas-phase diagnostics with the properties of YBaCuO films, we identified the deposition precursors for obtaining fine YBaCuO films. A YBaCuO powder target, Ar/O<sub>2</sub> mixture gas and a conventional rf magnetron sputtering source at 13.56 MHz were used in this experiment. The densities of Y, Ba, and Cu atoms were measured with varying the O<sub>2</sub> flow ratio from 0 to 100% at a total gas pressure of 400 mTorr. The Cu density decreased gradually with the O<sub>2</sub> flow ratio from 0 to 100%, which may be due to the decrease in the plasma density with the O<sub>2</sub> flow ratio, resulting in the decrease in the sputtered Cu flux. In contrast, the Ba and Y densities decreased drastically with the O<sub>2</sub> flow ratio, which is due to oxidation reaction in the gas phase. We observed the increases in the YO and BaO densities with the O<sub>2</sub> flow ratio from 0 to 10%, indicating the production of YO and BaO from Y and Ba in the gas phase, while the CuO density was below the detection limit at all the discharge conditions. On the other hand, the O atom density increased with the O<sub>2</sub> flow ratio from 0 to 20% and was saturated at O<sub>2</sub> flow ratios higher than 20%. The O atom density was estimated to be much higher than the Cu density. According to the analysis of YBaCuO films deposited on MgO substrates (670 °C) placed at a distance of 3 cm from the target, fine YBaCuO films with high crystallinity were obtained at O<sub>2</sub> flow ratios from 50 to 70%. Therefore, it is known by the present work that the deposition precursors for obtaining fine YBaCuO films are Cu, YO, BaO, and O.

## Nanometer-scale Science and Technology

**Room: 616 - Session NS2+EM-WeA**

### Nanoscale Devices and Nanowires II

**Moderator:** D.K. Ferry, Arizona State University, F.M. Ross, IBM T. J. Watson Research Center

**1:40pm NS2+EM-WeA1 Real-time Studies of Metallic Nanodroplet Formation and Motion on Semiconductor Surfaces.** *J.H. Wu, W. Ye, T. Sun, H.-Y. Chen, K. Thornton, R.S. Goldman, University of Michigan*

Arrays of metallic nanodroplets are of interest for a broad range of applications including magnetic memory arrays, plasmonic waveguides, nanowire growth seeds, and negative index of refraction materials. Although nanometer-sized metallic droplets often form on compound semiconductor surfaces during epitaxial growth, thermal annealing, and/or ion irradiation, the mechanisms of their formation are not well understood. In this work, we are examining the formation and motion of metallic droplets during ion-irradiation of a variety of semiconductor surfaces. We use real-time imaging in a dual-beam focused-ion-beam system followed by quantitative analysis of the instantaneous positions, sizes, and velocities of the droplets in each movie frame. On GaAs and GaSb surfaces, randomly distributed nearly pure liquid-like Ga droplets are observed to form above a critical dose. Subsequent ion beam irradiation results in growth, motion, and coalescence of the droplets. Since droplets are not observed on Si surfaces prepared under similar conditions, the droplet formation is likely associated with the preferential sputtering of group V elements and liberation of Ga from the substrate as it is milled. Under ion beam irradiation, Ga droplet motion is observed, possibly due to Marangoni motion, which is usually driven by a surface tension gradient. Since the Ga droplets are essentially liquid spheres, the weak atomic bonds and droplet shape lead to enhanced sputtering in comparison with the surrounding substrate. The enhanced sputtering at liquid droplets leads to both thermal and surface tension gradients between the droplets and the substrate, thus providing the driving force for droplet motion. Interestingly, a higher droplet velocity is observed on GaSb than on GaAs surfaces, suggesting that droplet motion is

dependent on the energetics of the Ga-substrate interface. On GaAs surfaces, most droplets move in a direction opposite to the ion beam scanning direction, presumably due to the FIB-induced thermal gradient on the surface. In addition, the droplet velocity is size-dependent, with higher velocities for larger droplets, suggesting the thermal/surface tension gradients increase with droplet size. The velocity is apparently correlated with the rate of droplet size change, suggesting that a mass transfer/exchange process occurs during droplet motion. This phenomenon is less significant for droplets that have merged with other droplets.

**2:00pm NS2+EM-WeA2 A Periodic Table of Silicon-Metal Nano-Templates for Cluster-Assembled Materials, G.K. Gueorguiev, S. Stafström, L. Hultman, Linköping University, Sweden**

The structure and bonding properties of  $MSi_n$  clusters, containing 1 to 14 Si atoms together with one transition metal atom among 24 different elements: Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ti, Zr, Hf, V, Nb, Ta, Ni, Pd, Pt, Cu, Ag, Au, were studied by first-principles calculations. Some of these clusters are known to have been synthesized. The transition metal atoms work as nucleation sites for  $MSi_n$ . We find that species with  $n=3, 5, 7, 10, 12$  are stable and exhibit shapes independent on the metal atom involved which establishes a systematic behavior for  $MSi_n$ . For most metals, due to p-d orbital hybridization, both  $MSi_{12}$  and  $MSi_{10}$  (the smallest endohedral species) are highly symmetric, exhibiting the shapes of a hexagonal prism ( $D_{6h}$ ) and of a bicapped tetragonal antiprism ( $D_{4d}$ ), respectively. For such clusters, we predict similar packing rules, but considerably different electronic properties. Nano-wires (hexagonal nanocylinders) assembled from  $MSi_{12}$  are stable and with tunable electronic properties. These attributes suggest  $MSi_n$  as building blocks for cluster assembled materials. We have systematized the results on  $MSi_n$  by the organization of the transition metals in the Periodic Table.

**2:20pm NS2+EM-WeA3 Sc Silicide Epitaxial Nanowires on Si(001): A Comparison with Rare Earth Silicide Nanowires, J. Nogami, Y. Chai, University of Toronto, Canada, G. Ye, M.A. Crimp, Michigan State University**

Rare earth (RE) metals can form self-assembled silicide nanowires when grown epitaxially on Si(001) substrates. These nanowires form due to an anisotropy in lattice mismatch between the hexagonal form of the silicide and substrate, with extended growth occurring along the direction of low mismatch.<sup>1,2</sup> In this context, the growth of scandium silicides is interesting since  $Sc_2Si_5$  has the same crystal structure as the RE silicides, but with the direction of close match along the c rather than the a axis. This raises the intriguing possibility of growing nanowires that are naturally perpendicular to RE silicide nanowires. The initial stages of Sc silicide growth on Si(001) was studied by scanning tunneling microscopy, transmission electron microscopy (TEM) and atomic force microscopy. The nanostructures can be divided into two classes: tabular rectangular islands with small aspect ratios, and highly elongated nanowires with triangular cross section. Surprisingly, there is no indication that the common growth direction of the nanowires is rotated with respect to RE nanowires. At the same time, TEM shows that the triangular nanowires have a two phase crystal structure, with a Sc rich silicide growing on top of a Si rich silicide. The differences in growth behavior with respect to the RE silicides will be explained in terms of the differences in stable silicide phases seen in the phase diagrams of these systems.

<sup>1</sup>Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, Y. A. Chang, and R. S. Williams, Appl. Phys. Lett. 76, 4004 (2000).

<sup>2</sup>J. Nogami, B. Z. Liu, M. V. Katkov, C. Ohbuchi, and N. O. Birge, Phys.Rev.B 63, 233305 (2001).

**2:40pm NS2+EM-WeA4 Time-resolved X-ray Excited Optical Luminescence Characterization of Si Nanowires\*, R.A. Rosenberg, G.K. Shenoy, Argonne National Laboratory, P.S.G. Kim, T.K. Sham, University of Western Ontario, Canada**

Due to quantum confinement effects nanostructures often exhibit unique and intriguing fluorescence behavior. X-ray excited optical luminescence (XEOL) provides the capability to chemically map the sites responsible for producing low energy (1-6 eV) fluorescence. By taking advantage of the time structure of the x-ray pulses at the Advanced Photon Source (APS, ~80 ps wide, 153 ns separation) it also possible to determine the dynamic behavior of the states involved in the luminescence. In this presentation we show how this technique can be utilized to understand the XEOL from silicon nanowires (~50 nm diameter). Analysis of the XEOL spectra revealed the presence of three peaks at 475, 540, and 640 nm whose breadth increased with increasing wavelength. To gain insight into the dynamic nature of the luminescence, time-gated spectra were obtained as the x-ray energy was varied through the Si K edge. Data were obtained using 15-140 ns and a 0-10 ns gates. For the long time gate the areas are roughly evenly distributed among each of the peaks. However, in the short time gated data the 640 nm peak is dominant. This clearly demonstrates that the relative lifetime of this state is shorter than the other two. This is in contrast to the

conventional wisdom for homo-structured and single component materials, for which the lifetime usually increases with wavelength. By extracting the intensity of each peak as the x-ray energy is scanned thru the Si K edge we are able to demonstrate that the 540 nm luminescence emanates from the Si nano crystallites imbedded in the wire, the 475 nm peak originates from the oxide shell, and the 640 nm peak comes from defects located near the Si-SiO interface.

\*Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

**3:00pm NS2+EM-WeA5 Enhancement of CHEI Programming Efficiency Using Extended SixZr1-xO2 Interface Formed by ZrO2 Charge Trapping Layer, G. Zhang, W.J. Yoo, Sungkyunkwan Advanced Institute of Nano-Technology, Korea**

Channel hot electron injection (CHEI) programming is widely used for NOR Flash memory operations, whose efficiency is determined by both hot electron (HE) injection level and electron capture rate in which an electron excitation and relaxation process is involved.<sup>1</sup> Inelastic phonon scattering is considered as the main mechanism to cause HE relaxation, where HE energy loss rate decays with larger electron/phonon temperature divergence.<sup>2</sup> As a result, electron capture rate of deep traps decays sharply with the increase of HE temperature (Te).<sup>3</sup> We consider that phonon scattering occurs actively at interfacial junction of different layers, where regularity of lattice structure is disturbed. In this work, we investigated capture rate dependent CHEI programming efficiency for different junction widths or phonon temperatures (Tp). It is found that HES are injected into the gate stack as lucky electrons,<sup>4</sup> resulting in small capture rate or low programming efficiency; instead, warm electrons (WE), which are generated by thermally enhanced F-N tunneling, play a more important role in programming with higher capture rate. In this work, a practical method to effectively enhance programming speed using extended SixZr1-xO2 interfacial junction between tunnel SiO2 and ZrO2 trapping layer in SONOS type Flash memory is proposed. Cross-sectional TEM image shows that the ZrO2 is highly reactive with SiO2 to form a SixZr1-xO2 interface of graded composition over the thickness of ~2 nm. HfO2 has a similar band structure with ZrO2 but a thinner (0.5-0.7nm) interface and Si3N4 has a smaller conduction band energy offset to SiO2. We observed effectively enhanced programming efficiency at various operation temperatures for the devices using a charge trap layer of ZrO2, compared to those using Si3N4 by ~3.2 times and HfO2 by ~2.2 times. Furthermore, ZrO2 demonstrates clear advantages in low-voltage operation and large Vth window over Si3N4 and HfO2, being a very attractive material contender for next-generation NOR Flash application.

<sup>1</sup>B. Govoreanu, et. al., IEDM Tech. Dig., p479, 2006.

<sup>2</sup>W. Cai, et. al., Physical Review B, p8573, 1986.

<sup>3</sup>R. Passler, Solid-State Electronics, p155, 1984.

<sup>4</sup>S. Tam, et. al., IEEE Trans. Electron Devices, vol.31, n.9, p1116, 1984.

**4:00pm NS2+EM-WeA8 Nano-Structured Surface Fabrication for Higher Luminescent LED by Self-Assembled Block Copolymer Lithography, A. Fujimoto, K.A. Asakawa, Toshiba Corporation, Japan**  
**INVITED**

Light-Emitting Diodes (LEDs) are widely used for cell phones, display panels, LCD backlights, traffic signals, and automobile rear lamp. They are expected to be used for automobile head lamps, and interior illumination. Higher luminance LEDs are required for these purposes. The total efficiency of LEDs is determined by the product of the internal quantum efficiency and the extraction efficiency. The internal quantum efficiency has been improved more than 80 %. But, the extraction efficiency remains 10 %, because of the large difference of the refractive index between substrates ( $n=3-3.5$ ) and the air. Therefore, to improve the extraction efficiency is the key for higher luminance LEDs. In order to improve the extraction efficiency, we fabricated nanostructures having the antireflection and the diffraction effect onto the semiconductor surface. Nanostructures have the cone, cylinder, and the mesa part. Since nanostructures have the cone and the mesa part and the refractive index from the semiconductor to the air changes smoothly within the critical angle, the incident light within the critical angle can be extracted without a loss, and the transmittance increases about 30 % compared with that of the flat surface. Furthermore, since nanostructures have the cylinder and the cylinder has the diffraction effect, the incident light over the critical angle can be extracted as the -1st order light. Nanostructures having two functions can be expected to improve the light-extraction efficiency greatly. Such structures are usually fabricated by electron beam (EB) lithography, but are too costly for mass production. To overcome this challenge, block copolymer lithography was employed. The polystyrene (PS) - polymethyl methacrylate (PMMA) diblock copolymer was used in this study. The PMMA was removed by reactive ion etching (RIE) since the PMMA has a much faster etch rate than the PS by RIE. The gallium phosphide (GaP) substrate was dry-etched by chlorine-based inductively coupled plasma RIE using the remaining PS dots

as a mask. The optical extraction efficiency of the substrates with subwavelength columnar structures improved 2.6 times compared to unprocessed flat substrates; the pillars' height was 350 nm, diameter was 130 nm, and pitch was 180 nm. We also manufactured a real LED and increased light emission volume 1.8 times compared with conventional LED at the same energy consumption.

4:40pm **NS2+EM-WeA10 Current-Voltage Characteristic of Organic Molecular Wires by Conducting Atomic Force Microscopy**, *N.J. Lee, S.B. Kim, I.C. Hong, S.H. Koo, Y.J. Choi, J.W. Kim, Y.S. Kim, C.J. Kang*, Myongji University, Korea

Using an atomic force microscope (AFM), with a conducting cantilever, the current versus voltage (I-V) characteristics of difference group substituted carotenedithiol molecules are measured. The molecules are inserted into 1-methylsulfanyl-octadecane monolayer on gold surface, and an Au nanoparticle is attached to each molecule via the protruding thiol group. To measure the current, a gold-coated AFM probe is used to contact with the molecule through the Au nanoparticle. A self-assembled monolayer of 1-methylsulfanyl-octadecane was analyzed by surface plasmon resonance, ellipsometry, and X-ray diffraction, which were employed to identify suitable preparation conditions of the substrate. The I-V curves of two kinds of carotenedithiol molecules substituted for different end groups appear quite different because of the different electron transport properties; bromophenyl-substituted group put a crimp in electron transport. The phenyl-substituted carotenoid is significantly more conductive than the bromophenyl-substituted carotenoid. In this talk, we'll present the molecular wires possibility. The carotenoid candidate "molecular wire".

5:00pm **NS2+EM-WeA11 Fabrication, Dynamics, and Electrical Properties of Shielded Probes**, *P.D. Rack, B.J. Rodriguez, K. Seal, S. Jesse, A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Many biological systems respond to stimuli such as electrical bias. The application of naturally occurring local biases in biosystems can be mimicked with an atomic force microscope tip. In order to minimize capillary forces and obtain high-resolution images of biosystems, a liquid environment, typically with a high ionic strength, is required. A bias applied via traditional cantilevers will cause electrochemical reactions in the solution. The use of shielded probes may allow biases to be applied locally, and minimize any electrostatic force contribution to the signal being measured, whether the tip is used as an electromechanical probe or a probe of local electric force. In this case, the bias is applied locally and the signal is measured locally, both on the nanoscale. The fabrication of suitable shielded probes requires (a) good dynamic properties of the lever, (b) good insulation everywhere except for the apex, (c) high apex conductivity, and (d) apex geometry consistent with high resolution. In this presentation, we describe a process for fabricating shielded probes, and measure their dynamic and electrical properties. The commercial doped-Si tips were coated with an oxide prior to etching a small via (~200nm diameter) with a focused ion beam. Subsequent to the via etch, a tungsten contact was deposited in the via using electron beam induced deposition. The dynamic properties of the fabricated probes, as well as their performance in Piezoresponse force microscopy in ambient and liquid environment and I-V characteristics are discussed. The choice of other coatings or other metal plugs may allow for further improvements, and/or tunable properties. The use of shielded probes may allow precise control over the application and measurement of local fields in solution.

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# Thursday Morning, October 18, 2007

## Electronic Materials and Processing

Room: 612 - Session EM-ThM

### Zinc Oxide

Moderator: R.M. Wallace, University of Texas at Dallas

#### 8:00am EM-ThM1 Bulk and Surface Impurities and Point Defects in ZnO, D.C. Look, Wright State University **INVITED**

ZnO is a popular material at present because of potential photonic and electronic applications, such as UV LEDs and transparent transistors. As with most semiconductors, the bulk optical and electrical properties are controlled by impurities and defects acting as donors, acceptors, traps, and recombination centers. However, ZnO is somewhat unusual in that the surface also has donors and acceptors that produce electrical activity and can affect Ohmic and Schottky contact formation, among other things. Bulk donors and acceptors can be quantified by temperature-dependent Hall-effect (T-Hall) measurements, and their identities can often be determined by correlation with low-temperature photoluminescence (PL) and SIMS measurements in conjunction with doping and electron-irradiation experiments. Surface donors and acceptors, however, are much more difficult to quantify, although in this work we show that fairly reliable concentrations of surface donors (but not acceptors) can be determined by means of a low-temperature Hall-effect measurement and a room-temperature electrochemical C-V (ECV) measurement. Information on the possible identities of these surface donors can be obtained with XPS, SIMS, and other surface-sensitive techniques. We present T-Hall, PL, and ECV data on bulk, commercially available, ZnO samples grown by the vapor-phase, melt, and hydrothermal methods. Accurate concentrations of bulk donors and acceptors are obtained in all cases; the donors are tentatively assigned to various combinations of H, Al, Ga, and a Zn-interstitial complex, and the acceptors, to Li and the Zn vacancy. Fairly accurate densities of surface donors are also obtained in each case, and it is speculated that they are due to H complexes since their concentrations can be significantly increased by forming-gas anneals. To our knowledge, this is one of the first quantifications of surface donors in any semiconductor material, and the methodology should have general applicability.

#### 8:40am EM-ThM3 Correlation of Native Point Defects to Thermal Stability of Schottky Barrier Formation at Metal-ZnO Interfaces, H.L. Mosbacher, C. Zgrabik, S. El Hage, The Ohio State University, A. Swain, Columbus School For Girls, M. Kramer, The Ohio State University, G. Cantwell, J. Zhang, J.J. Song, Zn Technology, D.C. Look, Wright State University, L. Brillson, The Ohio State University

ZnO is an important semiconductor system for spintronic, nanoelectronic and optoelectronic devices. Important to realization of these devices is control and thermal stability of the metal-ZnO interface. We investigated this interface on bulk single crystal substrates grown by different methods from 5 different vendors. Using a remote oxygen plasma to remove ZnO surface adsorbates, subsurface defects and hydrogen, we studied Al, Au, Ir, Ni, Mo, Pd, Pt, and Ta contacts. Depth-resolved cathodoluminescence spectroscopy (DRCLS) reveals the presence of 3 defects at energies of 2.1, 2.5 and 3.0 eV. These deep level states vary in concentration with vendor, with depth from the interface, and with metal contact. Current-voltage measurements show that material containing high concentrations of defects in the subsurface strongly affects reverse currents, idealities and barrier heights acquired from current-voltage measurements. After annealing these contacts at temperatures of 350°C, 450 °C, 550 °C, and 650 °C in an argon ambient, DRCLS spectra identify defect formation that correlates to the nature of the metal-ZnO interface. Metals that form oxides show increased deep-level emissions that have been attributed to oxygen vacancies, while metals that form eutectics with Zn reveal increased luminescence from defects associated with Zn vacancies. Ta contacts annealed at 550 °C create blocking contacts to ZnO, and DRCLS in the interface region reveal the formation of a Ta oxide. Al contacts also form blocking contacts at temperatures that depend on the native point defect densities. DRCLS of the subsurface oxide interface reveal increases in a 2.5eV transition often associated with oxygen vacancies. Au contacts that are annealed above the eutectic temperature for Au-Zn exhibit an increase of the 2.1eV defect level that correlates to Zn vacancies. Elevated temperature results demonstrate that the thermal stability of Schottky barriers also correlates to the density of native point defects. These differences in native point defect densities have a significant impact on defect formation at both elevated and room temperatures. Samples with high native defect concentrations initially can

increase reactions in the subsurface, thus creating more defects associated with the metal-ZnO surface chemistry. Overall we find that metal-ZnO chemical reactions introduce interface native defects. These and native bulk defects dominate Schottky barrier properties and thermal stability.

#### 9:00am EM-ThM4 Separation of Surface and Bulk Conduction in ZnO using Variable Magnetic Field Hall Effect Measurements, C.H. Swartz, M.W. Allen, S.M. Durbin, University of Canterbury, New Zealand, T.H. Myers, West Virginia University

One of the major advantages of ZnO over other wide bandgap semiconductors is the availability of bulk, single crystal growth of high quality material using a variety of techniques. Of these, hydrothermally grown ZnO is somewhat unique in that it is highly resistive with carrier concentrations typically 2 - 3 orders of magnitude lower than other bulk ZnO, due to compensation from unintentionally introduced Li and Na acceptor impurities. This high resistivity makes the measurement of its electrical properties particularly susceptible to complications such as persistent photoconductivity, increased temperature sensitivity and surface conduction effects. The surface conductivity of ZnO is known to depend strongly on the ambient atmosphere and can increase significantly under vacuum conditions. After being placed in a vacuum, the expiration of atmospheric effects on the surface can take many hours and, even when equilibrium is reached, the surface conductivity remains a significant, and often dominant, contributing factor to electrical measurements. Variable magnetic field Hall effect measurements can be used to separate surface or interface conducting layers from the bulk conductivity of a given sample. In this paper, we report on the results of temperature dependent, variable magnetic field Hall effect measurements on hydrothermally grown ZnO single crystal wafers from Tokyo Denpa Co. Ltd. (Japan). Measurements were carried out over a temperature range of 80 - 300 K and magnetic field strengths up to 12 T. Multiple carrier fitting was used to remove surface conduction effects and produce temperature dependent mobility and carrier concentration data for the bulk carriers only, which was then theoretically fitted. A significantly higher bulk carrier mobility and an order of magnitude lower ionised impurity concentration was found than is apparent from standard single field Hall effect measurements. These results also indicate that the use of single field, temperature dependent Hall effect measurements to determine donor concentration and activation energies may be problematic unless surface conduction effects are first isolated.

#### 9:20am EM-ThM5 Nuclear Reaction Analysis Investigation of H-doped ZnO Grown by Pulsed Laser Deposition, Y.J. Li, T.C. Kaspar, T.C. Droubay, S. Shuthanandan, S. Thevuthasan, P. Nachimuthu, S.A. Chambers, Pacific Northwest National Laboratory

As a wide bandgap semiconductor with good light emission properties, ZnO has attracted much interest because of its potential as a multifunctional material. Recent developments in bulk crystal and epitaxial film growth, along with advances in characterization methods, have expanded our understanding of this material, and created possibilities for ZnO-based optoelectronic, spin electronic, and transparent electronic applications. However, progress has been impeded by a lack of understanding and control of dopants, impurities and defects in ZnO. Difficulties in p-type doping of ZnO result from high background donor compensation of acceptors. One of the suspected background shallow donors in ZnO is H, which has been suggested to be readily incorporated during growth.<sup>1,2</sup> Theoretical calculations have predicted that H can exhibit a substitutional (on the O site) multi-center bonding configuration (H<sub>0</sub>).<sup>3</sup> However, there is thus far no experimental evidence for H<sub>0</sub> in ZnO. The focus of this study is to use nuclear reaction analysis to determine the local structural environment of H in ZnO. ZnO films are being grown in ultra-high purity H<sub>2</sub> at 500°C by pulsed laser deposition. The H(<sup>15</sup>N,αγ)<sup>12</sup>C and H(<sup>19</sup>F,αγ)<sup>16</sup>O nuclear reactions are being used in channeling and random directions to determine the position of H in the lattice. Initial results indicate that growth of ZnO in 10 mTorr H<sub>2</sub> at 500°C results in a total H concentration of ~1 x 10<sup>20</sup> cm<sup>-3</sup>. High-resolution x-ray diffraction is being used to characterize out-of-plane and in-plane lattice parameters of the doped phase. The effects of growth conditions on crystallinity as well as H concentration and position in the lattice are being investigated, and will be described in this talk.

<sup>1</sup> C.G. Van de Walle, Phys. Rev. Lett. 85, 1012-1015 (2000).

<sup>2</sup> D.M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B.K. Meyer, S.B. Orlinskii, J. Schmidt, and P.G. Baranov, Phys. Rev. Lett. 88, 5504 (2002).

<sup>3</sup> A. Janotti and C.G. Van der Walle, Nature Materials 6, 44 (2007).

9:40am **EM-ThM6 Effects of Hydrogen Ambient and Film Thickness on ZnO:Al Electrical Properties**, *J.N. Duenow*, Colorado School of Mines, *T.A. Gessert*, National Renewable Energy Laboratory, *D.M. Wood*, Colorado School of Mines, *T.J. Coutts*, National Renewable Energy Laboratory

Transparent conducting oxide (TCO) thin films are a vital part of flat-panel displays, electrochromic windows, and photovoltaic cells. ZnO-based TCOs may allow cost advantages compared to indium-containing TCOs such as indium tin oxide (ITO) or indium zinc oxide (IZO). Undoped ZnO and ZnO:Al (0.1, 0.2, 0.5, 1, and 2 wt.% Al<sub>2</sub>O<sub>3</sub>) films were deposited by RF magnetron sputtering. Controlled incorporation of H<sub>2</sub> in the Ar sputtering ambient, for films grown at substrate temperatures up to 200°C, results in mobilities exceeding 50 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> when using targets containing 0.1 and 0.2 wt.% Al<sub>2</sub>O<sub>3</sub>. Because high conductivity is achieved through high mobility at lower carrier concentration, these films demonstrate decreased infrared absorption compared to films containing the commonly used 2 wt.% Al<sub>2</sub>O<sub>3</sub>. ZnO:Al films grown in H<sub>2</sub> partial pressure (ZnO:Al:H) show no detectable changes in electrical properties during temperature-dependent Hall measurements conducted up to 170°C. Reduction in ZnO:Al mobility and carrier concentration with decreasing film thickness has been reported in the past, but mechanisms for these changes remain uncertain. Our studies show that ZnO:Al:H electrical properties are suboptimal if film thickness is less than ~300 nm. In attempts to improve the electrical properties of these thinner films, depositions were performed at room temperature with and without a 60-nm undoped ZnO nucleation layer. Results show that mobility values indeed benefit from this nucleation layer for film thicknesses less than 350 nm. However, films grown without the nucleation layer reached higher mobility values at thicknesses greater than 350 nm. This abstract is subject to government rights.

10:00am **EM-ThM7 Metallic Conductivity in Transparent Al:ZnO Films**, *O. Bamiduro*, *A.K. Pradhan*, Norfolk State University

Recently, transparent conductive oxide electrode, such as Ga or Al-doped ZnO, has attracted much attention not only as a powerful candidate material generally used for InSnO<sub>2</sub> (ITO) transparent electrodes, but also has a potential to replace ITO due to low cost, non-toxicity, and high stability in H<sub>2</sub> plasma atmosphere with good electrical and optical properties. Here we report on the metal-like conductivity in highly crystalline transparent (>85% in the visible region) Al:ZnO films grown on sapphire and glass substrates by the pulsed-laser deposition technique. Crystalline quality, surface morphology were studied on both types of films. Temperature dependent resistivity measurements of the films grown on sapphire and glass show metal-like conductivity with electrical resistivity, ~0.17 mOhm-cm and ~0.39 mOhm-cm, respectively, at room-temperature followed by either residual conductivity or a metal-semiconductor transition at low temperature due to the localization effect caused by the defects.

10:20am **EM-ThM8 Mixed Anion ZnOTe Thin Films by Pulsed Laser Deposition**, *W. Wang*, *W. Bowen*, *J. Phillips*, The University of Michigan Ann Arbor

deposition Zinc oxide and related wide-bandgap II-VI oxide alloys have received much interest for their potential application for optoelectronic and electronic devices. The primary challenges for this material remain the achievement of p-type material for junction devices, and alloy heterostructures to span the visible and ultraviolet spectral regions. The majority of recent research on ZnO and related alloys to address these challenges has focused on the doping of ZnO by group-V elements, and the investigation of mixed cation alloys CdZnO, MgZnO, and BeZnO. Very little attention has been given to mixed anion alloys related to ZnO. ZnTe is a II-VI compound semiconductor with a 2.29eV direct band gap, and typically exhibits p-type behavior. Furthermore, ZnTe has shown the ability for controllable p-type doping by nitrogen with hole concentrations of up to 1e20 cm<sup>-3</sup>. The ability to achieve p-type characteristics and the direct bandgap of ZnTe make mixed anion alloys based on ZnO and ZnTe attractive for optoelectronic devices including visible light emitters and solar cells. In this work, we report on mixed cation ZnOTe thin films deposited by pulsed laser deposition. Thin films were deposited on sapphire and GaAs substrates using a pulsed excimer laser, ZnTe target, and varying ambients oxygen, nitrogen, and high vacuum. Deposition under high vacuum resulted in crystalline ZnTe thin films with optical bandgap energy of approximately 2.3 eV based on transmission and reflectance measurements. Deposition under nitrogen ambient shows a significant red shift in optical bandgap energy, likely due to energy states introduced by nitrogen doping. Deposition of ZnTe under oxygen ambient results in a large blue shift in optical bandgap to more than 3.1 eV, with a strong dependence on oxygen partial pressure. The structural, electronic, and optical properties of these ZnOTe thin films will be presented.

10:40am **EM-ThM9 STM, LEED and ARXPS Study of MOCVD Grown a-plane ZnO and Mg<sub>x</sub>Zn<sub>1-x</sub>O (0 <= x <= 0.3) Thin Films**, *O. Dulub*, *E.H. Morales*, *U. Diebold*, Tulane University, *G. Saraf*, *Y. Lu*, Rutgers University

ZnO and Mg<sub>x</sub>Zn<sub>1-x</sub>O (0 <= x <= 0.3) thin films with a-plane orientation were grown on r-plane (011bar2) sapphire substrates using metal-organic chemical vapor deposition (MOCVD). The surface morphology of ZnO films with various thickness (20 - 2000 nm) was characterized by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) in ultrahigh vacuum (UHV). LEED patterns show well-ordered (1x1) surfaces. STM images reveal uniform surfaces with small, rectangular terraces during the initial growth stage (20 nm-thick film). Films with thicknesses of 100 and 450 nm have a characteristic wave-like surface morphology with needle-shaped domains running along the crystallographic c-direction. Films with a thickness of 2000 nm exhibit more flat surfaces with 20-100 nm wide domains running perpendicular to the c-axis, indicating variation in the strain effect caused by mismatch between substrate and film. On these thickest films, areas with facets of a different surface termination were observed as well. Angle-resolved x-ray photoemission spectroscopy (ARXPS) analysis of Mg<sub>x</sub>Zn<sub>1-x</sub>O films show that Mg atoms substitute for Zn atoms in the lattice. LEED shows that the incorporation of Mg atoms into the lattice reduces the surface roughness.

# Thursday Afternoon, October 18, 2007

## Electronic Materials and Processing

Room: 612 - Session EM-ThA

### High-K/High Mobility Substrates and Power Electronics

Moderator: C. Eddy, Naval Research Laboratory

2:00pm **EM-ThA1 Growth and Characterization of III/V Compound Semiconductors on Silicon.** *S.F. Cheng, R.L. Woo, L. Gao, R.F. Hicks,* University of California, Los Angeles

III-V materials are promising materials for high speed, low power devices in next-generation integrated circuits. However, a roadblock to implementing these materials in integrated circuit applications is the heteroepitaxial growth of III-V on silicon. Here, we have developed a process flow for the selective-area metalorganic vapor-phase epitaxy (MOVPE) of GaAs on Si (100) substrates. Arsenic passivation was demonstrated in the reactor environment at a temperature of 650 °C. The subsequent deposition of GaAs was carried out in a two-step process, with nucleation at 250-550 °C and second-step growth at 630 °C. High-resolution x-ray diffraction of films nucleated at 350°C or below exhibited polycrystalline grains, whereas films nucleated at 400 °C and above were single crystal. A clear  $c(4\times 4)$  LEED pattern of GaAs deposited on a blanket Si substrate is demonstrated for the first time. Growth on patterned Si indicates improved crystallinity as determined by XRD and plane-view TEM. The photoluminescence of SA-MOVPE GaAs on Si is shown to be nearly identical to homoepitaxial GaAs. The potential of these materials for the fabrication of high-speed devices will be discussed at the meeting.

2:20pm **EM-ThA2 STM Imaging of Selective Bonding of Hf, O, and HfO<sub>2</sub> on InAs(001)-(4x2)/c(8x2).** *J.B. Clemens, A.C. Kummel,* University of California, San Diego

Hafnium oxide (HfO<sub>2</sub>) has been successfully used as a high- $\kappa$  gate oxide on Si(100) and is being investigated as a high- $\kappa$  gate oxide for high mobility III-V semiconductors. To form an electronically passive interface on a III-V semiconductor is challenging because the bonding to the group III and group V atoms must be distinct to leave both atoms in their bulk oxidation states with an unchanged electronic structure. The bonding of Hf, O, and HfO<sub>2</sub> on the InAs(001)-(4x2)/c(8x2) surface was probed with scanning tunneling microscopy (STM) to determine the exact bonding positions at low coverage. The InAs(001)-(4x2) surface is advantageous for these studies since it has a row and trough structure with In atoms at the center of the rows and As atoms at the edges of the rows which are easy to image in STM. Furthermore, the InAs(001)-(4x2) surface contains no As-As dimers so surface atoms are rarely displaced during oxide and oxygen dosing. Although the sticking probability for O<sub>2</sub> on this surface is very low (~0.015%), it is found that O<sub>2</sub> bonds preferentially to the first layer undercoordinated In rows. This is consistent with O-metal bond formation being thermodynamically more favorable than As-O bond formation. Furthermore, the As atoms on the edge of the row have only half-filled dangling bonds so they are poor electron donors and less likely to react with oxygen than As dimer atoms found on other III-V reconstructions. Conversely, STM shows that Hf bonds initially to the second-layer tricoordinated As atoms along the edges of the In rows of the InAs(001)-(4x2) surface. This is consistent with the Hf atoms donating electrons to the unfilled dangling bonds of the second layer tricoordinated As atoms. In order to investigate the bonding geometry of HfO<sub>2</sub> on the InAs(001)-(4x2) surface, Hf and O<sub>2</sub> are co-deposited. Current work will show the result of annealing these surfaces in order to create ordered submonolayer coverages of HfO<sub>2</sub>.

2:40pm **EM-ThA3 Materials and Process Needs for Power Electronic Integration.** *K.D.T. Ngo, G.Q. Lu,* Virginia Tech, *P. Chow,* Rensselaer Polytechnic Institute

INVITED

A typical switched-mode converter contains semiconductor, conductive, magnetic, dielectric, and thermal-management elements. The wide variations in materials and processes employed to make these components, the large dimensions, and the requirements for low losses have limited the chance for integration. \*\*\* The integration strategy pursued divides the power electronic converter into three building blocks: Active, Passive, and Filter Integrated Power Electronics Modules (AIPEM, PIPEM, and FIPEM). Electro-magneto-thermal structures are described for realization of the functionalities expected from the structures. Materials and processes have been identified to verify the operation of the integrated structures. While the entire converter cannot be integrated using current technologies,

the equipment and process steps to fabricate the three types of IPEMs are similar. \*\*\* The AIPEM structure (e.g., an "embedded-power" module) contains the semiconductor devices, the associated ancillary functions (e.g., gate drives, sensing, and protection), and thermal management elements (e.g., heat spreader, heat sink, and micro-channel coolers). Interacting with the AIPEM to shape the conversion gain is the PIPEM (e.g., an integrated inductor/capacitor/transformer network) containing passive components designed to propagate energy at the switching frequency. The FIPEM (e.g., an integrated lossy transmission line for EMI filtering), on the other hand, contains passive components designed to attenuate at the switching frequency, or the frequencies beyond the useful power bandwidth. \*\*\* Semiconductor materials employed include silicon, silicon carbide, and gallium nitride. Nano-material technology has been developed for bonding and interconnects, and multiferroic nano-composites for passive integration. Other common metals, polymers, and ceramics are also used. \*\*\* Exemplified processes include "Metal Post Interconnected Parallel Plate Structure," "Flip Chip on Flex," "Dimple-Array Interconnect," and "Embedded Power." Sputtering, plating, etching, spin-coating, screen-printing, tape casting, sintering, and solder reflowing are typical process steps. New materials and processes are needed for high yield and reliable operations under wide ranges of temperature, fields, vibration, pressure, and other environmental conditions.

3:40pm **EM-ThA6 DFT Molecular Dynamics Simulation of Ge-O-Al Selective Bond Formation at the a-Al<sub>2</sub>O<sub>3</sub>/Ge(001) Interface.** *E.A. Chagarov, A.C. Kummel,* University of California, San Diego

Density-Functional Theory simulations of interface formation between amorphous Al<sub>2</sub>O<sub>3</sub> oxide and Ge(001)-(2x4) surface were performed to model the chemical bonding at the oxide-semiconductor interface. A realistic DFT sample of amorphous Al<sub>2</sub>O<sub>3</sub> was developed using "melt and cool" hybrid Classical-DFT Molecular Dynamics (MD) approach. Initially, 24 samples of 100 atoms were prepared by classical MD runs by melting initially crystalline sample. The spatial distribution of the atoms in each sample was quantified using Radial Distribution Functions (RDF), coordination distribution, and average coordination number. The sample with an atomic spatial distribution closest to the experimental geometry was DFT annealed to obtain a more realistic fully relaxed DFT geometry. The DFT annealed a-Al<sub>2</sub>O<sub>3</sub> sample was placed on a 8 layer Ge(001)-(2x4) slab and partially relaxed for 200 steps with the fixed Ge atoms allowing the a-Al<sub>2</sub>O<sub>3</sub> to adjust to Ge surface topography and to form oxide-Ge bonds. Subsequently, the top 5 layers of Ge were unfrozen, and the whole a-Al<sub>2</sub>O<sub>3</sub>-Ge system was annealed, cooled and relaxed to form a-Al<sub>2</sub>O<sub>3</sub>-Ge interface. DFT simulations of a-Al<sub>2</sub>O<sub>3</sub>-Ge interface revealed that during annealing, Al atoms migrate out of interface, while O atoms migrate into the interface. The bonding of a-Al<sub>2</sub>O<sub>3</sub> to Ge occurs mainly through O atoms forming a low density Al-O-Ge bonds to the Ge dangling bonds on the surface. It was found that several O atoms diffused into Ge bulk forming interstitials. Electronic structure analysis of the interface demonstrated that Density of States (DOS) of the interface region was approximately a superposition of a-Al<sub>2</sub>O<sub>3</sub> and Ge(001)-(2x4) DOS curves without significant new features. The oxygen-rich a-Al<sub>2</sub>O<sub>3</sub>/Ge interface is consistent with Al forming stronger bonds to O than to Ge and with experimental results. The small changes in electronic structure for a-Al<sub>2</sub>O<sub>3</sub>/Ge interface formation are consistent with the oxide reducing the number of Ge dangling bonds and only forming a low density of weakly ionic Al-O-Ge bonds.

4:00pm **EM-ThA7 Band Alignments of Y<sub>2</sub>O<sub>3</sub> on Different Group IV Substrates.** *S.Y. Chiam,* Imperial College London, UK, *W.K. Chim,* National University of Singapore, *A.C. Huan,* Institute of Materials Research and Engineering, Singapore, *J. Zhang,* Imperial College London, UK, *S.J. Wang, J.S. Pan,* Institute of Materials Research and Engineering, Singapore, *S.G. Turner,* Imperial College London, UK

Band alignment is an important property for oxides-semiconductor lineup especially for MOS devices. Band offsets for many oxides-semiconductor has and can be predicted by charge neutrality level (CNL) model (gap states model). This model however is based on an essentially "bulk" phenomenon of gap states dipoles. There have been, however, differences in the measured valence band offsets (VBO) and conduction band offsets (CBO) of oxides (especially rare-earth oxides) and the predicted offsets from the CNL model. In this work, we present the experimental data for rf-sputtered Y<sub>2</sub>O<sub>3</sub> on Si, Ge, strain-Si, strain-SiGe and relaxed SiGe. The virtual substrates were grown by GSMBE. Some of these substrates expect differences (based on various sources, investigating changes in conduction and valence band) in the valence and conduction band of less than 0.1eV. However, the VBO and CBO between the oxide and these substrates amounts often to >0.5eV. In addition, we have pre-sputtered a thin mono-

layer of Y metal before deposition of the Y<sub>2</sub>O<sub>3</sub> (in-situ). This reduces the valence band offset for the films on all the substrates. This can be explained by changes in either interface structure and/or chemical nature at the interface (dipoles). Our work shows the importance of the nature at the interface in determining the offsets between an oxide and semiconductor.

4:20pm **EM-ThA8 High-k/III-V Integration: from GaN to InSb, P.D. Ye**, Purdue University **INVITED**

The principal obstacle to III-V compound semiconductors rivaling or exceeding the properties of Si electronics has been the lack of high-quality, thermodynamically stable insulators on GaAs (or on III-V materials in general). For more than four decades, the research community has searched for suitable III-V compound semiconductor gate dielectrics or passivation layers. The literature testifies to the extent of this effort with representative, currently active approaches including sulfur passivation, silicon interface control layers (Si ICLs), in situ molecular beam epitaxy (MBE) growth of Ga<sub>2</sub>O<sub>3</sub>(Gd<sub>2</sub>O<sub>3</sub>), ex situ atomic layer deposition (ALD) growth of Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>, jet vapor deposition (JVD) of Si<sub>3</sub>N<sub>4</sub>, ALD, PVD or MBE of HfO<sub>2</sub> + Si or Ge ICL, Al<sub>2</sub>O<sub>3</sub> plasma nitridation or AlN passivation. The research on ALD approach is of particular interest, since the Si industry is getting familiar with ALD Hf-based dielectrics and this approach has the potential to become a manufacturable technology. In this talk, the authors will review some of our previous work on integration of ALD high-k dielectric Al<sub>2</sub>O<sub>3</sub> on GaAs, InGaAs and GaN, and demonstration of high performed depletion-mode III-V MOSFETs. But for very large scale integrated (VLSI) circuits or high-speed digital applications, enhancement-mode (E-mode) III-V MOSFETs within the Si CMOS platform are the real devices of interest. We will discuss on the detailed CV measurements (high frequency-low frequency CV, Quasi-static CV, split-CV, and photo-CV) on high temperature annealed ALD Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> dielectrics on GaAs and InGaAs. InGaAs includes In<sub>0.2</sub>Ga<sub>0.8</sub>As/GaAs, In<sub>0.53</sub>Ga<sub>0.47</sub>As/InP and other In-rich InGaAs materials. We will focus on some new results on inversion-type E-mode NMOSFET fabricated on p-type In<sub>0.53</sub>Ga<sub>0.47</sub>As, and InP surfaces using ALD Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> dielectrics. The maximum inversion current of ~ 400 mA/mm and G<sub>m</sub> of ~ 130 mA/mm and the middle gap interface trap density D<sub>it</sub> of low 10<sup>11</sup>/cm<sup>2</sup>-eV to 2x10<sup>12</sup>/cm<sup>2</sup>-eV is achieved at these material systems. We will also briefly report on some new CV results on high-k/InSb surface. The work is in close collaborations with G.D. Wilk, Y. Xuan, H.C. Lin, Y.Q. Wu, T. Shen, T. Yang, Z. Cheng, A. Lochtefeld, J. Woodall, M. Lundstrom, M.A. Alam, R.M. Wallace, J.C.M. Hwang, A. Liu, W. Wang, M. Santos. We also would like to thank B. Yang, M. Hong, R. Kwo, H. Gossmann, K.K. Ng, J. Bude and others who contributed significantly at the initial stage of this research.

5:00pm **EM-ThA10 Study of High-κ Dielectrics on InGaAs for CMOS Applications, F.S. Aguirre-Tostado, C. Hinkle, K.J. Choi, M. Milojevic, S.J. McDonnell, J. Kim, M.J. Kim, E. Vogel, R.M. Wallace**, University of Texas at Dallas

Scaling and performance of integrated circuits has been pushed to the limit where the substitution of Si itself by higher mobility channel materials. Bulk electron mobilities for GaAs and InGaAs are well above those obtained for Si. At room temperature, the electron mobility of InGaAs exceeds the 10,000 cm<sup>2</sup>/V-s making this material a good candidate for high-performance logic applications. In this paper we will describe chemical, structural and electrical properties of high-κ dielectrics on InGaAs channels. The chemistry and structural properties of LaAlO<sub>3</sub>, HfAlO<sub>3</sub> and HfO<sub>2</sub> on InGaAs will be presented using in-situ XPS and LEISS analysis as well as HRTEM and XRD analysis. The thermal stability for relevant thermal budgets associated with dopant activation in a surface channel MOSFET InGaAs based device is examined in view of the electrical characteristics of MOS capacitors. This work is supported by the MARCO MSD Focus Center.

## Surface Science

**Room: 611 - Session SS2+EM+TF-ThA**

## Organics and Carbon Films on Silicon

**Moderator: A.A. Baski**, Virginia Commonwealth University

2:00pm **SS2+EM+TF-ThA1 Reactivity of n-type/p-type H:Si(111) for Photoadsorption of CH<sub>3</sub>Br, T. Yamada**, RIKEN, Japan, *H. Ozawa*, The University of Tokyo, Japan, *H.S. Kato*, RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

Ultraviolet photo-assisted adsorption of CH<sub>3</sub>Br gas was examined on hydrogen terminated Si(111)-(1x1) surfaces of n-type (P-doped, resistivity 7-10 Ωcm) and p-type (B-doped, 10-40 Ωcm) substrates. After treatment of Si substrates at 1x10<sup>-5</sup> Pa of CH<sub>3</sub>Br pressure with simultaneous irradiation by high-pressure Hg lamp (100W) for 10 min - 3 hours at room temperature, high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) were applied to detect the adsorbate. On n-type H:Si(111), hydrocarbon adsorbates were observed, and on p-type H:Si(111), Si-Br stretching signal (450 cm<sup>-1</sup>) was exclusively detected. To survey the mechanism of reaction, we divided this adsorption process into UV irradiation in ultrahigh vacuum (UHV) and following CH<sub>3</sub>Br introduction without UV. Although a small amount of hydrocarbon contaminant was deposited on both n-type and p-type substrates during UHV UV irradiation, the post-adsorption of CH<sub>3</sub>Br resulted in increase of only hydrocarbons on n-type, and only Br on p-type. This result indicates that the irradiation of UV on H:Si(111) promoted photo-assisted desorption of H and leaves hydrogen vacancies, namely, dangling bonds. The difference of adsorption product between the n-type and p-type should be associated with the electronic structure of substrate modified with dopant atoms. We performed molecular-orbital calculations of various H-terminated Si(111) model clusters (sized from 32 Si atoms to 400 Si atoms) with H vacancies on the surface and a few Si atoms replaced with P or B atoms, on the basis of density functional theory (DFT). It was demonstrated that the orbital protruding over the dangling bond was the highest filled electronic orbital on P-doped cluster, whereas on B-doped, it was the lowest unoccupied orbital. This result did not change if we change the number of dangling bonds or dopant atoms. Although this approximation is too rough because of orders-of-magnitude higher dopant level than the real substrates, the result matches the classical formalism of semiconductor band bending near the surface. We further performed DFT calculations on the dangling bond coordinated with a CH<sub>3</sub>Br molecule. The dangling bond on n-type/p-type substrate attracts the CH<sub>3</sub> group/Br atom, respectively. It was recognized that the effects of dopant are crucial for the adsorption selectivity of surface dangling bonds towards organic molecules.

2:20pm **SS2+EM+TF-ThA2 Effects of Dative Bond Formation on Si(114) Reaction Pathways, D.E. Barlow**, Nova Research, Inc., *S.C. Erwin, A.R. Laracuente, L.J. Whitman, J.N. Russell, Jr.*, Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface with a single domain-like surface reconstruction composed of parallel rows of dimers, rebonded atoms, and tetramers.<sup>1</sup> We have used transmission FTIR, STM, and DFT to compare the reactions of ethylene and acrylonitrile at the Si(114)-(2x1) tetramer sites. These sites have a diene-like structure, allowing us to investigate the potential Diels-Alder reactivity of an unusual Si surface structure.<sup>2</sup> In particular, we have investigated the effects of conjugated, electron-withdrawing substituents on the dieneophile. For organic reactions, such substituents typically increase the reaction rate, often by several orders of magnitude. Ethylene reacts as the dieneophile in a Diels-Alder reaction at the tetramer site with a reaction probability of ~10<sup>-2</sup>. Surprisingly, however, we find that acrylonitrile does not undergo the Diels-Alder reaction at the tetramer sites. Rather, exposure of the clean Si(114) surface to acrylonitrile leads to three distinguishable ketenimine (-C=C=N-) structures in the FTIR spectra. Polarized transmission FTIR results indicate the presence of ordered ketenimine arrays, with strong registry to the Si(114) surface and site-dependent orientation. We have distinguished the acrylonitrile adsorption structures at the tetramer sites from those at the dimer and rebonded atom sites by analyzing site-dependent heterofunctionalized Si(114) surfaces on which we have first passivated a large portion of rebonded atom and dimer sites with ethylene, allowing the acrylonitrile to preferentially react with the remaining tetramer sites. From the polarized FTIR spectra, we conclude that the -C=C=N- structures are aligned parallel to <110> at the rebonded atom and dimer sites, but perpendicular to <110> at the tetramer sites. The differing ethylene and acrylonitrile reactivities on

Si(114) further emphasize the variable reaction pathways possible for dative bonding on reconstructed Si surfaces.

<sup>1</sup> S. C. Erwin, A. A. Baski, and L. J. Whitman, *Phys. Rev. Lett.* 77, 687 (1996).

<sup>2</sup> D. E. Barlow, et al., *J. Phys. Chem. B* 110, 6841 (2006).

**2:40pm SS2+EM+TF-ThA3 Surface Chemistry of Silicon: Making the Connection to Molecules, J.M. Buriak, D. Wang, Y. Qiao, J. Chai, University of Alberta, Canada INVITED**

The chemistry of semiconducting surfaces is a field of intense interest, not only for the prospect of exciting cutting edge applications, but also from a fundamental perspective.<sup>1</sup> Control over the surface reactivity of silicon and other semiconducting materials is critical for interfacing new molecular devices on chips and other nanotechnological applications, and to perhaps replace oxide overlayers as feature sizes on transistors become smaller than 50 nm. In this talk, we will attempt to provide a preliminary reactivity 'road map' towards understanding the organometallic surface chemistry of silicon that, interestingly, can vary greatly from that of silicon-based molecules. For example, by using the silicon surface as an electrode, electrochemistry can drive reactions that have no obvious parallels with molecular chemistry. As a result, molecules as diverse as alkynes and tetraalkylammonium salts can serve as organic sources to prepare organic monolayers directly on silicon, bound through Si-C bonds.<sup>2</sup> We will also discuss our latest results concerning the patterning of silicon surface reactivity on the nanoscale (feature sizes < 30 nm); both conjugated organic monolayers and monodisperse metallic nanocrystallites can be interfaced directly to the surface of silicon for a variety of applications.

<sup>1</sup> Buriak, J. M. "Organometallic Chemistry on Silicon and Germanium Surfaces", *Chemical Reviews*, 2002, 102, 1271-1308.

<sup>2</sup> Wang, D.; Buriak, J. M. "Trapping Silicon Surface-Based Radicals", *Langmuir*, 2006, 22 6214-6221.

**3:40pm SS2+EM+TF-ThA6 Liquid Methanol Reaction with H-terminated Silicon Surfaces, D.J. Michalak, University of California, Berkeley, S. Rivillon Amy, Air Products and Chemicals, Inc., A. Esteve, LAAS, France, Y.J. Chabal, Rutgers University**

The reaction of hydrogen-terminated Si(111) and oxide terminated silicon surface with neat anhydrous liquid methanol (CH<sub>3</sub>OH) has been studied with high resolution Fourier transform infrared spectroscopy (FTIR) to determine several factors regarding the surface chemistry. First, a high temperature reaction of atomically smooth H-Si(111) surfaces in neat anhydrous CH<sub>3</sub>OH liquid produces methoxylated surfaces that are virtually free of subsurface oxidation. At long reaction times (t > 3h), the surface saturates with Si-OCH<sub>3</sub> sites covering ~30% of a monolayer, with a residual ~70% comprised of Si-H sites. The virtually-oxide free surface facilitates two important conclusions. First, surface reaction mechanisms involving the insertion of oxygen atoms in the subsurface Si-Si back bonds can be ruled out. Because subsurface oxidation often presents deleterious surface electrical trap states, the absence of significant oxidation also holds important implications for the use of alcohol-terminated precursors in the functionalization of surface chemistry for use in electronics devices. Second, the vibration modes of the clean surface are very sharp and allow a more careful analysis of surfaces that contain subsurface oxidation. Specifically, it has been observed previously that, despite the presence of subsurface oxidation on some methoxyl-terminated surfaces, no evidence for subsurface oxygen atoms has been observed directly below Si-H sites. This is surprising from the standpoint that the surface still retains nearly 60-70% unoxidized Si-H sites. It was proposed that the oxidation may reside underneath Si-OCH<sub>3</sub> sites. In this work, comparison of partially oxidized surfaces with the virtually oxide-free surfaces demonstrates that the presence of blue shifted Si-OCH<sub>3</sub> vibrational modes is correlated with the presence of subsurface oxidation. This assignment is corroborated by studies performed on oxide-terminated surfaces that present similar, but blue shifted modes to those observed on the oxide-free H-Si(111) surface. Thus, this work demonstrates that while virtually oxide-free surface can be made, there is a large selectivity towards the formation of oxide underneath atop Si-OCH<sub>3</sub> sites relative to the Si-H sites, which retain almost exclusively unoxidized backbonds. Finally, mechanisms for the formation of oxide are presented with regard to these new results.

**4:00pm SS2+EM+TF-ThA7 Dissociative Electron Attachment Induced Growth of Thin Graphite Films or Graphene on Si(111)-7×7, D. Oh, H. Abernathy, N. Sharma, P.N. First, M. Liu, T.M. Orlando, Georgia Institute of Technology**

There is currently keen interest in developing good strategies for the growth of a few layers of graphite or graphene on substrates such as Si. We are exploring the use of low-energy electron induced dissociation of adsorbed benzene, naphthalene and phenylacetylene in the production of graphite/graphene films with good lateral heterogeneity. In this study, benzene, naphthalene or phenylacetylene is chemisorbed onto reconstructed Si(111)-7×7 surfaces. These adsorbates are fragmented via low-energy

electron bombardment at energies which are dominated by dissociative electron attachment resonances. In general, the incident electron beam can be captured by low-lying  $\pi^*$  states of the chemical precursors and can lead to controlled dissociation and the formation of reactive radicals and negative ions. These fragments can then react to form a network structure of predominantly  $sp^2$  hybridization. The deposited carbon overlayer is examined with Auger electron spectroscopy, Raman spectroscopy and scanning tunneling microscopy. The quality of the deposit and the viability of this non-thermal growth strategy will be discussed.

**4:20pm SS2+EM+TF-ThA8 Adsorption Irregularities of 1,3-Cyclohexadiene and Naphthalene on Silicon(100) Investigated by STM, DFT and an Extended Frontier Orbital Analysis, P.M. Ryan, CRANN, Trinity College Dublin, Ireland, L.C. Teague, National Institute of Standards and Technology, J.J. Boland, CRANN, Trinity College Dublin, Ireland**

We consider the reactions of 1,3-cyclohexadiene (1,3-CHD)<sup>1,2</sup> and Naphthalene on Si(100) and examine possible origins for the surface adsorption selectivity evident from STM measurements. The major adsorption products for both molecules are identified by STM. DFT calculations are carried out in order to examine the energetics of the major products and their associated structural analogs. The calculations reveal that the theoretical product distributions based on thermodynamics alone, for both systems, differ significantly from the experimental ones. We explain, using an extended frontier orbital analysis, that secondary orbital interactions which can discriminate between certain concerted reactions and are unavailable at the  $\Gamma$  point due to symmetry considerations become feasible at other  $\kappa$  points in the surface Brillouin zone. We propose that these interactions play a role in the kinetics of the adsorption process and may account for the observed reaction selectivity.

<sup>1</sup> Teague, L.C. and J.J. Boland, STM Study of Multiple Bonding Configurations and Mechanism of 1,3-Cyclohexadiene Attachment on Si(100). *Journal of Physical Chemistry B*, 2003, 107(16): p. 3820-3823.

<sup>2</sup> Teague, L.C., D. Chen, and J.J. Boland, DFT Investigation of Product Distribution Following Reaction of 1,3-Cyclohexadiene on the Si(100) Surface. *Journal of Physical Chemistry B*, 2004, 108(23): p. 7827-7830.

**4:40pm SS2+EM+TF-ThA9 CNTs on a Si(100) Surface: Dry Deposition, STM/STS, and Contacts, B. Naydenov, Trinity College Dublin, Ireland, J.J. Boland, Trinity College Dublin and CRANN, Ireland**

We present a cryogenic STM study of carbon nanotubes (CNTs) deposited on Si(100) surfaces. Imaging and spectroscopic results by means of LT-STM will be demonstrated and analyzed. Using STM-manipulations, contacts (different metals) with the CNTs are formed and characterized. Aspects of the CNTs purity, preparation, and interaction with the substrate will be discussed.

## Electronic Materials and Processing

Room: 4C - Session EM-ThP

### Electronic Materials and Processing Poster Session

**EM-ThP1 Electrical Characteristics of Aluminum Oxide Films Deposited by Spray Pyrolysis in the Presence of Ammonia**, *S. Carmona, M. Aguilar-Frutos, CICATA-IPN, Mexico, M. Garcia-Hipolito, J. Guzman, IIM-UNAM, Mexico, C. Falcony, CINVESTAV-IPN, Mexico*

Aluminum oxide films deposited by ultrasonic spray pyrolysis in the presence of a mist of H<sub>2</sub>O-NH<sub>4</sub>OH show an improvement of the overall electrical characteristics. The films were deposited on (100) silicon wafers at temperatures in the range of 400 to 550 °C. Films 200 to 300 Å thick incorporated in a metal-oxide-semiconductor structure present dielectric constants of 8, interface densities of the order of 5x10<sup>10</sup> 1/eV-cm<sup>2</sup> at midgap and a dielectric strength higher than 2MV/cm for samples deposited at 550°C. The average surface roughness for these films was of the order of 10 Å and the refraction index of about 1.6. Also the IR-transmittance spectra of these films suggest the presence of a silicon oxide interlayer for deposition temperatures above 500 °C.

**EM-ThP2 The Influence of Si Content on the Work Function of WSi<sub>x</sub> Gate Electrode**, *C.M. Lin, J.-S. Chen, National Cheng Kung University, Taiwan*

Metallic gate electrodes (including metals, metal nitrides and metal silicides) are potential candidates desirable to replace the poly-Si gate electrode for reducing the gate depletion, gate resistance, and dopant penetration problems. In addition, threshold voltage modification is necessary to achieve high-performance NMOS and PMOS devices. Refractory metal silicides have received attention for decades in MOS technology. Among the various metal silicides, tungsten silicide is of particular interest due to its low resistivity, good adhesion and high-temperature stability. The variation of nitrogen content in WN<sub>x</sub> will lead to the change of work function of W was confirmed in our previous work. In this study, we try to tune the work function of tungsten by adding Si. The W:Si ratio of WSi<sub>x</sub> is experimentally controlled. The microstructure and the C-V curves of the (WSi<sub>x</sub>/SiO<sub>2</sub>/Si) MOS structure are measured. The work function of WSi<sub>x</sub> films is extracted from the plot of flatband voltage versus SiO<sub>2</sub> thickness. For W and WSi<sub>0.56</sub> films, the work functions are 4.67 and 4.78 V, respectively. The correlation between work function and the materials characteristics of WSi<sub>x</sub> films will be discussed.

**EM-ThP3 Reduction of Defects at the SiO<sub>2</sub>/SiC Interface by MeV Electron Beam Irradiation**, *C. Jeon, J.H. Nam, W. Song, D.H. Oh, J.R. Ahn, C.-Y. Park, Sungkyunkwan University, Republic of Korea, M.-C. Jung, H.J. Shin, Pohang Accelerator Laboratory, Republic of Korea, Y.H. Han, B.C. Lee, Korea Atomic Energy Research Institute, Republic of Korea*

Among wide-band gap semiconductors, SiC has attracted interests in part because a stable native oxide SiO<sub>2</sub> can be grown only on SiC. However, metal-oxide-semiconductor field effect transistors (MOSFETs) based on SiC have shown lower electric performance than expected from bulk SiC properties.<sup>1</sup> The low electrical performance has been known to be related to defects at the SiO<sub>2</sub>/SiC interface. The defects produce fixed charges and interface trap states lowering electric performance. Several experiments using x-ray photoelectron spectroscopy have shown that the defects are Si suboxides (Si<sup>3+</sup>, Si<sup>2+</sup>, and Si<sup>1+</sup>) and Si oxycarbides (Si-C-O).<sup>2,3</sup> Therefore, the reduction of defect density at the SiO<sub>2</sub>/SiC interface is one of crucial issues for device applications of the promising wide-band gap SiC. In this study, 1 MeV electron beam was irradiated on a SiO<sub>2</sub>/SiC wafer at room temperature and ambient condition to reduce the defect density at a SiO<sub>2</sub>/SiC interface, where a native SiO<sub>2</sub> film with a thickness below 1 nm was naturally grown on a 6H-SiC(0001) wafer in air. The effect of the irradiation on the SiO<sub>2</sub>/SiC interface was investigated schematically by using synchrotron radiation scanning photoelectron microscopy with various incident photon energies (hv's). This makes it possible to measure spatially-resolved core-level spectra along directions parallel and perpendicular to a surface. Spatially-resolved Si 2p spectra show that 1 MeV electron beam irradiation reduces inevitable defects, Si suboxides (Si<sup>3+</sup>, Si<sup>2+</sup>, and Si<sup>1+</sup>) and Si oxycarbides (Si-O-C), at the SiO<sub>2</sub>/SiC interface with an ultrathin SiO<sub>2</sub> film leaving an abrupt SiO<sub>2</sub>/SiC interface. It is meaningful that the defect reduction by the irradiation succeeds at room temperature and ambient condition. Therefore, MeV electron beam irradiation is a promising method in producing a high quality SiO<sub>2</sub> and an abrupt SiO<sub>2</sub>/SiC interface.

<sup>1</sup> Silicon carbide, A Review of Fundamental Questions and Applications to Current Device Technology, edited by W. J. Choyke, H. M. Matsunami, and G. Pensl (Akademie, Berlin, 1998), Vol. I and II.

<sup>2</sup> F. Amy, P. Soukiasian, Y. K. Hwu, and C. Brylinski, Phys. Rev. B 65, 165323 (2002).

<sup>3</sup> C. Virojanadara and L. I. Johansson, Phys. Rev. B 71, 195335 (2005).

**EM-ThP4 Study on Characteristics of ZnO Thin Film by Chemical Mechanical Polishing**, *G.-W. Choi, W.-S. Lee, S.-W. Park, Chosun University, Korea, Y.-J. Seo, Daebul University, Korea, Y.-K. Lee, Chosun University, Korea*

As a semiconductor material, ZnO has many useful properties such as excellent transmittance for visible light, very high piezoelectricity and high gas sensitivity. Such properties make them well suited for the realization of many optoelectronic applications including transparent conductive oxides in display devices and solar cells, photodetectors, and transparent thin film transistors. In this paper, The electrical and the optical properties were investigated to find the optimum microstructure of ZnO thin films deposited by RF magnetron sputtering. To achieve high transmittance and low resistivity, we examined the various film deposition conditions such as deposition time, working pressure, annealing temperature, and substrate temperature. Then, electric characteristics, transmittance and surface roughness of ZnO thin films were measured by Hall effect measurement, UV-VIS spectrometer and AFM. Next, in order to improve the surface quality of ZnO thin film, we performed the chemical mechanical polishing (CMP) by change of process parameters, and compared the electrical and optical properties of the polished ZnO thin film. The thickness of ZnO films was measured by a-step. The spectral transmittance of ZnO thin films was measured in the wavelength range 200-900 nm by a UV-VIS spectrometer. This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

**EM-ThP5 Characterizations of Zn(1-x)Mn(x)O Thin Film Grown by Pulsed Laser Deposition**, *D.-R. Liu, C.-Y. Su, National Applied Research Laboratories, Taiwan*

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magnetooptical switches. ZnMnO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, the Zn(1-x)Mn(x)O (0.04 < x < 0.30) thin films were grown on sapphire(0001) substrates by Nd:YAG pulsed laser deposition(PLD). The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR). Atomic force microscopy (AFM) and magnetic force microscopy (MFM) were employed to characterize the surface properties of these films. The high-resolution x-ray diffraction was used to evaluate the crystal quality of the films. The magnetic properties of the ZnMnO thin films were measured by a superconducting quantum interference device (SQUID) magnetometer. Photoluminescence (PL) spectroscopy and ellipsometer were used to characterize the optical properties. The results show that oxygen is very important for the properties of ZnMnO thin films.

**EM-ThP6 Effect of Buffer Layer on InN Films Grown by UHV RF-MOMBE**, *W.C. Chen, C.-C. Kei, H.C. Pan, National Applied Research Laboratories, Taiwan, S.Y. Kuo, Chang Gung University, Taiwan, J.S. Chen, C.N. Hsiao, National Applied Research Laboratories, Taiwan*

InN nitride films were grown by using a metal-organic molecular beam epitaxy system. Trimethyl-indium and RF radical nitrogen were used as group III and V sources, respectively. Ga-doped ZnO and AlN buffer layers were used to improve the film quality of InN on silicon substrate. The growth rate of InN film can reach 25nm/min by using the Ga-doped ZnO buffer layer. According to X-ray diffraction and field emission transmission electron microscope results, the InN films are polycrystalline wurtzite with (0002) preferred orientation. Compared with the AlN buffer, the Ga-doped ZnO film can improve the film quality of InN. Photoluminescence result suggests that the band gap of InN film is around 0.65eV. Hall effect measurement reveals that the sheet carrier concentrations of InN film is 5 × 10<sup>17</sup> cm<sup>-2</sup>. The growth kinetic of InN films could be controlled by adjusting the III/V ratio, RF plasma power and growth temperature.

**EM-ThP7 Preparation and Characterization of HfO<sub>2</sub> Thin Films Prepared by Atomic Layer Deposition on Silicon**, *K.T. Kim, G.H. Kim, J.C. Woo, C.I. Kim, Chungang University, Korea*

In recent years, the continuous downward scaling of dynamic random access memory capacitors, requires exploitation of capacitive devices of advanced topology, i.e. stacked or trenced structures. In choosing the replacement high-k materials for SiO<sub>2</sub> for the transistor gate region several challenging factors should be taken into account such as: a) the dielectric-

silicon interface quality and stability b) the relation between the dielectric constant and the energy level configurations (energy band gap) c) energy band offsets, which could lead to an increase in the leakage current d) defect density at the interface. Among the many possible candidate high-k (15-30) dielectric materials, HfO<sub>2</sub> emerging as a promising gate dielectric material, due to its high dielectric constant and superior thermal stability on Si substrates. Moreover, the ALD (atomic layer deposition) method is preferred for obtaining these high quality high-k dielectric layers, because of its excellent thickness controllability and low thermal budget. In the present study, HfO<sub>2</sub> thin films were atomic layer deposited from the liquid hafnium precursor TEMA (Hf[N(CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)]<sub>4</sub>) precursor and O<sub>3</sub> oxidation and were characterized using angle resolved X-ray photoelectron spectroscopy, scanning transmission electron microscopy, and electron energy loss spectroscopy.

**EM-Thp8 Characterization of Plasma Etching Induced Interface States at Ti/p-SiGe Schottky Contacts, M. Mamor, Sultan Qaboos University, Sultanat of Oman**

SiGe/Si heterojunctions are particularly attractive in microelectronic and optoelectronic applications such as in heterojunction bipolar transistors, modulated doped field effect transistors and infrared detectors. SiGe/Si heterostructures provide new possibilities to engineer the bandgap in a material compatible with mature Si technology and they are now widely used to release novel devices integrated with silicon-based circuits. Plasma etching is widely used in the semiconductor industry as it offers the capability of performing many processes in vacuum without exposing the semiconductor surface to the atmosphere. However, these plasma-etching techniques also result in lattice damage at and below the surface, which alters the electrical and optical properties of the etched semiconductor surface. We have used electrical measurements (DLTS) complemented by current-voltage (I-V) and capacitance-voltage (C-V) over a wide temperature range (100-300 K) at frequencies of 10-100KHz for assessment of the defects introduced in Si<sub>0.95</sub>Ge<sub>0.05</sub> by argon plasma sputter etching. From DLTS, defect concentration depth profiling was extracted and revealed that the main defect introduced during argon plasma sputtering is located very close to the surface. I-V and C-V analysis shows that the electrical characteristics deviated from the ideal case and indicates the presence of lateral inhomogeneities of the barrier height, resulting from the plasma etching induced surface states at Ti/SiGe interface. From the low frequency and high frequency C-V plots, the interface states density and their energy distributions were extracted.

**EM-Thp9 DC-to-RF Dispersion Effects in AlGaIn/GaN HEMTs Operated Under High Stress, P.B. Shah, B. Huebschman, E. Viveiros, K. Kingkeo, A. Hung, K.A. Jones, US Army Research Laboratory**

Communication and radar applications place strong requirements for linearity, efficiency, gain and power handling capability on high power, high frequency AlGaIn/GaN HEMT performance. In AlGaIn/GaN HEMTs, the surface, interface and bulk traps have been identified as the cause of nanosecond and microsecond range drain-source current transients present during device turn-on and turn-off. These transients drain power from the source, degrade transmitted information, and affect system operating life. Therefore, it is important to understand the causes of these transients and to reduce their effects, through modeling, and characterization. We focus on physics based and empirical spice models because, once developed, these models will allow design and optimization of MMICs taking into account the transients. Both, unpassivated and AlGaIn HEMTs passivated with Si<sub>3</sub>N<sub>4</sub>, and SiO<sub>2</sub> are considered. The surface traps act as virtual gates, and to model them we are paralleling HEMT and FET models available in Agilent's ADS software with passive elements subcircuits. Adjusting the modulating pulse duty cycle, and gate and drain voltage biases have provided high-power / high-temperature operation data. Results indicate that although Si<sub>3</sub>N<sub>4</sub> mitigates drain lag effects at low power levels, the transients still appear at higher operation power levels. Also, the transients are not as clearly related to pre- and post-kink regions on the I-V characteristics. The drain lag ratio (off state drain current overshoot value / drain current steady state value) increases with device heating due to large ID and large VDS (20V). Furthermore, the slope of the drain current decay is also influenced by the gate bias present after the drain bias has returned to zero. Gate lag measurements on a number of AlGaIn/GaN HEMTs indicate that the turn-on transient is much shorter (~35 ns) than the turn-off transient (~70 ns) and the drain-current waveform when the HEMT is switched on will have different profiles -- in some cases concave and other cases convex. Furthermore, only in some devices as the time interval with low gate bias (VGS = 0) increases, the drain current in the device's on-state increases, even if most of the turn-on pulse at the gate is applied while VDS = 0, due to carrier heating. With accurate modeling to match the DC I-V, gate lag and drain lag transients, and S-parameter device data, models were verified and used to reverse engineer the AlGaIn/GaN HEMT.

**EM-Thp10 Ohmic Contacts to n- and p-type GaN Based on TaN, TiN, and ZrN, L.F. Voss, L. Stafford, R. Khanna, B.P. Gila, C.R. Abernathy, F. Ren, I.I. Kravchenko, University of Florida**

We examined the potential of transition metal nitrides as a diffusion barrier for Ti/Al-based Ohmic contacts to n-GaN and Ni/Au-based Ohmic contacts to p-GaN. The annealing temperature (600-1000°C) dependence of Ohmic contact characteristics using either Ti/Al/X/Ti/Au (n-Ohmics) or Ni/Au/X/Ti/Au (p-Ohmics) metallization schemes, where X is TaN, TiN, or ZrN, deposited by plasma-assisted sputtering were investigated by contact resistance and Auger Electron Spectroscopy (AES) measurements. For n-GaN ( $n \sim 3 \times 10^{17} \text{ cm}^{-3}$ ), the as-deposited contacts were rectifying and transitioned to Ohmic behavior for annealing at  $\geq 600^\circ\text{C}$ . A minimum specific contact resistivity of  $\sim 6 \times 10^{-3} \Omega \cdot \text{cm}^2$  was obtained after annealing over a broad range of temperatures (600-900°C for 60 secs), comparable to that achieved using a conventional Ti/Al/Pt/Au scheme on the same wafer. The contact morphology became considerably rougher at the high end of the annealing range. The long-term reliability of the contacts was also examined—each contact structure showed an increase in contact resistance by a factor of 3-4 over 24 days at 350°C in air. AES profiling showed that long-term aging had little effect on the nitride-based contact structure. For annealing temperatures greater than 500°C, the contacts to p-GaN ( $p \sim 10^{17} \text{ cm}^{-3}$ ) displayed Ohmic characteristics and reached a minimum specific contact resistance of about  $2 \times 10^{-4} \Omega \cdot \text{cm}^2$  after annealing at 700°C for 60 s. The specific contact resistance was stable on annealing up to at least 1000°C. However, at high temperatures the morphology of the contacts became very rough and a large degree of intermixing between the metallic layers was observed. The thermal stability of these contacts were found to be superior as compared to conventional Ni/Au, which displayed poor characteristics at anneal temperatures greater than 500°C.

**EM-Thp11 XPS and LEISS Study of GaAs Surface Preparation using Ammonium Hydroxide, F.S. Aguirre-Tostado, M. Milojevic, S.J. McDonnell, R.M. Wallace, University of Texas at Dallas**

The use of high-mobility channel materials, such as GaAs and InGaAs in addition to high-κ dielectrics has attracted substantial interest as a means to maintain integrated circuit scaling and performance. For ultra-thin dielectric films, the quality of the high-κ/semiconductor interface plays a crucial role in determining the electrical properties of a device. GaAs surface preparation plays an important part in controlling the interfacial chemistry.<sup>1</sup> Previous photoemission studies<sup>2,3</sup> have examined the effects of etching GaAs with HCl, HF and NH<sub>4</sub>OH in a controlled atmosphere (argon,<sup>2</sup> nitrogen<sup>3</sup>). This paper examines the chemistry of the GaAs surface after a NH<sub>4</sub>OH-based cleaning procedure, without the use of a controlled atmosphere, for high-κ dielectric deposition. In-situ anneals up to 450 °C promote As-oxide dissociation resulting in the formation of Ga-oxide and As desorption. An in-situ bulk and interface study of sputter deposited LaAlO<sub>3</sub> on GaAs is also presented on this surface. This work is supported by the MARCO MSD Focus Center.

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**EM-Thp12 Study on Scalability of MTJ Cells Using SPM, S. Kim, K. Kim, I. Chung, Sungkyunkwan University, Korea**

We investigated various sizes of magnetic tunneling junction (MTJ) cells which are considered as an alternative nonvolatile storage due to its unique characteristics such as high speed, low operation voltage and high endurance. We studied switching field variations in terms of the sizes of sub-micron MTJ cells by measuring the I-V characteristics of MTJ cells and I-H loops, which was obtained by measuring the tunneling current with sweeping a magnetic field. In addition, We obtained magnetic domain images utilizing magnetic force microscope (MFM) for MTJ cells to understand the variation in I-H loop. We found that the switching field of the MTJ cell tends to increase as the size decreases due to the demagnetization field.

**EM-Thp13 The Effect of Synthesis Methods on the Properties of ZnO:Ga Nanoparticle Ceramic Scintillators, D.M. DeVito, B. Kesanli, B.L. Armstrong, J.O. Ramey, C.J. Rawns, J.Y. Howe, Oak Ridge National Laboratory, N. Giles, West Virginia University, L.A. Boatner, J.S. Neal, Oak Ridge National Laboratory**

A number of different radiation detection applications require scintillators with high light output, good attenuation power, low afterglow, and very fast decay times. Fast decay times are of primary importance in positron emission tomography (PET) and nuclear physics experiments. Zinc oxide doped with gallium is known for its fast scintillation properties (sub-nanosecond decay time) under a variety of excitation conditions (alpha, gamma, UV). The expanded development of synchrotron radiation for the

investigation of advanced materials has only underscored the need for continued development. This work investigates the effect that synthesis method (urea precipitation, solution phase, combustion synthesis) has on gallium incorporation, particle size and distribution and resulting emission using a wide variety of analytical techniques.

**EM-ThP14 Magnetic Field Dependent Electrical Properties of Vertically Grown Ni Single Nanowire, A.-Y. Koo, H. Yang, C.J. Kang, Y.S. Kim, Myongji University, Korea, J.Y. Cho, Korea University, South Korea, Y.J. Choi, Myongji University, Korea, Y.K. Kim, Korea University, South Korea**

Magnetotransport of nickel nanowires has been widely investigated due to its potential application to magnetic memory devices. However, because of the difficulty to make a good electrical interconnects between single nanowire and metal pad, most magnetotransport studies have been performed on bundles of nanowires embedded in a template or a single nanowire with e-beam lithographically patterned metal contact. In order to overcome the averaged-out information of the bundles of nanowire and the complexity in patterning metal pads, we developed a novel and simple method to measure the magnetotransport properties of Ni single nanowire electrodeposited in an AAO template by adopting scanning probe microscopy technique. In addition to the magnetotransport properties, we studied the electrical properties of Ni single nanowire using the Electrostatic Force Microscopy (EFM) and Scanning Capacitance Microscopy (SCM). We will discuss the magnetic field dependent electrical property variation due to the crystallographic structure of Ni nanowire.

**EM-ThP15 Photoluminescence Study of Silicon Nanoclusters Embedded in a SiO<sub>2</sub> Matrix Deposited by Reactive Sputtering and Implanted with Si Ions, J. Carrillo, G. Garcia, Universidad Autonoma de Puebla, Mexico, M. Melendez, Centro de Investigación y Estudios Avanzados-IPN, Mexico, W. Calleja, Instituto Nacional de Astrofisica, Optica y Electronica, Mexico**

The search for a luminescence material compatible with silicon-based integrated circuit processing technology is a need for optoelectronic applications, and has received great attention in recent years. The optical properties of silicon nanocrystals in SiO<sub>2</sub> have been studied extensively since visible room temperature photoluminescence (PL) was first observed in such systems. Several models have been suggested in attempts to clarify the origins of the PL properties of indirect-gap group-IV semiconductor nanocrystals. For example, some researchers explain their results using a three-dimension quantum confinement model, while others believe that interface defects and emitting centers are responsible for PL emission. In this paper, the dependence of silicon nanoclusters embedded in a Si-implanted SiO<sub>2</sub> matrix deposited by reactive sputtering and after annealing is presented. Red photoluminescence has been observed at room temperature from deposited films and its intensity exhibits a strong dependence on the temperature and time of annealing. High-resolution transmission electron microscopy, Fourier transform infrared transmission spectra and PL results are used to discuss the emission mechanisms. We acknowledge the partial financial support of VIEP-BUAP through the project 06/EXC/06-G.

**EM-ThP16 Particle Emission from Zinc Oxide during 193-nm Excimer Laser Irradiation<sup>1</sup>, E.H. Khan, S.C. Langford, J.T. Dickinson, Washington State University**

We report observations of particle and light emission from single crystal and anodic ZnO during pulsed 193-nm irradiation by quadrupole mass selected time-of-flight measurements and photoluminescence spectroscopy. The particle emissions in particular are relevant to thin film production by laser ablation deposition. At fluences between 50 and 600 mJ/cm<sup>2</sup>, the only ion observed from single crystal ZnO at our level of sensitivity is Zn<sup>+</sup>. The mean kinetic energy of  $3.3 \pm 1.6$  eV is consistent with electrostatic ejection from defect sites with a net positive charge. Zinc ions absorbed on top of surface electron traps would experience a repulsive force when the underlying trap is photoionized. During prolonged irradiation, the Zn<sup>+</sup> intensity drops quickly, reflecting the depletion of surface defects by the emission process. Consistent with the radiation hardness of ZnO, single crystal remains transparent during prolonged irradiation. However, the sample photoluminescence evolves from greenish-blue, to deep blue, and to violet. At fluences above 600 mJ/cm<sup>2</sup>, the Zn<sup>+</sup> intensities increase rapidly and other positive ions appear, including O<sup>+</sup> and O<sub>2</sub><sup>+</sup>. Neutral O and O<sub>2</sub> appear, followed by neutral Zn at 775 mJ/cm<sup>2</sup>. Analyses of the neutral time-of-flight distributions indicate effective surface temperatures near 600 K at 800 mJ/cm<sup>2</sup> and near 1100 K at 1.2 J/cm<sup>2</sup>. These temperatures are well below the melting point of ZnO, suggesting that the observed neutral species are produced photochemically and desorb thermally. At these fluences, intense ion emissions persist for many thousands of laser pulses; defects consumed in the emission process are continuously replenished. Emissions from anodic black ZnO are similar to the emissions from single

crystals except that comparable emission intensities are achieved at lower fluences for the black ZnO. Weak emissions are also observed from the native oxide on electropolished Zn plate.

<sup>1</sup>We thank Dr. L. Boatner of Oak Ridge National Laboratory for providing single crystal ZnO. This work is supported by the DOE grant DE-G03-02ER45988.

**EM-ThP17 Pentacene TFTs with Ferroelectric Gate Insulators for Non-Volatile Memory Element, W. Choi, S.H. Noh, J.M. Choi, D.K. Hwang, S. Im, Yonsei University, Korea**

Field effect transistors using ferroelectric materials as a gate insulator (FeFET) could be next generation-memory elements because of its attractive characteristics: non-volatile data retention, small size, non-destructive read-out, and fast programming speed. Recently, thin-film transistors (TFTs) with organic ferroelectric gate insulators have been studied since the fabrication of FeFET is possible at the low temperature compatible with glass substrates. While previous researches showed high performances in terms of good retentions and large hysteresis loop, they have some problems such as high programmable voltage (~100 V), a low mobility (~10<sup>-3</sup> cm<sup>2</sup>/V s). To overcome aforementioned drawbacks, we fabricated pentacene based FeFET with the gate insulator composed of stacking multi-layers. In this presentation, we report on the fabrication of pentacene thin-film transistor with a poly-4-vinylphenol (PVP)/Poly(vinylidene fluoride/trifluoroethylene) (P(VDF/TrFE))/PVP triple-layer gate insulator. A triple-layer polymer gate insulator is deposited on an indium-tin oxide (ITO)/glass substrate by sequential spin-casting processes: 45 nm-thick PVP for a smoothing layer, 130 nm-thick P(VDF/TrFE) for a ferroelectric layer and 240 nm-thick PVP for a buffer layer. Each layer has own role for non-volatile memory thin film transistor. Our FeFET with the PVP/P(VDF/TrFE)/PVP triple layer exhibits a field effect mobility of 0.2 cm<sup>2</sup>/V s at each memory state and ~15V threshold voltage shift in the transfer characteristics which originates from the polarization of the ferroelectric layer by 50V writing voltage. The retention time was measured for 10<sup>4</sup> second under constant read condition. More and advanced details will be discussed in coming presentation.

**EM-ThP18 Flexible Organic Thin Film Transistor using Al<sub>2</sub>O<sub>3</sub>-PVP Nano-Composite Gate Dielectrics, H.Y. Noh, Y.G. Seol, S.I. Kim, N.-E. Lee, Sungkyunkwan University, Korea**

Organic TFTs with low threshold voltage (V<sub>T</sub>), low-leakage current, and high current on-off ratio are needed for various applications in flexible electronics. Employment of organic/inorganic nano-composite gate dielectrics may provide a low V<sub>T</sub> and flexibility improvement in OTFT devices. For this purpose, the nano-composite gate dielectric layers composed of the PVP polymer matrix and alumina nano-particle filler were investigated in this work. Treatment of alumina nano-particles by a coupling agent was carried out for improved dispersion of the nano-particles and their chemical binding with the PVP matrix. Flexible organic thin film transistors were fabricated using pentacene semiconducting layer and electroplated nickel (Ni) gate electrode on flexible polyimide substrate. Electroplated gate electrode fabricated on the plasma-treated polyimide substrate also provides a good adhesion. PVP/Al<sub>2</sub>O<sub>3</sub> nano-composite layer with different volume fractions was spin-coated. Pentacene and gold source-drain electrodes were thermally evaporated on the gate dielectric layer using a shadow mask in vacuum chamber. Leakage current of the nano-composite gate dielectric was reduced by two order magnitude compared to that of pure PVP layer for the same film thickness. Electrical measurements of the OTFT devices showed the electrical performance of a field-effect channel mobility of 0.94 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>, an on/off current ratio of 10<sup>5</sup>, a threshold voltage of -11.5V. Flexible tests indicated that the device with the nano-composite gate dielectric has the electrical performance superior to the device with pure PVP gate dielectric with repetitive cyclic bending.

**EM-ThP19 Fabrication and Characterization of Pentacene Thin Film Transistor with a Polymer Insulator As Gate Dielectric, C. Lee, K. Seo, J. Ko, J. Lee, I. Chung, Sungkyunkwan University, Korea**

Interfacial properties between semiconductor and insulator are critical to determine the performances of organic thin film transistors (OTFTs). In this study, we have fabricated OTFT with a back gate structure on the patterned pentacene active region. We studied the variation of electrical properties in terms of polyvinyl cinnamate (PVCN) which was used as a gate dielectric with different mole concentrations (6%, 7%, 8%). We investigated the leakage current behavior by obtaining topology and its current image simultaneously using scanning probe microscope (SPM). Also, we extracted the electrical properties such as mobility, threshold voltage V<sub>T</sub> and On/Off ratio from IDS-VDS, IDS-VGS characteristics of OTFTs.

**EM-ThP20 Differentiating True Tunneling from Defect Dominated One, Using Current-Voltage Curve Fitting.** *A. Vilan*, Weizmann Institute of Science, Israel

The shapes of current-voltage curves which originate from either true tunneling across the insulating film or from metallic shorts through the film (defects) are extremely similar.<sup>1,2</sup> While this problem is known since the 1960's,<sup>3</sup> there is yet no direct solution for it. An evidence for tunneling is received only by complementary observations such as characteristic vibronic features (IETS, molecules)<sup>4</sup> or magneto-resistance below  $T_c$  (superconductors).<sup>2</sup> The uncertainty regarding defect transport means that the nominal junction's geometry (namely contact area and insulator thickness) is not necessarily relevant. This motivated a search for a simplified modeling of charge transfer which avoids any prerequisite input parameters and relies solely on graphically extracted parameters. In my talk, I will show that the two popular, highly non-linear current-voltage (I-V) relations of inelastic tunneling (Simmons model<sup>5</sup>) and nonresonant super-exchange (Mujica-Ratner model<sup>6</sup>) can be reasonably approximated by simple cubic relations of two characteristic parameters: the equilibrium conductance ( $G_0$ ) and the shape factor ( $\rho$ ).<sup>7</sup> Both  $G_0$  and  $\rho$  depend on barrier height and width while contact area contributes only to  $G_0$ . Therefore, correlating between  $G_0$  and  $\rho$  is highly informative in evaluating the actual junction parameters. In case of defect dominated transport, the extracted contact area would be much smaller than the nominal one, providing a direct experimental indication for the quality of the junction. This approach can be extended also to the Fowler-Nordheim relations describing field emission at high bias range. The proposed analysis would be demonstrated on various experimental and simulated I-V's.

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**EM-ThP21 Dye Doped Red Organic Light-emitting Diode.** *L. Li*, China Aerospace and Technology Corporation No.513 Institute, China

Full color display is the goal of organic light-emitting diode(OLED), but the making of stable red organic light-emitting diodes is a great barrier in mass production of OLED and is also the most interesting study nowadays. Some red light-emitting diodes have been realized by doping a dye rubrene with different dopant concentrations in light-emitting layers, the configuration of devices is ITO/CuPc/NPB/Alq3:rubrene:DCJTB /Alq3/LiF/ Al, where NPB and Alq3 is used respectively as hole transport layer and electron transport layer. By using the theories of Forster and energy band, it is found that the main energy transfer mechanism in doped red OLED is not Forster energy-transfer but sequential carrier trapping mechanism, and rubrene can assist energy transfer from Alq3 to DCJTB more efficiently, which greatly improves the luminescence efficiency and performances of devices.

**EM-ThP22 Photoluminescence Characterization of Polythiophene Films Doped with Highly-Functional Molecules.** *H. Kato, S. Takemura, H. Koba, Y. Mori, Y. Matsuoka, Y. Watanabe, K. Shimada, T. Hiramatsu, N. Namba, K. Matsui*, Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with highly-functional molecules such as copper phthalocyanine (CuPc), fullerene C60, rhodamine B and TCNQ was synthesized and characterized by photoluminescence measurements in order to fabricate organic optical hybrid materials. The electrochemical polymerization was performed in acetonitrile containing thiophene monomer and (Et)4NBF4 as a supporting electrolyte and the polymerization on an ITO substrate was conducted by applying positive voltage to the anode. The molecule was injected by electrochemical and diffusion methods. A photoluminescence emission peak was observed at 594 nm in the case of PT doped sample with CuPc by diffusion method. The emission peak was observed at 540 nm shifted to the lower wavelength in the case of electrochemically positive voltage applied sample after CuPc was diffused into the PT. Fourier transform infrared spectroscopy (FTIR) measurements suggested the partial deformation of the aromatic structure of CuPc and a polymer-CuPc linkage. Adding C60 molecules to the CuPc diffused PT sample by the diffusion method made the emission peak shift to the higher wavelength at 730 nm suggesting the molecular interaction between CuPc and C60 in the photoluminescence emission process because double emission peaks were observed at 590 and 735 nm in the case of single doping of C60. Double doping of C60 and CuPc in PT was also investigated by FTIR. In the case of single doping of C60, successive electrochemical process made the double emission peaks a single peak at 580 nm. The FTIR measurements suggested charged states of C60 or a polymer-C60 linkage. The present work clarified that the photoluminescence emission peak position varied and was controlled by

electrochemically applying voltage or adding specific molecules. This work was supported by High-Tech Research Center Project aided by MEXT.

**EM-ThP23 Effect of Water Immersion and Surface Compositional Profile of Photoacid Generator Molecules in Photoresist Materials.** *S. Sambasivan, V.M. Prabhu, D.A Fischer*, National Institute of Standards and Technology, *L.K. Sundberg, R.D. Allen*, IBM Almaden Research Center

Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to quantify the surface composition and depth profiling in the top 2 to 6 nm range of photoacid generators (PAG) in thin film photoresist materials. By considering model compositional profiles, NEXAFS distinguishes the surface molar excess within the top 6 nm from the bulk. A surface enriched system, triphenylsulfonium perfluorooctanesulfonate (TPS-PFOS), is contrasted with a perfluorobutanesulfonate (TPS-PFBS) photoacid generator, which displays an appreciable surface profile within a 6 nm segregation length scale. A comparative study of the surface composition of PAG (TPS-PFOS, TPS-PFBS and TPS-Triflate) in photoresist system before and water immersion was monitored via NEXAFS. Results reveal that the loss of PAG occurs after the water immersion in all the three different PAG system examined. Detailed quantification of the PAG loss due to water immersion was seen to critically depend on the size of the PAG and its solubility in water. TPS-PFOS photoacid generator largest in size despite its least solubility in water showed the maximum loss after water immersion followed by TPS-PFBS and TPS-Triflate. These results, while applied to 193-nm photoresist materials, highlight a general approach to quantifying NEXAFS partial electron yield data and find application to immersion lithography fundamentals.

**EM-ThP24 Improvement of Ferroelectric Properties of Pb(Zr,Ti)O3 Thin Film Capacitor Fabricated by Chemical Mechanical Polishing through Post Cleaning Process.** *Y.-K. Jun, P.-G. Jung, P.-J. Ko*, Chosun University, Korea, *N.-H. Kim*, Sungkyunkwan University, Korea, *W.-S. Lee*, Chosun University, Korea

Chemical mechanical polishing (CMP) process was proposed to fabricate the ferroelectric Pb(Zr,Ti)O3 capacitor instead of plasma etching process for the vertical profile without plasma damage in our previous study. Our previous study showed that good removal rate with the excellent surface roughness compared to plasma etching process were obtained by CMP process for the patterning of Pb(Zr,Ti)O3 thin film. The post cleaning process was also one of the very important parameters influenced on ferroelectric properties of Pb(Zr,Ti)O3 thin film capacitor. The ferroelectric properties were degraded without post cleaning process. However, the optimized post cleaning process for Pb(Zr,Ti)O3 thin film was not reported. In this study, the effects on the degradation of Pb(Zr,Ti)O3 thin film capacitors of the contaminations such as slurry residues were investigated. And the exclusive cleaning chemicals for Pb(Zr,Ti)O3 thin film were developed in this work. The improved ferroelectric properties of Pb(Zr,Ti)O3 thin film capacitor were obtained with the optimized post cleaning process after fabrication of Pb(Zr,Ti)O3 thin film capacitor by CMP process. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2006-005-J00902).

**EM-ThP25 Pressure Damage to BLT Thin Film Capacitor Fabricated by Chemical Mechanical Polishing Process.** *P.-G. Jung, Y.-K. Jun, S.-H. Shin, P.-J. Ko*, Chosun University, Korea, *N.-H. Kim*, Sungkyunkwan University, Republic of Korea, *W.-S. Lee*, Chosun University, Korea

BLT thin films have many advantages such as highly fatigue resistance, low processing temperature, and large remanent polarization for high-density ferroelectric memories. However, the problems by plasma etching in patterning process of BLT thin films such as the angled sidewall preventing the densification of ferroelectric memory and being apt to receive the plasma damage were reported. Chemical mechanical polishing (CMP) process was proposed to fabricate the ferroelectric capacitor instead of plasma etching process for the vertical profile without plasma damage. CMP characteristics were presented in E-MRS 2006 spring meeting. CMP characteristics such as the removal rate and WIWNU% were improved by the increase of CMP pressure; however, the ferroelectric properties including polarization-electric field (P-E) characteristics of BLT capacitor fabricated by CMP process with the highest CMP pressure condition were disappeared. Bi content of BLT thin film was rapidly decreased as the increase of CMP pressure surface analysis. This means that Bi was easily removed in high CMP pressure. Therefore, the CMP pressure was controlled in CMP process for BLT thin film capacitor although the removal rate of BLT thin film became lower. Ferroelectric properties of BLT thin film capacitor were recovered with the vertical sidewall without the plasma damage. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

**EM-ThP26 A Study on the Electrochemical Reaction of Cu Electrode using Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) Method.** *Y.-K. Lee, S.-W. Park, S.-J. Han, G.-W. Choi*, Chosun University, Korea, *Y.-J. Seo*, Daebul University, Korea, *W.-S. Lee*, Chosun University, Korea

Chemical mechanical polishing (CMP) is the most commonly used planarization technique in semiconductor process for ULSI applications. As its name indicates, CMP process depending on the chemical interaction of the slurry with polishing wafer and mechanical down force applied to the wafer. Recently, the application of CMP has been especially popular in the fabrication of Copper damascene structures. However, the low-k materials at 65nm and below device structures because of fragile property, requires low down-pressure mechanical polishing for maintaining the structural integrity of under layer during their fabrication. Also, the problems faced by copper CMP process is the lower removal rate due to the low mechanical down force required by the low k dielectric and to reduce dishing and erosion. To solve these problems, in this paper, we studied electrochemical mechanical polishing (ECMP) as an epoch-making technology that uses electrical current and voltage for copper CMP process. In this experiment, 2 x 2 Cu disk of 99.99% pure was used as experimental samples in a standard two-electrode with Cu working electrode (WE), Pt counter electrode (CE). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) Method were plotted for each of the electrolyte (NaNO<sub>3</sub>) and concentration level. And then, we investigated that how this chemical affect the process of voltage induced material removal in ECMP of Copper. This work was supported by grant No. (R01-2006-000-11275-0) from the Basic Research Program of the Korea Science & Engineering Foundation and by Korea Research Foundation Grant (KRF-2006-005-J00902).

**EM-ThP27 Voltage-Activated Electrochemical Reaction of Cu Electrode for Electrochemical Chemical Mechanical Polishing (ECMP) Application.** *S.-J. Han, S.-W. Park, Y.-K. Lee, G.-W. Choi*, Chosun University, Korea, *Y.-J. Seo*, Daebul University, Korea, *W.-S. Lee*, Chosun University, Korea

The chemical mechanical polishing (CMP) process has been widely used to obtain global planarization of inter-metal dielectric (IMD) layers, inter-layer dielectric layers (ILD) and pre-metal dielectric (PMD) layers. Also, several semiconductor device and materials manufacturers have used this method. Especially, copper CMP has become an integral part of multilevel interconnection process. However, for the fabrication of 65nm and beyond technology nodes with fragile low k dielectric and copper, the down force of CMP process must be greatly reduced or eliminated to manage the low mechanical strength of low k film. To overcome these problems, we developed a new planarization technology that uses electrolyte chemistry instead of abrasive slurry. The current-voltage (I-V) curves were employed, in this paper, to evaluate the effect of electrolyte concentration on the reaction trend. From the I-V curve, the electrochemical states of active, passive, transient, and trans-passive could be characterized. The scanning electron microscopy (SEM) was used to observe the surface profile. The energy dispersive spectroscopy (EDS) spectrum was employed to analyze metallurgical components on the surface. From these analyses, it was important to understand the electrochemical mechanisms of the electrochemical chemical mechanical polishing (ECMP) technology. This work was supported by grant No. (R01-2006-000-11275-0) from the Basic Research Program of the Korea Science & Engineering Foundation and by Korea Research Foundation Grant (KRF-2006-005-J00902).

**EM-ThP28 SEM Image Analysis and Resistance Measurements of Cu Via with Defects on a Test Wafer.** *S. Suzuki, K. Umemura, T. Sunaoshi, Y. Nakano*, Hitachi High-Technologies Corporation, Japan

In LSI process, it is necessary for improvement of yield to inspect and analyze internal defects (e.g. void, etching-stop) of Cu interconnects after an electrical probing test. However, there are complicated and time-consuming procedures that consist of inspection of defects, samples making with focused ion beam (FIB) and cross section observation with scanning electron microscope (SEM). Therefore we have proposed more effective analysis system combined of SEM inspection and electrical probing equipment. This paper presents a relation between voltage contrast (VC) of SEM images and electrical resistance of via on a simple test wafer. The Via patterns of oxide (diameter of 160-300nm, depth of 500nm) were fabricated on double blanket layers which were made up of W layer (thickness of 200nm) to bring conductivity and SiO<sub>2</sub> layer to completely insulate from Si substrate. Next, TaN, Ta and Cu layer were buried in the via and planed with CMP at typical single damascene process. Two kinds of defects were in the via on the test wafer. With SEM inspection equipment and analyzing brightness of SEM images, these were classified into normal via and two kinds of defects via. Bright, gray and dark images of via correspond to normal, void and etch stop via respectively. Current-voltage (I-V) measurements of each via to calculate resistance were performed by electrical probing equipment with SEM, and one probe was contacted to W

layer as ground line fabricated by FIB, another to Cu surface at the top of the via. First, I-V measurements were performed for normal via with a diameter of 160 - 300nm. The current, which was about 0.2mA at a voltage of 10mV, was continuous and ohmic, so it was sufficient to calculate a resistance. The resistance of several  $\Omega$  was reasonable for a resistance generally performed in measurements of via chain. The resistance was in inverse proportion to the square of diameter, as expected, and its variation increased for small size via. Second, I-V measurements were performed for etch-stopped or void via with a diameter of 160nm. The resistance of void via was about 10 times of normal via and its variation was larger than variation of normal via. This suggests that variation of resistance dues to variation of void size in Cu. Furthermore, investigation of correlation between the resistance and brightness of SEM images presented numerically allows to know detailed information of defects. Finally, the combination of SEM inspection and electrical probing equipment can enable the estimate of resistance of via. In LSI process, it is possible to monitor defects directly and quantitatively by using SEM inspection equipment.

**EM-ThP29 Aluminum (Al) Contaminants & Copper (Cu) Debris Control in Wire Bonding Process: A Novel Ionization Application.** *O.A. Janducayan, G. Nuneza*, Fairchild Semiconductor Inc, Philippines

The effect of ionization is already proven over the years in so many fields and most of the positive effect of this can be manifested in the field of semiconductor. Specific in the wire bonding technology, broken welds are one of the most common failure signature in the industry today and the resolution of this failure varies depending on the failure mechanism. Ionization or the neutralization of static energy during wire bonding of aluminum wires in power packages were proven to have beneficial effects; such effects can be utilize to control metal to metal adhesion in the surrounding environment, i.e. adhesion of conductors through Copper (Cu) contaminants against another metal surface, Aluminum (Al) build up in wedge tools, etc. The neutralization of static energy during the processing of these metals can be effectively utilized to improve overall quality of the process. The framework of this paper presents a study of the beneficial effect of ionization that can contribute in the elimination of broken weld cause by the Aluminum build up and the integration feasibility of ionization application in the original equipment manufacturers Wire Bonding process.

**EM-ThP30 Novel Photoresist for Improvement in Pattern Collapse on Silicon Nitride.** *H.-J. Yun, D.-Y. Kim, Y.-G. Kwon, B.-D. Kim, Y.-H. Kim, T.-S. Kim, Y.-B. Koh*, Samsung Electronics, Korea

Silicon nitride is useful in semiconductor industry for surface passivation as a hard mask. Recently, even at optimum exposure dose (Eop), it was found that photoresist patterns collapsed on silicon nitride which underwent ashing and stripping due to former step failure. The cause of pattern collapse is thought to be adhesion insufficiency resulted from a large discordance between the surface tension of substrate and that of resist. A polymer which has hydrophilic ester moiety was synthesized, and a resist based on this polymer shows better adhesion to silicon nitride. 42 nm line and space patterns were delineated using 193nm lithography tool without pattern collapse.

## Electronic Materials and Processing

Room: 612 - Session EM-FrM

### Hf-based Dielectrics and Their Interfaces

Moderator: R.L. Opila, University of Delaware

8:00am **EM-FrM1 Electrical Properties of High k Dielectrics Improved by Atomic Scale Nitrogen Depth Profile**, *W.J. Maeng, H. Kim*, POSTECH in Korea

Nitrogen incorporation produces several benefits in the performance of high k gate oxides. However, since too much nitrogen incorporation at the interface of gate dielectric can result in device degradation, the atomic scale control of nitrogen depth profile is desirable. In this study, we have improved the electrical properties of gate oxides, including dielectric reliability and interface state density, by depth profile control using in situ nitrogen incorporation during plasma enhanced atomic layer deposition (PE-ALD). The PE-ALD HfO<sub>2</sub> films with oxygen plasma and PE-ALD HfO<sub>x</sub>N<sub>y</sub> films with N/O mixture plasma were prepared at various growth conditions, changing nitrogen profile (bottom, middle and top) and N/O flow ratio (from 0 to 4). The best electrical properties in terms of hysteresis, EOT, and interface state density were obtained when the nitrogen was incorporated in the middle of the thin film with the N/O ratio of 2, which has not been achievable by other nitridation techniques. The EOT and interface state density of middle nitridation sample was reduced to 0.95nm (HfO<sub>2</sub> : 1.10nm) and  $0.75 \times 10^{11} \text{cm}^{-2} \text{eV}^{-1}$  (HfO<sub>2</sub> :  $1.20 \times 10^{11} \text{cm}^{-2} \text{eV}^{-1}$ ). Also, the 50% failure electric field was improved from -10.3 MV/cm to -12.2 MV/cm.

8:20am **EM-FrM2 Effect of Annealing Temperature on the Chemical Composition, Chemical Depth Profile, and Film Morphology of High-k Gate Dielectrics by AR-XPS and AFM**, *G. Conti, G. Peydaye, C.C. Wang, T. Sato, Y. Uritsky, S. Hung, P. Liu*, Applied Materials

Hf-based films are alternative gate dielectric films to SiON because of their high dielectric constant and their relatively wide band gap. These films should stay amorphous after activation annealing at T>1000 °C because grain boundaries may serve as paths of dopant diffusion. Pure HfO<sub>2</sub> is not a good gate dielectric film because it crystallizes at a low temperature of 500 °C. In this work the effect of different annealing temperatures on chemical composition, and atomic depth profile of HfSiON films is studied by AR-XPS, AFM and TEM. HfSiON films with different N concentrations were annealed at temperatures ranging from 500C to 1050C. These films are thermally stable up to T=1000°C. AR-XPS analysis shows that Hf concentration remains constant, while the N concentration increases linearly with decoupled plasma nitridation power (DPN). All the samples show one layer of HfSiON on Si substrate with thickness of about 20Å. The AR-XPS depth profile shows that Hf and N are evenly distributed in the films, and carbon is observed as a contaminant element on the film surface. The film roughness by AFM is RMS=2Å. The temperature of T=1050C is most commonly used in the CMOS processes, because it is the temperature of Si recovery after dopants implantation. At this temperature the film should remain amorphous and thermodynamically stable. The set of films previously studied, was then annealed at T=1050C. AR-XPS analysis shows that the concentrations of both Hf and N drop significantly, while the N concentration still increases as the DPN power increases. The resulting films consist of two stacked layers of SiO<sub>x</sub>/HfSiON/Si whose total thickness ranges between of 24Å and 36Å. The AR-XPS depth profile shows that Hf is closer to the Si interface, N is buried in the middle of the film and a significant fraction of carbon is present both in the surface and in the bulk. These AR-XPS results can be explained only if crystallization occur. TEM images show the appearance of micro islands. AFM analysis shows that the film roughness increases by a factor of 20 compared to that of the film annealed at T=1000C. Based on the high film roughness, we conclude that AR-XPS technique on films at T=1050C produces meaningless results in term of composition and depth profile data. However, increasing the amount of N in the film prevents film crystallization. These films show a relative low roughness, and the AR-XPS results are similar to those of the samples annealed below T=1000C.

8:40am **EM-FrM3 Suppression of Ge-N Bonding at Ge-HfO<sub>2</sub> and Ge-TiO<sub>2</sub> Interfaces: Deposition on Nitrided Ge Surfaces, and Post-Deposition Annealing at 800°C**, *G. Lucovsky, S. Lee, J.P. Long*, North Carolina State University, *J. Luening*, SSRL

Differences in length scales for nano-scale order in thin film nanocrystalline HfO<sub>2</sub> and TiO<sub>2</sub> deposited on i) remote plasma-nitrided Ge(100) substrates, and ii) Si(100) substrates with ultra-thin (~0.8 nm) SiON interfacial layers are addressed. Near edge X-ray absorption spectroscopy (NEXAS) is used to determine nano-scale order through the presence or absence Jahn-Teller (J-T) distortion removal of band-edge d-state degeneracies. These studies identify a new and novel application for NEXAS based on the resonant character of the respective N K<sub>1</sub> and O K<sub>1</sub> edge absorptions; these absorptions, respectively, provide a novel way to probe correlated changes in buried interfaces and nano-scale order for as-deposited and 800°C Ar annealed HfO<sub>2</sub> and TiO<sub>2</sub> thin films. After an 800°C anneal, N K<sub>1</sub> edge spectra indicate an essentially complete elimination of interfacial GeN interfacial bonding on the Ge substrates, but no changes in SiON interfacial layer bonding on Si substrates. As-deposited films 2 nm, 4 nm and 6 nm thick on Ge and Si with interfacial transition regions do not display J-T splittings. This has been attributed to kinetically hindered nanocrystalline grain dimensions smaller than 2 nm. In contrast, after annealing, HfO<sub>2</sub> and TiO<sub>2</sub> films on Ge display spectroscopic evidence for J-T splittings, independent of film thickness. Annealed films on SiON interfaces display J-T splittings, but only for film thickness >3 nm in which grain size is not dimensionally constrained. The spectral signature of the J-T splittings for HfO<sub>2</sub> films on Ge is qualitatively different than for HfO<sub>2</sub> films SiON interfaces on Si. This is attributed to the TM oxide bonding directly to a Ge surface devoid of interfacial GeN serving as a template for mosaic in-plane controlled HfO<sub>2</sub> and TiO<sub>2</sub> grain growth to >3.5 nm. This grain size is sufficient to promote observable J-T splittings in O K<sub>1</sub> spectra. Equally significant, and consistent with the mosaic template description, the half-width-half-maximum of the O K<sub>1</sub> edge for annealed TiO<sub>2</sub> films is smaller for Ge substrates, 0.5 eV as compared with 0.6-0.7 eV for SiON interfaces on Si.

9:00am **EM-FrM4 Effect of Strain Localization and Percolation on Defect States by Controlled Nitrogen Incorporation in Hf Si Oxynitride Alloys**, *S. Lee, G. Lucovsky, L.B. Fleming*, North Carolina State University, *J. Luening*, Stanford Synchrotron Radiation Laboratory

There are two qualitatively different ternary alloy regimes with markedly different properties that are obtained by incorporation of nitrogen in the form of Si<sub>3</sub>N<sub>4</sub> bonding into TM silicates. These differentiated by i) strain localization and/or strain percolation, and more importantly iii) strain reduction associated with chemical bonding self-organizations that reduce macroscopic strain by more than compensating reductions in alloy atom entropy. In order to realize strain minimization, compositional optimization by remote plasma process processing was utilized for deposition of Hf, Ti and Hf,Ti alloy Si oxynitride dielectrics. For example, the effect of Si<sub>3</sub>N<sub>4</sub> content in (HfO<sub>2</sub>)<sub>x</sub>(Si<sub>3</sub>N<sub>4</sub>)<sub>y</sub>(SiO<sub>2</sub>)<sub>1-x-y</sub> pseudo-ternary alloys has been studied spectroscopically, and also shows systematic changes in electrical properties, including reduction of electrically-active traps, and minimization of tunneling leakage. Results from soft X-ray photoelectron spectroscopy (SXPS) valence band studies indicate no detectable hole traps for Hf Si oxynitrides with Si<sub>3</sub>N<sub>4</sub> content ~35 - 40%, and with equal concentrations of HfO<sub>2</sub> and SiO<sub>2</sub>, ~30-32%. These alloys show no evidence for chemical phase separation, as do Hf silicates, and other Hf Si oxynitride compositions. Optimized alloys are stable to at least 1100°C annealing. Derivative near edge x-ray absorption spectroscopy (NEXAS) comparisons for O K<sub>1</sub> edges of HfO<sub>2</sub> and optimized Hf Si oxynitride alloys display significantly decreases in electron trapping. The unique properties of optimized Hf Si oxynitrides are correlated with a four-fold coordination of Hf, in contrast with the 7-fold coordination of Hf in HfO<sub>2</sub>. C-V measurements indicate a dielectric constant of ~12 in optimized Hf Si oxynitrides, and a predicted value of 16-18 in Hf,Ti Si oxynitrides. Combined with low electron trapping similar to SiO<sub>2</sub>, and more than a 4 order of magnitude reduction in tunnel leakage, optimized TM Si oxynitride alloys are predicted to yield EOTs <1 nm, and possibly as low as 0.6 to 0.5 nm for aggressively scaled CMOS devices.

9:20am **EM-FrM5 A Comparison of the Nucleation and Growth of HfO<sub>2</sub> Thin Films Deposited by ALD Using TEMAH and TDMAH Precursors**, *J.C. Hackley*, UMBC, *J.D. Demaree*, Army Research Laboratory, *T. Gougousi*, UMBC

A hot wall Atomic Layer Deposition (ALD) flow reactor has been used for the comparison of two different HfO<sub>2</sub> ALD chemistries: tetrakis (ethylmethylamino) hafnium (TEMAH) and H<sub>2</sub>O, and tetrakis

(dimethylamino) hafnium (TDMAH) with H<sub>2</sub>O on H-terminated Si and SC1 chemical oxide starting surfaces. Spectroscopic ellipsometry (SE) confirms linear growth of the films with a growth rate of ~1.2 Å/cycle at 250°C for the TEMA process, and ~1.0 Å/cycle at 275°C for the TDMAH process. Nucleation and initial growth behavior of the films were examined using x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). RBS indicates an initial 4-7 cycle nucleation barrier for the Si-H surface with both metal-organic precursors, before the growth rates on that surface match those on SC1. Steady-state coverage is attained after a 'conditioning' period of about 45 ALD cycles for TEMA, as opposed to only 20 cycles with TDMAH. However, TEMA results in a higher steady-state coverage rate of 3.1x10<sup>14</sup> Hf/cm<sup>2</sup> on both starting surfaces, compared to 2.4x10<sup>14</sup> Hf/cm<sup>2</sup> and 2.7x10<sup>14</sup> Hf/cm<sup>2</sup> for the Si-H and SC1 surfaces with TDMAH. A comparison of the growth rate measurements with RBS and SE indicates that the HfO<sub>2</sub> films grown from TEMA appear to reach about 85% of their bulk density on both starting surfaces while TDMAH results in 85% bulk density for the Si-H surface and 95% density on the SC1 surface. XPS is implemented to examine the Si/HfO<sub>2</sub> interfacial region for films grown on the Si-H starting surface. Angle-resolved scans ranging from 0-60° (measured from the surface normal) are taken for samples prepared with both precursors, ranging from 4-25 ALD cycles. For the TEMA films, we detect a ~7 Å SiO<sub>x</sub>/silicate interfacial layer which remains practically unchanged up to 50 ALD cycles as indicated by HRTEM data. In the TDMAH/H<sub>2</sub>O process, the interface appears to be initially unstable, and the interfacial layer increases from ~6 Å at 4 cycles up to ~18 Å at 25 cycles. This unstable interface may be due to a more porous film structure, and/or the slightly higher deposition temperature than that of the TEMA process (275 vs. 250 °C) which may enhance interface oxidation.

9:40am **EM-FrM6 Material Characteristics and Electrical Properties of Hafnium Silicate Films Synthesized by Plasma Enhanced Atomic Layer Deposition**, J.R. Liu, R.M. Martin, M. Sawkar, J.P. Chang, University of California at Los Angeles

Pseudo-binary (HfO<sub>2</sub>)<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> has attracted much attention due to the interesting possibility of combining the high breakdown field of SiO<sub>2</sub> (E<sub>g</sub> = 9 eV) and high dielectric constant (22-25) of HfO<sub>2</sub> in a complex material to keep a relatively high dielectric constant and a low leakage current.<sup>1,2</sup> In this work, (HfO<sub>2</sub>)<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> composite films were deposited from hafnium tetratertert-butoxides (HTB) and tetraethylorthosilicate (TEOS) precursors by using a plasma-enhanced atomic layer deposition (PEALD) process. The film thickness increased almost linearly with increasing number of precursor-oxygen plasma cycles. An optimal control over the final composition was achieved by setting the deposition cycles of HfO<sub>2</sub> and SiO<sub>2</sub>. Fourier Transform Infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) analysis showed that the composite films were fully oxidized. The Si-O-Hf bonds were formed in the PEALD deposited composite films. The band gap determined from the XPS O 1s plasmon loss spectrum increased from 5.6 to 5.98 eV with increasing the Si content in the as-deposited films, and it increased slightly after the composite films were annealed at 600 and 900°C, respectively. Time-of-flight static secondary ion mass spectrometry (TOF-SSIMS) depth profiles showed that Hf is almost uniformly distributed throughout the films, and Hf and O exhibited a sharp decay at the Si interfacial substrate. Some Hf presence at the interface with Si could be attributed to ion beam-induced mixing of Hf into the interfacial layer. The low carbon content in these films, which is confirmed by XPS, resulted from the ambient surface contamination. The as-deposited and annealed films at 900°C were determined to be amorphous by x-ray diffraction (XRD), suggesting that the introduction of SiO<sub>2</sub> into HfO<sub>2</sub> matrix prevented crystallization and kept the film amorphous at high temperature. The as-deposited (HfO<sub>2</sub>)<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> composite films showed superior electrical properties, including dielectric constants from 5.3 to 11.5 and leakage current density several orders of magnitude lower than that of SiO<sub>2</sub> at the same equivalent oxide thickness.

<sup>1</sup> R. M. Wallace and G. Wilk, MRS Bulletin, 192, 27 (2002).

<sup>2</sup> R. Puthenkovilakam, M. Sawkar, and J. P. Chang, Appl. Phys. Lett., 202902, 86 (2005).

10:00am **EM-FrM7 Band Alignment in Metal/Oxide/Semiconductor Stacks**, S. Rangan, E. Bersch, R.A. Bartynski, E. Garfunkel, Rutgers University

Understanding band alignment in a Metal/Oxide/Semiconductor (MOS) structure is both a fundamental physical chemistry challenge and a crucial technological issue for nanoelectronics as the correct band offsets across a MOS stack is essential to prevent undesirable leakage currents in device applications. A recurrent problem in the evaluation of the band offsets is the lack of reproducibility between measurements on nominally identical samples and between measurements performed using different experimental methods. In this study, we have performed ultra-violet photoemission and inverse photoemission spectroscopy measurements in the same UHV system on a variety of high-κ dielectric films (HfO<sub>2</sub>, Hf<sub>0.8</sub>Si<sub>0.2</sub>O<sub>2</sub>, SiO<sub>2</sub>,

Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>) on different semiconductor substrates (Si, Ge, GaAs). This experimental setup allows the direct determination of band gaps, electron affinities, metal work functions, and band offsets across MOS structures. We have also explored the effect of subsequent metallization of the high-κ film in UHV with either of metals (Ru, Ti, Al) chosen for their very different work function and oxygen affinity. By examining the line shape of the shallow core levels using synchrotron radiation-excited x-ray photoemission spectroscopy, we determined the chemical state of the metal, the oxide and the substrate. Ru and Ti are found to remain metallic upon deposition on all oxide films used in this study. In contrast, strong changes in the chemistry of the entire stack are observed upon Al deposition. An Al<sub>2</sub>O<sub>3</sub> interface layer is always present at the Al/Oxide interface, and evidence for reduction of the semiconductor/high-κ interface oxide is also observed. Consistent with the observed level of reactivity, our measured Metal/Oxide band offsets are in good agreement with the values predicted by the interface gap state model for as-deposited Ru and Ti. In the case of Al, owing to an additional Al<sub>2</sub>O<sub>3</sub> interface layer between the oxide and the Al, our measured values are in poor agreement with the interface gap state model. This indicates that for reactive metal, the band offset is not well described by this simple model.

10:20am **EM-FrM8 Thermal Stability of Rare Earth Oxides as High-κ Gate Dielectrics**, S. Van Elshocht, C. Adelman, T. Conard, A. Delabie, A. Franquet, IMEC vzw, Belgium, P. Lehnen, ALXTRON, Germany, L. Nyns, O. Richard, IMEC vzw, Belgium, J. Swerts, ASM Belgium, S. De Gendt, IMEC vzw, Belgium

Chip performance has drastically increased during the past decades, pushed forward by the ITRS roadmap that projects a doubling of the amount of transistors on a chip every two years. This task has been mainly accomplished by down scaling the dimensions of the transistor, including the gate dielectric thickness down to a few atomic layers. As a result, gate leakage current densities have reached unacceptable levels. As a solution alternative gate dielectrics, replacing the standard SiON, were researched, leading to the identification of Hf-based dielectrics, recently announced to be integrated in the 45-nm technology node. Another class of alternative dielectrics that receives a lot of attention is the rare earth oxides, both as binary or ternary compounds. Rare earth oxides are being explored for their property to shift the work function of a metal gate towards n-type, which is of interest to engineer a proper transistor threshold voltage. In addition, ternary rare earth oxides have been studied because of their thermal stability that allows obtaining a material that remains amorphous during the entire CMOS process. We have studied the thermal behavior and stability of rare earth based oxides, such as Dy<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, LaAlO<sub>3</sub>, HfLaO<sub>x</sub>, and DyScO<sub>3</sub>, as function of anneal temperature, time, and ambient, as well as function of their composition. Observations were made by Spectroscopic Ellipsometry, Time-Of-Flight-Secondary Ion Mass Spectroscopy, Transmission Electron Microscopy, X-Ray Reflectometry, and X-Ray Diffraction. The rare earth oxide strongly intermixes with the SiO<sub>2</sub> layer underneath, in agreement with the tendency of rare earth elements to form silicates.<sup>1</sup> More interestingly, for ternary rare earth oxides, this behavior is heavily dependent on the composition of the deposited layer. The system evolves to a stable composition that is controlled by the thermal budget and the rare earth content of the layer. Understanding this behavior is important, since it provides a better insight in the behavior of these dielectrics during the thermal treatments inherent to a CMOS process flow. Finally, as an increased Si-content, resulting from silicate formation, can increase the thermal stability of a material, proper care needs to be taken interpreting thermal stability measurements, most often based on X-Ray Diffraction.

<sup>1</sup> H. Ono et al., Appl. Phys. Lett., 78, 1832 (2001).

10:40am **EM-FrM9 Diffusion of La-based Layers on HfO<sub>2</sub>/SiO<sub>2</sub>/Si Dielectric Stacks**, M.I. Medina-Montes, The University of Texas at Dallas and Cinvestav-Queretaro, Mexico, M.V. Selvidge, F.S. Aguirre-Tostado, The University of Texas at Dallas, A. Herrera-Gomez, The University of Texas at Dallas and Cinvestav-Queretaro, Mexico, R.M. Wallace, The University of Texas at Dallas

Although there is a consensus regarding the use of Hf-based dielectrics as an alternative to SiO<sub>2</sub> in MOS structures, the search for a suitable metal for n-MOS is still open. The addition of a La-based layer to Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub>/SiO<sub>2</sub>/Si dielectric stacks has proven to allow for the engineering of the work function to appropriate levels when TaN or TiN is employed as the metal gate. It has been suggested that the La diffuses into the Hf layer with thermal treatment. We performed high resolution Angle Resolved X-Ray Photoelectron Spectroscopy experiments to study the chemical depth profile distribution of La<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub>/SiO<sub>2</sub>/Si dielectric stacks exposed to a nitridation treatment by NH<sub>3</sub> at 700°C. The expected stoichiometry and distribution of the HfO<sub>2</sub> and SiO<sub>2</sub> layers was reproduced from self consistent analysis of the ARXPS data. Regarding La, this study clearly shows that it diffuses to the top of the SiO<sub>2</sub> layer, and that subsequent Rapid Thermal Annealing at 1000°C for 5s does not change significantly that distribution. A similar

conclusion was derived by Sivasubramani et al. from FTIR analysis.<sup>1</sup> In addition, back-side Secondary Ion Mass Spectroscopy results presented by Alshareef et al. are consistent with a location for La close to the HfO<sub>2</sub>/SiO<sub>2</sub> interface.<sup>2</sup> The quantitative results for the location and amount of La, together with the associated uncertainties, will be discussed in extent in the presentation.

<sup>1</sup> P. Sivasubramani, T. S. Boscke, J. Huang, C. D. Young, P. D. Kirsch, S.A. Krishnan, M.A. Quevedo-Lopez, S. Govindarajan, B.S. Ju, H.R. Harris, D.J. Lichtenwalner, J.S. Jur, A.I. Kingon, J. Kim, B.E. Gnade, R.M. Wallace, G. Bersuker, B.H. Lee, and R. Jammy, VLSI (2007).

<sup>2</sup> H.N. Alshareef, M. Quevedo-Lopez, H.C. Wen, R. Harris, P. Kirsch, P. Majhi, B.H. Lee, R. Jammy, D.J. Lichtenwalner, J.S. Jur, and A.I. Kingon. Applied Physics Letters 89, p. 232103 (2006).

11:00am **EM-FrM10 Physical and Chemical Properties of Hf-based High-κ Dielectrics on Ge(001) for CMOS Applications**, *F.S. Aguirre-Tostado, M. Milojevic, S.J. McDonnell, M.J. Kim, R.M. Wallace*, University of Texas at Dallas

The growth of High-κ dielectrics on Ge has attracted substantial interest as a means to maintain integrated circuit scaling and performance. High-κ dielectrics on Ge studies have shown promising results in terms of low equivalent oxide thickness<sup>1</sup> and enhanced hole mobility.<sup>2,3,4</sup> For MOSFET applications, the thermal stability of gate dielectrics is a requirement for an appropriate CMOS flow. This paper will describe the thermal stability studies of HfGeON gate dielectrics on Ge for several nitrogen concentrations. The structure and chemistry of the HfGeON/Ge(001) layers are studied using HRTEM, XRD and in-situ XPS and LEISS. Sputter deposited HfGeON films on atomically clean Ge epi-layers grown by MBE on Ge(001) substrates are investigated. Corresponding electrical characterization of the associated devices will also be described in view of the thermal budget where the maximum process temperature is ~500°C. This work is supported by the MARCO MSD Focus Center.

<sup>1</sup>C.O. Chui, S. Ramanathan, P.C. McIntyre, and K.C. Saraswat, IEEE Elec. Dev. Lett. 23, (2002) 473.

<sup>2</sup>C. H. Huang, et. al., in Symp. VLSI Tech. Dig., 2003, pp. 119-120.

<sup>3</sup>C. Chui, H. et.al., in IEDM Tech. Dig., Dec. 2002, pp. 437-440.

<sup>4</sup>W. P. Bai, et.al., in Symp. VLSI Tech. Dig., 2003, pp. 121-122.

## Surface Science

Room: 611 - Session SS2+EM+TF-FrM

## Organic Films II: Semiconductors and C<sub>60</sub>

Moderator: J.E. Reutt-Robey, University of Maryland

8:00am **SS2+EM+TF-FrM1 Unravelling Molecular Contrast Formation Obtained by NC-AFM on Titania**, *R. Bechstein, J. Schütte, P. Rahe, A. Kühnle*, University of Osnabrueck, Germany

The (110) surface of TiO<sub>2</sub> constitutes an interesting model substrate for molecular adsorption studies due to its importance in applications such as organic solar cells and light emitting diodes. Several experiments revealed that organic molecules can be anchored to the surface through carboxylic groups both under ultra-high vacuum conditions<sup>1</sup> as well as from solution.<sup>2</sup> We investigated a perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI) derivative without carboxylic anchor groups by non-contact atomic force microscopy (NC-AFM) under ultra-high vacuum conditions. The molecules were deposited at room temperature onto TiO<sub>2</sub> (110) by evaporation from a Knudsen cell. We achieved true atomic resolution on the bare substrate as well as submolecular resolution on individual molecules. The molecules were observed to align along the [001] direction with the ability to move along this direction. They are found to be homogeneously distributed on the terraces without any tendency to cluster at step edges even at elevated temperature. Two molecular contrast modes are clearly distinguished. In one mode the molecules appear cloudy and are observed to be centred on top of bright rows. In the other mode the molecules are imaged with a dark bone-shaped centre and a bright rim, centred on top of dark rows. Scanning tunnelling microscopy measurements allow to conclude that the molecules are always centred on top of the bridging oxygen rows, demonstrating a contrast reversal between the two NC-AFM imaging modes. By comparing these results with previous NC-AFM studies,<sup>3</sup> we can assign the two modes to positive and negative terminated tips showing that in NC-AFM imaging strongly depends on the tip termination.

<sup>1</sup> A. Sasahara, H. Uetsuka, and H. Onishi, J. Phys. Chem. B 105, 1 (2001)

<sup>2</sup> C. L. Pang, T.-a. Ishibashi, and H. Onishi, Jpn. J. Appl. Phys. 44, 5438 (2005)

<sup>3</sup> J. V. Lauritsen, et al., Nanotechnology 17(14), 3436 (2006).

8:20am **SS2+EM+TF-FrM2 Characterization of Para-Sexiphenyl Thin Films Grown on KCl Substrates**, *A. Andreev*, Univ. of Leoben, Austria, *A. Montaigne*, Univ. Linz, Austria, *T. Haber*, Graz Univ. of Tech., Austria, *A. Kadashchuk*, National Academy of Sci. of Ukraine, *G. Hlawacek*, Univ. of Leoben, Austria, *D.-M. Smilgies*, Cornell Univ., *R. Resel*, *A. Winkler*, Graz Univ. of Tech., Austria, *H. Sitter*, *N.S. Sariciftci*, Univ. Linz, Austria, *C. Teichert*, Univ. of Leoben, Austria

Para-sexiphenyl (6P) films grown on mica(001) and KCl(001) substrates show large morphological and optical anisotropy, which makes them attractive for nano-scale photonic devices. In this work we use Atomic Force Microscopy (AFM), electron microscopy, x-Ray diffraction (XRD), and photoluminescence (PL) in order to find the parameters controlling film morphology, structure, and quality. It is shown that the initial growth stage of 6P on KCl(001) is characterized by the formation of μm-long needles, generating a rectangular network in accordance with the substrate surface symmetry. With increasing coverage, terraced mounds composed of upright standing molecules developing between the needles are observed and subsequent growth is characterized by a coexistence of both features. It is demonstrated that both features grow directly on the substrate surface, i.e., there is no wetting layer during the deposition of 6P on KCl(001). It is also found that both needles and terraced mounds grown on KCl(001) are single crystalline, in contrast to mica(001), where different oriented 6P domains are formed inside of the chains. PL studies have shown that, as in 6P films on mica, the emission spectra contain two different components - a conventional structured spectrum due to intrinsic excitons and a broad red-shifted band ascribed to some kind of defects. The latter band most clearly can be distinguished in delayed fluorescence spectra of the studied films. It is remarkable, however, that the relative intensity of the defect band was much weaker in the films grown on KCl substrates comparing to that on mica, which corresponds well with results of morphological and structural investigations. This finding confirms the high quality of the films and implies that the defect band is rather sensitive to the structure and morphology of the films. We also discuss a correlation between growth condition of 6P and a relative intensity of the defect PL band.

8:40am **SS2+EM+TF-FrM3 A Nanoengineering Approach to Regulate The Lateral Heterogeneity of Self-Assembled Monolayers**, *J.-J. Yu, Y.H. Tan, X. Li*, University of California, Davis, *P.K. Kuo*, Wayne State University, *G.-Y. Liu*, University of California, Davis **INVITED**

Using a scanning probe lithography method known as nanografting in conjunction with knowledge of self-assembly chemistry, regulation of the heterogeneity of self-assembled monolayers (SAMs) is demonstrated. It is known that phase segregated domains would form if SAMs are grown from thiol solutions of mixed compositions. The size and distribution of these domains depend on the interplay between reaction kinetics and dynamics, which can be regulated by varying the reaction conditions including concentration, temperature and reaction time. The reaction mechanism in nanografting, however, differs significantly from self-assembly in the conventional mix-and-grow methods. The spatial confinement in nanografting bypasses the lying-down to standing up transition process, and thus leads to a much fast kinetics. Knowledge of the reaction pathways enables development of methods for shifting the interplay between the kinetics and thermodynamics in SAM formation, and thus the heterogeneity of mixed SAMs. By varying fabrication parameters such as shaving speed, and reaction conditions such as concentration and ratio of the components, the lateral heterogeneity can be adjusted ranging from near molecular mixing to segregated domains of several to tens of nanometers.

9:20am **SS2+EM+TF-FrM5 Mechanistic Aspects of Organic Thin Film Growth from Energetic Sources: Insights from Experiment and Molecular Dynamics Simulations**, *J.E. Goose, A.S. Killampalli, P. Clancy, J.R. Engstrom*, Cornell University

We have used a combination of experiments and molecular dynamics simulations to investigate the fundamental molecular mechanisms contributing to the evolution and final morphology of thin films of pentacene deposited at hyperthermal incident kinetic energies ( $E_i = 1-10$  eV). Experimentally, using supersonic molecular beam scattering techniques and atomic force microscopy we have characterized the adsorption probability as a function of both  $E_i$  and the angle of incidence ( $\theta$ ). Interestingly, we observe differences in the dynamics of adsorption for pentacene interacting with a clean SiO<sub>2</sub> substrate (submonolayer growth) vs. a SiO<sub>2</sub> substrate covered by a pentacene thin film (multilayer growth). Specifically, for  $E_i$  greater than ~1-2 eV, contribution of a new mechanism for pentacene adsorbing on pentacene is implicated. To determine the nature of this mechanism, we have used the non-reactive empirical MM3 potential to model the collision of pentacene molecules with a pentacene thin film using molecular dynamics. Our simulation cell consists of ca. 100 molecules, and includes an upper terrace of 4 x n unit cells, bounded by (010) step edges. Accounting for impacts both near the middle of the terrace and near the step edge, our results from simulation for the probability of

adsorption compare very well with those measured experimentally. In particular, adsorption is found to decrease with increasing  $E_i$ , and, in general, with increasing  $\theta_i$ . More importantly, the simulations give us insight into nature of the events that occur at high incident kinetic energies. For thermal incident kinetic energies we observe mostly simple trapping (molecular adsorption), with near unit probability. At higher  $E_i$  of 1-5 eV, a significant fraction of molecules (~30%) are found to directly insert into the upper terrace, whereas a higher fraction (~90%) of molecules impacting near the step edge in this same energy regime also end up incorporating into the upper terrace. Indeed, direct molecular insertion into the pentacene crystal structure is the dominant interlayer process when both the molecule's orientation and incident angle are aligned normal to the surface, which leads to the formation of interstitials for the time scale of these simulations.

**9:40am SS2+EM+TF-FrM6 Growth of Pentacene Thin Films from a Supersonic Source: Unexpected Behavior in the Presence of Molecular Cluster Formation.** *A. Amassian, S. Hong, S. Bhargava, A.R. Woll, T.W. Schroeder, A.S. Killampalli, J.D. Ferguson, J.D. Brock, G.G. Malliaras, J.R. Engstrom*, Cornell University

We have examined the growth of pentacene thin films on SiO<sub>2</sub> using supersonic molecular beam techniques and in situ real-time synchrotron x-ray scattering. At low-to-moderate rates of deposition [ca. 0.001 to 0.1 monolayer(ML)/s] we observe an abrupt transition from 2D, layer-by-layer growth to 3D, islanded growth after deposition of the first few monolayers of pentacene on SiO<sub>2</sub>. At high rates of deposition (ca. 1 ML/s), however, we find persistent 2D crystal growth, and the development of a highly textured film possessing significantly flatter and smoother surface morphology than at low rates of deposition. Concomitantly, in this regime we also observe new polymorphs of pentacene, as significant changes occur in the crystalline structure of the thin films. The transition to this anomalous, yet promising growth behavior corresponds very strongly with the onset of the formation of van der Waals clusters of pentacene within the supersonic expansion. We suggest that the presence of clusters in the incident flux acts to change the dynamics of growth due to a variety of reasons which we discuss. These findings raise the distinct possibility that organic crystals may be synthesized with ultra-flat surface morphology, making them suitable for use in a number of electronics applications where the requirement for abrupt and smooth interfaces has traditionally defaulted to the use of amorphous organic thin films.

**10:00am SS2+EM+TF-FrM7 Vibrational and Structural Investigation of Ferrocene Adsorption on Au(111) Surfaces.** *G. Pirug, M. Kazempoor*, Forschungszentrum Jülich, Germany, *J. Myslivecek*, Charles University in Prague, Czech Republic, *B. Voigtländer*, Forschungszentrum Jülich, Germany

The adsorption of ferrocene (Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>) on Au(111) surfaces has been studied spectroscopically applying HREELS and XPS as well as structurally by means of LEED and STM under UHV conditions. The vibrational modes observed by HREELS indicate reversible molecular adsorption of ferrocene at temperatures of about 110 K. The corresponding frequencies are not significantly shifted with respect to IR or Raman data from solution, indicating a weak adsorbate - substrate interaction. Multilayer adsorption can be distinguished from the physisorbed first layer based on the sequential appearance and relative intensity changes of vibrational modes. In the monolayer regime vibrational modes with a perpendicular dipole moment from ferrocene molecules with an upright standing molecular axis dominate, as concluded from on- and off-specular HREEL spectra applying the surface dipole selection rules. Dissociation into cyclopentadienyl ring radicals (C<sub>5</sub>H<sub>5</sub>) can be excluded due to the missing related vibrational losses, such as the wagging mode expected at about 760 cm<sup>-1</sup>. For multilayer coverages the orientation of the condensed ferrocene molecules is no longer exclusively perpendicular to the surface which results in the appearance of additional vibrational losses. Molecular self assembly yields a well ordered surface structure as shown by topographical STM pictures and LEED pattern.

**10:20am SS2+EM+TF-FrM8 Uncovering Molecular Dewetting: Growth and Morphology of C<sub>60</sub> and PTCDA on Insulators.** *S.A. Burke, J.M. Mativetsky, S. Fostner, P. Grutter*, McGill University, Canada

Despite considerable interest in recent years in the properties and structural characteristics of molecular deposits for organic based devices, there has been only limited study of growth and morphology of molecular materials on insulating substrates. The majority of traditional surface science tools are significantly hindered by the use of an insulating substrate due to complications with charging and surface damage. Over the past decade, non-contact atomic force microscopy (nc-AFM) has proven a powerful surface science tool, and is increasingly being applied to molecular studies on insulators. The power of the technique lies in its ability to image in real-space with sub-angstrom resolution as well as measure structure up to the

micron scale allowing for a connection between molecular scale structures and the overall growth morphologies. The nc-AFM technique, operated in UHV, has been applied to two prototypical organic semiconductors: C<sub>60</sub> and PTCDA, on two well-known insulating surfaces: KBr (001) and NaCl(001). Both systems showed island growth modes with evidence for dewetting, though the resulting morphologies differ considerably. C<sub>60</sub> on both of these alkali halides forms distinctive branched island shapes. A quantitative analysis of the morphology and its connection to the underlying epitaxy will be discussed. The formation of this branched morphology appears to be a dewetting process which was observed directly in a series of nc-AFM images. The energetics of this system will also be discussed in terms of annealing and deposition onto a heated substrate. PTCDA on NaCl also undergoes a dewetting process, though in a rather different manner. At low coverages, monolayer islands are observed in a highly strained c3x3 epitaxy. However, at larger coverages these single layer islands are seen to coexist with tall crystallites exhibiting the same morphology and herringbone structure as observed for PTCDA on KBr, indicating a coverage induced dewetting transition between 0.7 and 0.8 ML. The dewetting was also induced by annealing of the single layer islands yielding molecular crystals up to several microns long with the familiar herringbone structure of the PTCDA (102) plane. Dewetting has recently been recognized in several other organic systems as a significant factor in the growth and morphology of thin films. The examples presented here may indicate that dewetting is also an important consideration in molecule-on-insulators systems as well.

**10:40am SS2+EM+TF-FrM9 STM/STS Studies of C<sub>60</sub>:Pentacene Interface Formation.** *D.B. Dougherty*, National Institute of Standards and Technology, *W. Jin, W.G. Cullen, G. Dutton, J.E. Reutt-Robey*, University of Maryland at College Park, *S.W. Robey*, National Institute of Standards and Technology

The most efficient small-molecule organic solar cells employ heterojunctions between donor and acceptor materials.<sup>1</sup> In order to push the performance of such devices into a regime of cost-effective power generation, it is necessary to develop a detailed understanding of organic-organic interface morphology and its relationship to electronic band alignment. We have approached this question by studying the technologically relevant<sup>2</sup> system of C<sub>60</sub> deposited onto pentacene, using STM/STS to provide clues to the relative importance of competing intermolecular interactions. When C<sub>60</sub> is deposited onto a pentacene bilayer on a Ag(111) surface,<sup>3</sup> STM measurements show two unique structures in the first layer. The pentacene bilayer forms a well-ordered structure on Ag(111) with the long molecular axis nearly parallel to the surface. At the lowest coverages, C<sub>60</sub> forms linear chains whose direction is templated by the underlying pentacene rows, with C<sub>60</sub> molecules located between rows of pentacene molecules. The details of the observed structural arrangement are related to electrostatic interactions between C<sub>60</sub> and the pentacene bilayer structure. Information on local relative band alignment for these structures is measured using constant-current distance-voltage spectroscopy.<sup>4</sup> The local transport gap for C<sub>60</sub> linear chains is 4.4±0.2 eV compared with a gap of 3.7±0.2 eV for the surrounding pentacene bilayer. The magnitudes of the gaps are influenced by local polarization energies in each structure. At higher coverage, domains of C<sub>60</sub> with no discernable long range order dominate the first layer. This disorder probably arises from frustrated intermolecular interactions between the two different chemical species. The lateral interactions between C<sub>60</sub> molecules (favoring hexagonal ordering) cannot be optimized simultaneously with the comparable strength interactions between C<sub>60</sub> and the underlying pentacene film (favoring an oblique unit cell). \*This work has been partially supported by the Dept. of Commerce through the NIST Center of Nanomanufacturing and Metrology and the NSF-funded MRSEC via DMR-05-20471.

<sup>1</sup>P. Peumans, J. Appl. Phys. 93, 3693 (2003).

<sup>2</sup>S. Yoo et al., Appl. Phys. Lett. 85, 5427 (2004).

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<sup>4</sup>S.F. Alvarado, et al., Phys. Rev. Lett. 81, 1082 (1998).

**11:00am SS2+EM+TF-FrM10 Potassium Induced Long Range Superstructure on C<sub>60</sub>/Ag (111) Surface.** *C.-C. Kuo, W.W. Pai*, National Taiwan University

Various long range superstructures were observed for potassium (K) doped C<sub>60</sub> monolayer on Ag (111) by scanning tunnelling microscopy (STM). Pristine C<sub>60</sub> monolayer exhibits a bright-dim contrast in the most stable (2√3×2√3)-R30 phase, whereas the molecular contrast is uniform in other metastable phases (denoted as R12 or R48 phases). Upon K doping, K segregate into compact islands at room temperature and the bright-dim contrast in the R30 phase is eliminated. Furthermore, ordered quasi-hexagonal patterns with periodicities of ~7 nm to ~40 nm appear. The ordered superstructures show distinct characteristics in each C<sub>60</sub> phase. Close inspection reveals that the super lattices are not exactly hexagonal but exhibit uni-directional distortion. Therefore, the finding is perplexing as it

cannot be explained by, e.g., Morie patterns. We propose that the superstructures are due to overlaying an orthorhombic one-dimensional polymerized  $KC_{60}$  phase over the hexagonal silver lattice. This is supported by high-resolution STM images showing the signature of [2+2] covalent bond formation.

11:20am **SS2+EM+TF-FrM11 Thiol-Modified Diamondoid Monolayers on Silver and Gold Studied with Near-Edge X-ray Absorption Fine Structure Spectroscopy**, *T.M. Willey*, Lawrence Livermore National Lab., *J.D. Fabbri*, Stanford Univ., *J.R.I. Lee*, Lawrence Livermore National Lab., *P.R. Schreiner*, *A.A. Fokin*, *B.A. Tkachenko*, *N.A. Fokina*, Justus-Liebig Univ. Giessen, Germany, *J.E. Dahl*, *R.M.K. Carlson*, *S.G. Liu*, MolecularDiamond Tech., *T. van Buuren*, Lawrence Livermore National Lab., *N.A. Melosh*, Stanford Univ.

Higher diamondoids, hydrocarbon cages with a diamond-like structure, have evaded laboratory synthesis and have only recently been purified from petroleum sources. Initial calculations on these unique diamond-like molecules show they may have negative electron affinity, a desirable property for electron emission. Readily available adamantane, the smallest diamondoid, can be thiolated and has shown to adsorb on gold with high coverage. The availability of adamantane, triamantane, and tetramantanes opens new possibilities for surface-modification as multiple sites are available for thiol or other chemical functionalization. Surface-attached diamondoids have technological possibilities as high-efficiency electron emitters, as well as crystals for diamond growth or other nanotechnological applications, and fundamental studies of the electronic and structural properties of these molecular monolayers are a necessary precursor. We have investigated the effects of thiol substitution position, polyamantane order, and metal substrate on diamondoid film morphology. Using Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) we show that the orientation of the diamondoids within each type of monolayer depends highly upon these parameters. We thus demonstrate control over the assembly, and hence the surface properties, of this exciting new class of diamond-like carbon molecules.

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Garfunkel, E.: EM-FrM7, 31  
Gateau, R.: EM+NS-MoA2, 3  
Gellman, A.J.: EM+NS-TuA4, 7  
Gergel-Hackett, N.: EM-TuM9, 5  
Gessert, T.A.: EM-ThM6, 21  
Gila, B.P.: EM-ThP10, 26  
Giles, N.: EM-ThP13, 26  
Ginger, D.S.: EM+NS-TuA10, 7; EM-MoM11, 2  
Goldman, R.S.: EM+NS-MoA8, 4; NS2+EM-WeA1, 17  
Goose, J.E.: SS2+EM+TF-FrM5, 32  
Gorman, C.B.: EM-TuM5, 5  
Gougousi, T.: EM-FrM5, 30  
Grandider, B.: NS+EM-WeM12, 12  
Grutter, P.: SS2+EM+TF-FrM8, 33  
Gueorguiev, G.K.: NS2+EM-WeA2, 18  
Gundlach, D.J.: EM-MoM3, 1  
Guzman, J.: EM-ThP1, 25

## — H —

Ha, S.D.: SS2+EM+TF-WeM1, 12  
Haber, T.: SS2+EM+TF-FrM2, 32  
Hacker, C.A.: EM-TuM9, 5  
Hackley, J.C.: EM-FrM5, 30  
Hamadani, B.H.: EM-MoM3, 1  
Han, S.-J.: EM-ThP26, 29; EM-ThP27, 29  
Han, S.M.: EM-WeM10, 10  
Han, Y.H.: EM-ThP3, 25  
Herrera-Gomez, A.: EM-FrM9, 31  
Hesse, D.: EM-WeA1, 16  
Hicks, R.F.: EM-ThA1, 22; NS+EM-WeM5, 11

Hill, D.: EM+NS-MoA2, 3  
Hinkle, C.: EM-ThA10, 23  
Hiramatsu, T.: EM-ThP22, 28  
Hlawacek, G.: SS2+EM+TF-FrM2, 32  
Hong, I.C.: NS2+EM+WeA10, 19  
Hong, S.: SS2+EM+TF-FrM6, 33  
Horn, K.: EM+NS-TuA11, 7  
Howe, J.Y.: EM-ThP13, 26  
Hsiao, C.N.: EM-ThP6, 25  
Huan, A.C.: EM-ThA7, 22  
Huang, M.: NS+EM+WeM1, 11  
Huebschman, B.: EM-ThP9, 26  
Hullavarad, N.: EM+NS-MoA1, 3  
Hullavarad, S.: EM+NS-MoA1, 3  
Hultman, L.: NS2+EM+WeA2, 18  
Hung, A.: EM-ThP9, 26  
Hung, S.: EM-FrM2, 30  
Hwang, D.K.: EM-MoM5, 1; EM-ThP17, 27

— I —

Im, S.: EM-MoM12, 2; EM-MoM5, 1; EM-ThP17, 27  
Inoue, M.: EM-WeA11, 17

— J —

Janducayan, O.A.: EM-ThP29, 29  
Janes, D.B.: EM-TuM10, 6; EM-TuM6, 5  
Jen-La Plante, I.: EM+NS-TuA10, 7  
Jeon, C.: EM-ThP3, 25  
Jesse, S.: EM-WeA1, 16; NS2+EM+WeA11, 19  
Jin, W.: SS2+EM+TF-FrM9, 33; SS2+EM+TF-WeM6, 13  
Jin, Y.: EM+NS-MoA8, 4  
Joly, A.G.: EM-WeM2, 9  
Jones, K.A.: EM-ThP9, 26; EM-WeM13, 11  
Jones, T.E.: SS2+EM+TF-WeM4, 13  
Joubert, O.: EM-WeA9, 17  
Jun, Y.-K.: EM-ThP24, 28; EM-ThP25, 28  
Jung, M.-C.: EM-ThP3, 25  
Jung, P.-G.: EM-ThP24, 28; EM-ThP25, 28  
Jung, S.H.: EM-MoM12, 2  
Jurchescu, O.D.: EM-MoM3, 1

— K —

Kadashchuk, A.: SS2+EM+TF-FrM2, 32  
Kahn, A.: SS2+EM+TF-WeM1, 12  
Kahn, M.: EM-WeA9, 17  
Kalinin, S.V.: EM-WeA1, 16; NS2+EM+WeA11, 19  
Kang, C.J.: EM-ThP14, 27; NS2+EM+WeA10, 19  
Kang, H.B.: EM-WeM9, 10  
Kantorovich, L.: SS2+EM+TF-WeM2, 13  
Kaspar, T.C.: EM-ThM5, 20  
Katalinic, S.: EM+NS-MoA2, 3  
Kato, H.: EM-ThP22, 28  
Kato, H.S.: SS2+EM+TF-ThA1, 23  
Kavanagh, K.L.: EM+NS-TuA1, 7; EM-TuM11, 6  
Kawai, M.: SS2+EM+TF-ThA1, 23  
Kawazoe, H.: EM+NS-MoA4, 3  
Kazempoor, M.: SS2+EM+TF-FrM7, 33  
Kei, C.-C.: EM-ThP6, 25  
Kelly, R.: SS2+EM+TF-WeM2, 13  
Kensanli, B.: EM-ThP13, 26  
Kern, K.: SS2+EM+TF-WeM13, 14  
Khan, E.H.: EM-ThP16, 27  
Khanna, R.: EM-ThP10, 26  
Killampalli, A.S.: SS2+EM+TF-FrM5, 32; SS2+EM+TF-FrM6, 33  
Kim, B.-D.: EM-ThP30, 29  
Kim, C.I.: EM-ThP7, 25  
Kim, D.-Y.: EM-ThP30, 29  
Kim, G.H.: EM-ThP7, 25  
Kim, H.: EM-FrM1, 30; EM-WeM9, 10  
Kim, H.J.: NS+EM+WeM1, 11  
Kim, J.: EM-ThA10, 23

Kim, J.H.: EM-MoM12, 2; EM-MoM5, 1  
Kim, J.W.: NS2+EM+WeA10, 19  
Kim, K.: EM-ThP12, 26  
Kim, K.H.: EM-MoM1, 1  
Kim, K.T.: EM-ThP7, 25  
Kim, M.J.: EM-FrM10, 32; EM-ThA10, 23  
Kim, N.-H.: EM-ThP24, 28; EM-ThP25, 28  
Kim, P.S.G.: NS2+EM+WeA4, 18  
Kim, S.: EM-ThP12, 26  
Kim, S.B.: NS2+EM+WeA10, 19  
Kim, S.I.: EM-ThP18, 27  
Kim, T.-S.: EM-ThP30, 29  
Kim, Y.B.: EM-WeA10, 17  
Kim, Y.-H.: EM-ThP30, 29  
Kim, Y.K.: EM-ThP14, 27  
Kim, Y.S.: EM-ThP14, 27; NS2+EM+WeA10, 19  
Kimura, T.: EM-WeA11, 17  
Kingkeo, K.: EM-ThP9, 26  
Kizilkaya, O.: NS+EM+WeM13, 12  
Ko, J.: EM-ThP19, 27  
Ko, P.-J.: EM-ThP24, 28; EM-ThP25, 28  
Kobayashi, S.: EM+NS-MoA4, 3  
Kobayashi, Y.: NS+EM+WeM5, 11  
Kobe, H.: EM-ThP22, 28  
Koeble, J.: NS+EM+WeM12, 12  
Koh, Y.-B.: EM-ThP30, 29  
Kondratenko, Y.: EM+NS-MoA9, 4  
Koo, A.-Y.: EM-ThP14, 27  
Koo, S.H.: NS2+EM+WeA10, 19  
Kramer, M.: EM-ThM3, 20  
Kravchenko, I.I.: EM-ThP10, 26  
Kühnle, A.: SS2+EM+TF-FrM1, 32  
Kuikka, M.A.: EM-TuM11, 6  
Kukuruznyak, D.: EM-WeA5, 16  
Kumar, V.: EM-WeM6, 10  
Kummel, A.C.: EM-ThA2, 22; EM-ThA6, 22  
Kuo, C.-C.: SS2+EM+TF-FrM10, 33  
Kuo, P.K.: SS2+EM+TF-FrM3, 32  
Kuo, S.Y.: EM-ThP6, 25  
Kurdak, C.: EM+NS-MoA8, 4  
Kurtz, R.L.: NS+EM+WeM13, 12  
Kushmerick, J.G.: EM-TuM3, 5  
Kwok, C.T.Z.: EM+NS-MoA9, 4  
Kwon, T.: EM-MoM1, 1  
Kwon, Y.-G.: EM-ThP30, 29

— L —

Lagally, M.G.: NS+EM+WeM1, 11  
Lai, P.-Y.: EM+NS-MoA10, 4  
Langford, S.C.: EM-ThP16, 27  
Langner, A.: SS2+EM+TF-WeM13, 14  
Laracuate, A.R.: SS2+EM+TF-ThA2, 23  
Lee, B.C.: EM-ThP3, 25  
Lee, C.: EM-ThP19, 27  
Lee, G.-R.: EM-MoM6, 1  
Lee, H.H.: EM-MoM1, 1  
Lee, J.: EM-ThP19, 27  
Lee, J.R.I.: SS2+EM+TF-FrM11, 34  
Lee, J.W.: EM-WeM9, 10  
Lee, N.-E.: EM-ThP18, 27  
Lee, N.J.: NS2+EM+WeA10, 19  
Lee, S.: EM-FrM3, 30; EM-FrM4, 30  
Lee, U.: EM-WeM13, 11  
Lee, W.-S.: EM-ThP24, 28; EM-ThP25, 28; EM-ThP26, 29; EM-ThP27, 29; EM-ThP4, 25  
Lee, Y.-K.: EM-ThP26, 29; EM-ThP27, 29; EM-ThP4, 25  
Lehnen, P.: EM-FrM8, 31  
Leonhardt, D.: EM-WeM10, 10  
Leung, K.T.: EM+NS-TuA5, 7  
Li, L.: EM-ThP21, 28  
Li, Q.: EM-WeM10, 10  
Li, W.: EM-TuM11, 6  
Li, X.: SS2+EM+TF-FrM3, 32  
Li, Y.: EM+NS-TuA8, 7  
Li, Y.J.: EM-ThM5, 20

Lin, C.M.: EM-ThP2, 25  
Lin, C.-T.: EM-MoM6, 1  
Lin, N.: SS2+EM+TF-WeM13, 14  
Liu, D.-R.: EM-ThP5, 25  
Liu, F.: NS+EM+WeM1, 11  
Liu, G.-Y.: SS2+EM+TF-FrM3, 32  
Liu, J.R.: EM-FrM6, 31  
Liu, M.: SS2+EM+TF-ThA7, 24  
Liu, P.: EM-FrM2, 30  
Liu, S.G.: SS2+EM+TF-FrM11, 34  
Long, J.P.: EM-FrM3, 30  
Look, D.C.: EM-ThM1, 20; EM-ThM3, 20  
Loppacher, C.: EM-TuM13, 6; EM-TuM2, 5  
Lovejoy, T.C.: EM-WeM2, 9  
Lu, C.Y.: EM-WeM2, 9  
Lu, G.Q.: EM-ThA3, 22  
Lu, J.: EM-WeA8, 16  
Lu, P.: EM-TuM12, 6  
Lu, Y.: EM+NS-MoA2, 3; EM-ThM9, 21  
Lu, Y.-J.: EM-MoM4, 1  
Lucovsky, G.: EM-FrM3, 30; EM-FrM4, 30; EM-WeA10, 17  
Luening, J.: EM-FrM3, 30  
Luning, J.: EM-FrM4, 30

— M —

Maeng, W.J.: EM-FrM1, 30  
Mahapatro, A.K.: EM-TuM6, 5  
Maier, M.: NS+EM+WeM12, 12  
Malliaras, G.G.: SS2+EM+TF-FrM6, 33  
Mallouk, T.: NS+EM+WeM5, 11  
Mamor, M.: EM-ThP8, 26  
Mao, Y.: EM-WeA4, 16  
Marder, S.R.: SS2+EM+TF-WeM1, 12  
Martin, F.: SS2+EM+TF-WeM5, 13  
Martin, N.: SS2+EM+TF-WeM5, 13  
Martin, R.M.: EM-FrM6, 31  
Mativetsky, J.M.: SS2+EM+TF-FrM8, 33  
Matsui, K.: EM-ThP22, 28  
Matsuoka, Y.: EM-ThP22, 28  
McChesney, J.L.: EM+NS-TuA11, 7  
McCullough, R.D.: EM-MoM10, 2  
McDonnell, S.J.: EM-FrM10, 32; EM-ThA10, 23; EM-ThP11, 26  
Medina-Montes, M.I.: EM-FrM9, 31  
Melendez, M.: EM-ThP15, 27  
Melosh, N.A.: SS2+EM+TF-FrM11, 34  
Michalak, D.J.: SS2+EM+TF-ThA6, 24  
Miller, M.A.: EM-WeM11, 10  
Milojevic, M.: EM-FrM10, 32; EM-ThA10, 23; EM-ThP11, 26  
Miranda, R.: SS2+EM+TF-WeM5, 13  
Moad, A.J.: EM-MoM3, 1  
Mohney, S.E.: EM-WeM11, 10  
Montaigne, A.: SS2+EM+TF-FrM2, 32  
Moore, A.M.: EM-TuM1, 5  
Morales, E.H.: EM-ThM9, 21  
Mori, Y.: EM-ThP22, 28  
Morozovska, A.N.: EM-WeA1, 16  
Mosbacher, H.L.: EM-ThM3, 20  
Mullen, T.J.: SS2+EM+TF-WeM3, 13  
Munro, A.M.: EM+NS-TuA10, 7  
Muralidharan, B.: EM-TuM6, 5  
Myers, T.H.: EM-ThM4, 20  
Myslivecek, J.: SS2+EM+TF-FrM7, 33

— N —

Na, J.-S.: EM-TuM5, 5  
Nachimuthu, P.: EM-ThM5, 20  
Nakano, Y.: EM-ThP28, 29  
Nam, J.H.: EM-ThP3, 25  
Nanba, N.: EM-ThP22, 28  
Naydenov, B.: SS2+EM+TF-ThA9, 24  
Neal, J.S.: EM-ThP13, 26  
Ngo, K.D.T.: EM-ThA3, 22

Nguyen, N.: EM-WeA5, 16  
Nigra, M.M.: EM+NS-TuA4, 7  
Nikiforov, M.P.: EM-TuM13, 6; EM-TuM2, 5  
Nogami, J.: NS2+EM-WeA3, 18  
Noh, H.Y.: EM-ThP18, 27  
Noh, S.H.: EM-ThP17, 27  
Northrup, J.E.: EM-MoM8, 2  
Nuneza, G.: EM-ThP29, 29  
Nyns, L.: EM-FrM8, 31

— O —

Ogletree, D.F.: NS+EM-WeM11, 12  
Oh, D.: SS2+EM+TF-ThA7, 24  
Oh, D.H.: EM-ThP3, 25  
Ohta, T.: EM+NS-TuA11, 7  
Ohuchi, F.S.: EM-WeM2, 9  
Okojie, R.S.: EM-WeM3, 9  
Olmstead, M.A.: EM-WeM2, 9  
Opila, R.L.: EM-WeM1, 9  
Orlando, T.M.: SS2+EM+TF-ThA7, 24  
Otero, R.: SS2+EM+TF-WeM2, 13; SS2+EM+TF-WeM5, 13  
Ozawa, H.: SS2+EM+TF-ThA1, 23

— P —

Pai, W.W.: SS2+EM+TF-FrM10, 33  
Pan, H.C.: EM-ThP6, 25  
Pan, J.S.: EM-ThA7, 22  
Park, C.-Y.: EM-ThP3, 25  
Park, M.H.: EM-WeM9, 10  
Park, S.W.: EM-MoM12, 2  
Park, S.-W.: EM-ThP4, 25  
Park, S.-W.: EM-ThP26, 29  
Park, S.-W.: EM-ThP27, 29  
Park, S.Y.: EM-MoM1, 1  
Park, T.-H.: EM-TuM13, 6; EM-TuM2, 5  
Parsons, G.N.: EM-TuM5, 5  
Pearnton, S.J.: EM+NS-MoA7, 4  
Pei, Y.: EM-WeA8, 16  
Petuskey, W.T.: NS+EM-WeM6, 12  
Peydaye, G.: EM-FrM2, 30  
Phillips, J.: EM-ThM8, 21  
Pi, T.-W.: EM-MoM6, 1  
Picraux, S.T.: NS+EM-WeM2, 11; NS+EM-WeM6, 12  
Pingree, L.S.C.: EM-MoM11, 2  
Pirug, G.: SS2+EM+TF-FrM7, 33  
Poole, P.J.: EM+NS-MoA6, 3  
Porter, L.M.: EM-MoM10, 2  
Prabhu, V.M.: EM-ThP23, 28  
Pradhan, A.K.: EM-ThM7, 21  
Pradhan, D.: EM+NS-TuA5, 7

— Q —

Qiao, Y.: SS2+EM+TF-ThA3, 24

— R —

Rack, P.D.: NS2+EM-WeA11, 19  
Rahe, P.: SS2+EM+TF-FrM1, 32  
Rajadurai, C.: SS2+EM+TF-WeM13, 14  
Ramesh, R.: EM-WeA1, 16  
Ramey, J.O.: EM-ThP13, 26  
Rangan, S.: EM+NS-MoA2, 3; EM-FrM7, 31  
Rawn, C.J.: EM-ThP13, 26  
Raymond, S.: EM+NS-MoA6, 3  
Reason, M.: EM+NS-MoA8, 4  
Ren, F.: EM+NS-MoA7, 4; EM-ThP10, 26  
Ren, T.: EM-TuM6, 5  
Resel, R.: SS2+EM+TF-FrM2, 32  
Reutt-Robey, J.E.: SS2+EM+TF-FrM9, 33; SS2+EM+TF-WeM6, 13  
Richard, O.: EM-FrM8, 31  
Richter, C.A.: EM-TuM9, 5  
Richter, L.J.: EM-MoM3, 1; EM-TuM9, 5

Ritz, C.S.: NS+EM-WeM1, 11  
Rivillon Amy, S.: SS2+EM+TF-ThA6, 24  
Robertson, M.D.: EM+NS-MoA6, 3  
Robey, S.W.: SS2+EM+TF-FrM9, 33  
Rodovsky, D.B.: EM-MoM11, 2  
Rodriguez, B.J.: EM-WeA1, 16; NS2+EM-WeA11, 19  
Rosenberg, R.A.: NS2+EM-WeA4, 18  
Ross, F.M.: NS+EM-WeM3, 11  
Rotenberg, E.: EM+NS-TuA11, 7  
Ruben, M.: SS2+EM+TF-WeM13, 14  
Russell, Jr., J.N.: SS2+EM+TF-ThA2, 23  
Ryan, P.M.: SS2+EM+TF-ThA8, 24

— S —

Saavedra, H.M.: SS2+EM+TF-WeM3, 13  
Sambasivan, S.: EM-ThP23, 28  
Sanchez, L.: SS2+EM+TF-WeM5, 13  
Saraf, G.: EM-ThM9, 21  
Sariciftci, N.S.: SS2+EM+TF-FrM2, 32  
Sasaki, K.: EM-WeA11, 17  
Sato, T.: EM-FrM2, 30  
Sauve, G.: EM-MoM10, 2  
Sawkar, M.: EM-FrM6, 31  
Schiettekatte, F.: EM+NS-MoA6, 3  
Schlom, D.G.: EM-WeA2, 16  
Schneider, S.: EM-TuM2, 5  
Schock, M.: SS2+EM+TF-WeM2, 13  
Schreiner, P.R.: SS2+EM+TF-FrM11, 34  
Schroeder, T.W.: SS2+EM+TF-FrM6, 33  
Schütte, J.: SS2+EM+TF-FrM1, 32  
Schwartz, J.: SS2+EM+TF-WeM9, 14  
Scott, A.: EM-TuM10, 6  
Seal, K.: NS2+EM-WeA11, 19  
Seebauer, E.G.: EM+NS-MoA9, 4  
Sekharan, A.K.: NS+EM-WeM13, 12  
Selvidge, M.V.: EM-FrM9, 31  
Senevirathne, L.: NS+EM-WeM13, 12  
Seo, H.: EM-WeA10, 17  
Seo, K.: EM-ThP19, 27  
Seo, Y.-J.: EM-ThP26, 29; EM-ThP27, 29; EM-ThP4, 25  
Seol, Y.G.: EM-ThP18, 27  
Seyller, T.: EM+NS-TuA11, 7  
Shah, P.B.: EM-ThP9, 26; EM-WeM13, 11  
Sham, T.K.: NS2+EM-WeA4, 18  
Sharma, N.: SS2+EM+TF-ThA7, 24  
Shenoy, G.K.: NS2+EM-WeA4, 18  
Shimada, K.: EM-ThP22, 28  
Shin, H.J.: EM-ThP3, 25  
Shin, S.-H.: EM-ThP25, 28  
Shtinkov, N.: EM+NS-MoA6, 3  
Shukla, N.: EM+NS-TuA4, 7  
Shutthanandan, S.: EM-ThM5, 20  
Silien, C.: SS2+EM+TF-WeM10, 14  
Singh, K.A.: EM-MoM10, 2  
Sitter, H.: SS2+EM+TF-FrM2, 32  
Smilgies, D.-M.: SS2+EM+TF-FrM2, 32  
Sokolov, A.: EM-MoM2, 1  
Song, J.J.: EM-ThM3, 20  
Song, W.: EM-ThP3, 25  
Sprunger, P.T.: NS+EM-WeM13, 12  
Stafford, L.: EM+NS-MoA7, 4; EM-ThP10, 26  
Stafström, S.: NS2+EM-WeA2, 18  
Street, R.A.: EM-MoM8, 2  
Su, C.-Y.: EM-ThP5, 25  
Subramanian, S.: EM-MoM3, 1  
Sugai, H.: EM-WeA11, 17  
Sun, Q.: EM+NS-TuA8, 7  
Sun, T.: EM-WeM6, 10; NS2+EM-WeA1, 17  
Sunaoshi, T.: EM-ThP28, 29  
Sundberg, L.K.: EM-ThP23, 28  
Suzuki, S.: EM-ThP28, 29  
Swain, A.: EM-ThM3, 20  
Swartz, C.H.: EM-ThM4, 20  
Swerts, J.: EM-FrM8, 31

— T —

Tait, S.L.: SS2+EM+TF-WeM13, 14  
Takemura, S.: EM-ThP22, 28  
Talin, A.A.: EM+NS-TuA1, 7  
Tan, Y.H.: SS2+EM+TF-FrM3, 32  
Tani, Y.: EM+NS-MoA4, 3  
Tao, C.G.: SS2+EM+TF-WeM6, 13  
Teague, L.C.: SS2+EM+TF-ThA8, 24  
Teichert, C.: SS2+EM+TF-FrM2, 32  
Tersoff, J.: EM+NS-TuA2, 7  
Therein, M.J.: EM-TuM13, 6  
Therien, M.J.: EM-TuM2, 5  
Thevuthasan, S.: EM-ThM5, 20  
Thornton, K.: NS2+EM-WeA1, 17  
Tkachenko, B.A.: SS2+EM+TF-FrM11, 34  
Torres, V.M.: EM-WeM5, 9  
Trant, A.G.: SS2+EM+TF-WeM4, 13  
Turner, K.: NS+EM-WeM1, 11  
Turner, S.G.: EM-ThA7, 22

— U —

Umemura, K.: EM-ThP28, 29  
Uritsky, Y.: EM-FrM2, 30

— V —

Vaidyanathan, R.: EM+NS-MoA9, 4  
Vallee, C.: EM-WeA9, 17  
van Buuren, T.: SS2+EM+TF-FrM11, 34  
Van Elshocht, S.: EM-FrM8, 31  
Vilan, A.: EM-ThP20, 28  
Viveiros, E.: EM-ThP9, 26  
Vogel, E.: EM-ThA10, 23  
Voigtländer, B.: SS2+EM+TF-FrM7, 33  
Voss, L.F.: EM+NS-MoA7, 4; EM-ThP10, 26  
Vrejoiu, I.: EM-WeA1, 16

— W —

Walker, A.V.: EM-TuM12, 6  
Wallace, R.M.: EM-FrM10, 32; EM-FrM9, 31; EM-ThA10, 23; EM-ThP11, 26  
Wang, A.: EM+NS-TuA8, 7  
Wang, C.C.: EM-FrM2, 30  
Wang, D.: SS2+EM+TF-ThA3, 24  
Wang, H.T.: EM+NS-MoA7, 4  
Wang, L.: EM-WeM12, 10  
Wang, S.J.: EM-ThA7, 22  
Wang, W.: EM-ThM8, 21  
Wang, Y.: SS2+EM+TF-WeM5, 13  
Warren, A.P.: EM-WeM6, 10  
Watanabe, M.: EM-WeA11, 17  
Watanabe, Y.: EM-ThP22, 28  
Watson, B.M.: NS+EM-WeM13, 12  
Weidner, T.: SS2+EM+TF-WeM11, 14  
Weiss, P.S.: EM-TuM1, 5; SS2+EM+TF-WeM3, 13  
West, K.G.: EM-WeA8, 16  
Whang, J.M.: EM-MoM12, 2  
Whitaker, K.M.: EM+NS-MoA3, 3  
Whitman, L.J.: SS2+EM+TF-ThA2, 23  
Willey, T.M.: SS2+EM+TF-FrM11, 34  
Winkler, A.: SS2+EM+TF-FrM2, 32  
Wolf, S.A.: EM-WeA8, 16  
Woll, A.R.: SS2+EM+TF-FrM6, 33  
Woo, J.C.: EM-ThP7, 25  
Woo, R.L.: EM-ThA1, 22; NS+EM-WeM5, 11  
Wood, D.M.: EM-ThM6, 21  
Wu, C.-C.: EM-MoM4, 1; EM-MoM6, 1  
Wu, C.-I.: EM-MoM4, 1; EM-MoM6, 1  
Wu, J.H.: NS2+EM-WeA1, 17  
Wu, P.: EM+NS-MoA2, 3

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Xiao, J.: EM-MoM2, **1**  
Xu, B.: SS2+EM+TF-WeM6, **13**  
Xu, J.: EM+NS-TuA8, **7**  
Xu, W.: SS2+EM+TF-WeM2, **13**

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Yamada, T.: SS2+EM+TF-ThA1, **23**  
Yamamoto, A.: EM-WeA5, **16**  
Yang, C.W.: EM-WeM9, **10**  
Yang, H.: EM-ThP14, **27**  
Yang, Y.: EM-WeM5, **9**

Yao, B.: EM-WeM6, **10**  
Ye, G.: NS2+EM-WeA3, **18**  
Ye, P.D.: EM-ThA8, **23**  
Ye, W.: NS2+EM-WeA1, **17**  
Ying, J.: EM-TuM6, **5**  
Yitamben, E.N.: EM-WeM2, **9**  
Yoo, W.J.: NS2+EM-WeA5, **18**  
Yu, H.Z.: EM-TuM11, **6**  
Yu, J.: EM-WeA8, **16**  
Yu, J.-J.: SS2+EM+TF-FrM3, **32**  
Yun, H.-J.: EM-ThP30, **29**

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Zangmeister, C.D.: EM-TuM9, **5**

Zerwek, U.: EM-TuM13, **6**; EM-TuM2, **5**  
Zgrabik, C.: EM-ThM3, **20**  
Zhang, G.: NS2+EM-WeA5, **18**  
Zhang, J.: EM-ThA7, **22**; EM-ThM3, **20**  
Zhang, Q.: SS2+EM+TF-WeM1, **12**  
Zhang, R.: EM-MoM10, **2**  
Zhang, W.H.: SS2+EM+TF-WeM12, **14**  
Zhao, W.: NS+EM-WeM13, **12**; SS2+EM+TF-WeM12, **14**  
Zharnikov, M.: SS2+EM+TF-WeM11, **14**  
Zheleva, T.S.: EM-WeM13, **11**  
Zhu, J.F.: SS2+EM+TF-WeM12, **14**  
Zhu, T.: EM+NS-TuA8, **7**