Topical Conference on Renewable and Alternate Energy
Room 304 - Session EN-SuA

Renewable and Alternate Energy

Moderators: R. Ahrenkiel, University of Denver, G. Parsons, North Carolina State University

3:00pm **EN-SuA1 Scientific Challenges in Sustainable Energy Technology*, N.S. Lewis,*** California Institute of Technology **INVITED**

This presentation will describe and evaluate the challenges, both technical, political, and economic, involved with widespread adoption of renewable energy technologies. First, we estimate the available fossil fuel resources and reserves based on data from the World Energy Assessment and World Energy Council. In conjunction with the current and projected global primary power production rates, we then estimate the remaining years of supply of oil, gas, and coal for use in primary power production. We then compare the price per unit of energy of these sources to those of renewable energy technologies (wind, solar thermal, solar electric, biomass, hydroelectric, and geothermal) to evaluate the degree to which supply/demand forces stimulate a transition to renewable energy technologies in the next 20-50 years. Secondly, we evaluate the greenhouse gas buildup limitations on carbon-based power consumption as an unpriced externality to fossil-fuel consumption, considering global population growth, increased global gross domestic product, and increased energy efficiency per unit of globally averaged GDP, as produced by the Intergovernmental Panel on Climate Change (IPCC). A greenhouse gas constraint on total carbon emissions, in conjunction with global population growth, is projected to drive the demand for carbon-free power well beyond that produced by conventional supply/demand pricing tradeoffs, at potentially daunting levels relative to current renewable energy demand levels. Thirdly, we evaluate the level and timescale of R&D investment that is needed to produce the required quantity of carbon-free power by the 2050 timeframe, to support the expected global energy demand for carbon-free power. Fourth, we evaluate the energy potential of various renewable energy resources to ascertain which resources are adequately available globally to support the projected global carbon-free energy demand requirements. Fifth, we evaluate the challenges to the chemical sciences to enable the cost-effective production of carbon-free power on the needed scale by the 2050 timeframe. Finally, we discuss the effects of a change in primary power technology on the energy supply infrastructure and discuss the impact of such a change on the modes of energy consumption by the energy consumer and additional demands on the chemical sciences to support such a transition in energy supply.

3:40pm **EN-SuA3 Our Solar Power Future: The U.S. PV Industry Roadmap for 2030 and Beyond*, A.M. Barnett,*** University of Delaware*; R. Resch,* Solar Energy Industries Association **INVITED**

The next 10 years are critical for worldwide solar power development. Actions by industry and government will determine whether solar power is catapulted to a new level and whether the United States will regain its position at the forefront of solar power development. Investment decisions over the next decade for research, new manufacturing, and creating new markets will determine where solar power will thrive-and where it will merely survive. Solar power can provide great value in residential and commercial grid-connected applications, for individual consumers and businesses, as well as for utilities and the communities they serve. Our goals for 2030 are solar power system costs of $2.33 per watt, solar electricity prices of 3.8 cents per kilowatt-hour (kWh) delivered to the customer, installed solar power generation of 200 gigawatts (GW), and direct employment of 260,000 people.

4:20pm **EN-SuA5 Hydrogen and Chemicals from Fossil and Renewable Fuels by Autothermal Reforming*, L.D. Schmidt,*** University of Minnesota **INVITED**

Autothermal reactors have great promise for hydrogen and chemicals production because they have reactor residence times of 10-3 seconds and require very simple reactors. We describe the production of hydrogen and olefins from fossil fuels from methane to diesel and from renewable fuels such as ethanol and biodiesel in millisecond reactors. For successful vaporization and mixing of heavy fuels the use of fuel injectors for rapid vaporization and mixing is essential to suppress flames and carbon formation. For ethanol to hydrogen we obtain 80% selectivity to hydrogen at nearly 100% conversion of ethanol and oxygen for an ethanol-air feed. By adding water we obtain 110% (H2 from ethanol and water) in a single stage reactor and 130% H2 selectivity in a staged reactor where a cooler section undergoes the water gas shift reaction. For biodiesel (the methyl ester of C18 fatty acids from soy oil), we can obtain 80% H2 selectivity at C/O=0.8 and 80% selectivity to olefins at C/O=1.5. At higher C/O ratios the ester linkage also survives to produce olefinic esters. Modeling with detailed surface and homogeneous chemistry is used to simulate and understand these processes.

5:00pm **EN-SuA7 Fuel Cells from the Viewpoint of a Skeptical Optimist*, T. Zawodzinski,*** Case Western Reserve University **INVITED**

Fuel cells have been the subject of hype and backlash of late. The hype took various forms, including the 'We'll have a product next year' variety as well as inflated estimates system efficiency, simplicity, etc. Hopes have been dashed because of failure to adequately anticipate the difficulty of some technical and practical problems and from the short duration over which present-day configurations have been tested. The backlash has evolved from reaction to not meeting promises as well as from the realization of the aforementioned problems. Also, fuel cells are linked in many minds to the Hydrogen Economy, which has its own set of detractors. After reviewing these promises and pitfalls, this talk will discuss the current state of development of fuel cells, highlighting technical state of the art. Significant achievements and substantial activities to address some of the major challenges posed by the combination of cost, reliability and performance/functionality factors will be highlighted. By presenting a realistic assessment of these aspects, we hope to leave people with 'reasons to believe' in the promise of fuel cell technology in some applications

Electronic Materials and Processing
Room 310 - Session EM+NS-MoM

Novel Approaches in Wide Bandgap Semiconductors

Moderator: C.R. Eddy Jr., U.S. Naval Research Laboratory

8:20am **EM+NS-MoM1 Halide Chemical Vapor Deposition of SiC Crystals**, ***M. Skowronski***, *A.Y. Polyakov, H.J. Chung, S. Nigam, S.W. Huh,* Carnegie Mellon University*; M.A. Fanton,* Pennsylvania State University **INVITED**

A novel approach to the high growth rate deposition of silicon carbide single crystals and layers is described. The Halide Chemical Vapor Deposition (HCVD) process uses tetrachlorosilane, propane, and hydrogen as reactants . The use of halogenated Si source and separate injection of Si and C precursors allows for preheating the source gases up to the growth temperature (2300 K) without causing premature chemical reactions. This is a distinct advantage over approaches employing silane as the Si precursor. The stoichiometry of HCVD crystals can be controlled by changing the C/Si flow ratio and can be kept constant throughout growth, in contrast to the Physical Vapor Transport technique. HCVD allows for growth of high crystalline quality, very high purity 4H- and 6H-SiC crystals with growth rates in 0.1-0.3 mm/hr. The densities of deep electron and hole traps are determined by growth temperature and C/Si ratio and can be as low as that found in standard CVD epitaxy. At high C/Si flow ratio, the resistivity of HCVD crystals exceeds 1E5 Ohm cm. The properties of crystals grown by HCVD make an attractive method for applications in high-frequency and/or high voltage devices.

9:00am **EM+NS-MoM3 Nm-Resolution Study of Various Quantum-Well Inclusions in 4H-SiC using Ballistic Electron Emission Microscopy: Quantum-Well Energy Depth and Local Transport Behavior**, ***K.-B. Park***, *J.P. Pelz,* The Ohio State University*; M. Skowronski, J. Grim, X. Zhang,* Carnegie Mellon University*; M.A. Capano,* Purdue University

Thin planar inclusions with local cubic stacking can form in hexagonal SiC during device operation, processing, or growth. These have been found to behave as electron quantum wells (QWs), and strongly impact material and device property. We have used nm-resolution Ballistic Electron Emission Microscopy (BEEM)@footnote 1@ to study the electronic properties of individual "single stacking-fault (1SF)" cubic inclusions forming during p-i-n diode operation in (1 1 -2 0) oriented 4H-SiC, where the inclusions intersect a Pt Schottky Barrier (SB) interface. BEEM indicates a QW energy depth of ~0.25 eV below the host 4H-SiC for these 1SF inclusions, comparable to a previous calculated energy of ~0.22 eV@footnote 2@ and a reported ~0.282 eV energy measured by luminescence quenching.@footnote 3@ We are also currently studying inclusions of a different structure forming during CVD growth on 8° miscut n-type 4H-SiC substrates. BEEM indicates a QW energy depth of ~0.40 eV for these inclusions, between the measured ~0.25 eV depth of 1SF inclusions and the ~0.53 eV depth we previously measured on "double" SF inclusions forming during high-temperature processing@footnote 1@. We also observe that the local BEEM current amplitude and SB height on the surrounding 4H-SiC material are quite different on either side of these inclusions, possibly due to strong spontaneous polarization in 4H-SiC and/or subsurface scattering from the 8° inclined inclusion. Work supported by ONR and NSF. @FootnoteText@ @footnote 1@ Y. Ding, K. -B. Park, J. P. Pelz, K. C. Palle, M. K. Mikhov, B. J. Skromme, H. Meidia, and S. Mahajan, Phys. Rev. B 69, 041305(R) (2004).@footnote 2@ H. Iwata et al., Mater. Sci. Forum 389-393, 533 (2002).@footnote 3@ S. G. Sridhara et al., Appl. Phys. Lett. 79, 3944 (2001).

9:20am **EM+NS-MoM4 Quantitative Assessment of Diffusivity and Specularity of Textured Surfaces for Light Extraction in Light-Emitting Diodes**, ***Y.A. Xi***, *X. Li, J.K. Kim, F. Mont, Th. Gessmann, H. Luo, E.F. Schubert,* The Future Chips Constellation

Light extraction in GaN-based light-emitting diodes (LEDs) is limited by the large difference of the refractive index between GaN and the ambient material. The texturing of surfaces and interfaces can improve the light-extraction efficiency into the surrounding medium. Surface-textured reflectors fabricated by natural lithography and ion-beam etching are shown to have a specular as well as a diffusive component of the reflectivity. The diffusely reflected power and the specularly reflected power of surface-textured reflectors are measured and analyzed quantitatively in terms of a new theoretical model. The diffusivity, that is diffusive-power-to-total-power ratio, is determined and shown to strongly depend on the surface texture. Diffusivities of 38.1% and 42.8 % are obtained for the reflectors masked with 445 nm and 740 nm nano-polystyrene balls, respectively, much higher than the 0.35 % of a planar Silver reflector. The light-extraction efficiency from a waveguide, clad by a partially diffuse reflector, is analyzed and shown to be enhanced. In addition, the spatial transmittance pattern of the textured surface is also measured and analyzed by using the same theoretical model. Our study shows that this model can be used to quantitatively assess the dependence of the light-extraction efficiency on the diffusivity of textured surfaces in GaN-based LEDs.

9:40am **EM+NS-MoM5 MOCVD Growth of Al-rich AlGaN Alloys: Materials for Deep-UV Emitters**, ***A.A. Allerman***, *M.H. Crawford, S.R. Lee, D.M. Follstaedt, P.P. Provencio, K.H.A. Bogart, A.J. Fischer,* Sandia National Laboratories **INVITED**

Solid-state light sources emitting at wavelengths less than 300nm would enable technological advances in many areas such as fluorescence-based biological agent detection, non-line-of-sight (NLOS) communications, water purification, and industrial processing. Emitters achieving such emission wavelengths have been fabricated using, almost exclusively, Al-rich alloys of AlGaN. However the growth of Al-rich AlGaN alloys, and especially AlN, has proven problematic owing to their extreme sensitivity to growth conditions in addition to the lack of a native substrate. Even though AlN substrates are being developed commercially, nearly all LEDs emitting in the deep UV are grown on sapphire substrates. Typical LED structures start with an AlN buffer layer which establishes much of the basic crystal structure for the device. The AlN layer typically exhibits threading-dislocation densities exceeding 1x10@super 10@cm@super -2@ and will experience stress-induced cracking when the layer exceeds approximately 1µm in thickness. In this presentation, we will describe a method for AlN film growth that produces threading-dislocation densities less than 5x10@super 9@cm@super -2@. This method involves manipulation of growth conditions following initial film nucleation and has been used to grow crack-free AlN films exceeding 3µm in thickness. Using these AlN films as template layers, we produced Si-doped AlGaN films (with ~50-70% AlN mole fractions) that have improved electron mobilities and higher doping efficiencies. These improvements suggest a reduced level of compensation in the AlGaN film due to reductions in dislocation density. The presentation will also include the performance of LEDs emitting in the deep UV (<300nm) that have been fabricated with lower dislocation density AlN-AlGaN films. Sandia is a multiprogram laboratory operated by Sandia Corporation, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-ACO4-94AL85000. This work is also supported by DARPA under the SUVOS program managed by LTC J. Carrano.

10:20am **EM+NS-MoM7 High Reflectance GaN-based Distributed Bragg Reflectors Grown on Si Substrates**, ***M.A. Mastro***, *R.T. Holm, N.D. Bassim, D.K. Gaskill, C.R. Eddy Jr., R.L. Henry, M.E. Twigg,* U.S. Naval Research Laboratory

Presently, GaN based optoelectronic devices are primarily grown on expensive sapphire and SiC substrates. Substituting these substrates with inexpensive Si substrates would represent a major shift in the economics of the visible optoelectronic market. The primary limitation to this device structure is light absorption by the opaque Si substrate. Insertion of a high reflectance distributed Bragg reflector (DBR) between the substrate and the active region would increase light extraction by approximately a factor of two. The second major impediment to this device structure is the poor quality of group III-nitride films grown on Si substrates. High densities of dislocations and cracks can form in the (Al,Ga,In)N layers due to their large lattice and thermal expansion mismatch with the Si substrate. Thus low internal quantum efficiency is commonly observed for GaN based devices grown on Si substrates. This paper presents the first high-reflectance (>90%) (Al,Ga)N quarter-wave DBR grown on a Si (111) substrate. In-situ reflectometry of the MOCVD growth process allowed exact control of each individual layer thickness to yield DBR reflectance approaching the calculated theoretical level. Nominally crack free structures were obtained by controlling the distribution of the strain in the structure. Specifically, the DBR structure acted as a distributed buffer layer (DBL) for the thick GaN cap layer. TEM revealed a fall-off in screw-type dislocations throughout the DBL. This development presents the opportunity to significantly advance GaN based optoelectronics, including light emitting diodes (LEDs), resonant cavity light emitting diodes (RCLEDs) and vertical cavity surface emitting lasers (VCSELs), on Si substrates.

10:40am **EM+NS-MoM8 Synthesis of Aligned Arrays of III-Nitride Nanowires and Heterostructure Nanowires via MOCVD*, G.T. Wang*,** *J.R. Creighton, P.P. Provencio,* Sandia National Laboratories*; D. Werder,* Los Alamos National Laboratory

Nanowires based on the direct bandgap semiconductor Group III nitride (AlGaInN) materials system are attractive due to their potential in novel optoelectronic applications, including LEDs, lasers, high power transistors, and sensors. We have employed a MOCVD process to synthesize highly aligned arrays of single-crystalline GaN nanowires in a standard cold-wall rotating disk reactor on 2-inch diameter sapphire wafer substrates without patterning or the use of a template. Building on this process, we have also been able to synthesize novel core-shell heterostructure nanowires consisting of a GaN cores and various III-nitride shell materials, including AlN, InN, and AlGaN, and InGaN. In this presentation, several challenges and issues regarding control of the growth process will be discussed, including selectivity of VLS growth versus film nucleation, control of nanowire alignment and density, as well as the ability to control shell-layer uniformity in heterostructure nanowires will be discussed. Data on the optoelectronic and electrical properties of the nanowires and heterostructure nanowires will also be presented. The growth processes and reactor environment employed in this study are typical of those used to synthesize device-quality III-nitride films and should be scalable to larger commercial reactors and substrates. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

11:00am **EM+NS-MoM9 Large-scale Synthesis of GaN Nanowires by Direct Reaction of Gallium with Ammonia*, C.-H. Hsieh,*** National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chou,* National Tsing Hua University, Taiwan, R.O.C., Taiwan, R.O. C.

High-density GaN nanowires were synthesized on a large-scale Si substrate by direct reaction of metal gallium vapor under ammonia and hydrogen gases at 680~700°C. The morphology, composition and crystal structure were characterized by field-emission scanning electron microscope (FESEM, JSM-6500F), field-emission transmission electron microscope (FETEM, JEM-3000F) and X-ray spectrometer (SHINMADZU), respectively. From SEM images, the morphology of GaN nanowires is vermicular-like with average diameter of 200 nanometer and the length of up to 20 micrometer. The compositional line profile of TEM analysis revealed the vermicular-like GaN nanowires were uniformly doped with silicon and oxygen. The correspondent electron diffraction pattern indicated the vermicular-like GaN nanowires exhibiting poly-crystal structure. The XRD results of vermicular-like GaN nanowires show the hexagonal wurtzite structure. Furthermore, the cathodoluminescence (CL) characteristics demonstrate a broad band in the energy range of 2.1-3.1eV.

11:20am **EM+NS-MoM10 Optical and Ellipsometric Studies on InN Layers Grown by High-Pressure CVD*, N. Dietz*,** *M. Alevli, M. Strassburg, V.T. Woods, U. Perera,* Georgia State University*; N.A. Stoute,* North Carolina State University, US*; D.E. Aspnes,* North Carolina State University

The fabrication of emerging detector and emitter structures as well as high-frequency/high-power devices operating at high temperature(s) that are based on group III-nitride compound alloys is presently limited by the challenging difficulties in the growth of high quality In-rich group-III-nitride alloys and heterostructures. Even though recent improvements in MBE-grown InN material established a band gap near 0.65 eV, other data show a band gap near 1.85 eV. The origin of this bandgap difference is not understood. Here, we focus on the analysis of optical data obtained both by absorption spectroscopy and spectroscopic ellipsometry (SE) on InN material grown by high-pressure chemical vapor deposition (HPCVD) in the 10 to 15 bar pressure range as a function of growth temperature, flow rate, and flow ratios of ammonia and trimethylindium (TMI). With HPCVD we can compensate the inherent volatility of nitrogen and stabilize indium-rich conditions and grow group-III-nitride alloys at temperatures comparable to those used for GaN and AlN. The optical data indicate that the decrease in optical absorption edge from 1.85 eV to 0.63 eV is caused by a series of absorption centers appearing at 1.6 eV, 1.35 eV, 1 eV, 0.87 eV and below 0.65 eV. The appearance of these centers correlates with the indium-to-nitrogen ratio, which is controlled through the flow rates of ammonia and TMI. For InN layers grown near 1100 K and molar ammonia/TMI ratios less than 200, an InN absorption edge below 0.63 eV is observed. For material with absorption edges near 1.9 eV a strong peak is observed, which appears to be excitonic in nature.

11:40am **EM+NS-MoM11 Determining Composition of HPCVD Indium Nitride with Auger Electron Spectroscopy*, R.P. Bhatta,*** *B.D. Thoms, V.T. Woods, M. Alevli, N. Dietz,* Georgia State University

Indium Nitride (InN), a wurtzite structure III-V semiconductor with a direct bandgap, has potential for use in many optoelectronic applications. In addition, alloys of InN, GaN, and AlN cover a large spectral range from 0.6 eV up to 6 eV which can be utilized in many novel optoelectronic devices. The low growth temperatures usually needed for growth and stability of InN have limited the use of widely varying alloy compositions in the same device. High pressure chemical vapor deposition (HPCVD) allows InN to be grown at temperatures similar to those of GaN and AlN. There has recently been considerable debate regarding the value of the energy bandgap of InN and its relationship to the concentration of oxygen in the film. The optical analysis of InN layers grown under HPCVD shows that the shift of the absorption edge down to 0.63 eV is caused by a series of absorption centers. The appearance of these absorption centers is closely related to the indium and nitrogen point defect chemistry, which can be controlled through the molar flow ratio of the precursors. In this contribution, the compositional analysis of HPCVD grown InN films by Auger Electron Spectroscopy (AES) is presented. The proximity of the nitrogen and indium AES peaks makes determination of nitrogen to indium ratios more difficult. It has been reported that ion sputtering reduces the nitrogen content in InN films. While this study also reports that sputtering reduces the relative peak-to-peak height for dN/dE spectra, a substantial reduction is not observed in the relative integrated intensities for undifferentiated spectra. We conclude that sputtering has a large effect on the lineshape of nitrogen AES peaks but does not substantially reduce the nitrogen concentration. The concentrations of contaminants such as carbon and oxygen were analyzed and correlated with film properties measured by Raman and absorption spectroscopy.

Electronic Materials and Processing
Room 309 - Session EM-MoM

Electronic Properties of High-k Dielectrics and their Interfaces

Moderator: S.A. Chambers, Pacific Northwest National Laboratory and Univ. of Washington

8:20am **EM-MoM1 Electronic Properties of High-K Dielectrics and their Interfaces*, J. Robertson,*** University of Cambridge, UK **INVITED**

The continued scaling of CMOS devices means that SiO2 must be replaced as gate oxide by a dielectric of higher dielectric constant (K) to minimise gate leakage.@footnote 1@. The presently preferred candidates are HfO2, its silicates and nitrided alloys. La oxide and LaAlO3 are possible in the future. The reasons for this selection in terms of band offsets will be given,@footnote 2@ including their measurement and calculation. Despite much success in developing growth methods for high K oxides, including ALD, presently the performance of FETs with HfO2 are worse than those with SiO2 in terms of threshold voltage shifts, carrier mobility and trapped charge. This arises partly from the more complicated interface structure and greater bonding possibilities than at an Si:SiO2 interface. We show it is possible to define an ideal abrupt Si:HfO2 interface in terms of its bonding; only Hf-O and Si-O bonds or only Hf-Si bonds.@footnote 3@ In fact, a number of high symmetry and lower symmetry abrupt interfaces are possible. The structure, electronic structure and band offsets for these are given. It is then possible to define a defective interface; one containing mixed bonding. It is shown how such mixed bonding at the "back interface" between the HfO2 and poly-Si gate may be the cause of the excessive gate threshold voltages.@footnote 4@@FootnoteText@@footnote 1@ J Robertson, "High dielectric constant oxides", Euro Phys J Appl Phys 28 265 (2004) @footnote 2@ J Robertson, "Band offsets of wide band gap oxides and implications for future electronic devices", J Vac Sci Technol B 18 1785 (2000) @footnote 3@ P W Peacock, J Robertson, "Bonding, energetics and band offsets of Si-ZrO2 high-dielectric constant gate oxide interfaces", Phys Rev Letts 92 057601 (2004) @footnote 4@ K Xiong, P W Peacock, J Robertson, "Fermi level pinning and Hf-Si bonds at HfO2: poly-Si gate electrode interfaces", App Phys Lett 86 012904 (2005).

9:00am **EM-MoM3 The Effect of Nitrogen Incorporation on the Material and Electrical Properties of HfO@sub 2@ on Si*, M. Sawkar,*** *J. Choi, R. Puthenkovilakam, J.P. Chang,* UCLA

Alternative gate dielectrics are required in the future generation of MOSFET devices to enable their rapid down-scaling. One of the most

promising candidates is HfO@sub 2@. Unfortunately, HfO@sub 2@ has a low crystallization temperature, resulting in its structural change from amorphous to polycrystalline under high-temperature processing, which results in grain boundaries that serve as a path for leakage current, oxygen diffusion, and impurity diffusion. The incorporation of nitrogen in HfO@sub 2@ films increases the temperature at which the grain boundaries form allowing these films to remain amorphous at higher temperatures. This paper discusses the effect of nitrogen incorporation on the material and electrical properties of HfO@sub 2@. XPS, ellipsometry, and HRTEM are used to characterize the material properties. To characterize the electrical properties, MOS capacitors are fabricated to examine the capacitance-voltage (C-V) and current density-voltage (J-V) characteristics. Preliminary results showed that the leakage current density of the nitrogen incorporated samples is approximately three orders of magnitude lower than the as-deposited HfO@sub 2@. We also performed first-principle simulations within the framework of density functional theory to assess the effect of nitrogen incorporation on the bulk electronic properties of HfO@sub x@N@sub y@, as well as on the dielectric/Si interface properties. The simulation shows that the N 2p state is extended further toward the conduction band and the ionic character of Hf-N bonding is less pronounced with increasing nitrogen incorporation, resulting in a reduction in the band gap. The band alignment at the HfO@sub x@N@sub y@/Si interface calculated using the (HfO@sub 2@)(Hf@sub 3@N@sub 4@) structure as a model stoichiometry revealed an estimated valence-band offset of 1.14 eV, which is significantly lower than that reported for HfO@sub 2@/Si.

9:20am **EM-MoM4 Suppression of Fixed Charge at Internal Interfaces between SiO@sub 2@ and Dual-Layer High-k Gate Dielectrics: HfO@sub 2@-Al@sub 2@O@sub 3@**, ***C.L. Hinkle***, *G. Lucovsky,* North Carolina State University

A reduction in interfacial fixed charge between SiO@sub 2@ and high-k dielectrics has been studied using a dual layer high-k stack to match intrinsic bonding properties at interfaces. Previous studies of Al@sub 2@O@sub 3@ on SiO@sub 2@ have shown a large amount of fixed charge at the interface, effectively eliminating Al@sub 2@O@sub 3@ from the discussion of alternative gate dielectrics. However, a self-organization occurs for Zr and Hf oxides and silicates after anneal that leaves low interfacial charge at the interface of those materials and an SiO@sub 2@ buffer layer. The density of interfacial defects has been shown to scale with the step in bonds per atom at the interface, D@sub int@ @alpha@ [N@sub av@(A) - N@sub av@(B)]@super 2@. Using this scaling as a guide, internal interfaces can be engineered from materials that match the average bonds per atom on both sides of the interface thereby reducing the number of defects and suppressing the fixed charge. A gate stack using SiO@sub 2@-HfO@sub 2@-Al@sub 2@O@sub 3@ has been produced using these techniques. The SiO@sub 2@-HfO@sub 2@ interface becomes self-organized and relatively defect low after anneal at 800°C whereas the HfO@sub 2@-Al@sub 2@O@sub 3@ interface has a matchup of N@sub av@ intrinsically. Electrical characterization of the gate stacks was done using C-V measurements to analyze the flatband voltage shift in these materials. The flatband voltage for the SiO@sub 2@-HfO@sub 2@-Al@sub 2@O@sub 3@ stack is effectively the same as a film of SiO@sub 2@ showing the reduction in fixed charge expected from the theory mentioned above. Different thicknesses of each layer have been studied as well as frequency dependent C-V to determine trapping at the internal interfaces. Using this proposed method extends the range of usable high-k materials.

9:40am **EM-MoM5 Self-organization of Thin Film Dielectrics and Their Interfaces in Gate Stacks for Advanced Si Devices**, ***G. Lucovsky,*** NC State University*; J.C. Phillips,* Rutgers University

Self-organizations which inhibit percolation of network bond-strain are addressed. These occur i) within multi-atom gate dielectrics, Si@sub 3@N@sub 4@:H and Si@sub 3@N@sub 4@-SiO@sub 2@-ZrO@sub 2@ alloys, ii) at Si-SiO@sub 2@ interfaces, and iii) at internal interfaces in multi-layer dielectrics. All are driven by the same mechanism, but the dimensionalities of the materials systems are different. The dielectric films are 3-dimensional, but interfaces are 2-dimensional. The self-organizations of Si@sub 3@N@sub 4@:H and Si@sub 3@N@sub 4@-SiO@sub 2@-ZrO@sub 2@ dielectrics arise from stressed-rigid bonding, and prevent percolation of bond-strain at processing temperatures greater than the deposition temperatures. For the Si@sub 3@N@sub 4@:H and Si@sub 3@N@sub 4@-SiO@sub 2@-ZrO@sub 2@ alloys, compositions are identified that prevent chemical phase separation, and subsequent degradation of device properties. At the Si-SiO@sub 2@ interface the self-organization is at a molecular scale in a layer ~0.3-0.5 nm thick. This self-organization relieves in-plane strain, and provides for the first time a quantitative understanding for roughness scattering of channel electrons/holes in field effect transistors. This self-organization has enabled the information science revolution to proceed by down-sizing of Si integrated circuits and making Moore's Law for performance, cost and increased functionality a reality. Finally, self-organization at SiO@sub 2@-high-k internal interface is enabling for continuing Moore's Law scaling with alternative high-k dielectrics such as HfO@sub 2@ and Al@sub 2@O@sub 3@.

10:00am **EM-MoM6 Physical and Electrical Properties of LaAlO@sub 3@, Potential Candidate for High K Gate Dielectric**, *V. Edon,* ***M.C. Hugon****, O. Voldoire, B. Agius,* Universite Paris Sud, France*; I.J.R. Baumvol, L. Miotti, K.P. Bastos,* Universidade Federal do Rio Grande do Sul, Brazil

There is currently an extensive research effort to find an alternative gate dielectric to replace SiO@sub 2@ in metal oxide semiconductor field effect transistors (MOSFETs). LaAlO @sub 3@ is a promising material: it has a dielectric constant in the range 20-27. RuO@sub 2@ is proposed as a gate electrode. LaAlO@sub 3@ films were deposited by rf magnetron sputtering of a LaAlO@sub 3@ target in argon atmosphere. Thin film properties are studied as a function of deposition parameters (rf power, process pressure) and thermal annealings (in @super 16@O@sub 2@ or @super 18@O@sub 2@ atmospheres - temperatures from 450 to 1000 °C). Physical properties of as deposited material (composition, density), as determined by RBS, NRA, and X-ray reflectometry, are seen to depend slightly on deposition parameters. The films are stoichiometric and present a density of 5.5 ± 0.5g.cm@super -3@ close to the bulk material one (6.5g.cm@super -3@). The thermal stability of LaAlO@sub 3@ has been investigated under typical conditions of a MOSFET processing. O and Al transport during annealings are investigated with sub-nanometric depth resolution via the narrow resonances of @super 18@O(p,@alpha@)@super 15@N at 151 keV (fwhm=100eV) and @super 27@Al(p,@gamma@)@super 28@Si at 404.9keV (fwhm=40eV) respectively. The interfacial characteristics of LaAlO@sub 3@/Si were measured by spectroscopic ellipsometry, X ray reflectometry. The initial measurements subject the presence of an interfacial layer. We have performed high frequency (1MHz, 100kHz) C-V and I-V characteristics on RuO@sub 2@/LaAlO@sub 3@/Si MIS structure. After a thermal treatment at 600°C, the C-V curves exhibit well defined accumulation, depletion and inversion regimes which indicate a low interface state density. With the device biased in accumulation regime, a permittivity of 15 was deduced. Low leakage current is detected for films deposited at 0.5Pa or 5Pa and annealed at 600°C under 1 atm of oxygen.

10:20am **EM-MoM7 Magnesium Oxide as a High-K Gate Dielectric**, ***L. Yan,*** *C.M. Lopez, E.A. Irene,* University of North Carolina-Chapel Hill

The presently considered candidate high @Kappa@ dielectric materials are reactive with Si and SiO@sub 2@ and most metals yielding undesirable interfacial electronic properties. While magnesium oxide (MgO) does not have as high of a @Kappa@ value (about 9.8 for bulk material) as many of the other candidate dielectrics (e.g., ZrO@sub 2@ and HfO@sub 2@), it has its unique advantages such as chemical inertness enabling sharp interfaces and wide bandgap (7.3 eV) for large band offsets with silicon (Si) to minimize leakage. In this study, MgO thin films were deposited via reactive rf sputtering on both bare Si and SiO@sub 2@ coated Si. In situ spectroscopic ellipsometry (SE) and Mass Spectrometry of Recoiled Ions (MSRI) were used to monitor the film growth in real time and cross-sectional transmission electron microscopy and atomic force microscopy were used to determine interface and surface roughness, respectively. Capacitance versus voltage (C-V) and conductance (G(@omega@)) versus gate voltage (G(@omega@)-V) measurements were performed on capacitor structures in order to determine @Kappa@, and the density of interface states (D@sub it@), respectively. Thus far a value of about 8 was obtained for the static dielectric constant for 10 nm films and interface charge and D@sub it@ results are comparable with SiO@sub 2@ on Si. Based on our measured properties it is concluded that thin MgO films can provide a high K dielectric for many electronic applications. @FootnoteText@ This work is supported by the National Science Foundation (NSF) Materials Research Division.

10:40am **EM-MoM8 Spectroscopic Studies of Band Alignment in Metal/High-k Dielectric/Si Gate Stacks**, ***E. Bersch,*** *S. Rangan, O. Celik, W. Jiang, C.L. Hsueh, E. Garfunkel, R.A. Bartynski,* Rutgers University

The continued scaling of CMOS devices requires the replacement of SiO2 with a higher dielectric constant oxide, and of the doped poly-silicon gates with metal electrodes. The band alignment at these interfaces is critical in that there must be sufficient valence and conduction band offsets (> 1.0eV)

to limit the leakage current across the dielectric to a tolerable level. We have measured the conduction and valence band offsets of metal/high-k/Si gate stacks with inverse photoemission and photoemission, respectively, for various combinations of candidate gate metals and alternate dielectrics, in situ. Using inverse photoemission, the conduction band minimum (ECBM) is found to be 2.2 eV above the Fermi level ALD grown HfO2/Si films. This value is reduced by ~ 0.3 eV on films annealed to 700oC. The energy of the CBM of hafnium silicate films grown on Si that were subjected to a 1000oC anneal is found to be independent of silicate concentration, while similarly processed nitrided hafnium silicate films annealed exhibit in increase in the CBM energy with increasing silicate concentration. Upon metallization with Ru, ECBM of each of these systems decreases by ~ 0.3eV. We have also measured these offsets on the same samples with x-ray absorption spectroscopy and internal photoemission. The results of all of these methods will be compared to each other, and the merits of each method will be discussed.

11:00am **EM-MoM9 Characterization of Nitrided Hafnium Silicates for High-@kappa@ Dielectrics Using Photoelectron Spectroscopy***, **A. Mathew**, K. Demirkan,* University of Delaware*; C.-G. Wang, G. Wilk,* ASM America*; R.L. Opila,* University of Delaware

Nitrided hafnium silicates are strong contenders to replace the silicon dioxide gate dielectric in transistors for low standby power applications. Photoelectron spectroscopy with its sensitivity to local chemical bonding is an invaluable tool for investigating this dielectric. Hafnium silicates were deposited using Atomic Layer Chemical Vapor Deposition and subsequently nitrided. Nitrogen incorporation prevents dopant diffusion from the poly-silicon. Rapid thermal annealing of the nitrided and as deposited films can induce spinodal decomposition of these films. The Hf 4f and Si 2p binding energies in unannealed, non-nitrided films change as a function of Hf/Si composition. This shift in binding energy is attributed to the electronegativity of second nearest neighbors. After annealing, the Hf 4f and Si 2p peaks do not vary as a function of composition, but are not at the silica 2p and hafnia 4f positions. The distribution of nitrogen in the film can be determined from photoelectron spectra collected as a function of take off angles. Results suggest that nitrogen replaces oxygen. The variation in the Hf 4f, Si 2p and N 1s binding energies as a function of annealing temperature and phase composition will be discussed. The effect of nitrogen upon the binding energies of the Hf 4f, O 1s and Si 2p before and after annealing, as well as its role in the phase decomposition upon annealing will be discussed.

11:20am **EM-MoM10 Surface Functionalization and Interface Characterization for HfO@sub 2@ Growth by Atomic Layer Deposition***, **Y. Wang**, M.-T. Ho, L.S. Wielunski, L.V. Goncharova, T. Gustafsson, Y.J. Chabal,* Rutgers University*; N. Moumen,* Sematech*; M.P. Boleslawski,* Aldrich Chemical Co.

Hafnium oxide is a promising candidate to replace SiO@sub 2@ and prevent current leakage in nanoscale transistors. For fabricating ultra-thin films, atomic layer deposition (ALD) is the preferred growth method. However, formation of interfacial SiO@sub 2@ during the ALD growth significantly increases the equivalent oxide thickness (EOT), partly negating the value of high-@kappa@ dielectrics. Our approach to minimizing interfacial SiO@sub 2@ formation during HfO@sub 2@ deposition is based on surface pretreatment of H-passivated silicon surfaces with Cl@sub 2@ and NH@sub 3@, followed by studies of the effect of post annealing on the nature of the interface. Using various surface/interface analytical techniques, such as in situ infrared spectroscopy, ex situ Rutherford back scattering spectroscopy (RBS) and medium energy ion scattering spectroscopy (MEIS), we have found that surface termination/passivation by hydrogen, chlorine, or silicon nitride can effectively prevent silicon oxidation during HfO@sub 2@ ALD growth, while fostering a linear growth of HfO@sub 2@ (~0.09 nm per ALD cycle). In situ IR studies show a linear incorporation of hydroxyl within the HfO@sub 2@ film during growth, constituting a source of excess oxygen within the film. Upon annealing above 400@super o@C, interfacial SiO@sub 2@ is formed as the hydroxyl content of the film decreases down to less than 10% of the initial value. The initially amorphous HfO@sub 2@ film begins to crystallize at 500@super o@C, as reflected in the appearance of a sharper HfO@sub 2@ phonon mode (~780 cm@super -1@) and in the angular dependence in the MEIS. Preliminary electrical properties measurement indicates the leakage current of the ALD-grown HfO@sub 2@ is small on the pre-functionalized silicon substrate.

11:40am **EM-MoM11 Differences in Band Edge Electronic Structure between Nanocrystalline ZrO@sub 2@ and HfO@sub 2@ Thin Films, and Bulk Crystals and Thin Films of Cubic Zironia (ZrO@sub 2@-Y@sub 2@O@sub 3@) and Hafnia (HfO@sub 2@-Y@sub 2@O@sub 3@)***, **N.A. Stoute**,* North Carolina State University, US*; H. Seo, C.C. Fulton, D.E. Aspnes, G. Lucovsky,* North Carolina State University

There is considerable interest in the band edge electronic structure of high-k oxides for applications as gate dielectrics in advanced semiconductor devices. This paper compares band edge electronic structure of nanocrystalline (nc) thin films of ZrO@sub 2@ and HfO@sub 2@, with i) bulk crystals of cubic zirconia and hafnia, e.g., ZrO@sub 2@ that is cubic as a result of incorporation of 5%-30% Y@sub 2@O@sub 3@, as well as ii) thin alloys of nanocrystalline ZrO@sub 2@-Y@sub 2@O@sub 3@ over a wider composition range. The band edge electronic structure of these alloy dielectrics has been studied by visible-near UV optical transmission and visible-near-UV-VUV spectroscopic ellipsometry. Band edge structure is also compared with ab initio calculations. For (Y@sub 2@O@sub 3@)@sub 0.095@(ZrO@sub 2@)@sub 0.905@ we observe a sub-bandgap absorption onset at ~4 eV, an absorption edge at ~5.3 eV and a weak d-state structure at ~6.3 eV. In contrast, nc-ZrO@sub 2@ has an absorption edge at ~5.7eV, and prominent d-state features at ~6.2 and 7.0 eV. Cubic (Y@sub 2@O@sub 3@)@sub 0.15@(HfO@sub 2@)@sub 0.85@ displays sub-bandgap absorption at ~ 4 eV, an absorption edge at ~5.9 eV, and a weak, broad d-state feature at ~7.5 eV, compared with an absorption edge at ~5.8 eV and sharp d-state features at ~6 and 7.2 eV in nc-HfO@sub 2@. The end-member ZrO@sub 2@ and HfO@sub 2@ nanocrystalline thin films display Jahn-Teller distortions that remove band edge d-state degeneracies that are not present in the Y@sub 2@O@sub 3@-stabilized cubic phases. The Y@sub 2@O@sub 3@-stabilized cubic phases display sub-bandgap absorption attributed to deep electronic states associated with the O-vacancies, while the nc-thin films display defects ~0.5 to 0.8 eV below the conduction band edge. These have been assigned to nanocrystalline grain boundary defects.

Thin Films
Room 306 - Session TF+EM-MoM
Thin Films for Photovoltaic and Energy Applications

Moderator: B.C. Holloway, College of William and Mary

8:20am **TF+EM-MoM1 Hydrogen - The World of Tomorrow?***, **G.N. Richter**,* Chevron Fellow Emeritus **INVITED**

We have all heard of the coming world of hydrogen, and how it will become our energy carrier of choice, both clean and efficient, a major input for many chemical processes and, perhaps, our saviour. I am sure that this is coming, and it will bring a major change to many things we do. It will take a revolution to bring this about and it won't be until some time in the future. The question isn't if it will happen, but when will it come and what is needed to bring it about? Others at this meeting are telling us of the uses of hydrogen, its promises and its behaviour. But, there are also important questions to ask about where will the hydrogen come from and the infrastructure needed for us to be able to use it. It is the difficulty in answering these questions that is holding back the revolution. And it is these points that I would like to discuss with you today. Not the promises we have all heard, but how we can get to this "promised" land, as well as some of the things we might all do to get there sooner. What are the needs and opportunities for all of us to address?

9:00am **TF+EM-MoM3 Carbon Nanotube Catalyst for PEM Fuel Cells***, **J. Narayanamoorthy**, S. Durairaj, J. Choi,* Wayne State University

Carbon nanotubes have unique properties for future fuel cell applications such as diverse electrical properties, large surface area to volume ratio, chemical inertness, etc. The role of carbon nanotubes for the polymer electrolyte fuel cell has been investigated. First, the morphological, electrical, and mechanical role of the carbon nanotubes in the catalyst layer was studied. There was minimal cracking and maximal interconnect in the layer with carbon nanotubes. The resistance of the catalyst layer reduced due to the presence of carbon nanotubes and mechanical properties also showed good improvement. Further, carbon nanotubes themselves were employed as catalyst in place of noble metals and were optimized by tuning the electronic properties of carbon nanotubes. In this presentation, we will discuss the correlation between catalytic activity and the electronic structure of carbon nanotubes.

9:20am **TF+EM-MoM4 Growth of CIGSS Thin Film Solar Cells on Flexible Stainless Steel Substrates of Various Thicknesses**, ***A. Kadam***, *A. Jahagirdar, N.G. Dhere,* University of Central Florida

The article presents the effect of surface roughness and thicknesses of stainless steel(SS) substrates on the growth behavior of CuIn@sub 1-x@Ga@sub x@Se@sub 2-y@S@sub y@(CIGSS) absorber thin film solar cells. The work was carried out on 430 grade SS of thicknesses 25 µm, 50 µm and 127 µm. Surface roughness gradually decreased from 254 Å for 25 µm to 62.3 Å for 127 µm substrate. Thinner foil has higher surface roughness as it required more processing steps. Deposition sequence was Mo/SS/Mo/CIGSS/CdS/i:ZnO/ZnO:Al/Ni/Al. Mo back contact and Cu-Ga-In metallic precursors were deposited by DC magnetron sputtering. Mo was deposited on both the sides of SS to prevent the reaction of selenide and sulfide gases with SS during processing. Mo was deposited in a three-layer sequence. Mo layer deposited at low DC power and high argon gas pressure develops tensile stress while that deposited at high power and low pressure exhibits compressive stress. Tensile layer was sandwiched between two compressive layers to reduce the overall stress and to build the thickness of 500 nm. Identical parameters were used for deposition of metallic precursors on all three substrates. The elemental stack was selenized at 400@super o@C for 10 minutes followed by sulfurization at 475@super o@C for 20 minutes. CdS, n-type hetero-junction partner was deposited by chemical bath deposition. Window bilayer of i:ZnO and ZnO:Al were deposited by RF magnetron sputtering and Ni/Al contact fingers were deposited by e-beam evaporation. The crystal structure, surface morphology, chemical variation and cell efficiency were studied using the characterization technique such as x-ray diffraction, scanning electron microscopy, Auger electron spectroscopy, transmission electron microscopy, current-voltage and quantum efficiency measurement to bring out the variation in the growth behavior and cell efficiency on substrates having varied physical properties.

9:40am **TF+EM-MoM5 Surfactant-assisted Growth of CdS Thin Films for Photovoltaic Applications**, ***C.L. Perkins***, *F.S. Hasoon,* National Renewable Energy Laboratory

A common non-ionic surfactant, Triton X-100, was used to modify the chemical bath deposition (CBD) of CdS "buffer" layers on Cu(In,Ga)Se@sub 2@ (CIGS) thin films. X-ray photoelectron spectroscopy and Auger electron spectroscopy data demonstrate that films produced with the surfactant have about the same levels of impurities as films grown without it. It was found that Triton X-100 allowed the use of CdS layers that were 3-4 times thinner than those used normally in high efficiency CIGS-based devices, with no loss in cell performance. For these thin CdS layers and relative to devices made without the surfactant, average absolute cell efficiencies were increased from 10.5% to 14.8%, or by a relative 41%. Visual inspection of the CdS depositions reveals one possible mechanism of the surfactant's effects: bubbles that form and adhere to the CIGS surface during the chemical bath deposition are almost completely eliminated with the addition of the TX-100. Thus, pinholes and thin areas in the CdS layers caused by poor wetting of the substrate surface are sharply reduced, leading to large increases in the open circuit voltage in devices produced with the surfactant.

10:00am **TF+EM-MoM6 Surface Energies and Surface and Grain Boundary Nanochemistry of Cu(In,Ga)Se@sub 2@**, *C. Lei, D. Liao, A. Hall, I.M. Robertson,* ***A. Rockett***, University of Illinois

A combination of angle-resolved photoelectron spectroscopy, atomic force microscopy, and analytical high-resolution transmission electron microscopy including nanoprobe energy dispersive spectroscopy (EDS) and angular darkfield imaging have been used to characterize the surfaces and grain boundaries in a wide variety of Cu(In,Ga)Se@sub 2@ epitaxial single crystal and polycrystalline thin films. We have observed the formation of a wide variety of nanoscale and microscale voids in polycrystalline grain boundaries and in heteroepitaxial interfaces. It is argued that these are Kirkendall voids. Likewise, trapped internal voids within grains are observed in dislocation cores and at twin termination boundaries. These have been analyzed and a Wulff construction developed to characterize the surface energies in the material. The results show that the polar metal-terminated (112) planes are the lowest energy surfaces, followed by the Se-terminated (112) planes. These results are consistent with the surface morphology of growing epitaxial layers of various orientations, indicating that the surface faceting is a largely equilibrium rather than kinetically-determined result. Other planes are stable when covered by a surfactant layer of Cu@sub 2@Se, which occurs naturally when the film is deposited in an average Cu-rich condition. Grain boundaries are also found to exhibit faceted growth. Surprisingly, in spite of these surfaces being polar, no chemistry change is observed with nanoprobe EDS in the grain boundaries relative to the bulk grains for films grown at high temperatures. For low temperature depositions (below 450°C), non-equilibrium grain boundary compositions are observed. Clean metal-terminated (112) surfaces are shown to have Fermi energies higher in the energy gap when treated in various ways than the corresponding Se-terminated surfaces. The results are related to solar-cell device performances, the primary application of these materials.

10:20am **TF+EM-MoM7 Preparation and Characterization of Transparent Conducting ZnTe:Cu Back Contact Interface Layer for CdS/CdTe Solar Cell**, *U. Avachat,* ***N.G. Dhere***, University of Central Florida

This paper presents preparation and characterization of transparent conducting ZnTe:Cu back contact interface layer for CdS/CdTe thin film solar cells for multijunction thin film PV applications. Polycrystalline ZnTe:Cu thin films were grown by Hot Wall Vacuum Evaporation technique. Hot wall set up was developed to obtain highly stoichiometric films with better material yield and thickness uniformity. 500 nm ZnTe:Cu films were prepared on glass and characterized for stoichiometry, structural properties and optical transparency by electron probe microanalysis, optical transmission spectroscopy and X-ray diffraction technique respectively. Highly stoichiometric ZnTe:Cu films were obtained on glass with optical transparency in the range of 70-80 % in near IR region. X-ray diffraction patterns revealed face-centered cubic phase of ZnTe with preferred {111} orientation. CdS/CdTe solar cells were completed with configuration, CdS/CdTe/ZnTe:Cu/ZnO:Al/Ni-Al and CdS/CdTe/ZnTe:Cu/ITO/Ni-Al. ZnO:Al and ITO thin film layers were deposited by RF magnetron sputtering and Ni-Al contact fingers were deposited by e-beam vacuum evaporation through metallic mask. Completed CdS/CdTe solar cells were characterized for their I-V characteristics using current voltage measurements.

10:40am **TF+EM-MoM8 CuPc:C60 Blend Film: A Photoemission Investigation**, ***L. Lozzi***, University of L'Aquila and INFM-CNR, Italy; *V. Granato,* University of L'Aquila, Italy; *S. La Rosa,* Sincrotrone Trieste Scpa, Italy; *S. Santucci,* University of L'Aquila and INFM-CNR, Italy

Recently a strong research effort has been devoted to study the application of organic-inorganic multiplayer films for the preparation of photovoltaic devices. Generally these devices are composed by a multilayer of an organic film which is the active layer, a charge acceptor (to reduce the electron-hole recombination probability) and the two metallic contacts to collect the charges (as ITO, Au and Al). The most used compounds are Copper Phthalocyanine (CuPc), as organic layer, and the C60, as electron acceptor. An improved system, showing an higher efficiency, can be prepared depositing, between the metallic contacts, a blend of active layer and charge acceptor. With this design one of the most important parameter, the exciton diffusion length (which is quite small in the organic systems), becomes less important because it is obviously much higher then the CuPc-C60 distance when these molecules are bonded. The realization of these blend films determines the strong reduction of the luminescence of the CuPc film, but it is not clear if in this blend film there is the formation of bonds between CuPc and C60 molecules or if its electronic structure is simply the sum of the electronic states of the two single compounds. In this contribution we will show the results obtained using soft X-ray photoemission spectroscopy on CuPc:C60 blend films, with different concentrations. These films have been deposited in ultra high vacuum by thermal evaporation. We will show a variation of the HOMO states as a function of the concentration ratio. This HOMO level moves towards the Fermi level, influencing the interface properties with the metallic contacts. The intensity and position of this level is strongly influenced by the CuPc:C60 ratio. This result could be related to the variation of the optical properties of these films.

11:00am **TF+EM-MoM9 Silicon Thin Films from Trichlorosilane for Electron Beam Recrystallized Solar Cells**, ***C. Groth***, *K. Ong,* Hamburg University of Technology, Germany

The project's aim is to produce polycrystalline thin film solar cells on low cost substrates, especially on float glass. The chemical processing is entirely dry, which leads to high efficiency and throughput. There is no size limitation using this sequence of processing; even the in-line production of complete solar panels is feasible. An intermediate Tungsten (W) layer of approximately 1 µm is used to maintain mechanical stability at high temperatures. Furthermore, it is used as diffusion barrier during the recrystallisation process and serves as back surface reflector and electrical contact. Two deposition processes are currently under investigation: DC-magnetron sputtering and plasma enhanced chemical vapour deposition

(PECVD) using tungstenhexafluoride (WF@sub 6@) as precursor. Both processes are using substrate temperatures of ~400 °C. Analysis using XRD (x-ray diffraction) shows formation of @alpha@-W for sputtered layers while PECVD layers consist of @alpha@- and @beta@-W, depending on the process parameters. The silicon (Si) basis with a thickness of 15 µm is deposited by PECVD directly from trichlorosilane (SiHCl@sub 3@) as precursor at high rates of ~200 nm/min. Substrate temperature during the process is ~550 °C. RF frequencies of 13.56 MHz are used in both PECVD processes. P-doping of the basis is done in-situ using borontrichloride (BCl@sub 3@). The nanocrystalline silicon film is recrystallised by a line-shaped electron beam at high velocities of about 60 mm/s. This leads to grain sizes of up to several 100 µm. A PECVD deposited amorphous silicon layer will be used as hetero emitter to complete the solar cell.

11:20am **TF+EM-MoM10 Plasma-Assisted Co-Evaporation of Thin Films for Photovoltaic Applications***, S. Kosaraju, J.A. Harvey,* ***C.A. Wolden,*** Colorado School of Mines

This presentation describes the development of plasma-assisted co-evaporation (PACE) and its application to the formation of @beta@-In@sub 2@S@sub 3@ and InN thin films. The former is an alternative window layer for copper indium diselenide based devices and the latter is a potential absorber. In PACE metals are supplied by conventional thermal evaporation, while the chalcogen or nitrogen gas precursors are activated by an inductively coupled plasma (ICP) source. The performance of the ICP source to activate both H@sub 2@S and N@sub 2@ was measured and optimized using a combination of optical emission spectroscopy and mass spectrometry. Transport modeling was used to quantify the flux distributions of both the co-evaporated metal and the reactive species from ICP source impinging upon the substrate. The source geometries were positioned asymmetrically so that the influence of composition and absolute rate could be ascertained from a single deposition experiment in a combinatorial approach. Model predictions were compared and validated using measurements of film thickness, composition, and quality. Through the deposition of @beta@-In@sub 2@S@sub 3@ and InN it was demonstrated that PACE provides substantial improvements in both materials utilization and substrate temperature reduction. For the case of @beta@-In@sub 2@S@sub 3@ it was observed that film quality was highly sensitive to the S/In ratio. The buffer layer was formed as low as 100 °C, and it was found that both the morphology and optical band gap were strong functions of temperature. In the case of InN the most important parameter was the excitation of nitrogen in the ICP source. It was shown that the introduction of argon was beneficial to nitrogen activation as evidenced by measurements of crystal quality and electronic properties.

11:40am **TF+EM-MoM11 Anomalously High Seebeck Coefficient Observed in V@sub 2@O@sub 5@ Thin Films***,* ***S. Iwanaga****, N.T. Nguyen, R.B. Darling, F.S. Ohuchi,* University of Washington

Vanadium oxides, especially vanadium pentoxide (V@sub 2@O@sub 5@), have gained recent attention for a wide range of applications such as ion storage layers in solid-state batteries, windows for photovoltaic cells, and electro- and photo-chromic devices. Various transport properties have been investigated in the past; however, its thermoelectric properties have not been well characterized. Recently, we observed an anomalously high Seebeck coefficient from sol-gel deposited V@sub 2@O@sub 5@ thin films. Seebeck coefficients of between - 500 to - 700 µV/K were measured, with corresponding electrical conductivities ranging from 0.005 to 0.1 @ohm@@super -1@ cm@super -1@. Unlike conventional materials, the Seebeck coefficients and electrical conductivity act in parallel, suggesting that the carrier concentration increases while maintaining a high Seebeck coefficient. This peculiar transport characteristic appears to be related to polaron hopping. The power generation of the film was further estimated by current-voltage (I-V) measurements to assess the thermoelectric performance of the films. The I-V measurements were performed while applying a temperature gradient to the film by applying a current source in such a way that the thermopower current was suppressed by applying the current in the opposite direction. The I-V characteristics at different applied @DELTA@T were thus obtained, from which the output power (load characteristic, P) was calculated from the I-V data.

Electronic Materials and Processing
Room 309 - Session EM-MoA

High-k Dielectric Growth and Processing

Moderator: S.A. Chambers, Pacific Northwest National Laboratory and Univ. of Washington

2:00pm **EM-MoA1 Peter Mark Award Lecture: Synthesis and Patterning of Multifunctional Oxides*, J.P. Chang*[1]**, University of California, Los Angeles **INVITED**

The continuous down-scaling of the microelectronic and optoelectronic integrated circuits dictates the development of atomic layer deposition and high fidelity pattern transfer processes to synthesize and integrate novel materials, such as multifunctional oxides, into nanometer scaled devices. In this talk, I will first discuss current research progress in atomic layer deposition for synthesizing transition metal oxides which can be used as a gate dielectric material on semiconductors in transistors, or as a waveguide core material for planar miniature optical amplifiers. The interfacial composition and dipole are found to control the band alignment at the dielectric/semiconductor heterojunctions, while the short range order as determined by extended x-ray absorption fine structure analysis governs the electronic and optoelectronic properties. To integrate these oxide materials into future generations of devices, a viable etching process is needed to its realization. I will address the design of plasma chemistries to selectively pattern these oxide materials, including the individual and synergistic effects of ions and radicals, and their impact on device integration.

2:40pm **EM-MoA3 DFT Investigation of the Initiation of HfO@sub2@ ALD on H-Si(100)-2x1 and Nitrided Si Surfaces*, Y. Xu,*** *C.B. Musgrave,* Stanford University

Atomistic mechanisms for the initiation of atomic layer deposition (ALD) of hafnium oxide (HfO@sub2@) on hydrogen terminated and nitrided silicon surfaces were investigated using density functional theory (DFT). There are two possible pathways for the reaction of the precursor Hf[N(CH@sub3@)@sub2@]@sub4@ and Si-H surfaces. One is to form a Si-Hf bond through a ligand exchange mechanism. One H atom from the Si-H* surface site and one N(CH@sub3@)@sub2@ group of the precursor combine through a four-centered transition state to form NH(CH@sub3@)@sub2@, which subsequently desorbs. The second pathway is one H atom will be transferred from Si-H surfaces to one CH@sub3@ group from precursor to form Si-N-Hf bond. Alternatively, Hf[N(CH@sub3@)@sub2@]@sub4@ and residual water in the reactor can react to form Hf[N(CH@sub3@)]@subx@(OH)@suby@. Subsequently, Hf[N(CH@sub3@)]@subx@(OH)@suby@ can react with Si-H* to form Si-O-Hf structures of the reacted precursor. This reaction is more kinetically favorable than both of the reaction of Hf[N(CH@sub3@)@sub2@]@sub4@ with Si-H surfaces and it is important for understanding the interface structure between silicon surface and HfO@sub2@ films. We have also investigated the reactions of Hf precursors with the nitrided Si(100) surface and found that alkylamide precursors can react with SiNH* sites to initiate ALD whereas HfCl@sub4@ reactions with the nitrided surface are kinetically unfavorable.

3:00pm **EM-MoA4 Hafnium Based High K Dielectrics for Advanced ULSI Technology*, S. Muthukrishnan,*** *S. Kher, P. Narwankar, R. Sharangapani, T. Goyani, Y. Ma, K. Ahmed, G. Conti,* Applied Materials Inc.

Hafnium based high k dielectric has emerged as a primary candidate for advanced ULSI technology due to its thermal stability property and leakage current reduction potential in comparison to other high k materials. We have successfully developed a hafnium based gate dielectrics, HfO2 and HfSiOx, using both ALD and MOCVD techniques. The materials are thermally stable up to source/drain activation temperature of 1050C and above when nitrogen is incorporated into the high k film. The nitrogen is incorporated into the high k film through plasma nitridation. We have been able to incorporate as high as 25% nitrogen in the high k film. The benefit of the plasma nitridation is in its capability of engineering the nitrogen profile in the gate stack. The nitrogen can be engineered to maintain the highest concentration in the bulk of the film and prevent nitrogen from going to the dielectric and channel interface. This profile provided the High K film with low leakage current. X-ray Photoelectron Spectral analysis showed that nitrogen is primarily bonded to the silicon. Besides high k deposition, process integration is critical not only for the gate dielectric performance but also for its scaling capability. By controlling the silicon surface coverage prior to high k deposition and surface adsorption from clean room environment, additional scaling can be achieved with processing steps in integrated clustered tools.

3:20pm **EM-MoA5 Plasma-enhanced ALD for CMOS Applications*, G. Wilk,*** *S. Marcus, P. Raisanen,* ASM America*; Y.M. Yoo, D.Y. Kim,* ASM Genitech **INVITED**

Plasma-enhanced ALD (PEALD) is a novel deposition technique which allows low-temperatures and a wide selection of precursors. PEALD films result in substantial leakage current benefit compared to thermal ALD films for dielectrics, and result in low-resistivity metals compared to thermal ALD metals. This process also maintains the benefits of standard Atomic Layer Deposition, including outstanding thickness control and conformality. Several applications will be shown to have excellent capacitance, leakage and breakdown characteristics, including metal gates and MIM capacitors. A range of dielectrics and metals will be presented, including Al2O3, HfO2, Ta2O5 and TiN.

4:00pm **EM-MoA7 LPCVD of Thin TiO@sub 2@ Films using TDEAT as Ti Source Gas and NH@sub 3@ as a Catalyst*, X. Song,*** *C.G. Takoudis,* University of Illinois at Chicago

Thin TiO@sub 2@ films were deposited using Tetrakis(diethylamino)titanium (TDEAT) and O@sub 2@ as source gases, and NH@sub 3@ as a catalyst. The deposition temperature was 100 - 250°C and the system pressure was on the order of 1 torr. Real-time reactor gas analysis was carried out with a Residual Gas Analyzer. The TiO@sub 2@ film thickness was probed using spectroellipsometry. Time of flight secondary ion mass spectroscopy (ToF-SIMS) was utilized to study the depth profile of oxygen and other elements in the deposited films. The bonding states and atomic compositions of the samples were analyzed with x-ray photoelectron spectroscopy (XPS). It is found that when the TDEAT feed flow rate increases, the TiO@sub 2@ deposition rate increases. The growth rate of TiO@sub 2@ films deposited using NH3 is substantially higher than that of films deposited without NH@sub 3@; for example, at 200°C, the growth rate increases from 4.7 nm/min (without NH@sub 3@) to 38 nm/min (in the presence of NH@sub 3@). XPS data show that the as-deposited Titanium Oxide films are stoichiometric, even when NH@sub 3@ is used. ToF-SIMS depth profile analysis of as-deposited and annealed TiO@sub 2@ is done using Cesium primary ion beam sputtering. The annealing is performed in Oxygen, at 750°C for 10 min. The Oxygen distribution profiles along the depth of both as-deposited and annealed films are found to be uniform; this indicates that Oxygen is incorporated during deposition rather than diffusion during annealing. The impurity levels of C, H, and N are found to be lower in the annealed films than those in the as-deposited films. This study shows that TiO@sub 2@ can be deposited at low substrate temperature and high deposition rates with low impurity levels using TDEAT and O@sub 2@ as source gases and NH@sub 3@ as a catalyst. The impurities in the films can be further reduced with post annealing if desired.

4:20pm **EM-MoA8 MOCVD of ZrO@sub 2@ Thin Films Using the Novel Single Precursor Zirconium 3-methyl-3-pentoxide, Zr(mp)@sub 4@***, W. Cho, K.-S. An, Y.K. Lee, T.-M. Chung,* Korea Research Institute of Chemical Technology, South Korea*; D. Jung,* Sungkyunkwan University, South Korea*; **Y. Kim,*** Korea Research Institute of Chemical Technology, South Korea

Thin films of zirconium dioxide, ZrO@sub 2@, have been deposited on silicon substrates by metal organic chemical vapor deposition (MOCVD) using the novel single precursor, zirconium 3-methyl-3-pentoxide {Zr[OC(CH@sub 3@)(C@sub 2@H@sub 5@)@sub 2@]@sub 4@, Zr(mp)@sub 4@}, with no additional oxygen source, and the CVD reaction mechanism was also investigated. In its thermogravimetric analysis (TGA), Zr(mp)@sub 4@ showed an excellent one-step weight loss and a low residual weight (less than 2.5%). The deposition rate was found to be ~30 Å/min at the substrate temperature of 400 °C and the activation energy of deposition was 33.3 kJ/mol which is similar to that of zirconium tert-butoxide, Zr(O@super t@Bu)@sub 4@. By gas chromatography/mass spectroscopy (GC/MS) and nuclear magnetic resonance (NMR) analyses of the thermally decomposed vapor phase products collected during the deposition of ZrO@sub 2@ films, it was clearly found that the films were grown via @beta@-hydrogen elimination processes of the Zr(mp)@sub 4@ single precursor. Negligible carbon contamination of the ZrO@sub 2@ films, examined by x-ray photoelectron spectroscopy (XPS), indicates that, except for the @beta@-hydrogen elimination processes, no additional decomposition and/or recombination processes contributed to the

[1] **Peter Mark Memorial Award Winner**

ZrO@sub 2@ film growth. The morphology, crystallinity, and electrical properties of the ZrO@sub 2@ films were characterized by atomic force microscopy (AFM), x-ray diffraction (XRD), and capacitance-voltage (C-V) and current-voltage (I-V) measurements.

4:40pm **EM-MoA9 The Effect of Nitrogen Incorporation on the Thermal Stability of La, Hf-aluminate Gate Stacks on Silicon***, **P. Sivasubramani**, P. Zhao, F.S. Aguirre-Tostado, J. Kim, M.J. Kim, B.E. Gnade, R.M. Wallace,* University of Texas at Dallas

The International Technology Roadmap for Semiconductors (ITRS) 2003 predicts the need for the introduction of high dielectric constant (k) gate dielectrics by 2006 to meet continued scaling requirements in metal-oxide silicon field-effect transistor (MOSFET) digital logic technology. Hf, Zr, group III or rare earth oxides with N, Al and/or Si additions have been identified as possible high-k gate dielectric candidates for near term MOSFET scaling.@footnote 1@ The thermal stability of a high-k dielectric film in direct contact with the underlying Si substrate is essential because out-diffusion of metal impurity atoms into the channel region during processing can cause carrier mobility degradation and affect the electrical performance of integrated circuit. Evaluation of the thermal stability of molecular beam deposited LaAlO@sub 3@ thin films show crystallization and out-diffusion of La and Al into Si (100) substrate when subjected to rigorous rapid thermal anneals (RTA) at or above 950 °C, 20 sec. in N@sub 2@ ambient.@footnote 2@ In this study, the effect of nitrogen incorporated into the La- and Hf-aluminate thin films and at the Si (100) interface will be discussed. Films are fabricated using reactive sputter deposition in Ar + N@sub 2@ followed by subsequent UV-O@sub 3@ oxidation at room temperature. High resolution transmission electron microscopy, atomic force microscopy, x-ray photoelectron spectroscopy, x-ray reflectivity, x-ray diffraction, and secondary ion mass spectroscopy are utilized to characterize the gate stacks before and after RTA in the 850 to 1050 °C temperature range. This work is supported by the Semiconductor Research Corporation (SRC) FEP Transition Center. @FootnoteText@ @footnote 1@ITRS, Front End Processes, p. 33 [2003].@footnote 2@P. Sivasubramani, M. J. Kim, B. E. Gnade, R. M. Wallace, L. F. Edge, D. G. Schlom, H. S. Craft and J.-P. Maria, accepted for publication in Appl. Phys. Lett.

5:00pm **EM-MoA10 Atomic Layer Chemical Vapor Deposition and Characterization of Hf-silicate, Hf-silicate/Al2O3, and Hf-silicate/SiO2 Gate Dielectrics***, **J. Kim**, K. Yong,* POSTECH, Korea

Silicate or aluminate including hafnium components is considered to be the most promising alternative gate dielectrics, due to good thermal stability in direct contact with silicon. Hf-silicate (HfSi@sub x@O@sub y@) films were grown by ALCVD using the precursor combination of tetrakis-diethylamido-hafnium [Hf(NEt@sub 2@)@sub 4@] and tetra-n-buthyl orthosilicate [Si(O@super n@Bu)@sub 4@]. A highly conformal, uniform Hf-silicate films of a few nm was observed by high resolution-TEM. The Hf/(Hf+Si) was average 0.38 for the bulk film, indicating a Si-rich composition. However, the formation of Hf-silicide (Hf-Si@sub x@) at Hf-silicate/Si interfaces was induced by the reaction of metallic Hf atoms with Si substrate atoms. As a gate oxide becomes thinner, the interfaces have shown to play a key role in device performance. In order to improve the interface properties, the Al@sub 2@O@sub 3@ and chemical SiO@sub 2@ layers were introduced to fabricate the Hf-silicate/Al@sub 2@O@sub 3@ and Hf-silicate/SiO@sub 2@ stacks, respectively. Al@sub 2@O@sub 3@ films were deposited by ALCVD at 200 @super o@C using Al(CH@sub 3@)@sub 3@ and H@sub 2@O. The chemical SiO@sub 2@ of ~1.5 nm was formed by phirana (H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@=4:1) cleaning process. The Hf-silicate/Al@sub 2@O@sub 3@ bilayer showed amorphous characteristics, while Hf-silicate films showed a micro-crystalline structure. The Hf-Six formation was significantly decreased in the case of Hf-silicate/Al@sub 2@O@sub 3@ and Hf-silicate/SiO@sub 2@ bilayer. Compared with Hf-silicate, Hf-silicate/Al@sub 2@O@sub 3@ exhibited a lower leakage current density of 8.9 x 10@super -8@ A/cm@super 2@ at a gate bias of -1 V for an equivalent oxide thickness of 5.2 nm. Hf-silicate/Si and stacked Hf-silicate/SiO@sub 2@/Si were furnace annealed at 650, 750, and 850 @super o@C in the N@sub 2@O/Ar and N@sub 2@O/O@sub 2@ atmosphere. The phase transition (crystallization) was confirmed by XRD, FT-IR and Raman-IR results.

Electronic Materials and Processing
Room 310 - Session EM1-TuM

Defects, Interfaces, and Surface Passivation in Electronic Materials

Moderator: L.J. Brillson, The Ohio State University

8:20am **EM1-TuM1 The Role of Defects at Nanoscale Semiconductor Interfaces***, **Y.M. Strzhemechny**, H.L. Mosbacker, M.J. Hetzer, M. Gao, B.D. White,* The Ohio State University*; D.C. Look, D.C. Reynolds, C.W. Litton,* Wright-Patterson AFB*; M.A. Contreras, A. Zunger,* National Renewable Energy Laboratory*; L.J. Brillson,* The Ohio State University **INVITED**

Current understanding and control of semiconductor contacts increasingly require measurements sensitive to defects and chemical changes at nanoscale interfaces. We offer examples illustrating dramatic macroscopic effects occurring in semiconductor systems as a result of nanoscale interface phenomena. In some cases, there is an interplay of several competing defect-driven mechanisms. Elucidating them and finding the leading ones requires careful experimental approach. For single-crystalline ZnO, we study the role of near-surface defects on the formation of Au Schottky contacts. Among factors degrading rectifying characteristics of such contacts one should consider the following. High concentrations of shallow donors in the surface and subsurface regions lead to barrier thinning, resulting in increased tunneling. Alternatively, the presence of deep defects near contact interface promotes tunneling by defect-assisted hopping. Nanoscale electronic and chemical studies show that independent reduction of both shallow donors and deep defects significantly improves rectifying performance of the Au/ZnO contacts. We find that processing of ZnO with remote O and H plasma allows for controllable tailoring of chemical and physical properties of the surface. By the same token, nanoscale compositional and electrostatic variations between grain boundaries and grain interiors in thin polycrystalline films of Cu(In,Ga)Se@sub 2@, absorber layers in record-setting solar cells, show how nanoscale arrangement of near-surface stoichiometric defects may improve the overall photovoltaic efficiency. Confirming theory, we find a 50% reduction in Cu composition from grain interior to boundary and a p-type potential barrier that acts to reduce majority carrier hole recombination. These and related examples emphasize the practical significance of nanoscale chemical and electronic features at electronic material interfaces.

9:00am **EM1-TuM3 Interstitial Oxygen Related Defects and Current Leakage in UMOSFET on Epi/As++ Structure***, **Q. Wang**, M. Daggubati, H. Paravi,* Fairchild Semiconductor*; R. Yu, X. Zhang,* Lawrence Berkeley National Laboratory

Interstitial oxygen (O@sub i@) related defects and current leakage in UMOSFET on Epi/As++ structure has been investigated. The devices fabricated on heavily arsenic doped wafer with poly-silicon backside exhibited an increased yield loss in reverse current leakage with increasing O@sub i@ concentration in the wafer. For the wafers with the same O@sub i@ content, the leakage yield loss increases with decreasing device geometry. This leakage yield loss was attributed to the O@sub i@ related defects in active region (well junction). Transmission electron microscopy (TEM) study revealed, in the well junction region, the existence of extrinsic stacking faults and half-hexagonal dislocation punch-through defects, characteristic of oxygen precipitation. Defects created by the heavy body boron implantation seem to enhance O@sub i@ precipitation in the active region. In addition, the O@sub i@ is also found to diffuse to the interface of the poly-silicon layer and bulk silicon and precipitate out. This precipitation may consume the poly layer and reduce the gettering effect of poly silicon, which also leads to an O@sub i@ dependent current leakage. Similar experiments carried out with damaged backside wafers showed that current leakage yield loss was independent of O@sub i@ in the wafer and was low in general. The detailed TEM work indicated that the O@sub i@ did precipitate out in the bulk close to the back surface. The O@sub i@ precipitates may result in an intrinsic gettering and thus improve the current leakage yield. This comparative study between poly-silicon and damaged back-surfaces indicates that for heavily arsenic doped silicon wafers, intrinsic gettering is much better than extrinsic gettering due to the facts discussed above.

9:20am **EM1-TuM4 Control of Defect Concentrations in Silicon through Surface Chemistry***, **R. Vaidyanathan**, K. Dev, R.D. Braatz, E.G. Seebauer,* University of Illinois at Urbana-Champaign

Point defects govern many aspects of the behavior of crystalline solids, especially for semiconductors. We show through self-diffusion measurements that defect concentrations deep in the semiconductor bulk can be varied controllably over several orders of magnitude through submonolayer-level adsorption at the surface. For example, less than 0.01 monolayer of nitrogen adsorbed on silicon (100) that is undersaturated in defects lowers their concentration and inhibits diffusion, with the effects extending at least 0.5 µm into the bulk. The measurements have been made using a new method for determining key diffusion parameters via the short-time decay of an initial step concentration profile in an isotopic heterostructure. This method takes advantage of the relative ease with which step concentration profiles can be fabricated by thin film deposition, and in the limit of very short times provides particularly simple analytical means for obtaining parameters connected to diffusion length and defect formation. The adsorption phenomena discovered here open the possibility of precise defect engineering for numerous applications.

9:40am **EM1-TuM5 The Role of Etching in Film Growth during Wet Chemical Oxidation of H:Si(100)**, ***K.T. Queeney**, J.W. Clemens, S.K. Green, C.A. Shea,* Smith College

Exposure of hydrogen-terminated Si(100) to aqueous solutions is an integral part of most wafer cleaning processes in microelectronics manufacturing. The quality of the thin oxide films formed (either intentionally or unintentionally) during this processing can have a profound effect on ultimate device performance. We have used transmission infrared spectroscopy to study this wet chemical oxidation of H:Si(100), allowing us to monitor both the evolution of SiH@sub x@ species and the growth of Si-O modes from the oxide film. While dissolved O@sub 2(aq)@ is the primary oxidizing species in H@sub 2@O, etching of the Si(100) surface by OH@super -@ species in the water plays an important role in oxidation. Sharpening of the Si-H bending modes in the earliest stages of oxidation suggests that this etching creates a more homogeneous surface, which is consistent with the high quality of the single layer SiO@sub x@ as judged by the evolution of Si-O optical phonons during oxidation. Studying the subsequent oxidation of surfaces first etched in deoxygenated water provides some temporal separation of the concomitant etching and oxidation processes and reveals that the relative reactivity of sites exposed by this etching is distinct from reactivity of analogous sites on extended Si surfaces, highlighting the importance of defect-driven chemistry during oxidation.

10:00am **EM1-TuM6 Experimental and Theoretical Studies of Various Oxides on the Ge(100)-2x1/4x2 Surface: Deposition of SiO and Oxidation by O@sub 2@ and NO***, **T.J. Grassman**, A.C. Kummel,* University of California, San Diego

To further the development of a germanium-based metal-oxide-semiconductor field effect transistor (MOSFET) a suitable gate-oxide material must be found which yields a high-quality, electrically-unpinned interface. For this, the semiconductor/oxide interface needs to be free of charge traps and other such interfacial defects that can cause Fermi-level pinning. Unfortunately, germanium's native oxide has been shown to be inadequate for the task of providing a clean, unpinned interface. We have investigated the bonding and electronic structures of various oxides on the Ge(100)-2x1/4x2 surface using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density function theory (DFT) modeling, including correction for the infamous DFT band gap problem. We will present atomically resolved images of the clean Ge(100) surface, the Ge(100) surface after oxidation with both O@sub 2@ and NO, the Ge(100) surface after deposition of SiO at various coverages, and the Ge(100) surface after nitridation with a neutral nitrogen plasma. Our STM and DFT studies show that SiO, unlike O@sub 2@ or NO, spontaneously forms an oxide bilayer by way of molecular SiO trimers, without displacing Ge atoms or oxidizing the surface. STS and DFT studies show this bilayer SiO absorption leaves the Fermi level unpinned. Such a bilayer formation makes SiO a strong candidate for use as a passivating buffer layer for further gate oxide growth. Conversely, NO and O@sub 2@ dosing causes Ge displacement and does not spontaneously form oxide or nitride bilayers.

10:20am **EM1-TuM7 Optimized Chemical Cleaning Method for Producing Device Quality Ge(100) Surfaces**, ***S. Sun,*** Stanford University*; Y. Sun, Z. Liu, D. Lee, S. Peterson, P. Pianetta,* Stanford Synchrotron Radiation Laboratory

Ge(100) surfaces treated by aqueous HF solutions with three different concentration (1:2, 1:5, and 1:25) have been systematically studied by synchrotron radiation photoemission spectroscopy (SR-PES) at Stanford Synchrotron Radiation Laboratory (SSRL). After HF treatment, the sample surface is hydrophobic and hydrogen terminated. HF solutions with higher concentration leave the Ge surfaces with less oxide, but relatively larger roughness. Hydrogen coverage also depends on the HF concentration. HF:H@sub 2@O (1:5) is a good choice, since it leads to a Ge(100) surface with approximately 0.9 monolayer hydrogen and less than 0.1 monolayer carbon and oxygen. The residual carbon and oxide come from the aqueous solutions. Solutions with higher concentrations of HF do not improve the surface cleanness. Additionally, a 10% HCl solution was also used to clean the Ge(100) surface. A hydrophilic and Cl terminated surface is achieved after HCl treatment. Relatively more residual carbon and oxide are left on the surface, which is due to the hydrophilic nature of treated surface. More details of the work will be discussed in the oral presentation.

10:40am **EM1-TuM8 XPS Study of Se-passivated Si(100)**, ***F.S. Aguirre-Tostado**, R.M. Wallace,* University of Texas at Dallas*; J. Zhu, G. Larrieu, E. Maldonado, W.P. Kirk, M. Tao,* University of Texas at Arlington

The presence of strained and dangling bonds on the atomically clean Si(100) surface leads to a metastable surface structure not suitable for the growth of high-k oxides. In the present work, we have examined the passivation of the Si(100) surface with one monolayer of selenium upon thermal annealing. Ex-situ analysis by x-ray photoelectron spectroscopy reveals that while Se-oxide formation is below the limit of detection, SiO@sub 2@ formation is observed. Assuming a 2D Se layer growth, we speculate that the formation of SiO@sub 2@ takes place at the atomic steps on the surface and at defect sites in the Se layer. It is also possible that there exists a cooperative inter-diffusion of Se and topmost Si atoms, leading to SiO@sub 2@ formation on top of the Se layer. From in-situ thermal annealing studies up to 425 °C, we find that adventitious C concentrations are below detectible limits above 100 °C while Se-Si and SiO@sub 2@ species surface concentrations remain unchanged. From photoelectron attenuation measurements, the SiO@sub 2@ thickness is around 8 Å. The mechanism of formation of the Se layer and SiO@sub 2@ will be discussed. This work is supported in part by the Texas Advanced Technology Program and SEMATECH.

11:00am **EM1-TuM9 Surface Passivation of Semiconductors**, ***D.R.T. Zahn,*** Chemnitz University of Technology, Germany **INVITED**

Considering GaAs(100) very often chalcogen atoms, i.e. sulphur and selenium, are employed for passivating its surface. Passivation can be achieved by exposing the surface to a beam of chalcogen atoms under ultra-high vacuum conditions or employing an ex situ wet chemical treatment followed by annealing in vacuum. We have studied both types of preparation using photoemission as well as Raman spectroscopies. Both techniques are capable of determining the change of band bending resulting from the passivation process. It is quite accepted that the chalcogen passivation induces a considerable reduction in band bending for n-type substrate material. However, the band bending is increased when p-type GaAs is used indicating that the density of surface states is changed but not removed from the band gap of the semiconductor. Core level photoemission data reveal that there are two distinct chalcogen atom environments on the passivated surface and that very similar surfaces are prepared independent on the preparation technique. The core level spectra provide very a very important input for DFT-LDA structure calculations which indicate that the reconstruction is likely to be different from the previously suggested chalcogen dimer terminated one. Moreover, we probe the passivated surfaces by addition of sub-monolayer coverages of organic molecules. The sharpening of core level spectra upon absorption of the molecules is indicative of some inhomogeneities in surface band bending being healed. Finally we address the influence of the passivation on electrical transport in metal/semiconductor structures.

Electronic Materials and Processing
Room 312 - Session EM2-TuM

High-k Dielectric Characterization

Moderator: G. Wilk, ASM America

8:20am **EM2-TuM1 Characterization of High-@kappa@ Materials using High Resolution Ion Backscattering**, ***T. Gustafsson**, E. Garfunkel, L.V. Goncharova, R. Barnes, D. Starodub,* Rutgers University **INVITED**

Understanding the thermodynamics and kinetics of film growth during fabrication of high-@kappa@ gate stacks is vital to establish atomic level control of interfacial layers and to minimize defects. Annealing such films in different atmospheres may lead to diffusion and reactions with significant consequences on the electrical properties. Ion beam methods, in particular medium energy ion scattering (MEIS), are non-destructive, high resolution (sub-nm) tools for quantitative characterization of buried layers and interfaces. An attractive feature is the possibility to use isotope tracing, which allows a study not just of the structures of such ultrathin films, but also of the processes responsible for their formation. We will discuss some key materials issues relevant to films and interfaces in next-generation highly-scaled CMOS gate stack structures as investigated using ion beams. As one example, we will contrast the behavior of Hf and Ce oxides on Si during annealing in an oxide atmosphere. The Hf based system shows evidence for oxygen exchange, which could be suppressed by mixing the oxide with SiO@sub 2@. Little SiO@sub 2@ interfacial growth was observed. This reaction saturates with time and appears to be enhanced after film recrystallization. Annealing in nitrogen results in reduced oxygen incorporation and exchange. In contrast, Ce silicates exhibit rapid interface growth upon oxygen exposure. Materials changes occur in the ultrathin films and at the various interfaces during growth and processing at elevated temperature that strongly affect device properties. Changes in oxide and silicate interface composition and thickness, phase mixing and crystallization within the film, and film decomposition will be discussed also for high-@kappa@ films on Ge and GaAs. In general the native oxides on these materials are less stable than those of Si, leading to different high-@kappa@ layered structures and interface composition.

9:00am **EM2-TuM3 Fermi Level Pinning at Re/HfO@sub2@ Interface and Effective Work Function of Re in Re/HfO@sub2@/SiO@subx@/n-Si Stack**, ***Y. Liang**, J. Curless, C. Tracy, D. Gilmer, J. Schaeffer, D. Triyoso, P. Tobin,* Freescale Semiconductor Inc.

One of the challenges in metal/high-k/Si based CMOS devices is a need for a metal with work function aligned with the Si valence band edge (5.2 eV) for PMOS devices. While a number of metals have vacuum work functions equal or greater than 5.2 eV, their effective work functions in a MOS structure are often less than 5.2 eV due largely to Fermi level pinning in the metal/high-k/Si stack. We used x-ray and ultra-violet photoemission spectroscopy (XPS and UPS) in conjunction with capacitance-voltage (C-V) measurements to investigate Fermi level pinning in a Re/HfO@sub2@/SiO@subx@/n-Si stack. Evolution of the Re vacuum work function at different Re film thickness and the resulting band bending in HfO@sub2@ and Si were determined by in situ XPS and UPS techniques. Results showed that the Re vacuum work function reached a constant value of 5.5 eV when the film exceeded 30 Å thick. Photoemission results further showed that the Fermi level at the Re/HfO@sub2@ interface was partially pinned, resulting in an interface dipole of 0.5 eV and a 5.0 eV effective work function with respect with HfO@sub2@sub. C-V measurement of the Re/HfO@sub2@/SiO@subx@/n-Si stack resulted in a 4.8 eV work function of Re with respect to Si. The difference in work functions determined by photoemission and by C-V will be discussed in terms of the contribution of additional interface dipoles in the Re/HfO@sub2@/SiO@subx@/n-Si stack.

9:20am **EM2-TuM4 Oxygen Diffusion and Reduction of Interfacial Layer in high-k Metal Oxide Gate Stacks**, ***L.V. Goncharova,*** Rutgers University*; M. Dalponte,* Universidade Federal do Rio Grande do Sul, Brazil*; T. Gustafsson, E. Garfunkel,* Rutgers University

Deposition of high-k metal oxide films onto Si substrates is accompanied almost unavoidably by the formation of a thin interfacial SiO@sub 2@ layer as a result of oxidation of the Si surface. This layer grows during metal oxide deposition in an oxygen-rich atmosphere or as a result of post-growth annealing treatments. Recently it has been found that deposition of an oxygen-gettering overlayer such as Ti on top of the high-k metal oxide can result in reduction and even possibly elimination of the SiO@sub 2@ interfacial layer. In our the work reported here we use Medium Energy Ion Scattering (MEIS) to focus on understanding (i) the diffusion and thermal

stability of oxygen in multilayer high-k gate stacks and (ii) the reduction of interfacial SiO@sub 2@. HfO@sub 2@ films of different thickness were grown on Si(001) substrates with and without nitride incorporation on the interface. To study oxygen transport some of the films were re-oxidized in isotopically labeled @super 18@ O@sub 2@. The interfacial layer and the HfO@sub 2@ layer remain constant during deposition of the Ti overlayer at 300K, with the exception of a small amount of interdiffusion at the Ti/HfO@sub 2@ interface. There is no significant change in interfacial SiO@sub 2@. An ultra-high vacuum anneal (600K, P=10@super -9@ Torr) of the stack results in an immediate change in the oxygen region of the spectrum, accompanied by a lowering and broadening of Ti peak. This is clear evidence that some oxygen is moving towards the outer surface of the film and oxidizes Ti. The oxygen growth in the Ti layer occurs at least partially in parallel with a reduction of interfacial SiO@sub 2@ as it is suggested by a decrease of the interfacial Si peak. This process changes with increasing HfO@sub 2@ crystallinity, opening more permeable diffusive pathways via crystallite grain boundaries. Additional studies of the effects of nitrogen incorporation in the interfacial region and film thickness will be presented.

9:40am **EM2-TuM5 Characterization of High- and Low-k Dielectrics Materials using Secondary Ion Mass Spectrometry***, **J. Bennett,*** ATDF **INVITED**

The semiconductor industry continues to move forward with the introduction of high-k and low-k materials for use as gate dielectrics and interlayer insulators, respectively. The successful integration of these materials into the manufacturing process requires an understanding of the chemical, physical, and electrical properties of the new materials. Secondary ion mass spectrometry (SIMS) can provide valuable chemical information about high- and low-k materials, either using static SIMS to investigate surface chemistry or dynamic SIMS for depth profiling. However, these advanced materials are often complex mixtures of elements and physical phases that can complicate the analysis. This presentation will describe some of the current progress in the use of SIMS depth profiling to characterize both high- and low-k materials, and the challenges that remain. Examples from our lab will be used to demonstrate the difficulties (e.g., charging, beam damage) encountered when profiling new generation, porous low-k materials. Examples of backside SIMS to assess barrier metal diffusion will be also be shown. For high-k materials, particularly thin HfO@sub 2@ and HfSiO films, examples from our lab will be used to show the presence of several SIMS artifacts including preferential sputtering and sputter rate and ion variations. Also, the issue of dopant penetration through the films will be discussed.

10:20am **EM2-TuM7 Combined Electrical and Morphological Characterization of Al@sub 2@O@sub 3@ Films by Non-Contact AFM***, **J.M. Sturm,** A.I. Zinine, H. Wormeester, R.G. Bankras, J. Holleman, J. Schmitz, B. Poelsema,* University of Twente, The Netherlands

High-K Al@sub 2@O@sub 3@ films deposited on Si(001) by Atomic Layer Deposition (ALD) were investigated with non-contact AFM in ultra-high vacuum. Oxide charges in the film appear in the AFM images through the attractive interaction between the charge and its image charge in the conducting tip. The image contrast of the charge was found to depend on the tip-sample bias voltage. A spherical tip model based on the oxide charge, its image in the tip and the image of the tip in the substrate allows a quantitative description of the influence of the bias voltage. Most charges in the oxide film were identified as negative with a homogeneous depth distribution. Lateral variations of the Contact Potential Difference (CPD) and differential capacitance were recorded during acquisition of the topographic image with the aid of bias modulation and lock-in detection of the electrostatic force gradient at the first and second harmonic. CPD fluctuations with a typical magnitude of 20 to 50 mV on a lateral scale of ~50 nm were found. The lateral resolution of the CPD is limited with respect to the topography. This is attributed to charge screening with a length scale set by the effective Debye length. Al@sub 2@O@sub 3@ deposition on hydrogen-terminated Si (Si-H) resulted in a strong negative correlation between the differential capacitance and the surface topography (i.e. a large height correlates to low capacitance). For deposition on thermal SiO@sub 2@, this correlation was significantly reduced, whereas almost no correlation was observed for a SiO@sub 2@ film. The high correlation for deposition on Si-H is attributed to thickness variations due to substrate-inhibited ALD growth.

10:40am **EM2-TuM8 The Effect of Surface Pre-treatment upon the Growth of Hafnium Dioxide Layers on Silicon***, P. Mack, R.G. White, **J. Wolstenholme,*** Thermo Electron, UK*; T. Conard,* IMEC, Belgium

Angle resolved XPS (ARXPS) has been shown to be a powerful tool for the determination of the thickness of ultra-thin films. In the case of high-k dielectric layers, the technique is capable of measuring the thickness of both the high-k layer and intermediate layers of silicon dioxide or metal silicate. The values for layer thickness are in close agreement with those generated by a variety of other techniques. As well as knowing the thickness of these layers, it is important to determine whether the layers are continuous or whether the coverage of the high-k layer is only partial. Using ARXPS, a method has been developed to determine whether the coverage of the high-k material is continuous and, if not, to calculate the fraction of the surface that is covered. The method has been applied to HfO@sub 2@ layers produced using atomic layer deposition (ALD) on silicon wafers whose surfaces had received three different types of surface treatment. The way in which the layers grow and the nature of the resulting layer were found to depend upon the pre-treatment method. For example, growth on a thermal silicon dioxide surface resulted in complete coverage of HfO@sub 2@ after fewer ALD cycles than layers grown on an HF last surface. The results from ARXPS will be compared with those obtained from ToF SIMS that have been shown earlier to be a valuable alternative to the LEIS analysis.

11:00am **EM2-TuM9 Atomic Layer Deposition and Characterization of Hafnium and Aluminum Oxides and Hafnium Aluminates on Silicon***, **R.R. Katamreddy,** A. Deshpande,* University of Illinois at Chicago*; R. Inman, A. Soulet, G. Jursich,* American Air Liquide*; C.G. Takoudis,* University of Illinois at Chicago

In future minimization of transistor devices, alternative high dielectric constant materials are needed to replace SiO@sub 2@ and its first-generation replacement material- silicon oxy-nitride. Among the diverse number of possible candidates, HfO@sub 2@ and Al@sub 2@O@sub 3@ films are currently among the most promising replacement materials. Each of these materials has different advantageous and disadvantageous properties for the gate dielectric application. So a more optimal film may be a compositional mixture or nanolaminated structure of these two materials. In this study, the two oxide films are investigated individually on silicon in order to further investigate more complex combinations of the two metal oxides. Ultra-thin hafnium oxide and aluminum oxide films are grown on precleaned silicon substrate having approximately 10 Å residual oxide thickness. The deposition takes place in an ALD reactor using tetrakis(diethylamino)hafnium and tris(diethylamino)aluminum@footnote 1@ precursors respectively. The oxidizing co-reactant is water. After deposition, some of the resulting high-k films are annealed at 600 - 1000°C. Both deposition film and its interfacial region of annealed and non-annealed sample substrates are characterized using Fourier Transformed infrared spectroscopy, X-ray Photoelectron Spectroscopy, Scanning Transmission Electron Microscopy (STEM) and Electron Energy-Loss Spectroscopy in STEM. Our studies indicate that the as-deposited HfO@sub 2@ film is amorphous and there is no indication of silicate formation at the interface; upon annealing of these films, electron microscopy measurements reveal a novel interesting sequence of interfacial transformations as the temperature increases. Similar measurements on Al@sub 2@O@sub 3@ films will be discussed. Preliminary results on nanolaminate deposition of Al@sub 2@O@sub 3@ and HfO@sub 2@ films will also be presented. @FootnoteText@ @footnote 1@ US Patent Application Number 20050003662 A1 filed in May, 2004.

11:20am **EM2-TuM10 Measurement of Thicknesses of HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, and ZrSiO@sub 4@ Films on Silicon by Angle-Resolved XPS***, W. Smekal, W.S.M. Werner,* Vienna University of Technology, Austria*; **C.J. Powell,*** National Institute of Standards and Technology

We report on the use of a new NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) in measuring thicknesses of candidate high-@kappa@ gate-dielectric materials (HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, and ZrSiO@sub 4@) on silicon by angle-resolved XPS. Practical effective attenuation lengths (EALs) have been computed from SESSA as a function of film thickness and photoelectron emission angle (i.e., to simulate the effects of tilting the sample). EALs have been calculated in two ways. First, realistic (Mott) cross sections have been used to describe the elastic scattering of the signal electrons in the substrate and overlayer film; appropriate inelastic mean free paths have also been selected for each material. Second, the transport approximation (TA) has been utilized in which isotropic elastic-scattering is assumed; in addition, it

is assumed that elastic- and inelastic scattering parameters for the film can also be used for the substrate. These EALs have been compared with similar values obtained from the NIST Electron Effective-Attenuation-Length Database (SRD 82) that utilizes an algorithm based on the TA (and where it is again assumed that substrate and overlayer have similar scattering properties). Excellent agreement is found between EALs from SRD 82 and those from SESSA with the TA. Generally good agreement was found between these EALs and those from SESSA with the Mott cross sections, but there were some differences for film thicknesses less than the inelastic mean free path of the photoelectrons in the high-@kappa@ material. The SESSA EALs with the Mott cross sections are considered more reliable than those from the TA because realistic cross sections are used for both elastic and inelastic scattering in the film and substrate materials. These EALs should thus provide more accurate measurements of film thickness, particularly in applications where the film and substrate have different electron-scattering properties.

Electronic Materials and Processing
Room 310 - Session EM+MI-TuA

Spin Injection

Moderator: C.J. Palmstrom, University of Minnesota

2:40pm **EM+MI-TuA3 Characterization of Mn-based Contacts on GaAs***, **J.L. Hilton**[1], B.D. Schultz, S. McKernan, C. Adelmann, X. Lou, P.A. Crowell, C.J. Palmstrom,* University of Minnesota

Mn-based ferromagnetic materials, such as binary metals, Heusler alloys, diluted magnetic semiconductors, and digital alloys, are potentially useful as epitaxial spin injection contacts in GaAs-based spintronic devices. Defects and solid-state reactions at a ferromagnet/semiconductor interface have a significant influence on the spin injection efficiency of spintronic devices. Consequently, a detailed understanding of the interfacial interactions of Mn and Mn-based materials with GaAs is needed. In order to understand the thermodynamic phase behavior of the Mn-Ga-As ternary system, thin film Mn/GaAs structures were grown using molecular beam epitaxy. RHEED, LEED, STM, XPS, RBS, XRD, and cross-sectional TEM were used to characterize the Mn/GaAs interfacial reactions. These reactions initially resulted in the formation of a two-phase region of tetragonal Mn@sub 2@As and tetragonal @delta@-MnGa, with an average composition of Mn@sub 0.6@Ga@sub 0.2@As@sub 0.2@. The two phases formed an epitaxial lamellar layer on the GaAs substrate with Mn@sub 2@As(001) and @delta@-MnGa(001) // GaAs(001). Higher temperature anneals resulted in the dissociation of the Mn@sub 0.6@Ga@sub 0.2@As@sub 0.2@ region into a @delta@-MnGa layer near the sample surface and a Mn@sub 2@As layer near the GaAs substrate. Anneals of @delta@-MnGa films on GaAs suggest that @delta@-MnGa is thermodynamically stable in contact with GaAs over a narrow compositional range up to at least 400°C. For more Ga-rich Mn@sub 1-x@Ga@sub x@ films, no evidence of interfacial reactions with GaAs was observed, but there were significant structural changes within the film. Stable @delta@-MnGa films are especially desirable for use in spintronic devices due to their inherent perpendicular magnetization. Spin injection measurements utilizing @delta@-MnGa contacts on GaAs-based spin-LEDs will be presented. Supported by ARO, ONR, DARPA, NSF, and AFOSR.

3:00pm **EM+MI-TuA4 Interface Structure and Spin Injection Efficiency in a Ferromagnetic/Semiconductor Spin-LED***, **A.T. Hanbicki**, G. Kioseoglou, R. Goswami, T.J. Zega, O.M.J. van 't Erve, C.H. Li, R.M. Stroud, G. Spanos, B.T. Jonker,* Naval Research Laboratory

Considerable effort has been made to incorporate ferromagnetic metals into semiconductor spintronic devices. The nature of the interface between a magnetic contact and a semiconductor is expected to influence the spin-injection efficiency. Indeed, we have discovered interface effects play a role in the spin-injection efficiency for an all-semiconductor system.@footnote 1@ Recently we demonstrated robust spin injection from Fe into an AlGaAs/GaAs spin-LED. With this system, we have successfully injected spin polarized electrons with an electron spin polarization of 32% in the GaAs quantum well (QW).@footnote 2@ To correlate the interface structure with the observed QW polarization, we have characterized our Fe/AlGaAs contacts using high-resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy, and high-angle annular-dark-field (HAADF) imaging. HRTEM together with HAADF imaging provides compositional information that can also be used to determine the interfacial character. We have studied several samples with different detector heterostructures. Optimized annealing can improve the measured spin polarization, therefore for each sample several pieces were annealed to generate a systematic dataset. Enhancement in polarization is seen with anneals as low as 175°C, and the maximum increase in polarization occurs for anneals above 200°C. Measured spin polarizations increase by 8 to 10%, independent of the starting value. Preliminary results reveal a correlation between the GaAs QW spin polarization and the thickness of the Fe/AlGaAs interface. As the interface thickness increases from 0.5 to 0.9 nm, the measured polarization decreases from 27% to 18%. There are also indications that the Fe film is affected by annealing and implications toward spin injection will be discussed. This work was supported by the DARPA SpinS program and ONR. @FootnoteText@ @footnote 1@R.M. Stroud, et al, PRL 89 (2002)@footnote 2@A.T. Hanbicki, et al, APL 82 (2003).

[1] **Falicov Student Award Finalist**

3:20pm **EM+MI-TuA5 Gate-Controlled Electron Spin Transport for Nonmagnetic Spintronics***, **K.C. Hall**,* Dalhousie University, Canada*; K. Gundogdu, J.L. Hicks, A.N. Kocbay, M.E. Flatte, T.F. Boggess,* University of Iowa*; K. Holabird, A. Hunter, D.H. Chow, J.J. Zinck,* HRL Laboratories, LLC **INVITED**

The prospect of novel high-performance spin-based semiconductor technologies has lead to new research in spintronics, in which the fields of electronics, photonics, and magnetics merge with the promise of applications in ultra-low-power logic architectures, non-volatile reprogrammable gate arrays, and optoelectronic technologies. Innovation in these areas requires the development of efficient methods for spin injection and manipulation in semiconductor materials. Spintronic device architectures that do not require external magnetic fields or magnetic contacts are especially attractive as they would provide seamless integration with the materials and processing techniques of existing semiconductor devices, while avoiding undesirable stray magnetic fields that may hinder device performance. We show that highly spin-polarized electron spin injection may be achieved in side-gated resonant interband tunnel diodes (RITDs) based on nonmagnetic (110) InAs/GaSb/AlSb heterostructures.@footnote 1@ Due to the strong spin-orbit effects in this system, electron spin splittings due to bulk inversion asymmetry approach 40 meV, permitting operation of the spin-RITD at practical temperatures. A nonmagnetic spin field effect transistor incorporating RITD contacts and gate-controlled spin relaxation will be described, along with our recent experiments demonstrating low-threshold spin lifetime switching in this device.@footnote 2@@FootnoteText@This research is supported by DARPA MDA972-01-C-0002, DARPA/ARO DAAD19-01-1-0490, NSF ECS 03-22021, and NSERC. @footnote 1@K.C. Hall et al., Appl. Phys. Lett. 83, 2937 (2003); @footnote 2@K.C. Hall et al., to be published in Appl. Phys. Lett. (2005).

Electronic Materials and Processing
Room 309 - Session EM-TuA

Growth and Characterization of ZnO

Moderator: T.J. Coutts, National Renewable Energy Laboratory

2:00pm **EM-TuA1 Expanding Thermal Plasma Deposited ZnO Films: Effect of Al Doping on the Thin Film Growth***, **I. Volintiru**, M. Creatore,* Eindhoven University of Technology, The Netherlands*; J.L. Linden,* TNO Science and Industry, The Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Zinc oxide (ZnO) films have been extensively studied in the past decade due to their advantages over other transparent conductive oxides (TCOs) such as large exciton binding energy, possibility of wet chemical etching, non-toxic precursors, and low-cost production. For specific applications, a good control of the ZnO film electrical and optical properties, as well as the surface morphology (e.g. high roughness needed for light trapping within solar cells) is necessary. In this work, both undoped and Al-doped ZnO films are deposited on crystalline Si and glass substrates using an argon-fed expanding thermal plasma in which oxygen, diethylzinc (and trimethylaluminium for Al doping) are admixed downstream. The in-situ real-time spectroscopic ellipsometry (SE) and atomic force microscopy (AFM) performed on undoped ZnO point out towards a linear roughness development (about 10% of the film thickness) starting from 10 nm film thickness. Moreover, both AFM and X-ray diffraction (XRD) measurements indicate a polycrystalline film growth above 10 nm. The influence of Al doping on the ZnO film electro-optical properties, surface morphology and crystallinity obtained from Hall, in-situ SE, AFM and XRD, respectively, will be presented.

2:20pm **EM-TuA2 Carbon Passivation Effect in ZnO Thin Film***, **X. Li**, S. Asher, C.L. Perkins, B.M. Keyes,* National Renewable Energy Laboratory*; S. Limpijumnong,* Suranaree University of Technology, Thailand*; S.B. Zhang, S.-H. Wei, T.J. Coutts, R. Noufi,* National Renewable Energy Laboratory

Carbon impurity is commonly found in thin films fabricated by metal-organic chemical vapor deposition (MOCVD). The role of carbon in undoped and nitrogen-doped ZnO thin films was studied experimentally and theoretically to understand the possible compensation effect of carbon. ZnO thin films were fabricated by low-pressure MOCVD using diethylzinc and oxygen precursors. Nitrogen doping was achieved with nitric oxide (NO) gas. High levels of carbon incorporation were observed in the ZnO film, especially for nitrogen-doped ZnO film. Fourier transform infrared (FTIR) spectroscopy observed the possible C-H@sub x@ (x=1, 2,

and 3) defect complex in the unintentionally doped ZnO film. Both FTIR and X-ray photoelectron spectroscopy observed the possible N-C defect complex in the nitrogen-doped ZnO. The first-principles calculations predict that the N-C defect complex is 1+ charge state. Therefore, the existence of carbon and the N-C defect complex could compensate the nitrogen acceptor species.

3:20pm **EM-TuA5 Direct Formation of Nanoporous ZnO Networks by MBE**, ***S.M. Durbin***, *W.C.T. Lee, R.P. Millane, R.J. Reeves,* University of Canterbury, New Zealand*; Z. Liu, S. Ringer,* University of Sydney, Australia*; F. Bertram,* Otto-von-Guericke-University Magdeburg, Germany

Porous semiconductors have captured significant attention in the past decade, both as a result of visible luminescence from silicon structures and due to the potential for creating surface-active devices such as gas sensors. Porous networks of these materials are generally formed in conjunction with some form of anodic etching procedure, although some arc processing has been reported as well. In contrast, we have observed the direct formation of large-scale multi-level nanoporous ZnO networks grown using an RF plasma-assisted molecular beam epitaxy (RF-PAMBE) technique without the need for etching or other postprocessing. Elemental Zn was evaporated using a standard effusion cell, and active oxygen was supplied using an Oxford MDP21 plasma source with alumina components in the plasma chamber. In-situ reflection high-energy electron diffraction exhibited patterns consistent with c-axis oriented single crystal growth on the GaN/sapphire template. Initial estimates indicate a porosity of at least 20% based on analysis of field emission scanning electron microscopy images, which also show feature sizes on the order of tens of nanometres and pores of approximately 100 nm in diameter. Cross-sectional transmission electron microscopy confirms the presence of a porous network on top of a 20 nm thick continuous ZnO layer. Low temperature photoluminescence reveals a broad feature near the bandedge of ZnO, which is near the short wavelength limit of the measurement apparatus. The driving mechanism underlying the formation of the nanoporous layer is unclear, but may be related to preferentially-oriented surface features formed on the GaN buffer layer. This work is supported in part by the MacDiarmid Institute for Advanced Materials and Nanotechnology, and the University of Canterbury.

3:40pm **EM-TuA6 STM Study of Gold Nanoparticles on ZnO Film Annealed at Different Temperature**, ***R.S. Aga***, *A. Ueda, W.E. Collins, R. Mu,* Fisk University

ZnO nanowires are promising for photovoltaic applications. In addition, ZnO film may also be used as a transparent electrode. Direct growth of ZnO nanowires on ZnO film via gold nanoparticles may then provide a better transport of photogenerated charges from the nanowire to the electrode. Thus, it is important to understand the effect of thermal treatment on the microstructure and electronic properties of gold nanoparticles deposited on ZnO film. In this work, we use STM to study spin-coated gold nanopaticles on ZnO films annealed at different temperatures. The films were grown by electron beam deposition. Our results may be useful in optimizing nanowire properties as well as improving nanowire connectivity to the electrode.

Electronic Materials and Processing
Room Exhibit Hall C&D - Session EM-TuP

Electronic Materials and Processing Poster Session

EM-TuP1 Nano-scale Characterization of High-k Dielectric Materials by Conducting Atomic Force Microscopy*, S. Kremmer, H. Wurmbauer,* ***C. Teichert,*** University of Leoben, Austria*; G. Tallarida, S. Spiga, C. Wiemer, M. Fanciulli,* Laboratorio MDM - INFM, Italy

The steadily shrinking device dimensions in semiconductor industries demand for advanced electrical characterization methods operating on the nanometer scale. One suitable technique already used for the evaluation of silicon gate oxide quality@footnote 1,2@ is Conducting Atomic-Force Microscopy (C-AFM). C-AFM, operating in ultra high vacuum (UHV), is used to study different high-k dielectric thin films with regard to their electric properties and homogeneity. The UHV conditions are mandatory here to avoid surface modification during the experiment. ZrO@sub 2@ and HfO@sub 2@ films of different thickness have been grown by atomic layer chemical vapor deposition on silicon substrates. With increasing film thickness their structure changes from amorphous to polycrystalline with different phases. Therefore, local current-voltage measurements are used to obtain a statistical distribution of the leakage current as a function of applied voltage and film thickness. Further, two dimensional current scans are performed to obtain the local distribution of leakage current. These investigations provide a deeper insight into the influence of crystallites formation on nano-scale electrical properties of two selected dielectric materials. @FootnoteText@@footnote 1@ S. Kremmer, C. Teichert, E. Pischler, H. Gold, F. Kuchar, M. Schatzmayr, Surf. and Interf. Anal. 33 (2002), 168. @footnote 2@ S. Kremmer, H. Wurmbauer, C. Teichert, G. Tallarida, S. Spiga, C. Wiemer, M. Fanciulli, J. Appl. Phys. 97/7 (2005), 74315-1-7.

EM-TuP2 Production of a Hafnium Silicate Dielectric Layer For Use As a Gate Oxide by Solid-State Reaction*,* ***H.T. Johnson-Steigelman****, S.S. Parihar, A.V. Brinck, P.F. Lyman,* University of Wisconsin-Milwaukee

The formation of hafnium silicate films (HfSi@sub x@O@sub y@) for use as gate oxides with large dielectric constant by solid state reaction of Hf metal and high quality thermal oxide and native oxide SiO@sub 2@/Si(001) substrates was investigated using LEED, XPS, and AFM. Thin, fully reacted silicate films could be formed, and were thermally stable in vacuum to temperatures in excess of 800°C. Spectroscopic evidence indicates that the interface between a hafnium silicate layer and the silicon substrate was stable against SiO@sub 2@ formation. The observed binding energy (BE) shift provides evidence that the hafnium silicate/Si interface will be stable against interfacial SiO@sub 2@ formation (as predicted by Hubbard and Schlom@footnote 1@). The thermodynamic driving force for interfacial SiO@sub 2@ formation when most oxides are placed in contact with Si is the large heat of formation of the SiO@sub 2@ phase. While Si is rather electro-positive, Hf is even more electropositive, and HfO@sub 2@ has a higher heat of formation than does SiO@sub 2@. The shift of the Si oxide XPS feature to shallower BE indicates@footnote 2@ that Hf donates charge to the SiO@sub 2@ complexes in the newly formed silicate compound. This shift, therefore, corroborates that Hf is able to reduce SiO@sub 2@; conversely, Si will be unable to reduce HfO@sub 2@, and interfacial SiO@sub 2@ formation will be thermodynamically unfavorable. The morphology of the surface was determined by AFM to be smooth and featureless on the length scale of hundreds of nanometers. LEED results show the surface to be amorphous and free of pinholes. @FootnoteText@ @footnote 1@ K.J. Hubbard, D.G. Schlom: J. Mater. Res. 11, 2757 (1996).@footnote 2@ T.L. Barr: Crit. Rev. Anal. Chem. 22, 115 (1991).

EM-TuP3 Investigation of Annealing Effect and Suppression of Hydration and Silicate Formation of La@sub 2@O@sub 3@ Thin Films*,* ***D. Eom****, S.Y. No, C.S. Hwang, H.J. Kim,* Seoul National University, Korea

High dielectric constant materials (high-K) have attracted a great deal of interest because of the dramatic scaling down of Metal-Oxide-Semiconductor field effect transistor (MOSFET) device reaching its physical limit in terms of reduction of thickness. Among high-k materials, such as Al@sub 2@O@sub 3@, HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, La@sub 2@O@sub 3@ etc., have attracted a great deal of interest as a replacement for the conventional SiO@sub 2@ gate oxide. La@sub 2@O@sub 3@ is promising as a gate dielectric film in future CMOS devices because it has a large conduction band offset(~2.0eV), high didelectric constant(24~27) and good leakage current characteristic. However La@sub 2@O@sub 3@ films appears to be hydrated easily and become silicate films by react with Si substrate. Moreover improvement of thermal stability is needed like other high-k films. In this work AlN thiln films was deposited after La@sub 2@O@sub 3@ film deposition on Si substrate to suppress hydration of La@sub 2@O@sub 3@ films. From X-ray Photoelectron Spectroscopy(XPS) results the hydration was not shown. AlN thin film was also deposited on Si substrate before La@sub 2@O@sub 3@ film deposition as a barrier material to prevent reaction of La2O3 film with Si substrate. Without thermal annealing, AlN barrier film is effective to reduce silicate formation, but after 800@super o@C annealing the AlN film mixed with La@sub 2@O@sub 3@ film therefore barrier effect disappeared. And There were flat band shift toward negative voltage and degradation of electrical properties after annealing at 800@super o@C and over. From Auger Electron Spectroscopy and XPS results, it is considered to be because of a generation of oxygen vacancy during annealing. Low temperature annealing at O@sub 2@ ambient after 800@super o@C annealing recovered flat band voltage and electrical characteristics.

EM-TuP4 Nucleation Behavior of Ru Thin Films Prepared by MOCVD on TiN Substrate with TiCl@sub 4@ Pre-Treatment*,* ***B.S. Kim,*** *H.S. Seo, C.S. Hwang,* Seoul National University, Korea*; S.Y. Kang, J.Y. Kim, K.H. Lee, H.J. Lim, C.Y. Yoo, S.T. Kim,* Samsung Electronics Co., Ltd., Korea*; H.J. Kim,* Seoul National University, Korea

Due to the excellent characteristics, such as low electrical resistivity and good dry etching property, ruthenium (Ru) is considered as a candidate material for capacitor electrodes in gigabit scale dynamic random access memories (DRAMs). In a typical concave type storage node of gigabit scale DRAMs, the Ru bottom electrodes should be deposited on the TiN diffusion barrier. But the metalorganic chemical vapor deposition (MOCVD) of Ru on the TiN surface has been suffered from the poor nucleation behavior and rough surface morphologies, which makes the capacitor fabrication difficult. In this study, the Ru films were deposited by MOCVD using Ruthenium-(2,4-Demethylpentadienyl)(Ethylcyclopentadienyl)[Ru(DER)] on various substrates, such as Ta@sub 2@O@sub 5@, TiN, SiO@sub 2@ and TiO@sub 2@. The nucleation rate of Ru on the TiN surface was improved by the TiCl@sub 4@ pre-treatment which was done by atomic layer deposition (ALD). The Ru thin films deposited on Ta@sub 2@O@sub 5@ and TiO@sub 2@ with oxygen addition at 300°C have continuous and smooth surfaces while those on SiO@sub 2@ and TiN have discontinuous film morphologies. It is suggested that the different surface morphologies of Ru films were mainly attributed to the difference of bonding type of the substrates. The surfaces with highly ionic bonding characteristics, such as Ta@sub 2@O@sub 5@ and TiO@sub 2@, can share the surface electron cloud with the metallic Ru dimer resulting in lowering of nucleation barrier energy. Therefore surface modification of TiN surface that has highly covalent bonding characteristics can improve the nucleation rate of Ru. The pre-treatment with ALD-TiCl@sub 4@ enhanced the nucleation rate of Ru films mainly due to the partial oxidation of TiCl@sub 4@ that results in the formation of seed-like TiO@sub 2@ layer. The conformal deposition of Ru on the contact-hole structure and on the bottom TiN surfaces was successfully obtained via surface modification using TiCl@sub 4@.

EM-TuP5 Structural and Electrical Properties of PZT Thin Films Patterned by Chemical Mechanical Polishing Process for FRAM Applications*,* ***N.-H. Kim****, P.-J. Ko, G.-W. Choi,* Chosun University, Korea*; Y.-J. Seo,* Daebul University, Korea*; W.-S. Lee,* Chosun University, Korea

Ferroelectric random access memory (FRAM) has been considered as one of future memory devices due to its ideal memory properties such as non-volatility, high charge storage, and faster switching for the readywrite operations. The lead zirconate titanate (PZT) is one of the most attractive perovskite-type materials for realizing the ferroelectric products due to its higher remanant polarization and the ability to withstand higher coercive fields. The sol-gel solution of Pb@sub 1.1@(Zr@sub 0.52@Ti@sub 0.48@)O@sub 3@ was spin-coated on patterned substrate. The thin films were polished by chemical mechanical polishing (CMP) technique. The vertical sidewall of the PZT pattern was successfully achieved, because the patterning of the PZT thin films was performed by using a damascene process. In this study, the surface morphology and the electrical properties of PZT capacitors were evaluated after CMP process. The selectivities for end-point detection to top electrode materials and TEOS film were also studied. Surface morphology after CMP process was undergone with atomic force microscopy (AFM) of PSIA Company. The electrical properties were measured between the top and bottom electrodes. Capacitance and leakage current of PZT capacitors after CMP are examined. The capacitance was measured by using an HP 4192 impedance/gain-phase analyzer at 10 kHz, and the leakage current density was determined by using an HP 4145B semiconductor parameter analyzer. The crystal structure of the polished samples was investigated by X-ray diffraction (XRD) to observe the

variation of phases. The improved PZT capacitor with the high capacitance and the low leakage current could be obtained by analyzing correlation between electrical properties and various CMP process parameters. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2004-005-D00007).

EM-TuP6 Chemical Mechanical Polishing Characteristics of BTO Thin Films by BaTiO@sub 3@ Abrasive Slurry for High-Density DRAM Application*, **P.-J. Ko**, N.-H. Kim, J. Park,* Chosun University, Korea*; Y.-J. Seo,* Daebul University, Korea*; W.-S. Lee,* Chosun University, Korea

BaTiO@sub 3@ (BTO) high dielectric thin films have received much attention as one of the new dielectric materials for high density dynamic random access memories (DRAMs) because of their high relative dielectric constant and small variation in dielectric properties with frequency. It is well known that BTO films are difficult to be etched by wet etching, but high etch rate with good selectivity to pattern mask was required. Plasma etching provided the high etch rate with good selectivity, however, the problem of sidewall angle still remained to be solved. In this study, we examined the characteristics of submicron capacitors fabricated by chemical mechanical polishing (CMP) process with the vertical sidewall instead of plasma etching. The sputtered BTO thin films on the stopper layer were polished by CMP with commercial alumina (Al@sub 2@O@sub 3@) slurry and self-developed BTO (BaTiO@sub 3@) abrasive slurry. The polishing results of BTO thin films using the harder alumina slurry represented the high removal rate, while the polishing results using the softer BTO slurry shows the relatively low removal rate with insufficient within-wafer non-uniformity (WIWNU%). The polishing mechanism of BTO thin films by two kinds of slurry was investigated by the surface analysis by X-ray photoelectron spectroscopy (XPS) with the surface morphology by atomic force microscopy (AFM). The surface roughness and planarity were also strongly depended on the self-developed BTO slurry. The vertical sidewall of BTO patterns was successfully accomplished by the damascene process of BTO thin film. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2004-005-D00007).

EM-TuP7 Poly(3-hexylthiophene) Organic Thin Film Transistor on Polyimide using Electroplated Au Electrodes*, **J.G. Lee**, Y.G. Seol,* Sungkyunkwan University, South Korea*; N.-E. Lee,* Sungkyunkwan University, South Korea, Korea

Organic thin film transistors (OTFT) on flexible substrate utilizing electroplated Au electrodes have potential advantages in the fabrication of flexible devices requiring large area coverage, structural flexibility, low-temperature processing, and especially low cost. In particular, the application of electroplated electrode with the adhesion layer enables one to obtain reliable devices on the flexible substrate in terms of mechanical flexibility and thermal stability, as proved in the flexible printed circuit board (FPCB) technology. In this work, poly(3-hexylthiophene) (P3HT) OTFT devices with a top-gate structure were fabricated by utilizing the electroplated Au source and drain electrodes on polyimide substrate. First, since the adhesion of electrodes on the flexible substrate is of great importance for the application in flexible devices, the adhesion improvement of electroplated electrode structures was achieved by plasma treatment of polyimide substrate followed by a sequential sputter-deposition of Cr(adhesion) and metal seed layers. Au source/drain electrodes were electroplated into the patterned SU-8 mask by ultra-violet photolithography. After SU-8 ashing and Cr/Cu layer removal, spin-coating of P3HT layers, and gate dielectric formation, and Al electrode deposition were carried out. Here, organic-inorganic hybrid gate dielectric layers as well as organic PVP gate dielectric were employed. The channel length ranged between 5 and 110 µm, and the channel width was 800 µm. Electrical properties of fabricated OTFTs were characterized and the effect of various process conditions and structures on the performances of the fabricated devices will be discussed.

EM-TuP8 Scanning Tunneling Microscopy Study of Rubrene on Au(100) Substrate*, **Y.S. Cho**, Y.J. Song, H.J. Yang, S.H. Kim, Y. Kuk,* CSNS, Seoul National University, Korea

Rubrene has become a strong candidate for an organic thin film transistor (OTFT) because of its high mobility 8 cm@super 2@/Vs,@footnote 1@ and easy processing on various substrates, together with pentacene. It has been pointed out that interface states work as scattering centers and results in poorly reproduced potential barriers for various metal contacts in the transport measurement. In this work, we investigated the geometrical and electronic structures of a single rubrene molecule and up to 10-monolayer rubrene adsorbed on Au(100) surface with scanning tunneling microscopy and spectroscopy. In the geometry of metal-rubrene-metal transport measurement, the molecule is positioned as if it flat on the contact metal. This geometry can be achieved by adsorbing the molecule on a metal substrate. At low coverages, rubrene molecules grow as a single phase from step edges, showing step flow growth. They show well ordered growth pattern at high coverages. We will show the coverage dependence of the HOMO-LUMO gap states and possible implication to the transport measurement. @FootnoteText@ @footnote 1@Vikram C. Sundar et al., Science, 303, 1644 (2004).

EM-TuP9 Organic Light Emitting Diodes Using Alkaline-earth Metals as an Electron-injecting Layer and Their Semi-passivation*, **C.H. Jeong**, J.T. Lim, J.H. Lee, J.H. Lim, G.Y. Yeom,* Sungkyunkwan University, Korea

To obtain the high performance characteristics of the top-emitting organic light-emitting diodes (TEOLEDs) based on an electron-injecting layer of alkaline-earth metal with a low work function, devices consisted of glass/ITO/2-TNATA (60 nm)/NPB (15 nm)/Alq@sub3@ (45 nm)/alkali metal (x nm)/Al (2 nm)/Ag (10-y nm)/Au (y nm)/Alq@sub3@ (53 nm) were fabricated, where, alkaline-earth metals such as Ba, Ca, and Mg were used to reduce the energy barrier from the cathode into the organic layers by electron hopping. The top Alq@sub3@ layer was used to passivate the semitransparent conducting protecting layer (STCPL) composed of alkaline-earth metal/Al/Ag/Au and organic layers from the damaging environment. In addition, the Ag layer composed of STCPL was introduced into TEOLED to improve the adhesion between the Al layer and the Au layer. In this study, the electrical characteristics of the fabricated TEOLEDs semi-passivated with the Alq@sub3@ were measured using an electrometer and the luminescence characteristics were determined by measuring the photocurrent induced by light emission from the OLEDs using a picoammeter. Other properties such as optical transmittance and resistivity were measured using a UV-spectrometer and a four point probe, respectively.

EM-TuP10 Highly-efficient Top-emission Organic Light-emitting Diodes Using Alkali Metal as an Electron-injecting Layer and Their Semi-passivation*, **J.T. Lim**, C.H. Jeong, J.H. Lee, J.H. Lim, G.Y. Yeom,* Sungkyunkwan University, Korea

To obtain high-performance top-emission organic light-emitting diodes (TEOLEDs) with a high aperture ratio and high resolution, a device consisted of glass/ITO/2-TNATA (60 nm)/NPB (15 nm)/Alq@sub3@ (45 nm)/alkali metal (x nm)/Al (2 nm)/Ag (10-y nm)/Au (y nm)/Alq@sub3@ (53 nm) was fabricated. Especially, in this study, alkali metals such as Li and Cs with a low work function was used to reduce the energy barrier from the cathode into the organic layers by electron hopping and the top Alq@sub3@ layer was used to passivate the semitransparent conducting protecting layer (STCPL) composed of alkali metal/Al/Ag/Au and organic layers from the hostile environment. The Ag layer composing of STCPL was introduced into TEOLED to improve the adhesion between the Al layer and the Au layer. In this study, the characteristics of STCPL composed of TEOLEDs were investigated using a four-point probe and a UV-spectroscopy to measure the resistivity and the transmittance, respectively. Also, the current-voltage-luminance characteristics and electroluminescent spectra of the TEOLEDs semi-passivated with the Alq@sub3@ layer were investigated.

EM-TuP11 Oxygen Doping of DNA Molecules Using Rapid Thermal Processor at Low Temperature*, **M.W. Yoon**, J.M. Lee, K.-S. Kim,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

Recent studies on the electrical conduction of the deoxyribonucleic acid (DNA) strands reveal that they may act as semiconductor materials, suggesting that they might be used for the nano-electronic devices in the future. Furthermore, semiconducting properties can be controlled by gas (e.g., O@sub 2@) doping the DNA molecules. For example, it has been reported that O@sub 2@ doping of poly(dG)-poly(dC) DNA molecules at room temperature results in p-type semiconductor-like DNA molecules. In this work, we investigated the possibility of carrier doping of various types of DNA molecules including poly(dG)-poly(dC), DNA poly(dA)-poly(dT) and lambda DNA molecules at low temperature (e.g., room temperature, 90, 100, 130 °C) using a rapid thermal processor. Doping gases used in this work were N@sub 2@ and O@sub 2@. Annealing at low temperature in vacuum (i.e., without gas doping) was also performed to clarify the roles of both gas sources and heat treatment. Results obtained in this work show that both O@sub 2@ doping and heat treatment have certain roles to change the conduction properties of DNA molecules. Specifically, the conductivity of poly(dG)-poly(dC) molecules increases as annealing temperature raises regardless of the gas types. However, the highest value

of conductivity at given annealing temperature was always obtained from the samples annealed at O@sub 2@ ambient, suggesting that O@sub 2@ doping is more effective to make p-type semiconductor-like poly(dG)-poly(dC) molecules. On the contrary, O@sub 2@ doping of poly(dA)-poly(dT) and lambda DNA molecules results in the reduction of conductivity. This phenomenon suggests that poly(dA)-poly(dT) and lambda DNA molecules behave like a n-type semiconductor due to O@sub 2@ doping.

EM-TuP12 Field Effect Properties of M-DNA Molecules Observed by Changing Gate Voltages*, **J.M. Lee**,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

Recent studies on the electrical conduction of the deoxyribonucleic acid (DNA) strands reveal that they may act as semiconductor materials, suggesting that they might be used for the nano-electronic devices in the future. Consequently, on-going research efforts have been focused on ways to find the conduction properties of many different types of DNA strands. In addition, several research groups reported that the metallic nano-wires can be formed by utilizing the DNA molecules as templates. One of the examples is the formation of M-DNA (i.e., metallic DNA). M-DNA is a complex form of DNA molecules with the divalent metallic ions (i.e., Zn@super 2+@) replacing the imino proton of every base pair. Because of containing metallic ions at DNA helix, it has been reported that the current-voltage characteristic of M-DNA attached on the two-terminal electrode represents the metallic properties, although I-V data failed to show the ohmic property. In this work, we investigated the I-V characteristics of M-DNA molecules attached on the three-terminal electrode. We monitored the current variation measured between source and drain by sweeping the gate voltage. It has been reported that M-DNA can be made using poly(dA)-poly(dT), poly(dG)-poly(dC) or lambda DNA. For the current work, we report the experimental results obtained from M-DNA prepared using lambda DNA. Once M-DNA molecules were trapped on the top electrode, the sample chamber was evacuated to minimize the humidity effects on the measurement of I-V characteristics. We found that the current of M-DNA molecules measured between source and drain (I@sub DS@) increases as the gate voltage increases, although the degree of current modulation obtained through M-DNA was less than that of lambda DNA. Since the I@sub DS@ data obtained in this work were collected in vacuum, we suggest that the I@sub DS@ modulation caused by the gate voltage is due to the field effect.

EM-TuP13 Simple Patterning Techniques for Fabrication of Organic Thin Film Transistors*, **S.J. Jo**, W.J. Kim, C.S. Kim, H.K. Baik,* Yonsei University, Korea

Fabrication of any device requires patterning and this patterning for organic devices such as OTFTs presents a challenge because of the deleterious effects a solvent typically used in conventional lithography can cause. Particularly in the context of low cost, large volume manufacturing, there is a need to demonstrate that inexpensive material deposition and patterning processes can be integrated with existing device concepts with adequate performance. As an alternative to the vacuum deposition and photolithographic patterning of the various functional films, the use of high-resolution patterning techniques is of particular interest. We report simple microcontact printing techniques to form organic source/drain microstructure for organic thin film transistors (OTFTs). Fabrication of OTFTs with micron feature sizes demonstrates the approach. The performance of these transistors compares with that of similar devices constructed using conventional methods and Au source/drain.

EM-TuP14 Encapsulation of Pentacene Thin-Film Transistors with a Transparent Oxide/Organic Smoothing Layer*, **W.J. Kim**, W.H. Koo, S.J. Jo, C.S. Kim, H.K. Baik,* Yonsei University, Korea

The long-term stability of the pentacene thin-film transistors encapsulated with a transparent oxide which was prepared by ion-beam assisted deposition (IBAD) was investigated in terms of the electrical properties associated with material characterizations. A polymer layer had been deposited in vacuum prior to IBAD process not only for a buffer layer, but also for a smoothing layer. Our unique multi-layer encapsulation was found to effectively suppress water and oxygen permeation into the organic active layer so that our pentacene TFT with the encapsulation showed a greatly enhanced long-term stability. It is thus concluded that our encapsulation can be employed for stable operation of organic devices such as organic thin-film transistors (OTFTs) and organic light-emitting diodes (OLEDs) in air ambient.

EM-TuP15 Photo- and Electro-Luminescence Studies of Highly Alkyl-Substituted Templated Bis(8-Hydroxyquinoline) Derivatives for Organic Light Emitting Diodes*, **R.D. Torres**, P.H. Holloway, J.R. Reynolds,* University of Florida*; M. Albrecht,* RWTH Aachen, Germany

Aluminum tris(8-hydroxyquinoline) (Alq@sub 3@) is the most widely used electon transport and emissive material in organic light emitting diodes (OLEDs). Alq@sub 3@ is thermally and morphologically stable when vacuum deposited. The molecule is shaped to avoid exciplex formation, serves as a good green (@lambda@@sub max@ = 520 nm) emitter with excellent electron-transport properties, and the bandgap can be modified by attaching electron withdrawing/donating organic groups. In this study we have used solution and thin-film photoluminescence (PL) to characterize the emissive properties of new Alq@sub 3@ type derivatives: tetra-decyl-substituted ethylene-linked bis(8-hydroxyquinoline) (BHQ) ligands. The effects of different templating cations (K@super +@, NH@sub 4@@super +@, Rb@super +@, Cs@super +@) on optical emission from these complexes [(ligand)@sub 3@Al@sub 2@ and (ligand)@sub 3@Ga@sub 2@] were investigated. Solutions were prepared using only the complexes, or using the complexes with various molar concentrations of poly(methyl methacrylate) or polystyrene. The ratio of PMMA or PS was varied relative to the polymer repeat unit, and compared to similarly prepared Alq@sub 3@ solutions. Thin films were made by spin coating on glass substrates. The samples were excited with a 350 nm excitation, and spectra were recorded from 400 to 650 nm. Electroluminescent devices with structures of glass/ITO/PEDOT-PSS HTL/BHQ complexes ETL/LiF/Al were prepared. The current-voltage-luminescence characteristics of these devices were observed. These complexes show promise as Alq@sub 3@ derivatives that can be processed by methods other than vacuum evaporation.

EM-TuP16 A Study of the Optical and Electronic Properties of Poly(Vinylidene Fluoride-Trifluoroethylene) Copolymer Thin Films*, **Y.X. Li**,* Shandong University, China*; L. Yan, E.A. Irene,* University of North Carolina-Chapel Hill

Thin films of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] have been deposited by spin casting onto bare Si and SiO@sub 2@ coated on Si substrates. From trials with a variety of solvents methyl ethyl ketone (MEK) yielded the most uniform smooth films as determined using atomic force microscopy. The films were found to be optically transparent in the 280-830 nm (1.5-4.5eV) optical range. Spectroscopic ellipsometry (SE) was used to obtain the refractive index in the 1.5-4.5eV photon energy range that was found to decrease with thinner films. SE performed at several sensitive angles of incidence has revealed no measurable optical anisotropy. Annealing in vacuum caused about a 3% decrease in thickness and an increase of about 0.02 in the refractive index. Capacitance versus voltage (C-V) and conductance (G(@omega@)) versus gate voltage (G(@omega@)-V) measurements were performed on capacitor structures in order to determine K, interface charge and the density of interface states (D@sub it@), respectively. Thus far a value of about 9 was obtained for the static dielectric constant for 50nm films and interface charge and D@sub it@ results appear promising for the use of P(VDF-TrFE) as a gate dielectric and thin film piezoelectric for various electronic applications. @FootnoteText@ This research is supported by NASA URETI and the NSF.

EM-TuP17 Optical and Interfacial Electronic Properties of Spin Cast Poly(o-methoxyaniline) (POMA)Thin Films*, **R.P. Shrestha**, D.X. Yang, E.A. Irene,* University of North Carolina-Chapel Hill

Optical properties of semiconducting polymer, Poly(o-methoxyaniline)(POMA) thin films prepared by spin casting have been studied and using optical transmission spectroscopy and spectroscopic ellipsometry in the visible-near uv optical range. The dispersion in refractive index and extinction coefficient along with anisotropy, surface roughness and annealing results are reported.@footnote 1@ Small uniaxial anisotropy has been measured and annealing leads to some densification and surface smoothing. Capacitance versus voltage (C-V)and current versus voltage (I-V) measurements were performed on capacitor and thin film transistor (TFT) structures, respectively. The C-V results indicate to yield a value of about 5 for the static dielectric constant. The I-V yields TFT transfer characteristics are used to optimize the film formation process and the performance of thin film POMA as a P-type semiconductor for TFT's. @FootnoteText@ @footnote 1@R.P. Shrestha, D. Yang, and E.A. Irene, Ellipsometric determination of the Optical Properties of Poly(o-methoxyaniline), Thin Solid Films, submitted Feb 2005.

EM-TuP20 Contact Properties in Metal/Molecule/GaAs Devices*, P.D. Carpenter*, *S. Lodha, Q. Hang, D.B. Janes,* Purdue University

Molecular devices have typically been fabricated in a metal/molecule/metal configuration.@footnote 1@ However, the use of semiconductor contacts in molecular devices allows for control in device performance by varying the doping density and the surface properties of the semiconductor substrates. Semiconductors, such as GaAs, also allow for stable bonds to molecular layers. In this work, molecular devices have been fabricated in a metal/molecule/GaAs device structure using standard photolithography techniques and solution-based growth of self-assembled monolayers (SAMs).@footnote 2@ After SAMs were formed on the GaAs surface, a top metal contact was formed using an indirect path, low energy evaporation technique. The effect of the doping density (n-type and p-type) and surface properties of the substrates, including surface layers incorporating defect states, have been studied in devices employing both aromatic and alkanethiol SAMs. An electrostatic model was developed to calculate the energy band diagrams of the structures and to explain the current-voltage results. Upon examination of the I-V characteristics of the devices, we see an increase in conductivity from the fabricated metal/semiconductor control devices. It has been shown that the electrical performance of the device can be modulated by changing the coupling of the molecular monolayer with the top contact metal and the GaAs substrate. This coupling can be changed by varying the work-function of the metal contact, or by changing the doping type in the GaAs or by incorporating defect states near the GaAs surface.@footnote 3@ Alternate metallization techniques, including shadow masking approaches to avoid process-related damage to the SAM, have also been developed. @FootnoteText@ @footnote 1@ M. Reed, et. al., Science, vol. 278, pp. 252-254 (1997).@footnote 2@ S. Lodha and D. B. Janes, et al., Appl. Phys. Lett., vol. 85, 2809 (2004).@footnote 3@ S. Lodha, P. D. Carpenter, and D. B. Janes, unpublished.

EM-TuP22 Effect of Fluorine-Neutral Beam Irradiation on the Ohmic Contact Formation to n-type GaN*, H.C. Lee*, *J.W. Bae, B.J. Park, G.Y. Yeom,* Sungkyunkwan University, Korea

Irradiation of a fuorine-neutral beam to n-type GaN surface is expected to create nitrogen vacancy at the near surface region of the GaN due to the removal of nitrogen by forming NFx(x=1-3) volatile gases, which may act as donor impurities. In the case of n-type GaN contact formation, it is well known that the increase in the donor concentration at the surface region of the GaN is one of important factors to achieve a good ohmic formation. The increase of carrier concentration should lead to a decrease of the effective barrier height between n-GaN and contact material, implicating a decrease of the depletion region width. Consequently, more carriers can tunnel through the reduced barrier, resulting in ohmic contact behavior. To date, few investigators have been using chlorine-based plasmas to generate N-vacancies at the surface region of the GaN. However, these charged and energetic treatments may lead to an electrical damage to the GaN layer, which can be attributed to the deterioration of contact property. On the other hand, a treatment by a neutral beam may give no electrical damage to the GaN layer due to its neutrality. It is noteworthy that the creation of N vacancy without electrical damage causes an increase in the net carrier concentration in the near surface region of n-GaN, resulting in the decrease of the contact resistivity. Therefore, in this study, a fluorine-neutral beam is proposed to remove nitrogen atoms off at the surface of n-type GaN without electrical damage. The subsequent ITO-based contact schemes including ITO, Ti/ITO, and Cr/ITO have been investigated using a current-voltage measurement system, photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS). In this presentation, the advantage of fluorine-neutral beam treatment to modify n-GaN surface, as compared to a reactive ion treatment will also be discussed.

EM-TuP23 Effect of Nitrogen Contents (0%-5.3%) on the Temperature Dependence of Photoluminescence in InGaAsN/GaAs Single Quantum Wells*, F.-I. Lai,* National Chiao-Tung Univ., Taiwan*; S.-Y. Kuo,* National Applied Research Labs, Taiwan*; J.S. Wang,* Opto-Electronics & Systems Labs of the Industrial Technology Research Institute, Taiwan*; H.C. Kuo,* National Chiao-Tung Univ., Taiwan*; J.Y. Chi,* Opto-Electronics & Systems Labs of the Industrial Technology Research Institute, Taiwain*; S.C. Wang,* National Chiao-Tung Univ., Taiwan*; H.S. Wang, C.T. Liang, Y.F. Chen,* National Taiwan Univ.

A series of InGaAsN/GaAs single-quantum wells (SQWs) with N contents varied from 0 % to 5.3 % were grown by molecular-beam epitaxy using a solid As and nitro-gen plasma sources. The impact of nitrogen concentration on the optical properties, as determined by the temperature dependence of photoluminescence (PL), of a 6 nm SQW was investigated. In the low-temperature region, a pronounced temperature-dependent S-shaped peak positions was observed in PL spectra while increasing nitrogen concen-tration. Two approaches are used to estimate the localization energy and a strong cor-relation was observed. Quenching behavior reveals that the defect-related nonradiative processes might enhance in the highly nitrogen incorporated samples and thus influence the recombination dynamics. In addition, the evolution of the peak positions of In-GaAsN/GaAs samples was in agreement with the empirical Varshni model in the high-temperature region. A significant reduction in the temperature dependence of the emission peak position compared to the nitrogen-free InGaAs SQW is analyzed as well, and further confirms the prediction of proposed band anticrossing model of the elec-tronic structure of III-N-V alloys.

EM-TuP25 Preparation of Indium Nitride Thin Films by RF-MOMBE*, S.-Y. Kuo,* *C.-C. Kei,* National Applied Research Laboratories, Taiwan*; C.K. Chao,* National Central University, Taiwan*; C.Y. Su, C.N. Hsiao,* National Applied Research Laboratories, Taiwan

Indium nitride (InN) films have been prepared directly on the c-plane sapphire substrate by a self-designed radio-frequency plasma metal organic molecular beam epitaxy (RF-MOMBE) system. We have investigated the influence of growth temperature on the surface morphology and crystal structures by x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). At growth temperatures higher than 500 @super o@C, the hexagonal wurtzite InN films exhibit randomly oriented crystalline nature. Furthermore, a pronounced two-dimensional growth mode was observed at the growth temperature of 500 @super o@C, and this film shows highly orientation along the c-plane. These results indicate that the control of growth temperature is essential for engineering the growth of InN on Al@sub 2@O@sub 3@ (0001), and it might be also applicable for other lattice-mismatched III-V heteroepitaxial systems.

EM-TuP26 Electron Spin Resonance Investigation of the Crystallization of Silicon Carbide Thin Films*, M. Tabbal*, *E. Hannoun, T. Christidis, S. Isber,* American University of Beirut, Lebanon

Crystalline silicon carbide (SiC) is the material of choice to manufacture electronic devices that can function under extreme conditions such as high temperature, high power, high frequency and high radiation environments. This work consists of an electron spin resonance (ESR) study of paramagnetic defects in crystallized SiC thin films. The films were synthesized on silicon (Si) substrates by ablating a pure SiC target in vacuum using a pulsed KrF excimer laser. Crystallization of the films was performed by deposition at temperatures exceeding 1000 K and by subsequent high temperature annealing. ESR measurements were performed at various temperatures at X-Band and Q-Band frequencies. It is found that deposition at temperatures between 1000 and 1200 K lead to polycrystalline films with an ESR signal having a g-value of 2.0028, that is attributed to carbon defects. Increasing the deposition temperature lead to a decrease in the spin density as well as broadening of the ESR signal, with typical line-widths ranging between 5.5 and 8 G. In addition, the ESR line was found to be temperature dependent with lines narrowing down to 4.8 G for measurements performed at 77 K. Such broadening phenomena could be explained by an enhanced connectivity of the paramagnetic defects that could lead to conducting channels in the layers. Post-deposition annealing of the films, in vacuum, to 1400 K leads to a considerable decrease in spin density as well as to significant narrowing of the ESR signal down to 3.2 G. Furthermore, annealing was found to eliminate the temperature dependent contribution to the ESR line-width. These effects were found to occur along with an enhancement of the crystalline quality of the films, as deduced by XRD. A phenomenological model describing the effect of deposition temperature and subsequent annealing on the paramagnetic defects in polycrystalline SiC films will be presented.

EM-TuP27 Remote Plasma-Enhanced Chemical Vapor Deposition of Tantalum Diffusion Barrier*, E.R. Fisher,* ***P.R. McCurdy,*** Colorado State University

In recent years, copper (Cu) has become the interconnection material of choice, replacing aluminum (Al) and Al alloys in integrated circuits (ICâ?Ts). Cu is preferred over Al because of its lower resistivity and higher melting point. The lower resitivity is especially important in reducing the resistance-capacitance delay, which becomes dominant as the gate size continues to decrease. Unfortunately, Cu is susceptible to diffusion into SiO2, and suffers from poor adhesion to low dielectric constant materials. Therefore,

it is imperative to have a diffusion barrier that can also act as an adhesion layer to integrate Cu into ICâ?Ts. Currently, tantalum (Ta) and Ta nitrides are widely used for this purpose. Ta metal is especially attractive because of its low resistivity; however, because of the ever increasing aspect ratio of metal lines, tradition methods for depositing Ta metal are deficient. Physical vapor deposition is a line-of-sight method that does not work well on high aspect ratio trenches; alternative deposition methods must, therefore, be developed. One potential technique is plasma-enhanced-chemical-vapor-deposition (PECVD). This technique is especially promising for the deposition of Ta in high aspect ratio trenches because it gives extremely good step coverage and can be done at much lower temperatures than traditional CVD processes. We have successfully deposited high quality Ta films using H2 and TaCl5 in a remote PECVD system. Our Ta films show low levels of impurities and excellent step coverage on patterned Si substrates. Data on deposition rate, conformality, film composition, and electrical properties will be presented.

EM-TuP29 The Characteristics of ZnO:Al Film Using Reactive Magnetron Sputtering System for Touch Screen Applications*, **H.S. Jeong**, M.G. Kim, Y.W. Seo,* ITM Inc., Korea*; S.J. Kwon,* Kyungwon University, Korea

The ZnO:Al (AZO) films deposited on glass for touch screen panels were prepared by in-line reactive magnetron sputtering system. The target materials of magnetron sputtering system were ceramic ZnO:Al@sub2@O@sub3@ and metallic Zn:Al targets. We applied the dc-pulsed power to the targets with the change of duty ratio. To compare the AZO thin film properties with respect to the properties of typical ITO thin film used in touch screen panels, we also prepared ITO films on glass using the in-line reactive magnetron sputtering system and commercial ITO coated glass for touch screen panels. We analyze the electrical and optical characteristics of the AZO and ITO coated glass, and the environmental endurance properties (high-low temperature, temperature/humidity test, etc) of the touch screen panels (4-wire resistive type) made with the AZO and ITO coated glass. The typical range of electrical resistance and optical transmittance of the AZO and ITO coated glass were 400~500@ohm@/Sqr and about 92%, respectively. The electrical and optical properties of the films were measured with a surface profiler, an UV/Visible spectrophotometer, a 4-point probe, X-ray diffraction spectroscopy, and atomic force microscopy. @FootnoteText@ This work was supported by the Ministry of Commerce, Industry and Energy of the Republic of Korea through the National Research Laboratory program.

EM-TuP30 Large Nonlinear Optical Properties of Lead Magnesium Niobate-Lead Titanate Thin Films Grown by Pulsed Laser Deposition*, **D.-R. Liu,*** National Applied Research Laboratories,Taiwan, Taiwan*; P.-T. Cheng,* National Applied Research Laboratories,Taiwan*; S.-L. Ou,* National Taiwan Normal University, Taiwan*; J.-S. Chen,* National Applied Research Laboratories, Taiwan*; C.-P. Cheng,* National Taiwan Normal University, Taiwan

Thin film optical devices have been especially attractive because of their potential for the integration with electronic and optoelectronic systems. Owing to its ferroelectricity, high dielectric constant, and large electro-optic coefficients, Lead magnesium niobate-lead titanate (PMN-PT) can be used in many applications that include pyroelectric detectors, thin film capacitors, nonvolatile memory, and nonlinear optical devices. Because of good transparency over a wide wavelength range of 500nm-7000nm, PMN-PT best suited for almost all the visible to mid IR optical applications. In this study, highly textured thin films of lanthanum doped lead titanate were grown by pulsed laser deposition (PLD) on MgO substrates. The measurement of glancing-angle x-ray powder diffraction (GAXRD) was used to determine the structure of the PMN-PT films. The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR), and the complex refractive indices were measured in the range from 1.5 to 4.1 eV by spectroscopic ellipsometry (SE). The average oscillator strength and its associated wavelength were estimated by using a Sellmeier-type dispersion equation. Z-scan measurements were performed to study the third-order optical nonlinearity. It was found that the PMN-PT films grown on MgO substrates exhibited strong nonlinear optical effect. The results show that PMN-PT thin films are promising materials for nonlinear optics.

EM-TuP32 Electromigration Performance by Via Structure in Cu Dual-damascene Process*, **H.-K. Lee**, M.-H. Choi,* Chung-Ang Univ., Korea*; N.-H. Kim,* Chosun Univ., Korea*; S.-Y. Kim,* DongbuAnam Semiconductor Inc.*; E.-G. Chang,* Chung-Ang Univ., Korea

In order to improve the interconnect performance, Cu has been used as the interconnect material instead of Al. One of the advantages of using Cu instead of Al interconnects for ULSI circuits is high electromigration (EM) and low resistance and it is based alloys to copper interconnect leads to new via structure fabricated by dual-damascene process. Improved EM characteristic leads to not only high reliability but also high speed of ULSI. The effects of a Ta/TaN Cu diffusion barrier existence on the EM reliability and EM performance of Cu dual-damascene interconnects were investigated. In this study, EM experiments are performed on interconnect structures of via bottom in Cu dual-damascene interconnection system. In result of EM test by interconnect structure, a high EM performance for copper dual-damascene structures was observed with the conventional interconnect structure to remain Ta/TaN barrier layer at via bottom. The failure analysis of the EM investigated with the focused ion beam (FIB), scanning electron microscope (SEM), and transmission electron microscope (TEM) equipments. Failures in direct contact via (DCV) structure by using bottomless process were formed at copper lines. However the EM failures were found at the top of via through the Cu-SiN interface. DCV structure of via EM had lower activation energy than conventional interconnect structure. Via resistance was decreased DCV structure by using bottomless process. The existence of barrier layer at via bottom has the relation with the difference of EM failure mode. From the different via failure modes, it can be concluded that the barrier layer at via bottom was enhanced the back stress in conventional structure due to the blocking of Cu flow. Acknowledgement : This work was supported by grant No. R01-2002-000-00375-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

EM-TuP35 The Growth and Characterization of InN Films Grown by High-Pressure CVD*, **V.T. Woods**, M. Alevli, J. Senawiratne, M. Strassburg, N. Dietz,* Georgia State University

Group III-nitride material systems (e.g. AlN-GaN-InN) have generated considerable interest for use as the basis for advanced opto-electronic device structures. Fabrication of multi-tandem solar cells, high speed optoelectronics and solid state lasers operating in the higher energy wavelengths will be made possible using (Ga@sub1-y-x@Al@suby@In@subx@)N heterostructures due to their robustness against radiation and the wide spectral application range. As organometallic chemical vapor deposition (OMCVD) has proved to be the most efficient technique for commercial production of group III-V semiconductors, it would be expedient to gain insight in applying OMCVD to group III-nitride material systems. However, the growth of indium rich (In1-xGax)N thin films utilizing OMCVD has been unsuccessful, primarily due to the large thermal decomposition pressures in indium rich group III-nitride alloys at the optimum growth temperature. As shown in this contribution, high-pressure chemical vapor deposition (HPCVD) overcomes the limitations, enabling the growth of InN and indium rich group III-nitride alloys. This high pressure approach allows InN growth at temperatures of 1100K and above which is a major step forward towards the production of indium rich heterostructures, providing a closer match to the ideal processing temperatures of (Ga@sub1-x@In@subx@)N. Real-time optical characterization techniques are applied to study and control the gas phase kinetics and surface chemistry processes during he growth process. The ex-situ analysis of the InN layers indicates that the shift of the absorption edge from 1.85 eV down below 0.6 eV is caused by a series of absorption centers, that appear as the indium to nitrogen stoichiometry varies. This contribution will provide results from the real-time optical characterization of InN and will correlation the process parameter to results obtained by XRD, Raman spectroscopy and optical spectroscopy, in order to asses the film quality.

EM-TuP36 Characteristics of Lanthanum Oxide Prepared using La(iPrCp)@sub 3@ and H@sub 3@O*, **S.Y. No**, D. Eom, C.S. Hwang, H.J. Kim,* Seoul National University, Korea

According to scaling rule, high @kappa@ gate dielectric stack with equivalent oxide thickness (EOT) below 1 nm will be required for sub-0.1µm devices. La-based oxides are attractive candidates for this purpose because of high-@kappa@ value, good interfacial properties, and large band offset against the Si. In this report, we deposited lanthanum oxide thin films using La(iPrCp)@sub 3@ (Tris(isopropylcyclopentadienyl)Lanthanum) and H@sub 2@O. The La precursor and H@sub 2@O were injected alternately and purged by Ar gas between the injections. The deposited films underwent various rapid thermal annealing (RTA), and the property changes were investigated. The deposited films contained carbon impurity less than 1 at.% and showed smooth surface (root mean square roughness< 0.1 nm, ~5 nm film). The electrical properties of deposited films were measured on Pt/Lanthanum oxide/p-Si(100) structure, and small frequency dispersion and hysteresis

(<10 mV) were observed in capacitance vs. voltage measurement. The film structures were observed by high-resolution transmission electron microcopy, and the chemical states of interfacial and upper layer were analyzed by angle-resolved X-ray photoelectron spectroscopy. The film showed amorphous structure even after RTA at 900°C. However, chemical states were altered significantly with a change of valence band offset by the RTA. With optimized RTA condition, capacitance equivalent oxide thickness (CET) below 1.1nm was obtained with fairly reduced positive fixed charge density, and accompanied interfacial reaction lead to a decrease of interface trap density.

EM-TuP37 Zr-doped HfO2 High-k Dielectric with an Inserted HfNx Interface Layer*, J. Yan*, *J. Lu, S. Chatterjee, H.C. Kim, Y. Kuo,* Texas A&M University

Hafnium oxide (HfO2) is a popular high-k gate dielectric candidate. However, HfO2 is easily crystallized at a low temperature, such as < 600C. The effective dielectric constant of HfO2 is lowered due to the formation of a SiOx interface layer. Previously, there are reports that the k value of a high-k film can be increased by inserting a high-k interface layer between the high-k film and silicon substrate.@footnote 1@ In addition, the crystallization temperature of a high-k film can be increased by adding a certain amount of dopant.@footnote 2@ In this paper, authors will report new results on Zr-doped HfO2 films with or without an inserted HfNx interface layer. The leakage current is improved with the doping process as well as the addition of a HfNx interface layer. Other dielectric properties, such as the effective k value, interface density of states, trapped charges, and frequency dispersion, and the final interface layer material properties, such as the bond structure and thickness, of the new high-k gate stack will also be presented and discussed. @FootnoteText@ @footnote 1@ J. Lu, J. -Y. Tewg, and Y. Kuo, Engineering the nm-thick Interface Layer Formed Between a High-k Film and Silicon, MRS Symp. Procs. Integration of Advanced Nanoelectronic Devices - Critical Issues and Solutions, 811, 81-86 (2004).@footnote 2@ J.-Y. Tewg,Y. Kuo, and J. Lu, Suppression of Crystallization of Tantalum Oxide Thin Film by Doping with Zirconium, Electrochemical and Solid-State Letters, 8(1), G27-G29 (2005).

Electronic Materials and Processing
Room 309 - Session EM+SS-WeM

Contacts to Organic and Molecular Devices

Moderator: Y. Roichman, Princeton University

8:20am **EM+SS-WeM1 Energy Level Alignment at Interfaces in Organic Semiconductor Devices**, ***K. Demirkan***, *A. Mathew, S. Vaidyanathan, Z.I. Niazimbetova, H. Christian-Pandya, M.E. Galvin, R.L. Opila,* University of Delaware

Poly-phenylene vinylene based organic semiconductor polymers and oligomers were studied using X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron spectroscopy (UPS). Valence bands and highest occupied molecular orbitals (HOMOs) (with respect to Fermi level) for these organic structures were determined. Due to the high electron withdrawing property of the oxadiazole moiety, polymers, which have a higher oxadiazole density, are found to have lower energy levels. Using optical absorbance spectra, the lowest unoccupied molecular orbitals (LUMO) for some of the organic semiconductor materials were estimated and the basic energy level diagrams were established with respect to the underlying electrode. The valence band spectra of the polymers spin coated on different substrates did not show any substantial variation except for shifts in the entire spectra. In the Mott-Schottky limit, the energy difference between the electrode Fermi level and the HOMO of the organic layer is expected to follow the work function of the electrode. The interface slope parameter, a measure of the change in HOMO-Fermi level difference as a function of electrode work function, was found to vary between 0.4 and 0.9. These values are intermediate to Mott-Schottky and Fermi level pinning. We will explain the interface slope parameter in light of the interfacial dipole and charge neutrality level at organic/metal interfaces.

8:40am **EM+SS-WeM2 Towards Molecular Electronic Circuitry: Selective Deposition of Metals on Patterned Self-Assembled Monolayer Surfaces**, *C. Zhou, G. Nagy,* ***A.V. Walker,*** Washington University in St. Louis

We have developed a robust method by which to construct complex two- and three- dimensional structures based on controlling surface chemistry. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. Our method is extensible to many different types of materials, easily parallelized, affords precise nanoscale placement and is fully compatible with photolithographic fabrication processes. The method is based on the deposition of metals on UV-photopatterned self-assembled monolayers (SAMs). To demonstrate the method we have selectively vapor-deposited Mg on a patterned -CH@sub 3@/-COOH terminated alkanethiolate surface. The deposited metal penetrates through the -CH@sub 3@ SAM to the Au/S interface while reacting with the -COOH terminal group and accumulating on top of the other SAM.

9:00am **EM+SS-WeM3 Interface Disorder and Charge Injection into Organic Semiconductors**, ***M.A. Baldo***, *B.N. Limketkai,* MIT **INVITED**

In this talk, we examine the effect of structural disorder at the injection interface on the current-voltage (IV) characteristics of organic semiconductors. We find that structural disorder at the injection interface creates energetic disorder, which in turn may dominate the IV characteristics of these materials. We will describe the effects of interfacial disorder on charge injection in several model systems: flat metal electrodes, rough metal electrodes, and highly conductive polymer electrodes. Disorder is most important at interfaces with relatively small energetic barriers between the metal and semiconductor.

9:40am **EM+SS-WeM5 Modelling Inhomogeneities of Organic Device Contacts: Organic Film Growth on Nanostructured Surfaces**, ***M.G. Ramsey,*** *B. Winter, S. Surnev, G. Koller, F.P. Netzer,* Karl-Franzens-University Graz, Austria

In this contribution the growth, geometric and electronic structure of sexiphenyl films grown on clean Cu(110) and mesoscopically patterned Cu(110)-(2x1)O will be presented. The results highlight the effects of the atomic and nanometric substrate structure on the growth and electronic level alignment of active organic films. Scanning tunnelling microscopy (STM) reveals that on the clean Cu the molecules align parallel to each other and are highly mobile in one surface direction. By monolayer coverages a complete layer forms reminiscent of a smectic liquid crystal phase. Despite the lack of strict long range order the molecules align in strings with a periodicity determined by intermolecular interactions, while the periodicity between the strings is determined by the substrate periodicity. In contrast when the substrate is covered with a half monolayer of oxygen the molecules appear not to wet the surface and, apart from at defects, are not visible in STM. On the mesoscopically patterned Cu(110)-(2x1)O (stripes of clean and oxygen covered surface with a periodicity of ~ 7 nm) the molecules first appear at the Cu-CuO boundaries and then grow preferentially on the clean Cu stripes. Growth and electronic structure on the three basic substrate situations are also followed by angle resolved ultraviolet photoemission spectroscopy (ARUPS). These results highlight the problems of imaging such wide band gap materials with STM and indicate that the 6P does in fact wet the Cu(110)-(2x1)O and that the visibility of the molecule is dependent on charge transfer states in the gap. These ARUPS results will also be discussed in terms of the electronic level alignment on inhomogeneous surfaces where large band offsets between molecules on different regions occur.

10:00am **EM+SS-WeM6 The Influence of Alkyl Side-chains and Charge-Transfer Complex Formation on Sexithiophene/Metal Interface Energetics**, ***S. Duhm***, *H. Glowatzki,* HU-Berlin, Germany*; R.L. Johnson,* Hamburg University, Germany*; J.P. Rabe, N. Koch,* HU-Berlin, Germany

The energy level alignment at metal/organic interfaces is a key issue for improved performance of novel organic (opto-) electronic devices. In certain cases, solution-based processing of organic materials (i.e., spin-coating, ink-jet printing) is preferred over vacuum sublimation. Frequently, alkyl side-chains are attached to the conjugated moieties for improved solubility. In order to investigate the influence of alkyl side-chain addition on interface energetics, we studied interfaces formed between the organic molecules sexithiophene (6T) and @alpha@,@omega@-dihexylsexithiophene (DH6T) and the metal surfaces Ag(111) and polycrystalline Au with ultraviolet photoelectron spectroscopy (UPS). Samples were prepared by sublimation of the organic substances on clean metal surfaces in ultrahigh vacuum. Interestingly, we observed significantly lower hole injection barriers (0.2 - 0.4 eV) for DH6T on the metal surfaces than for 6T. We propose that the mechanism responsible for our observations is closely related to the "electron push-back effect" at metal/organic interfaces. Furthermore, the influence of molecular orientation will be discussed. Additionally, we demonstrate that the hole injection barrier at interfaces between 6T (DH6T) and metals can be further reduced by the formation of charge transfer complexes comprising tetrafluoro-tetracyanoquinodimethane (F4-TCNQ).

10:20am **EM+SS-WeM7 Top-contact Junctions for Molecules Electronics: Nano-transfer Printing**, ***K. Ojima,*** Osaka University, Japan*; K. Nakamatsu,* University of Hyogo, Japan*; Y. Otsuka, T. Matsumoto,* Osaka University, Japan*; S. Matsui,* University of Hyogo, Japan*; T. Kawai,* Osaka University, Japan

Recently, nanotransfer printing (nTP) attracts an attention as a method of producing the electrode. The electrode fabricated by nTP give the solutions for the problems of bottom contact-type electrode because electrodes are fabricated directly on the substrate after the deposition of molecules. In the previous reports, the nTP process needed chemical modification for the substrate in order to obtain well adhesiveness between the electrode and the substrate. This requirement has been serious limitation to fabricate molecular-scale devices. We have developed a nTP process for molecular devices without any modifications of substrate surfaces and evaluated the electrical properties of the electrodes fabricated by nTP. The use of the release agent enables us to print electrodes without any surface modification and heating the substrate. A test pattern of gold electrodes formed by the nTP on a DNA spread SiO2/Si substrate was examine by AFM. We found that the resistivity of a line of gold electrode is nearly equal to that of bulk gold. We also examined the electric contact between the electrodes and molecules using Kelvin force microscopy (KFM) under applying bias voltage to the electrode/molecules junctions. We will present the images of electric potential distribution for the junctions.

10:40am **EM+SS-WeM8 Orbital Alignment and Chemical Interaction at Macro-Molecular Contacts**, *M.M. Beerbom, B. Lagel, J.P. Magulick, A.J. Cascio,* ***R. Schlaf***, University of South Florida

Our experiments aim at the determination of the chemical and electronic structure of interfaces between macro-molecules and inorganic materials to determine charge injection barriers across the interfaces, the electronic structure of the highest occupied molecular orbitals (HOMO), and the chemical interaction between the materials in contact. Photoemission spectroscopy (PES) was used in combination with multi-step in-situ

deposition of macro-molecular materials on inorganic substrates. PES characterization between deposition steps yields a sequence of spectra allowing the determination of the orbital line-up. Multi-step deposition was achieved using either a unique electrospray thin film deposition system, or a glove-box based deposition procedure. This allowed the fabrication of pure and non-contaminated interfaces suitable for PES measurements. Results from a series of experiments on poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV),@footnote 1@ ribonucleic acid (RNA@footnote 2@) and L-cysteine (amino acid)@footnote 3@ interfaces will be presented. The electronic and chemical structure of these interfaces will be discussed as well as the measurement technique. @FootnoteText@ @footnote 1@N. Dam, M.M. Beerbom, J.C. Braunagel and R. Schlaf: "Photoelectron Spectroscopic Investigation of In-Vacuum Prepared Luminescent Polymer Thin Films Directly From Solution", J. Appl. Phys. 97(pp.024909 (2005).@footnote 2@N. Dam, B.V. Doran, J.C. Braunagel and R. Schlaf: "Charge injection barriers at a ribonucleic acid/inorganic material contact determined by photoemission spectroscopy", J. Phys. Chem. 109(2), pp.748-756 (2005).@footnote 3@M.M. Beerbom, R. Gargagliano and R. Schlaf: "Determination of the Electronic Structure of Self-Assembled L-cysteine/Au Interfaces Using Photoemission Spectroscopy", Langmuir Articles ASAP), (2005).

11:00am **EM+SS-WeM9 Self-assembled Monolayers with Reactive Endgroups: Studies of Inorganic-Organic Interfaces and the Initiation of Top Contact Formation**, ***A. Dube***, *M. Sharma, A.S. Killampalli, J.R. Engstrom,* Cornell University

Self-assembled monolayers (SAMs) have attracted considerable interest over the past several years in the field of molecular electronics. In such applications two interfaces become important, and understanding the formation of both is critical to effectively making use of SAMs in these devices. While formation of the bottom contact is a well studied area, the formation of top contacts is an immature field. We have been examining the reactions of transition metal coordination complexes, such as Ti[N(CH@sub 3@)@sub 2@]@sub 4@ and Ta[N(CH@sub 3@)@sub 2@]@sub 5@, with SAMs possessing different head group chemistries [e.g., RSiCl@sub 3@ on SiO@sub 2@, R-(thiophene) on Au] and endgroup functionalities (e.g., -CH@sub 3@, -NH@sub 2@ and -OH) in order to develop an understanding of interface and contact formation. In this presentation we will highlight our most recent work that includes the self-assembly and reactions of functionalized molecular wires (thiophenes with conjugated ethynyl-phenylene backbones) adsorbed on Au using in situ angle resolved x-ray photoelectron spectroscopy (ARXPS). Here we find that the saturation density of the SAM increases from ~ 2.1 to 3.4 x 10@super 14@ molecules-cm@super -2@ as the length of the conjugated backbone is roughly doubled. More importantly, these layers, which possess an isopropylamine endgroup, react via ligand exchange with Ti[N(CH@sub 3@)@sub 2@]@sub 4@ even at -50 °C, forming a structure that has a Ti:SAM stoichiometry of ~ 1:2. ARXPS shows conclusively that these Ti coordination complexes bond with the SAMs exclusively at the isopropylamine group, and can seed additional deposition of the top contact. We will discuss the importance of these and other results concerning what they say about designing an effective means to make top contacts to molecular monolayer structures.

11:20am **EM+SS-WeM10 Observation of Interface Gap-State between Pentacene Molecules and Gold Metal by Scanning Tunneling Spectroscopy**, ***Y.J. Song***, *S.H. Kim, Y. Kuk, K. Lee, J. Yu,* Seoul National University, Korea

Pentacene has been studied widely as a candidate for an organic thin film transistor (OTFT) because of its high mobility, and easy processing on various substrates. It has been pointed out that interface states work as scattering centers and results in poorly reproduced potential barriers for various metal contacts in the transport measurement. In this work, we investigated the electronic structure of a single pentacene molecule adsorbed on Au(100) surface with one dimensional spatially-resolved scanning tunneling spectroscopy (1D SR-STS) to map position-dependent local density of states (LDOS).@footnote 1@ In the geometry of metal-pentacene-metal transport measurement with a single crystal or a thin film pentacene, the molecule is positioned as if it flat on the contact metal. This geometry can be achieved by adsorbing the molecule on a metal substrate. Au(100) surface was chosen since it offers both near-hexagonal and square symmetry, depending on a location of the (5x20) reconstruction. We measured SR-STS at various sites on the Au(100)-(5x20) surface. Unlike previously observed spectroscopy results on an insulator surface,@footnote 2@ two dominant features are clearly resolved in the HOMO-LUMO gap of the spectroscopy: 1) Au surface state peaks of which energy level is position independent, and 2) a HOMO derived gap state which depend on the registry of the pentacene molecule on the substrate. We expect that these gap states work as a scattering center and change the barrier height between metal contact and organics in the transport measurement. A density functional theory (DFT) calculation confirms our observation. @FootnoteText@ @footnote 1@ Jhinhwan Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara and Young Kuk, Nature (London) 415, 1005 (2002)@footnote 2@ Jascha Repp, Gerhard Meyer, Sladjana M. Stojkovic´, Andre´ Gourdon and Christian Joachim, Phys. Rev. Lett. 94, 026803 (2005)

Surface Science
Room 202 - Session SS+EM-WeM
Self-Assembled Monolayers

Moderator: P.S. Weiss, The Pennsylvania State University

8:20am **SS+EM-WeM1 Investigation of Mixed Fluorocarbon/Hydrocarbon Self-Assembled Monolayers on Au by Reactive Ion Scattering Spectrometry**, ***X. Yang***, University of Arizona; *S. Ravindran,* University of Texas; *A. Graham, K. Nebesny,* University of Arizona; *T.R. Lee,* University of Houston; *N.R. Armstrong, V.H. Wysocki,* University of Arizona

A series of mixed self-assembled monolayers (SAMs) of CF@sub 3@CF@sub 2@(CH@sub 2@)@sub 14@SH (C16F2) and CH@sub 3@(CH@sub 2@)@sub 15@SH (C16) were prepared on polycrystalline gold. Surface composition and crystallinity were first examined by XPS, FT-RAIRS and contact angle. Homogeneously mixed and well-ordered surfaces were formed. Results showed that surface composition followed solution composition uniformly. Reactive Ion Scattering Spectrometry (RISS) utilizing low-energy (<100eV) ion-surface collisions was used to investigate the mixture monolayers. Experiments are carried out in a tandem quadruple mass spectrometer. Precursor ions selected by the first quadrupole collide onto the surfaces at given collision energies. Neutralization and fragmentation of projectiles, ion-surface reaction and sputtering of surface species occur upon collision of the projectile ions with the surface. Product ions are extracted and analyzed by the second quadrupole. Benzene, tungsten hexcarbonyl and d4-pyrazine positive radical ions were used as projectile ions. As C16F2 concentration increases on the surface, projectile neutralization decreases, the amount of methyl/hydrogen abstraction decreases non-linearly, and linear increases of translational to internal energy conversion upon collision of either benzene or tungsten hexcarbonyl are shown. RISS shows high sensitivity to composition and homogeneity of surfaces.

8:40am **SS+EM-WeM2 Surface Bonding and Dynamical Behavior of CH@sub 3@SH on Au(111)**, ***P. Maksymovych***, University of Pittsburgh; *D.C. Sorescu,* U.S. Department of Energy; *D.B. Dougherty, J.T. Yates, Jr.,* University of Pittsburgh

Alkanethiols are often used for the growth of self-assembled monolayers, which are ordered 2-D molecular films covalently bonded to a substrate, typically a gold surface. The bonding of alkanethiols to gold has remained a controversial issue. In particular, the bonding of the undissociated alkanethiols has not been addressed at the atomic scale so far. We have studied adsorption and surface chemistry of the smallest alkanethiol, CH@sub 3@SH, on the Au(111) surface using the Scanning Tunneling Microscopy (STM) at 5K and Density Functional Theory (DFT). It has been established that CH@sub 3@SH adsorbs and desorbs without dissociation. Using the STM, it was found that CH@sub 3@SH adsorbs on top of an Au atom on the defect-free surface, and undergoes hindered rotation at 5K. The barrier to rotation obtained by DFT calculations is ~0.1 kcal*mol@super -@@super 1@. The STM image of the rotating molecule has a shape of a flower with six petals. The pattern suggests that the potential minima directions occur for the rotating molecule at the six hollow sites surrounding the atop adsorption site. Furthermore, selective site occupation was observed on the length-scale of the herringbone reconstruction of the Au(111) surface. At very low coverage, the CH@sub 3@SH molecule was found to preferentially adsorb on the intrinsic defective sites on the surface, such as the herringbone "elbows" and random atomic step sites. At higher coverage preferential adsorption occured on the fcc-stacked regions of the herringbone reconstruction. The latter is explained by the variation of the surface stress across the Au(111) surface due to the herringbone reconstruction, which causes the mobile CH@sub 3@SH molecules to select the most exothermic adsorption sites available at various coverages. We thank the W. M. Keck Foundation and NEDO (Japan) for financial support of this work.

9:00am **SS+EM-WeM3 Diffusion and Aggregation of Thiol-Linked Organic Molecules on a Cu(111) Surface**, ***K.L. Wong***, *K.-Y. Kwon, X. Lin, L. Bartels,* University of California at Riverside

We have investigated the adsorption geometry and the detailed surface dynamic behavior of benzenethiol (BT) molecules on a Cu(111) surface at low temperatures (50-60K). We chose BT as a model system, because it contains both the aromatic moiety and the thiol linker common in molectronic molecules, yet it is sufficiently small to be treated at high resolution experimentally and theoretically. The BT molecule adsorbs onto Cu(111) in two types of adsorption sites. In both cases the sulphur atom is believed to be adsorbed near the fcc hollow site while the benzene group is located near parallel to the surface. The more stable adsorption configuration (I) have the benzene ring centered near an hcp hollow site while the less stable adsorption configuration (II) have the benzene ring centered near an on-top site. The molecule can change adsorption configurations by rotation around the sulphur atom. Rotation from (II) to (I) occurs more rapidly than in the opposite direction. In addition to rotations the molecule can diffuse to nearby adsorption site. The sulphur atom jumps to one of six nearby adsorption sites along the high symmetry axis of Cu(111)while the orientation of the molecule with respect to the substrate remains the same. The rate of rotations and translations has been measured at different temperatures in the range 50-60K. An Arrhenius fit to the measured data yields rotations and diffusion barriers of 120meV, 130meV and 150meV respectively. DFT calculations show good agreement with the STM data. At higher coverages the adsorbed BT molecules from stable aggregates. No stable aggregates larger than 7 molecules were found, instead the density of evenly distributed 7-molecule aggregates increases with the coverage. Abundance histograms of aggregates with different sizes and configurations reveal a delicate balance between molecule-substrate and molecule-molecule interactions.

9:20am **SS+EM-WeM4 Tunneling Spectroscopy of Self-Assembled Monolayers of 1-adamantanethiolate on Single Crystal Metallic Substrates**, ***A.R. Kurland***, *A.A. Dameron, P. Han, S.U. Nanayakkara, P.S. Weiss,* The Pennsylvania State University

We measure local barrier height and differential conductance using ultrahigh vacuum scanning tunneling microscopy (STM) at 4 K to investigate the work function and local density of states, respectively, of individual adamantanethiolate molecules on a range of single crystal metallic substrates. These techniques allow us to probe specific electronic characteristics while simultaneously resolving the molecular lattice of the adamantanethiolate monolayers. Previously, we have shown that adamantanethiolate molecules form well-ordered hexagonally close-packed monolayers on the Au{111} surface. The complex and highly symmetric cage structure of adamantanethiolate results in weaker intermolecular interactions than those of alkanethiolate self-assembled monolayers. Taking advantage of these properties, we have implemented adamantanethiolate molecules in thin-film molecular lattices and as nanolithography patterning inks. We aim to exploit and to incorporate the unique physical and electronic interactions of adsorbed adamantanethiolate to understand and to tailor self-assembled nanostructures.

9:40am **SS+EM-WeM5 Interaction Pathways of Vapor Deposited Metal Atoms with Self-Assembled Monolayers**, ***D. Allara***, *N. Winograd,* Pennsylvania State University*; A.V. Walker,* Washington University*; T. Tighe, T. Daniel, O. Cabarcos, S. Uppili,* Pennsylvania State University **INVITED**

With rapid progress being made in the fabrication and testing of molecule-based electronic devices in the past several years one of the critical issues that has arisen is the character of the metal-molecule interfaces and interphases of vapor-deposited top contact device structures. Results will be discussed that show a broad strategy for developing correlations between the interactions of a wide variety of metals with a range of alkanethiolate/Au{111} self-assembled monolayers (SAMs) carrying varied terminal groups. The metals include inert coinage metals, one-electron donor alkali metal and aggressively reactive metals such as Ti. The SAMs range from those with hydrocarbon surface character to others with high electron acceptor character (-NO@sub 2@, C=N, C=O moieties) and including "solvating" types of groups such as -OCH3. The use of 4-5 different in-situ surface characterization tools augmented by DFT calculations aids greatly in achieving incisive information ranging from metal atom surface scattering to the evolution of the metal-molecule interface chemistry and the metal film morphology. Details include the distribution of metal and reaction products throughout the SAM structure, both laterally and extending to the substrate interface. Coupling this information with the character of the SAM/base electrode interface can provide critical information to aid fundamental interpretations of device behavior.

10:20am **SS+EM-WeM7 Replicative Generation of Electrode Structures by SAM-templated Electrometallization**, *I. Thom, G. Haehner,* ***M. Buck***, University of StAndrews, UK

Self-assembled monolayers (SAMs) of thiols provide a convenient way to modify electrode surfaces and, thus, to control charge transfer at an electrochemical interface. Adjustment of electrode properties from conducting to blocking is achieved by variation of the SAM forming molecules. Since a variety of methods is available to pattern thiol monolayers, this type of SAM can serve as templates to confine electrochemical processes, e.g. metal deposition. However, in addition to the control of charge transfer, SAMs serve also to control adhesion between deposit and electrode and, therefore, make the generation of metal structures by electrochemical deposition and subsequent transfer to a different substrate possible. Copper structures were produced by electrochemical deposition onto SAM-modified polycrystalline gold electrodes. Selective metal deposition was achieved by use of thiols which differ in their electrochemical blocking properties, namely hexadecane thiol and @omega@-(4'-methyl-biphenyl-4-yl)-methanethiol. After deposition the metal patterns were easily transferred to an insulating substrate by glueing. Characterization of the transferred structures with atomic force microscopy shows that the flatness of the metal surface is essentially determined by the initial SAM carrying substrate electrode. Since the thiol pattern on the substrate electrode remains intact, it can be repetitively used. Therefore, the process allows an easy and fast fabrication of high quality electrode patterns.

10:40am **SS+EM-WeM8 Alkylidyne Self-Assembled Monolayers on Pt(111): A Novel System for Molecular Electronics Applications**, ***M. Yang***, *A.R. Laracuente, L.J. Whitman,* Naval Research Laboratory

Although many alkanethiols form well-understood self-assembled monolayers (SAMs) on gold, such systems are of limited utility for molecular electronics applications given the incompatibility of gold with conventional silicon devices. Moreover, it is now widely recognized that the gold-sulfur bond inhibits electrical transport between the substrate and the bound organic molecules. Because of these issues, there has been recent interest in more compatible metals such as Pd and Pt, along with non-thiol bonding schemes for organic molecules. We are developing a new type of SAM/metal system based on direct carbon-to-metal bonding. When 1-hexene (C@sub6@H@sub14@) is vapor-deposited on clean Pt(111) in ultra-high vacuum, it converts into hexylidyne (C@sub6@H@sub11@) to form a self-assembled monolayer (SAM) with an upright geometry. Scanning tunneling microscopy studies show that the hexylidyne SAM on Pt(111) is a commensurate (3x3) overlayer. We have also investigated the influences of pressure, temperature, and coadsorbed hydrogen on the formation of the alkylidyne SAMs. Given that many of the organic molecules of potential use for current transport are alkanes and perylenes, direct carbon-metal bonding may provide the most desirable metal-molecule junction. Therefore, we believe this system has significant potential for developing molecular electronic devices.

11:00am **SS+EM-WeM9 Vertically Aligned Chromophoric Molecular Assemblies on a Si Surface**, ***G.G. Jernigan***, *M.F. Pepitone, J.S. Melinger, O.-K. Kim,* US Naval Research Laboratory

Strong motivation for the development of molecular devices is the ability to synthetically create a molecule with desired optical and electronic properties through the linkage of different chemical moieties. The challenge remains, however, to integrate such a molecule with a physical device. Molecules can take various physical conformations and can interact with nearby molecules or surfaces resulting in a loss of optical and electronic properties. We have developed a method for encapsulating a 4-[4-(Dimethylamino) styryl]-1-docosylpyridinium bromide (DASP) chromophore in a helical amylose sheath to produce a supramolecular assembly as a molecular device. The benefits of the supramolecular assembly formation are attributed to the ability of the amylose to rigidify the conformation of the DASP molecule, to individually isolate DASP molecules, and to prevent the DASP molecules from interacting with other DASP molecules to form aggregates. When DASP forms aggregates, the fluorescence is quenched, but when DASP is encapsulated by amylose, the fluorescence intensity is maximized. We report that when the supramolecular assemblies are self-assembled onto a Si surface that DASP emits a strong fluorescence with a spectrum that is similar to that found in solution. More importantly, AFM images show that the assemblies

vertically self align at near monolayer coverage on the Si surface. We have subsequently linked a viologen species (electron acceptor) to the DASP (electron donor) through various hydrocarbon chain spacers resulting in distant-dependent electron transfer. We report this system as the basis for a molecular photodiode.

11:20am **SS+EM-WeM10 Laser Activation-Modification of Surfaces***, G. Jiang, M.C. Asplund,* ***M.R. Linford,*** Brigham Young University

We have recently developed a new and extemely rapid method for simultaneously functionalizing and patterning surfaces, which we term Laser Activation-Modification of Surfaces, or LAMS. This method consists of wetting a surface, e.g., Si or Ge, with a chemical and firing an intense, nanosecond pulse of laser light (355 or 532 nm) through the liquid onto the surface. The energy ablates a thin layer from the surface, exposing a highly reactive surface that appears to react instantaneously with the liquid it is in contact with. LAMS on silicon has been demonstrated with homologous series of 1-alkenes and 1-haloalkanes, and an epoxide and an alcohol. Unreactive compounds, such as octane and perfluorodecalin, also react in this manner; LAMS on Si with octane results in a functionalized surface. Surface modification is confirmed by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and chemical reactivity. Functionalized feature dimensions and morphology are shown by atomic force microscopy and imaging ToF-SIMS.

11:40am **SS+EM-WeM11 Temperature-Dependent Branching of Photochemical Reactions in Organic Layers and Biological Systems***,* ***M. Zharnikov,*** *A. Shaporenko,* Universität Heidelberg, Germany*; A. Baumer,* Walter Schottky Institut, Germany*; D. Menzel,* Technische Universität München, Germany*; P. Feulner,* TechnischeUniversität München, Germany

Radiation-induced damage represents a severe constraint for the characterization of organic materials, biological macromolecules, and cells by advanced electron or x-ray spectroscopy and microscopy. A possibility to reduce irradiation-induced degradation is cooling of the samples down to cryogenic temperatures. However, although the protecting effect of sample cooling against radiation damage is empirically well demonstrated, no detailed knowledge on its exact microscopic mechanism exists as yet. It is commonly assumed that the main effect is simply hindrance of mass transport in the object, whereas the basic irradiation-induced bond cleavage is believed to be unaffected. To prove this hypothesis we studied radiation damage of self-assembled monolayers, which are prototypes of thin organic layers and highly organized biological systems. We demonstrate that the effect of cooling is twofold. It freezes the structure, but by decreasing the mobility of fragments it also changes the branching of various photochemical reactions, thereby strongly modifying the cross sections as well as the products of irradiation induced processes. Two limiting cases could be identified. Reactions involving transport of single atoms and small fragments proceed nearly independent of temperature. Reactions requiring transport of heavy fragments are, however, efficiently quenched by cooling. We speculate that bonds can recombine if the fragments are forced to stay in place due to their reduced mobility at low temperatures. The results have direct implications for cryogenic approaches in advanced electron and x-ray microscopy and spectroscopy of biological macromolecules and cells.

Thin Films
Room 310 - Session TF+EM-WeM
In-Situ/ Ex-Situ & Real- Time Monitoring

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **TF+EM-WeM1 In-situ Infrared Absorption Spectroscopy of High-k Dielectrics Growth on Semiconductors***,* ***Y.J. Chabal,*** *S. Rivillon, Y. Wang, K. Bratland, M.-T. Ho,* Rutgers University **INVITED**

Atomic Layer Deposition (ALD) is a particularly attractive method to grow a variety of heterostructures on semiconductors. It makes it possible for instance to deposit ultra-thin and near stoichiometric high-k dielectric metal oxides films one layer at a time in a highly conformal manner. For microelectronics applications, controlling the nature of the semiconductor/oxide interface and the oxide film itself is critical. For instance, formation of an interfacial SiO2 layer during metal oxide growth or incorporation of excess oxygen in the oxide is a major detriment to the performance of future MOSFETs. This talk discusses the use of in-situ infrared (IR) absorption spectroscopy to optimize silicon and germanium wafer pretreatments, to monitor interface formation during growth and to control the nature of metal oxides. For this work, a simple ALD reactor has been designed to be compatible with efficient transmission IR spectroscopy. The effects of surface chemical functionalization of H-terminated Si and Ge surfaces with Cl, NH3 prior to and thermal annealing after Al2O3 and HfO2 deposition have been investigated with emphasis on identifying the presence and bonding of oxygen at the interface. The mechanism for oxygen incorporation have been identified resulting in a much better control of the interface.

9:00am **TF+EM-WeM3 Real-time Sensing for Process Dynamics and Metrology in Tungsten Atomic Layer Deposition***,* ***L. Henn-Lecordier,*** *W. Lei, G.W. Rubloff,* University of Maryland

Atomic layer deposition (ALD) has been investigated using a novel wafer-scale reactor which features an internal mini-reactor and in-situ mass spectrometry (MS) for chemical analysis during tungsten ALD using WF6 and SiH4. Downstream MS sampling system measures deposition kinetics directly and reaction product MS signal is used for real-time thickness metrology. MS signal reveals ALD reactant and product species in real time through ALD process cycle, with product generation and reactant depletion indicative of species consumption. Both the H2 product from SiH4 exposure and the SiF4 product from WF6 exposure show the kinetics of self-limiting adsorption/reaction on the surface, which enables process optimization to minimize cycle time. MS data also directly indicates the influence of process temperature and precursor dose on film growth, and can also been employed for process optimization. The integrated reaction product MS signal over each exposure, when plotted against ALD cycle number, reveals different stages of ALD film growth and provides a quantitative measure of film thickness. Our study demonstrated that integrated reaction product MS signal has a good linear relationship with ALD film thickness. This provides a promising approach to advanced process control in ALD manufacturing.

9:20am **TF+EM-WeM4 Twin Boundaries can be Moved by Step Edges during Film Growth***,* ***N.C. Bartelt,*** *W.L. Ling, K.F. McCarty,* Sandia National Laboratories*; C.B. Carter,* University of Minnesota

Considerable effort has been devoted to minimizing twins in a film's microstructure because they typically degrade a film's performance. Twins are generally believed to originate from the nucleation stage of film growth. That is, when film islands nucleate, not all of them contain the same stacking sequence of film layers. Twin boundaries then occur where islands with different stacking sequence impinge. Attempts to reduce the density of twins are usually based on minimizing their nucleation or by removing them by annealing. We track individual twin boundaries in Ag films on Ru(0001) using low-energy electron microscopy (LEEM). We find that twin boundaries can move readily during film growth but relatively little during annealing. The growth-driven motion of twin boundaries occurs as film steps advance across the surface -- as a new atomic Ag layer approaches an fcc twin boundary, the advancing step edge carries along the boundary, which intersects the film thickness. This process can produce twin-free regions that are over 10 Âµm wide. These observations show that there can be a close connection between morphological evolution and microstructural evolution in thin films. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

9:40am **TF+EM-WeM5 In-Situ Real Time Spectroscopic Ellipsometry Studies of the Growth of Amorphous and Epitaxial Silicon for Photovoltaic Applications***,* ***D.H. Levi,*** *C.W. Teplin, E. Iwaniczko, Y. Yan, T.H. Wang, H.M. Branz,* National Renewable Energy Laboratory **INVITED**

In-situ monitoring of material properties during thin film deposition provides researchers with a valuable tool for maximizing solar cell performance, while also enabling efficient exploration of deposition parameter space. In this presentation I will describe how our research team at NREL has utilized in-situ real time spectroscopic ellipsometry (RTSE) to maximize our productivity in two related projects. We are using hot wire chemical vapor deposition (HWCVD) for low-temperature (90 to 350@super o@C) deposition of very thin films of amorphous hydrogenated silicon (a-Si:H) for a-Si / crystal-Si (c-Si) heterojunction (SHJ) solar cells. We are also using HWCVD for low temperature (200 to 440@super o@C) deposition of epitaxial films of silicon (epi-Si) on c-Si substrates. We utilize RTSE as both an in-situ diagnostic and a post-growth analysis tool for SHJ solar cells and epi-Si films grown by HWCVD. RTSE enables precise thickness control of the 3 to 10 nm thick layers used in the SHJ devices, as well as monitoring crystallinity and surface roughness in real time. Post-growth analysis of the RTSE data has enabled us to determine the optical, electronic, and structural properties of the thin films used in the SHJ devices, as well as crystallinity vs. thickness in the epi-Si layers. This

information has been used to fine-tune the deposition parameters to optimize device performance and epi-Si thickness. Using input from RTSE analysis we have achieved a photovoltaic energy conversion efficiency of 17% on an Al-backed p-type float-zone c-Si wafer. Epi-Si films have been grown as thick as 500 nm utilizing parameter optimization based on RTSE analysis.

10:20am **TF+EM-WeM7 Analytic First-Order Solution for the Simultaneous Determination of Complex Refractive Indices and Thicknesses of Thin Films Deposited on Substrates***, **I.K. Kim**, D.E. Aspnes,* North Carolina State University

The problem of the simultaneous determination of the complex refractive index = n + i@kappa@ and thickness d of an isotropic thin film deposited on an isotropic substrate from polarimetric data (the so-called nkt problem) has never been solved analytically for a general , although solutions are available for the case of a transparent film (@kappa@ = 0). Here, we present an analytic solution for arbitrary n and @kappa@ that is valid to first order in d/@lambda@, where @lambda@ is the wavelength of light. The solution requires a knowledge of the change of pseudodielectric function <@epsilon@>, or alternatively the relative change @Delta@@rho@/@rho@ in the complex reflectance ratio @rho@, and either the relative change @Delta@Rp/Rp or @Delta@Rs/Rs, where Rp and Rs are the reflectances for p- or s-polarized light. Ranges of validity are obtained by comparing results to those obtained numerically using the exact three-phase-model expressions, and a procedure is presented for improving the accuracy. Numerical evaluation of the exact equations, which proceeds by least-squares analysis, is facilitated by using the first-order solution as a starting point. Depending on the sample the first-order solution is more effective at some energies than others, emphasizing the need for multiwavelength measurements over finite energy ranges. The most effective ranges can be determined from the correlation coefficients obtained in the least-squares analysis. As previously noted, the highest correlation generally occurs between n and d, although under some situations a high correlation can also occur between @kappa@ and d. The results should be particularly useful for systems involving reversible configurations, such as the cyclic adsorption and desorption of gases on clean surfaces, where accuracy can be improved by modulation techniques.

10:40am **TF+EM-WeM8 Linear Nanomechanical Measurements using a Novel AFM Technique***, **P.M. Hoffmann**,* Wayne State University **INVITED**

Atomic Force Microscopy has been extensively used to study roughness, adhesion and mechanical properties of surfaces and thin films. However, commonly used AFM techniques suffer from a variety of problems inherent to the technique: Snap-in instabilities in static AFM and non-linearities in dynamic AFM measurements. Here we present a new AFM technique that avoids these problems and is capable of stable, linear measurements of many systems, including atomic scale contact mechanics and atomic friction on surfaces. I will introduce the technique and present recent results, especially the finding that continuum mechanics applies in atomic contacts even if the number of atoms in the contact becomes very low and the observation of friction due to a single atomic defect.

Electronic Materials and Processing
Room 309 - Session EM-WeA

Contacts to Semiconductors

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

2:00pm **EM-WeA1 Effect of Si on the Ohmic Behavior of Ti/Al/Mo/Au Metallization for AlGaN/GaN HEMTs***, **F.M. Mohammed**, L. Wang, H.J. Koo, I. Adesida,* University of Illinois at Urbana-Champaign

The high breakdown voltage and high saturation current of AlGaN/GaN HEMTs present great potential for applications in power amplification. High performance devices for such application require low parasitic ohmic contact resistance. We present an investigation on the study of the effects of Si incorporation in Ti/Al/Mo/Au metallization scheme. Si is a commonly used n-type dopant in GaN alloys systems, and implantation and diffusion doping are utilized to increase carrier concentration at the surface of epilayers. In Ti/Si-based contact metallizations, the formation of TiSi@sub x@ at the interface is believed to lower the barrier height for conduction of current across the metal/GaN junction. In this study, we have carried out experiments to optimize the thicknesses of Si introduced in the metallization scheme. Impact of the place of insertion within the metallization scheme (e.g. Ti/Si/Al/Mo/Au vs. Ti/Si/Al/Si/Mo/Au) has also been studied. Si incorporation, surface treatment, and annealing are collectively optimized to induce a reduction in contact resistance. An example is the optimized Ti/Si/Al/Si/Mo/Au metallisation annealed at 850 @super o@C for which a contact resistance (R@sub c@) and specific contact resistivity (@rho@@sub c@) as low as 0.16 ± 0.02 @OMEGA@.mm and 6.77 ± 0.7 x 10@super -7@ @OMEGA@.cm@super 2@ were obtained, respectively. This represents a significant reduction when compared to what was correspondingly obtained for Ti/Al/Mo/Au at 0.41 @OMEGA@.mm and 4.78 x 10@super -6@ @OMEGA@.cm@super 2@, respectively. Atomic force microscopy (AFM) and Auger electron spectroscopy (AES) characterization are utilized to reveal the nature of ohmic contact formation and the evolution in surface morphologies of the metallization schemes and epilayers.

2:20pm **EM-WeA2 Non-uniform Interfacial Reactions of Ti/Al/Mo/Au Ohmic Contacts on n-AlGaN/GaN Heterostructure and its Effect on Carrier Transport***, **L. Wang**, F.M. Mohammed, I. Adesida,* University of Illinios at Urbana-Champaign

Ti/Al/Mo/Au multilayer metallization scheme has been demonstrated to have low ohmic contact resistance, high thermal stability, and sharp edge acuity on AlGaN/GaN high electron mobility transistors (HEMT). Transmission electron microscopy (TEM) is used to elucidate the cross-sectional interfacial microstructure and to gain insight into the formation mechanism of low-resistance ohmic contacts. It has been observed that reactions between the metallization and the AlGaN layer did not proceed uniformly. Localized penetration through AlGaN layer up to a depth of 130 nm was observed. Thinning of the AlGaN layer was noted where there was no penetration. Energy dispersive x-ray spectroscopy (EDS), and high resolution TEM (HRTEM) analysis confirmed that the reaction products were TiN. A strong correlation between the appearance of TiN islands and threading dislocations in the epitaxial layers was observed. Further analysis indicated that threading dislocations served as short-circuit diffusion channels, and thus are responsible for the non-uniform reaction. TiN islands have a large total area of intimate contact with the two-dimensional electron gas (2DEG), and since no tunneling of electron through the AlGaN is required, a low resistance ohmic contact is obtained. Methods for promoting and controlling the non-uniform interfacial reaction are proposed.

2:40pm **EM-WeA3 Polarization-enhanced Ohmic Contacts to GaInN-based Blue Light-Emitting Diodes***, **T. Gessmann**, Y.A. Xi, H. Luo, J.K. Kim, J.Q. Xi, K. Chen, E.F. Schubert,* Rensselaer Polytechnic Institute

Thin p-type Ga@sub 1-x@In@sub x@N cap layers have been grown on p-type GaN contact layers of blue light emitting diodes (LEDs) using metal-organic vapor phase epitaxy (MOVPE) with an AIX 200/4 RF-S reactor. The Ga@sub 1-x@In@sub x@N cap layers have thicknesses smaller than 4 nm and In-contents varying between x = 0.1 and 0.2. The LED structure consists of a GaN nucleation layer grown on c-oriented sapphire, a 2 µm-thick n-type GaN layer, 5 Ga@sub 0.86@In@sub 0.14@N quantum wells embedded in GaN-barriers, and a 0.2 µm-thick p-type GaN layer. Having a cap layer thickness below the critical thickness of Ga@sub 1-x@In@sub x@N on GaN, a piezoelectric field will be present in the cap layer resulting in increased carrier tunneling probabilities through the metal-semiconductor barrier. The In-content and the strain status of the cap layers have been analyzed using HR X-Ray diffractometry. For cap layer thicknesses smaller than 4 nm, pseudomorphic Ga@sub 1-x@In@sub x@N has been obtained for three different In-contents x = 0.1, 0.15 and 0.2. LEDs have been fabricated using standard photolithograpy processes, CAIBE mesa etching and electron beam deposition of Ni/Au and Ti/Al/Ni/Au contact metals. The specific contact resistance, diode series resistance, ideality factor and optical output power of the LEDs are determined and compared to devices without capping layer. A specific contact resistance @rho@@sub c@ = 1.8 x 10@super -4@ @Ohm@ cm@super 2@ has been obtained for samples with InGaN cap layer; this value is significantly smaller than @rho@@sub c@ of a sample without cap layer. The results will be discussed in terms of a model relating the cap layer thickness and In-content to the p-type contact resistance.

3:00pm **EM-WeA4 Indium-based Ohmic Contacts to n-GaSb and the Influence of Surface Passivation***, **J.A. Robinson**, S.E. Mohney,* The Pennsylvania State University

Gallium antimonide and related ternary and quaternary semiconductors have shown great potential for electronic devices as well as optoelectronic devices in the 0.3 - 8 µm wavelength range. High quality ohmic contacts help ensure device reliability and improve performance by providing a low resistance, a uniform interface morphology, and minimal semiconductor consumption. Pd-based contacts to n-GaSb that do not include In provide specific contact resistance values as low as 5 x 10@super -6@ @Omega@-cm@super 2@. However, by adding In, the specific contact resistance is reduced by 80%. We present two high quality In-based contacts that include Pd. Initial experiments included a Pd/In/Pd/Pt/Au contact that provides a specific contact resistance of 1.8 x 10@super -6@ @Omega@-cm@super 2@ using a modified pre-metallization surface treatment that involves 2.1% (NH@sub 4@)@sub 2@S. However, the surface and interfacial reaction morphology of the Pd/In/Pd/Pt/Au contact was less than optimal. As a result, sputtered Pd@sub 3@In@sub 7@/X/Au (X = Pt,W,WSi@sub 2@, or WSiN) contacts were explored as a means to improve reaction morphology and thermal stability. Contacts utilizing WSiN provide a specific contact resistance of approximately 3 x 10@super -6@ @Omega@-cm@super 2@ using a conventional surface treatment, and 1.8 x 10@super -6@ @Omega@-cm@super 2@ when the modified surface treatment is used. While the Pd@sub 3@In@sub 7@/WSiN/Au contact provides specific contact resistance values comparable to the best reported In-based contacts, this contact exhibits an improved reaction morphology and better thermal stability compared to other contacts.

3:20pm **EM-WeA5 Controlling Interfacial Reactions in Ferromagnetic Metal / GaAs Heterostructures***, **B.D. Schultz**,* University of Minnesota **INVITED**

Growth of epitaxial ferromagnetic metal contacts on compound semiconductors with atomically abrupt interfaces is often a challenge due to thermodynamic instabilities at the interface between the two materials and the subsequent formation of solid state reaction products. Elemental ferromagnetic metals, such as Fe and Co, can be grown by molecular-beam epitaxy (MBE) as single crystal films on GaAs; however, they are not thermodynamically stable and reacted phases form at the interface. The initial nucleation of Fe on GaAs surfaces is strongly influenced by the GaAs surface reconstruction, but results in little disruption of the reconstruction itself. Fe/GaAs reactions are reduced at lower MBE growth temperatures with a reacted layer thickness of approximately three monolayers at 15°C. Post-growth anneals at 250°C do not result in the reaction of additional GaAs, but the anneals significantly alter the electronic properties of the interface. Co is more reactive than Fe on GaAs and forms a reaction region composed of Co@sub 2@GaAs, CoGa, and CoAs. Thermodynamically stable metals such as ErAs can be used as epitaxial diffusion barriers to minimize Fe-Ga-As and Co-Ga-As interfacial reactions for growth temperatures as high as 225°C. This paper will emphasize the correlation between the structure, chemistry, magnetism and transport properties of Fe@sub x@Co@sub 1-x@/GaAs and Fe@sub x@Co@sub 1-x@/ErAs/GaAs contacts as determined by STM, RHEED, LEED, XPS, RBS, XRD and TEM. Supported by: ONR, DARPA, NSF/DMR, and AFOSR.

4:00pm **EM-WeA7 Molecular Beam Epitaxial Growth of Sc@sub x@Er@sub 1-x@Sb on III-V Compound Semiconductors***, **S.G. Choi**,* Univerrsity of Minnesota*; B.D. Schultz, C.J. Palmstrom,* University of Minnesota

Epitaxial metallic or semimetallic layers in semiconductors have potential application in novel electronic devices. Rare-earth group-V (RE-V)

compounds have received much attention since they are thermodynamically stable and epitaxial on III-V semiconductors. In particular, Sc@sub y@Er@sub 1-y@As alloys have been employed successfully in GaAs-based materials, however, application of Sc@sub y@Er@sub 1-y@As alloys to other III-V's has been less fruitful due to large lattice-mismatches. Therefore, RE-V alloys with lattice parameters close to InP or GaSb are of considerable interest and Sc@sub x@Er@sub 1-x@Sb is one of the promising candidates. The lattice parameter of Sc@sub x@Er@sub 1-x@Sb ranges from 5.85Å (ScSb) to 6.11Å (ErSb), and can therefore be lattice-matched to InP, InAs, and GaSb by controlling the Sc to Er ratio. In this work, Sc@sub x@Er@sub 1-x@Sb alloys have been grown on various III-V semiconductors by molecular beam epitaxy (MBE). The surface ordering was monitored in-situ by RHEED and LEED. ErSb grown on GaSb(100) exhibited a (1x1) surface ordering with high Sb incorporation and a mixed (1x4)/(4x1) with low Sb incorporation. In-situ XPS data showed no significant differences in Er and Sb coverage between the two surfaces, however, the amount of Ga riding on the two surfaces was different, which may cause the different surface ordering. One possible mechanism for Ga atoms to segregate on a 500Å-thick ErSb film can be explained in terms of an embedded growth model. Growth of Sc@sub x@Er@sub 1-x@Sb on InAs and InP is more challenging since intermixing of the different group-V elements at the interface would be expected to degrade the quality of interface. Different methods for minimizing the intermixing at the interface will be discussed. Supported by ONR, DARPA, and ARO.

4:20pm **EM-WeA8 Chemically-Induced Point Defects and Schottky Barrier Formation at Metal/4H-SiC Interfaces***, **L.J. Brillson**, S. Tumakha, M. Gao,* The Ohio State University*; S. Tsukimoto, M. Murakami,* Kyoto University, Japan*; D.J. Ewing, L. Porter,* Carnegie Mellon University

We have used depth-resolved cathodoluminescence and Auger electron spectroscopies, DRCLS and AES, respectively, to determine the role of chemically-induced defects on 4H-SiC barrier formation on a nanometer scale. DRCLS of 5 nm Au, Ag, Ti, and Ni overlayers reveal formation of mid-gap defect transitions at ~1.8 eV and 2.85 eV extending only nanometers away from the junction. These states vary in their ranges of depth and depend sensitively on interface reactivity and subsequent UHV annealing. Their pervasive appearance near morphological defects and the absence of new gap states indicates that native defects rather than metal-specific states produce the dominant interface levels. For thicker TiAl Ohmic contacts with 5 min 1000 C anneals, cross-sectional scanning electron microscopy, AES, and DRCLS reveal a continuous ternary Ti-Si-C interfacial layer ~100 nm thick, a 1.9 eV sub-band gap transition localized within this depth and a 2.8 eV emission extending into the SiC, indicating both reaction-induced compound and defect formation, respectively. Within annealed NiTiAl Ohmic contacts, Ni silicide and Ti carbide form with a qualitatively different ~ 1.6 eV transition extending beyond the reaction zone. AES showing C movement from SiC into the metal overlayer indicate formation of a C-deficient SiC point defect. Thus the major difference in TiAl and NiTiAl interfacial reactions induces different interfacial gap states. For Ni/SiC reacted diodes, DRCLS and current-voltage measurements show a close correspondence between the Schottky barriers and deep level defect energies from diode to diode. Furthermore, the range of energies bounded by these defects corresponds with Schottky barrier heights reported previously via electrical measurements. This correspondence between chemically-induced deep levels at bulk defect energies and the range of macroscopic Schottky barriers for SiC appears to be a more general phenomenon, extending to other compound semiconductors as well.

4:40pm **EM-WeA9 Metal Germanide Schottky Contacts to Relaxed and Strained Germanium***, **A. Khakifirooz**, O.M. Nayfeh, M.L. Lee, E. Fitzgerald, D.A. Antoniadis,* Massachusetts Institute of Technology

Significant mobility enhancement offered by germanium channel MOSFETs and especially strained-Ge devices makes them very attractive for the deca-nanometer transistor scaling. A low resistivity contact to the S/D junctions is, however, the key to successful integration of such devices. Since high doping levels are difficult to achieve in Ge, Schottky S/D MOSFET is considered as an interesting option that also relaxes the constraints on the S/D junction abruptness. A systematic study of the formation of different metal germanide phases has been recently performed and they were characterized in terms of their electrical resistivity.@footnote 1@ In this work we study the Schottky barrier formed between germanium and Ni, Pd, and Pt germanides that were previously identified as the low-resistivity phases and offer a relatively wide processing window. Metal germanide is formed by annealing a very thin layer of metal (~15 nm) deposited onto HF-last Ge samples and patterned by lift-off. Samples are annealed in a furnace for 15 min. or in an RTA chamber for 1 min at different temperatures in the range of 350-500°C. Some diodes are also fabricated on strained Ge epitaxially grown on relaxed Si@sub 0.4@Ge@sub 0.6@ buffer with an ultrathin silicon cap. In this case, the metal thickness is selected in a way to consume the Si cap and almost the entire strained-Ge layer without touching the SiGe buffer layer to avoid excessive leakage. XRD and XTEM analysis are performed to study the crystallinity and morphology of the germanide layers, whereas I-V and C-V measurements are used to characterize the Schottky barrier. While nearly ideal barriers (ideality factor as good as 1.01), with a barrier height of 0.55-0.57 eV are obtained on bulk germanium, diodes fabricated on strained-Ge samples show excessive leakage current and high ideality factor (~1.8). Possible mechanisms responsible for this non-ideality are discussed. @FootnoteText@ @footnote 1@S. Gaudet et al., AVS 51st Int. Symp., 2004.

5:00pm **EM-WeA10 Ni Diffusion Studies From NiSi/Hf-based High-K Dielectric Stack Into Si***, **P. Zhao**, M.J. Kim, B.E. Gnade, R.M. Wallace,* University of Texas at Dallas

Fully silicided NiSi has been studied as a metal gate electrode due to low resistivity, scability and work function tunability.@footnote 1,2,3@ However, there remain many challenges for the integration of NiSi metal gates, such as phase stability, incomplete silicidation and possible Ni diffusion. The interdiffusion of Ni from NiSi through dielectrics into the underlying Si substrate (channel) has not yet been reported in the literature to our knowledge. We have investigated the Ni diffusion from NiSi through SiO@sub X@N@sub Y@ and Hf-based gate dielectrics into the Si channel. SIMS profiles show that interdiffusion of Ni from NiSi through a 13Å SiO@sub X@N@sub Y@ into the Si channel can be observed after thermal anneal budgets even as low as 350°C for 60min, representative of a typical backend process. It is also found that the Ni penetration increases with temperature and time. Although the penetration is reduced for a stack with thicker HfSiON dielectrics (23Å), the diffusion is observed when the stack is annealed for 60min at 400°C. Compared to N@sub 2@ annealing, deuterated forming gas annealing appears to enhance the Ni penetration. Both backside and front side SIMS, XRD, and HRTEM results will be presented. The possible diffusion mechanism will be discussed. This work is supported by Texas Instruments and the Semiconductor Research Corporation. @FootnoteText@ @footnote 1@ Z. Krivokapic, W. Maszara, F. Arsnia, E. Patron, Y. Kim, L. Washington, et al., VLSI 2003, p. 131-132 (2003)@footnote 2@ J. Kedzierski, E. Nowak, T. Kanarsky, Y. Zhang, D. Boyd, R. Carruthers, et al., IEDM 2002, p.247-250 (2002)@footnote 3@ C. Cabral, Jr., J. Kedzierski, B. Linder, S. Zafar, V. Narayanan, S. Fang, A. Steegen, P. Kozlowski, R. Carruthers, and R. Jammy. 2004 Symposium on VLSI Technology Digest of Technical Papers, p.184-185 .

Magnetic Interfaces and Nanostructures
Room 204 - Session MI+EM-WeA

Magnetic Semiconductors

Moderator: A.T. Hanbicki, Naval Research Laboratory

2:00pm **MI+EM-WeA1 Effects Limiting the Formation of Ferromagnetic III@sub 1-x@Mn@sub x@V Alloys by Epitaxial Growth***, **J.K. Furdyna**,* University of Notre Dame **INVITED**

III@sub 1-x@Mn@sub x@V alloys (e.g., Ga@sub 1-x@Mn@sub x@As), comprised of Mn@super +2@ incorporating substitutionally for the group-III element in the III-V lattice are captivating the attention of the scientific community worldwide because of the promise they hold for spin-electronic applications. Incorporation of Mn into the III-V lattice in sufficient concentrations to render the III@sub 1-x@Mn@sub x@V alloy ferromagnetic must be carried out by non-equilibrium low-temperature epitaxy, whereby Mn concentrations x approaching 0.10 can be attained. The ferromagnetism of these alloys occurs because, in addition to providing magnetic moments, the Mn ions also act as acceptors, thus supplying large concentrations of holes that mediate the ferromagnetic interaction between magnetic moments of the Mn ions. A mean field theory projects that the Curie temperature T@sub C@ should scale as the product of the Mn concentration x and of the hole density p. Thus, in principle, one should expect above-room-temperature ferromagnetism for large values of the x·p product. Our research on Ga@sub 1-x@Mn@sub x@As and In@sub 1-x@Mn@sub x@Sb has shown, however, that the Fermi energies achievable in these materials cannot exceed a certain maximum E@sub Fmax@, corresponding to a maximum hole concentrations p@sub max@. This occurs because the relationship

between the creation energies for negatively-charged defects (such as the desired substitutional Mn acceptors Mn@sub III@, e.g. Mn@sub Ga@ or Mn@sub In@) and positively-charged defects (such as the unwanted interstitial Mn double donors, Mn@sub I@) is controlled by the Fermi energy. When E@sub F@ in the III@sub 1-x@Mn@sub x@V reaches E@sub Fmax@ due to the increasing free hole density, further formation of Mn@sub III@ becomes energetically unfavorable, and a high concentration of compensating Mn@sub I@ defects begins to form. The creation of Mn@sub I@ is deleterious to the ferromagnetism for multiple reasons: (1) compensation by the double Mn@sub I@ donors reduces the hole concentration, (2) interstitial Mn is RKKY-inactive (due to negligible p-d exchange), and (3) Mn@sub I@ forms antiferromagnetic pairs with Mn@sub III@, reducing further the density of Mn ions that contribute to the ferromagnetism of the III@sub 1-x@Mn@sub x@V alloy. Thus any increase of the Mn@sub I@ concentration automatically leads to lowering the value of T@sub C@. Ion-channeling experiments directly reveal this type of interstitial Mn creation whenever p approaches p@sub max@ due to a high Mn concentration. In this talk we concentrate on showing that substitutional vs. interstitial incorporation of Mn in III@sub 1-x@Mn@sub x@V alloys is determined by the Fermi level during the growth process itself, no matter what is the source of holes that establish the value of E@sub F@, and independent on the spatial location of the acceptors with respect to the magnetic Mn ions. To demonstrate this, we discuss two types of growth experiments that allowed us to vary the Fermi level independently of the Mn concentration, namely, experiments on Be co-doping of III@sub 1-x@Mn@sub x@V alloys; and on modulation doping of Al@sub 1-y@Ga@sub y@As/Ga@sub 1-x@Mn@sub x@As/Al@sub 1-y@Ga@sub y@As heterostructures by Be. Having established causes for the limit which nature imposes on incorporating substitutional Mn ions at the Group-III sites in III-Mn-V alloys, I will then discuss possible strategies for circumventing this obstacle, with an eye on increasing the Curie temperature of these novel ferromagnetic semiconductors.

2:40pm **MI+EM-WeA3 Structural Properties, Lattice Dynamics, and Optical Properties of GaMnN**, *W.E. Fenwick, M.H. Kane, M. Strassburg, A. Asghar, S. Gupta, H. Kang,* Georgia Institute of Technology*; Z. Hu,* Georgia State University*; S. Graham,* Georgia Institute of Technology*; U. Perera,* ***N. Dietz,*** Georgia State University*; I.T. Ferguson,* Georgia Institute of Technology

Dilute magnetic semiconductors (DMS) show promise as spintronic materials because of their electrical and magnetic properties. E.g., GaMnN exhibit ferromagnetism (FM) above room temperature (RT). Application of such materials for RT spintronic devices requires an understanding of the origin of this magnetism, which is still under debate in the literature. Knowledge of the structural properties is essential to determine the origin of the RT FM in GaMnN. Therefore this work provides structural and optical studies of GaMnN to reveal the crystalline quality, lattice dynamics, and some fundamental properties such as the optical constant. Increasing Mn concentration significantly affects long-range lattice ordering. The observation of a local vibrational Raman mode at 669 cm@super -1@ combined with the slight excess of metal components in the growth process and the incorporation of Mn acceptor states favors the formation of nitrogen vacancies. Such vacancies form shallow donor complexes and thus contribute to self-compensation, which may hamper carrier mediation. Raman spectroscopy also revealed a disorder-induced mode at 300 cm@super -1@. The intensity of both modes was found to be weaker by more than one order of magnitude compared to GaMnN grown by MBE or prepared by ion-implantation. This is a consequence of the improved MOCVD growth conditions. Crystalline integrity and the absence of major second phase contributions were confirmed by high resolution X-ray diffraction studies. Atomic force microscopy showed that optimized annealing conditions suppressed the formation of Mn-rich precipitates on the surface. Further investigations on the lattice dynamics and the determination of the optical constants were enabled by infrared reflectance spectroscopy. The GaN E1(TO) phonon frequency linearly increases with Mn composition, which is expressed by (558 + 2.7x) cm@super -1@. Meanwhile the peak values of the infrared dielectric functions of the GaMnN decrease with increasing Mn concentration.

3:00pm **MI+EM-WeA4 Epitaxial Growth of Ferromagnetic Mn@sub 3-delta@Ga Thin Films on Wurtzite GaN(0001) by Molecular Beam Epitaxy***,* ***E.D. Lu****, M.B. Haider, R. Yang, C. Constantin, G. Pokharel, D.C. Ingram, A.R. Smith,* Ohio University

Magnetic metal and/or alloy films on III-V semiconductor substrates have attracted considerable interest due to the potential applications for magnetic/spintronic materials and devices,especially as spin electron injection sources for spin-sensitive heterostructures as well. The binary MnGa alloy is one of several promising metallic ferromagnetic candidates with CuAu-I type ordering. It is a face-centered tetragonal (fct) structure with lattice constants a = 3.897 Å, c = 3.58-3.65 Å dependent on content of at.% Mn between 55-60%. The epitaxial ferromagnetic Mn@sub 3-Î´@Ga(111) thin films have been grown on wurtzite GaN(0001) substrates with Ga polar surface by molecular beam epitaxy through controlling the substrate temperature and flux ratio of manganese to gallium during the growth. Prior to growing Mn@sub 3-Î´@Ga thin films, the commercial MOCVD GaN substrates were directly heated for clean up and refreshed by growth of GaN layer by radio plasma MBE. The growth and structure of the Mn@sub 3-Î´@Ga thin films are monitored in situ by reflection high energy electron diffraction (RHEED). The RHEED pattern was spotty at the initial stage and gradually became streaky, indicating surface roughness at the beginning and finally a smoother surface at the end. Combined RHEED and ex situ XRD results have revealed the primarily structure of the CuAuâ?"I type fct Mn@sub 3-Î´@Ga thin films grown with (111) plane lying on GaN(0001) plane; due to double lattice constant of the Mn@sub 3-Î´@Ga(111) plane along [11-2] direction is a good match with that distance along [11-20] direction of GaN(0001) (less than 4% mismatch), the epitaxial relationship of the fct Mn@sub 3-Î´@Ga is (111)[01-1] MnGa // (0001)[1-100]GaN and (111)[11-2] MnGa // (0001)[11-20]GaN. Rutherford Backscattering Spectroscopy (RBS) has also confirmed composition of the Mn@sub 3-Î´@Ga thin films with the ratio of Mn to Ga about 1.5 to 1.

3:20pm **MI+EM-WeA5 Nanostructure of Ferromagnetic Mn-implanted Si***,* ***C. Awo-Affouda***[1]*, M. Bolduc, K.A. Dunn, M.B. Huang, F. Ramos, G. Agnello, B.L. Thiel, V.P. LaBella,* University at Albany-SUNY

Semiconductor devices which exploit the spin of the electron hold great potential to produce devices with increased functionalities. Making conventional semiconductors ferromagnetic via ion implantation of Mn will aid in fabricating future spintronic devices. We recently demonstrated that ferromagnetism can be achieved via Mn-ion implantation of n-type and p-type Si wafers. A Curie temperature greater than 400K was observed for the p-type samples. The structure of the implanted material was investigated in order to identify the source of the ferromagnetism. SIMS depth profiling of the as-implanted samples showed a typical Gaussian shape profile of Mn atoms in the silicon lattice, which peaks at 250 nm. Post-implant annealing was performed to heal the damage from the implantation process and resulted in a strong redistribution of the Mn atoms. Furthermore diffraction contrast TEM of the annealed samples revealed nanometer size precipitates distributed throughout the implanted region, along with a large band of dislocation and stacking faults. Selected area diffraction patterns gave strong evidence that these phases are MnSi@sub1.7@ crystallites. We will discuss the role of these precipitates on the observed ferromagnetism.

3:40pm **MI+EM-WeA6 Ferromagnetic Properties of Mn-implanted Si***,* ***M. Bolduc****, C. Awo-Affouda, M.B. Huang, F. Ramos, V.P. LaBella,* University at Albany - SUNY

Integrating spintronic device concepts with silicon may enable new possibilities for fabrication. In addition, theoretical calculations have predicted ferromagnetic ordering in Mn-doped group-IV semiconductors. This potential has motivated the search for a Si-based ferromagnetic semiconductor. We demonstrate that p-doped and n-doped Si crystals can be made ferromagnetic above room temperature through Mn-ion implantation. 300-keV Mn@super+@ ions were implanted at doses of (1-10)X10@super15@ cm@super-2@ reaching peak concentrations of (0.1-0.8) at.% as measured through SIMS profiling. Ferromagnetic hysteresis loops were obtained using a SQUID magnetometer at temperature of (10-300) K, yielding a saturation magnetization of 0.1-0.7 emu/g-sample. The Curie temperature is found >400 K with carrier concentration dependence. We will report on the dependence of the magnetic properties on the post-implant annealing temperature and Mn concentration. These results will be discussed in comparison with other ion implanted or MBE grown group-IV ferromagnetic semiconductors.

4:00pm **MI+EM-WeA7 Growth and Magnetic Properties of Doped ZnO Epitaxial Films and Nanocrystal***,* ***S.A. Chambers,*** Pacific Northwest National Laboratory and Univ. of Washington*; A.C. Tuan,* Pacific Northwest National Laboratory*; K.R. Kittilstved, D.R. Gamelin,* University of Washington**INVITED**

Since 2001, researchers around the world have been involved in a vigorous search for new ferromagnetic oxide semiconductors with Curie temperatures above ambient. Such materials are vitally important for the

[1] **Falicov Student Award Finalist**

practical realization of spintronics. Two wide bandgap oxide semiconductors have been of particular interest - TiO@sub 2@ anatase and ZnO. A number of claims of room temperature ferromagnetism (RTFM) in these host oxides with various dopants have been made. However, some of the results were based on poorly characterized material, often containing magnetic secondary phases, leading to illegitimate claims. Even for well characterized materials which are phase-pure magnetically doped oxides, the mechanism(s) of magnetism remain largely undetermined. We have used oxygen plasma assisted metal organic chemical vapor deposition along with direct wet chemical synthesis and spin coating to prepare Co@sub x@Zn@sub 1-x@O and Mn@sub x@Zn@sub 1-x@O epitaxial and nanoparticle films. Co(II) and Mn(II) substitute for Zn(II) in the wurtzite lattice in materials synthesized by both methods. Room temperature ferromagnetism in epitaxial Co:ZnO films can be reversibly activated by diffusing in Zn, which occupies interstitial sites and makes the material n-type. O-capped Co:ZnO nanoparticles, which are paramagnetic as grown, become ferromagnetic upon being spin coated in air at elevated temperature. Likewise, spin-coated N-capped Mn:ZnO nanoparticle films also exhibit room temperature ferromagnetism. However, the inverse systems, N-capped Co:ZnO and O-capped Mn:ZnO, are entirely paramagnetic when spin coated into films in the same way. Unfortunately, the nanoparticle films are not sufficiently conductive do perform magneto-transport measurements. Instead, we have carried out a detailed analysis of optical absorption, photovoltage, and magnetic circular dichroism spectra. This analysis reveals that the resonances Co(I) ↔ Co(II) + e@super -@@sub CB@ and Mn(III) ↔ Mn(II) + h@super +@@sub VB@ are energetically favorable, consistent with strong hybridization of Co (Mn) with the conduction (valence) band of ZnO. In contrast, the resonances Mn(I) ↔ Mn(II) + e@super -@@sub CB@ and Co(III) ↔ Co(II) + h@super +@@sub CB@ are not energetically favorable. These results indicate that Co(II)-derived states will strongly interact only with the conduction band, whereas Mn(II)-derived states interact strongly only with the valence band. These spectral results are consistent with the observed ferromagnetism in Co:ZnO (Mn:ZnO) being mediated by electrons (holes). @footnoteText@This work was performed in part in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering Physics. Work at UW was funded by the NSF (DMR-0239325 and ECS-0224138) and the Research Corporation.

4:40pm **MI+EM-WeA9 Effects of Differing Mn@sub Ga@/Mn@sub I@ on the Anomalous Hall Effect in (Ga,Mn)As***, Y.S. Kim, H.K. Choi, Z.G. Khim,* Seoul National University, Korea*; S.H. Chun,* Sejong University, Korea*; **Y.D. Park**,* Seoul National University, Korea

We report on the effect of differing ratios of substitutional and interstitial Manganese (Mn@sub Ga@/Mn@sub I@) on the Anomalous Hall Effect(AHE) in low temperature molecular beam epitaxy prepared (Ga,Mn)As diluted magnetic semiconductors. As-grown (Ga,Mn)As epifilms with Mn content from 2.4 % ~ 6.1 % exhibit ferromagnetic ordering below temperatures ranging from 60 to 110 K. Relatively differing Mn@sub Ga@/Mn@sub I@ ratios were achieved by careful annealing at moderate temperatures as evident in the differing resistivities (as low as 2.5 m@ohm@-cm)/ Hall carrier concentrations (as high as ~ 8 x 10@super 20@cm@super -3@) as well as T@sub C@ (as high as 150 K) with optimal annealing temperature found to be 250°C.@footnote 1@ AC-magnetotransport measurements conducted from 5 K to 300 K and with applied magnetic fields ranging to +/- 7 Tesla indicate similar field dependence of resistivity, AHE, and metal-insulator-like transition near T@sub C@ as reported by others.@footnote 2@ T@sub C@'s as found from Arrott plots from the resulting AHE measurements agree well with direct SQUID magnetometry measurements. Log-log plots of @rho@@sub xy@, d@rho@@sub xy@ /dH, and @rho@@sub xy@/M@sub S@ vs. @rho@@sub xx@, cumulated from AHE measurements at temperatures below T@sub C@ of differing as-grown Mn content and annealing conditions, indicate skew scattering to be the dominant mechanisms for AHE in (Ga,Mn)As regardless of as-grown Mn content or Mn@sub Ga@/Mn@sub I@ ratios and possibly regardless of presence of non-magnetic or magnetic Mn-rich nano-clusters. We will also discuss the results in light of theory@footnote 3@ of AHE in clean (Ga,Mn)As and experimental reports@footnote 4@ of AHE in DMS systems with ferromagnetic nano-clusters. @FootnoteText@ @footnote 1@T Hayashi et al. APL 78, 1691 (2001); KC Ku et al., APL 82, 2302 (2003).@footnote 2@M Tanaka, JVST B 16, 2267 (1998).@footnote 3@T Jungwirth et al., PRL 88, 207208 (2002).@footnote 4@SR Shinde et al., PRL 92, 166601 (2004).

Surface Science
Room 202 - Session SS+EM-WeA
Organic Film Growth and Characterization

Moderator: J.N. Russell, Jr., Naval Research Laboratory

2:00pm **SS+EM-WeA1 Comparison of the Electronic Structure of Ferroelectric Polymers***, **J. Xiao**, L.G. Rosa, M. Poulsen, D.Q. Feng, S. Ducharme,* University of Nebraska-Lincoln*; P.A. Dowben,* University of Nebraska-Lincoln, US

We compare the electronic structure of copolymers of polyvinylidene fluoride with trifluroethylene P(VDF-TrFE, 70%:30%) with polymethylvinylidenecyanide (PMVC). Crystalline thin films can be formed from both ferroelectric polymers and we find that in both cases the dipole is aligned along the surface normal. The P(VDF-TrFE) copolymer is generally observed to have the chemical potential close to the lowest unoccupied molecular orbital,@footnote 1@ with a band gap of about 6 eV.@footnote 2@ PMVC exhibits a much greater band gap, with the Fermi level placed roughly mid way within the highest occupied to lowest unoccupied molecular orbital (HOMO-LUMO) gap. The implications of these differences in electronic properties will be discussed, in particular with regard to electron-phonon coupling.@footnote 3@ @FootnoteText@ @footnote 1@Jaewu Choi, P.A. Dowben, S. Pebley, A. Bune, S. Ducharme, V.M. Fridkin, S.P. Palto, N. Petukhova, Phys. Rev. Lett. 80 (1998) 1328-1331@footnote 2@Chun-gang Duan, W.N. Mei, J.R. Hardy, S. Ducharme, J. Choi, P.A. Dowben, Europhys. Lett. 61 (2003) 81-87@footnote 3@Luis G. Rosa, Ya.B. Losovyj, J. Choi, and P.A. Dowben, J. Physical Chemistry B 109 (2005) 7817-7820.

2:20pm **SS+EM-WeA2 Energetics of Metals Adsorption on Polymers: Calorimetric Studies***, **J.F. Zhu**, S.F. Diaz, P. Goetsch, J.J.W. Harris, C.T. Campbell,* University of Washington

We report here the first calorimetric measurement of any metal adsorption energy onto any polymer surfaces wherein the sticking probability of the metal also was measured. The heat of adsorption and sticking probability were measured for Pb and Ca gas atoms adsorbing onto clean poly(methyl methacrylate) (PMMA) and electron-irradiated PMMA. The PMMA film was spin coated directly onto the heat detector, a pyroelectric polymer foil (polyvinylidene fluoride - PVDF) precoated on both sides with metal thin films to serve as electrodes. This provides a detector sensitivity of ~450 V/Jabs with a pulse-to-pulse standard deviation of 1.2 kJ/mol and an absolute accuracy within 2%. The Pb atoms interact very weakly with the outgassed pristine PMMA surface, with a sticking probability of 0.02 ± 0.02. They deposit a heat into the PMMA of 12.7 ± 0.7 kJ per mole of dosed Pb, independent of Pb exposure up to 10 ML. This is slightly less that would be expected even if no Pb atoms stuck to the PMMA, but if they completely thermally accommodated to the substrate temperature during their collisions with the surface. This proves that thermal accommodation is incomplete, highlighting the weakness of the Pb - PMMA interaction. Calcium interacts with pristine PMMA much more strongly, with an initial sticking probability of ~0.5 and an initial heat of adsorption above 240 kJ/mol. Damaging the PMMA surface with electrons causes an increase in reactivity with Pb, as evidenced by increases in the initial heat of adsorption up to 134.0 ± 0.7 kJ/mol and the initial sticking probability up to 0.51 ± 0.01. Both increase with increasing coverage toward values expected for Pb adsorption onto bulk Pb.

3:00pm **SS+EM-WeA4 Contrasting the Assembly and Molecular Architecture of N-heteroaromatic Molecular Films on Ag(111): ACA vs. INA***, **H. Li**, B. Xu, D. Evans, J. Reutt-Robey,* University of Maryland at College Park

Monolayer films of isonicotinic acid (INA) and 9-acridine carboxylic acid (ACA) were prepared by physical vapor deposition and investigated with complementary scanning tunneling microscopy (STM) and spectroscopy (XPS, RAIRS) under UHV conditions. These N-heteroaromatic acids offer the same H-bonding motifs, but varied sizes and electrostatic properties, which should impact film architecture. In the monolayer regime, STM images reveal that both molecules readily assemble at room temperature into ordered "2-D" structures with typical domain sizes exceeding 100 nm for INA and 1000 nm for ACA. Differences between the domain structures (INA domains being more anisotropic and with much sharper (molecularly smooth) boundaries) are related to differences in their intermolecular

forces. We propose structural models consistent with high resolution STM images and test these structural models with detailed spectroscopic measurements. XPS studies of N 1s and O 1s core level shifts identify a predominant H-bonding motif based upon N head-to- carboxyl tail interaction, in agreement with the proposed structural model. Surface infrared measurements of INA molecular films detect a pronounced out-of-plane aromatic H bending mode at 858 cm@super -1@, and an intensity analysis determines the aromatic plane to be tilted by ~20° from the substrate plane. The proposed structural model for ACA involves an arrangement of ACA molecules with greater and alternating tilt angles, which we are presently testing with infrared experiments. We will account for these distinct molecular film architectures with the differences in the intermolecular forces and discuss the generality of these effects.

3:20pm **SS+EM-WeA5 Intermolecular Interactions in Ultrathin Organic Films***, **N.V. Richardson**,* University of St Andrews, UK **INVITED**

Across the complexity of molecular systems, which have now been studied in great detail at well-defined, single crystal surfaces, particularly metal surfaces, there is a great variety in the strength, nature and significance of the interamolecular interactions which are possible. It is the balance of these interactions with the adsorbate/substrate interaction that is a key determinant of the two dimensional order, which can be achieved in the system. In the simplest cases, the interaction may be limited to Van der Waals' attractions balanced by local steric repulsion, while in more complex cases, highly directional H-bonding interactions can dominate the interadsorbate interaction. In the case of adsorption on relatively soft metals such as copper, silver and gold the strength of the interaction of the molecule with the surface atoms can be comparable with or even greater than that between the surface metal atoms, this can lead to the formation of highly ordered 2D adsorbate structures involving significant translocation of metal atoms, most likely in the form of metal adsorbate complexes, and consequential large scale restructuring of the surface. In this presentation, some examples of the relevance of intermolecular interactions in determining adsorbate structures in the sub-monolayer to monolayer regime will be given based on our studies of molecules ranging from aromatic hydrocarbons, through alkane and fluoroalkane thiols to simple biomolecules, such as amino acids and nucleic acid bases. In a somewhat more detailed description of two adsorbate-substrate systems, the role of a two dimensional monolayer in templating a novel three dimensional bulk structure will be described and, in the other example, the ability of a racemic mixture of adsorbing molecules to exploit intermolecular interactions leading to chiral phase segregation will be demonstrated.

4:00pm **SS+EM-WeA7 Conformational Changes and Chiral Ordering in Adsorbed Molecular Layers Investigated by Time-resolved STM***, **S. Weigelt**[1], C. Busse, L. Petersen, T.R. Linderoth, E. Rauls, B. Hammer, K.V. Gothelf, F. Besenbacher,* University of Aarhus, Denmark

Detailed understanding of intermolecular interactions and molecular dynamical processes is required to control, and ultimately exploit, molecular self-assembly on surfaces. Recently, self-assembled structures formed from molecules that become chiral once confined to the surface plane have received particular attention. In this contribution we investigate a family of organic molecules that surprisingly can switch chirality as well as switch between chiral and non-chiral forms after adsorption by undergoing spontaneous conformational changes. The molecules (oligo-(phenylene-ethynylene)'s) consist of a central benzene ring with two or three ethynylene spokes each terminating in a tert-butyl substituted salicylaldehyde moiety. Upon vapour deposition onto the Au(111) surface under UHV conditions, the molecules assume different surface conformers, distinguishable in STM images by the positions of the tert-butyl groups relative to the molecular backbone. Some of these surface conformers are chiral and the chirality of the conformers and the chirality of the assumed molecular tiling patterns are highly correlated. The correlation is enabled by an intra-molecular switching mechanism, allowing the adsorbed molecules to flip between different surface conformers (and hence between different chiral forms) by rotating their end groups around the axis of the ethynylene spoke. This chiral switching enable the molecules to form extended homo-chiral domains by dynamically accommodating to the chiral template found at domain perimeters. We have performed a detailed investigation of this intra-molecular dynamic process by monitoring the surface with time-resolved STM at substrate temperatures in the interval 150-220K. The rate for the conformational change follows an Arrhenius dependence on temperature with activation energy ~0.3 eV. Theoretical modeling is currently being performed to illuminate this novel intra-molecular dynamical process.

4:20pm **SS+EM-WeA8 Resonant Soft X-Ray Emission and Inelastic X-Ray Scattering Studies of Electronic Structure in Metal Phthalocyanines***, Y. Zhang, S. Wang, L. Plucinski,* Boston University*; J.E. Downes,* Victoria University of Wellington, New Zealand*; C. McGuinness,* Trinity College Dublin, Ireland*; P.A. Glans, T. Learmonth, **K.E. Smith**,* Boston University

We report synchrotron radiation-excited resonant soft x-ray emission (SXE) spectroscopy and resonant inelastic x-ray scattering (RIXS) studies of the electronic structure of thin films of metal phthalocyanines (M-Pc).@footnote 1@ SXE measures the element-resolved partial density of states (PDOS) in materials. At a core level resonance, SXE measures the non-ionized PDOS associated with specific chemical sites. Furthermore, RIXS features can be observed which are related to low energy excitations in the system. We discuss the application of SXE and RIXS in the study of M-Pc. Our results are in excellent agreement with theory, but differ significantly from previously published experiments. The films were found to be highly susceptible to beam damage. We successfully circumvented this effect by continuous film translation during measurement. Resonant SXE spectra from undamaged Cu-Pc samples show spectral features near the Fermi level (E@sub F@) that, although predicted, have not previously been observed.@footnote 2@ We have also studied vanadium oxide phthalocyanine (VO-Pc), and in addition to measuring the element resolved PDOS, have observed dipole forbidden V 3d - V 3d* and O 2p - V 3d* charge transfer transitions across the band gap. The ability to accurately measure states near E@sub F@ is significant, as is the discovery that many SXE studies of organic semiconductors are dominated by beam damage effects. @FootnoteText@ @footnote 1@ Supported in part by the ACS PRF, by NSF DMR-0304960, and by DOE DE-FG02-98ER45680. The spectrometer system is funded by U.S. ARO DAAD19-01-1-0364 and DAAH04-95-0014. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.@footnote 2@ J.E. Downes, C. McGuinness, P.-A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390, 203 (2004).

4:40pm **SS+EM-WeA9 Effects of Incident Kinetic Energy on the Nucleation and Morphological Evolution of Organic Thin Films***, A.S. Killampalli, T.W. Schroeder, **J.R. Engstrom**,* Cornell University

The deposition and growth of thin films of organic materials differs fundamentally from that of the more conventional inorganic materials. A key difference involves the presence of strong covalent and ionic bonding in the latter class of materials, whereas organic materials are often bound by rather weak dispersion forces. As a consequence, considerable promise exists in the use of energy tunable molecular beams for the deposition of organic thin films, as incident species with energies on the order of a few eV may produce substantial changes in the growth habit. We have been examining the deposition of pentacene thin films using a supersonic molecular beam source producing hyperthermal (E@subi@ = 1.4 - 10.6 eV) kinetic energies. In both the monolayer and multilayer regimes of growth of pentacene on SiO@sub2@ we find that as E@subi@ is increased from 1.5 to 6.7 eV, the growth rate at a fixed incident flux decreases, consistent with trapping-mediated adsorption. In the monolayer regime the data is well explained by nucleation theory, where the critical island size is 4.5 ± 1.3. The situation is more complex in the multilayer regime - here the decrease in the rate is less than that observed in the monolayer regime, and at sufficiently large E@subi@ (> 4 eV), the rate of deposition in the multilayer regime exceeds that in the monolayer regime by about a factor of 3. The evolution of surface roughness provides additional clues as to the dynamics of growth in the multilayer regime. For all incident kinetic energies, the growth exponent, @beta@, is greater than 0.5, indicative of rapid roughening. Our results demonstrate clearly that the morphological evolution of organic thin films can be modified substantially at high incident kinetic energies.

5:00pm **SS+EM-WeA10 Para-Sexiphenyl Thin Films Grown by Hot Wall Epitaxy on KCl(001) Substrates***, **A.Yu. Andreev**, A. Montaigne,* University Linz, Austria*; G. Hlawacek,* University of Leoben, Austria*; T. Haber, R. Resel,* Graz University of Technology, Austria*; H. Sitter,* University Linz, Austria*; C. Teichert,* University of Leoben, Austria

Para-sexiphenyl (p-6P) is a blue emitting organic semiconductor widely investigated for optoelectronic applications. Especially, p-6P thin films grown on mica(001) and KCl(001) substrates show large morphological, electrical and optical anisotropy, which makes them attractive for nano-scale optoelectronic and photonic devices. In this work, we use Atomic Force Microscopy (AFM) and X-Ray diffraction (XRD) to study the growth of

[1] **Morton S. Traum Award Finalist**

p-6P on crystalline KCl substrates, in order to find the process controlling parameters. It is shown that the growth process of p-6P on KCl(001) is quite complex and can be divided preliminary in two steps. The initial growth stage is characterized by the formation of the long needle-like crystallites build of "laying" molecules (as shown by XRD), generating a rectangular network in accordance with substrate surface symmetry. If the surface coverage increases, terraced crystalline mounds composed of upright standing molecules start to develop between the needles. These mounds are clearly formed due to repeated 2D nucleation of p-6P molecules. Consequently, all terraces found are in average about 2.6 nm high, which corresponds to one monolayer of standing p-6P molecules. Further, growth is characterized by a coexistence of the constantly growing needles and mounds, whereby the last ones cover finally almost the whole surface between the needles. By means of phase imaging in AFM tapping mode, it could be clearly demonstrated that both needle-like crystallites and flat terraced mounds grow directly on the substrate surface, i.e., there is no wetting layer formed during the deposition of p-6P on KCl(001).

Electronic Materials and Processing
Room 309 - Session EM1-ThM

Molecular Electronics

Moderator: D.B. Janes, Purdue University

8:20am **EM1-ThM1 Molecular Conductance and Contact Resistance Measured in Nanoparticle-Bridged Nanogap Structures***, **C. Chu**, G.N. Parsons,* North Carolina State University

Understanding molecular conduction and contact resistance at organic-metal junctions is crucial for advanced organic electronic materials and devices. We have developed an angled metal evaporation technique to form planar metal (Au and Al) electrodes with separation distances of <50nm and electrode width of several microns, and used 80nm Au nanoparticles to form conductance pathways between the nanometer-spaced electrodes. Multiple nanoparticles can be measured in parallel, and the conductance increases with the number of nanoparticles in the gap. Before Au nanoparticle deposition, various molecular monolayers were adsorbed onto the Au electrodes, resulting in bridging structures that enable conductance of sets of molecules to be characterized. The conductance and contact resistances are evaluated from current-voltage characteristics and compared to results obtained by conductive probe AFM (CP-AFM) on the same monolayers. Molecules studied include various length alkanethiols and alkylamines, as well as conjugated molecules including xylyl thiol and phenylene derivatives. Current vs voltage is observed to follow the coherent tunneling model, and contact resistance (R@sub o@) was evaluated by measuring the effect of alkyl chain length for both thiol and amine head groups. Alkanethiols show R@sub o@ of ~18 k@OMEGA@, whereas amine head groups give R@sub o@ ~1k@OMEGA@. The number of molecules probed is not precisely known, but resistance for the nanoparticle bridge is larger than measured by CP-AFM, suggesting a smaller number of molecules are probed in the bridge structure. Furthermore conjugated molecules show conductivity that is ~400 times larger than for alkanedithiols. Results show that the bridged nano-gap structure can be used to evaluate conductance and resistance on the molecular scale, and it is capable of characterizing a variety of molecular and nanostructured elements.

8:40am **EM1-ThM2 The Effects of Molecular Environments on the Electrical Switching with Memory of Nitro Molecules***, **N. Gergel-Hackett**,* University of Virginia, US*; N. Majumdar, Z. Martin, G. Pattanaik,* University of Virginia*; Y. Yao, J.M. Tour,* Rice University*; G. Zangari, N. Swami, L.R. Harriott, J.C Bean,* University of Virginia

Since memory behavior was first reported for the "nitro" molecule (an OPE molecule with nitro side groups),@footnote 1@ other researchers have reported various combinations of electrical switching, memory, and/or negative differential resistance.@footnote 2,3,4@ These reports employed test structures that differed in the number of nitro molecules simultaneously contacted: some reports describe devices that contact thousands of molecules,@footnote1,3@ while others contact just a few.@footnote 2,4@ To address a possible correlation between contacting a large area of nitro molecules and observing memory behavior, we report on experiments that use a nanowell device where nitro molecules are seperated by insertion into a secondary matrix of alkanethiols. We observe memory behavior for "pure" nitro monolayers, but not for the monolayers of nitro molecules inserted into alkanethiols. Additionally, insertion into alkanethiol matrices adds the variable of order. STM images reveal that alkanethiol matrices are ordered, yet "pure" nitro monolayers are disordered. A recent report suggests a correlation between the rate of electrical switching and the ordering of a nitro molecule's environment.@footnote 4@ To test for a relationship between memory behavior and an ordered matrix environment, we have developed ways of forming disordered matrices. This is done by changing the exposure time of the substrate to the alkanethiol solution or by using COOH-terminated alkanethiols (16-mercapto hexadecanoic acid). We will report the electrical behavior of nitro molecules inserted into these disordered alkanethiol matrices and contrast the results with those obtained for nitro molecules inserted into ordered matrices, as well as those for "pure" nitro monolayers. @FootnoteText@ @footnote 1@M.A. Reed et al, Appl. Phys. Lett. 78, 3735 (2001)@footnote 2@I. Kratochvilova et al, J. Mater. Chem. 12, 2927 (2002)@footnote 3@F.Fan et al, J. Am. Chem. Soc.124, 5550 (2002)@footnote 4@Z.J. Donhauser et al, Science 292, 2303 (2001).

9:00am **EM1-ThM3 Electronic Structure and Charge Addition Effects in Phenylene Ethynylene Oligomers: a Comparison of Pristine versus -NO@sub2@ Substituted Molecules***, **S.W. Robey**, C.D. Zangmeister, R.D. van Zee,* NIST

Interest in aromatic systems based on phenylene ethynylene oligomers (OPE) has been spurred by reports of intriguing transport behavior in metal-molecule-metal junctions. There have been reports of the observation of negative differential resistance (NDR) characteristics by substitution of electron-withdrawing -NO@sub2@ groups on the central ring of a three-ring phenylene ethynylene oligomer, whereas this behavior is not observed for the "pristine", unsubstituted molecule. In this contribution, the relevant @pi@ electronic structure near the Fermi level, determined via photoelectron spectroscopy for self-assembled monolayers on gold, is compared and contrasted for three-ring phenylene ethynylene oligomers with and without substitution of -NO@sub2@ groups. Further comparison with -NH@sub2@ substituted oligomers and results of ab inito calculations will also be discussed. In addition, theoretical work has invoked redox-like or polaronic effects to provide an explanation for NDR behavior. We have performed measurements to shed light on this issue by comparison of the influence of additional charge in pristine versus nitro-substituted OPE, added by "doping" with K. For pristine OPE, sequential addition of K leads to a gradual shift of levels to higher binding energy reminiscent of "rigid band" behavior, although some distortion/conformation change is suggested by relative shifts of @pi@ levels. For large charge addition, two new states are observed in the original @pi@ to @pi@* gap. For the nitro-substituted oligomer, a similar spectrum is observed for large K addition, but the behavior as a function charge addition is quite different. After an initial shift by ~ 0.6 eV, the spectrum is nearly pinned for subsequent K addition before a final shift brings it to near coincidence with the pristine oligomer spectrum. These results will be discussed in the context of polaronic/bipolaronic effects and the influence of unoccupied levels related to the -NO@sub2@ substitution.

9:20am **EM1-ThM4 Probing Silicon Based Molecular Electronics with Ultra-High Vacuum Scanning Tunneling Microscopy***, **N.P. Guisinger**, N.L. Yoder, M.C. Hersam,* Northwestern University

A cryogenic variable temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM) is utilized for measuring the electrical properties of isolated cyclopentene molecules adsorbed to the degenerately p-type Si(100)-2x1 surface at a temperature of 80 K. Current-voltage curves taken under these conditions show negative differential resistance (NDR) at positive sample bias in agreement with previous observations at room temperature.@footnote 1-3@ The enhanced stability of the STM at cryogenic temperatures was utilized for repeated measurements taken over the same molecule. Current-voltage curves on isolated cyclopentene molecules are demonstrated to be repeatable and possess negligible hysteresis for a given tip-molecule distance. Subsequent measurements with variable tip position show that the NDR voltage increases with increasing tip-molecule distance. Using a one-dimensional capacitive equivalent circuit and a resonant tunneling model, this behavior can be quantitatively explained, thus providing insight into the electrostatic potential distribution across a semiconductor-molecule-vacuum-metal tunnel junction. This model also provides a quantitative estimate for the alignment of the highest occupied molecular orbital (HOMO) of cyclopentene with respect to the Fermi level of the silicon substrate, thus suggesting that this experimental approach can be used for performing chemical spectroscopy at the single molecule level on semiconductor surfaces. Overall, these results serve as the basis for a series of design rules that can be applied to silicon-based molecular electronic devices. @FootnoteText@ @footnote 1@ Guisinger, N. P., Basu, R., Baluch, A. S. & Hersam, M. C. (2003) Ann. N. Y. Acad. Sci. 1006, 227-234.@footnote 2@ Guisinger, N. P., Greene, M. E., Basu, R., Baluch, A. S. & Hersam, M. C. (2004) Nano Lett. 4, 55-59.@footnote 3@ Guisinger, N. P., Basu, R., Greene, M. E., Baluch, A. S. & Hersam, M. C. (2004) Nanotechnology 15, S452-S458.

9:40am **EM1-ThM5 Metal Molecule Silicon Devices***, **A. Scott**, D.B. Janes,* Purdue University

While the majority of molecular electronic devices have employed metal contacts, semiconductor contacts could allow more stable chemical bonds and enhanced electrical functionality. Integrating molecular devices on silicon is a promising approach to molecular electronics@footnote 1@ and would leverage capabilities of the microelectronics industry. In this study, metal-molecule-silicon devices have been fabricated and characterized. Molecules are grafted to 111 silicon surfaces by electrochemical reduction

of diazonium salts,@footnote 2@ resulting in robust molecular layers that are covalently bound to the surface by C-Si bonds. Aromatic molecules with various headgroups have been grafted to Si and characterized using infrared spectroscopy and cyclic voltammetry. Metal top contacts are deposited using an indirect evaporation technique which minimizes metal penetration, as demonstrated previously on GaAs.@footnote 3@ Electrical testing of these devices indicates that transport can be modulated by both substrate doping and molecular chemistry. If a large metal-semiconductor barrier is present and the substrate is lightly doped, the current-voltage characteristics are only slightly modified by the addition of a molecular layer. N-type Si-Au Schottky diodes (N@sub D@=10@super 15@cm@super -3@) have current densities of 3 A/cm@super 2@ at 0.5 volt, and the addition of a molecular layer reduces the current density by less than an order of magnitude. In devices where the barrier height is small and the substrate heavily doped, transport is more dominated by molecular effects. P+ (N@sub A@=10@super 19@cm@super -3@) Si-Au Schottky diodes exhibit current densities of 10@super 6@ A/cm@super 2@, and the addition of a molecular layer decreases this by 1 to 4 orders of magnitude depending on the molecular species. @FootnoteText@ @footnote 1@Guisinger et al., Nano Let. 55-59, 2004@footnote 2@Allongue et al.,JEAC 161-174, 2003@footnote 3@Lodha and Janes, APL, 2809-2811, 2004.

10:00am **EM1-ThM6 Chemically Resolved Electrical Measurements within Monomolecular Layers*, H. Cohen*, *R. Yerushalmi, N. Granit, A. Shukla, M.E. van der Boom, A. Scherz,* Weizmann, Israel

Interesting electrical characteristics within monomolecular layers are revealed by chemically resolved electrical measurements (CREM).@footnote 1,2@ The method is based on slightly modified X-ray photoelectron spectroscopy (XPS), using energy-filtered electrons as fine and flexible electrodes. Our recent results manifest breakthrough capabilities for future molecular electronics applications. @FootnoteText@ @footnote 1@ H.Cohen, Applied Physics Letters 85, 1271 (2004).@footnote 2@ H. Cohen, C. Nogues, I. Zon and I. Lubomirsky, J. Appl. Phys., in press.

10:20am **EM1-ThM7 Conduction through Cytochrome c Molecules*, T. Matsumoto*,** *M. Kataoka, T. Kawai,* Osaka University, Japan

Cytochrome c, which mediates electron transfer in biological system, is a candidate molecule with the suitable structure for electronic elements that comprise insulating and active parts. Since this redox center is isolated from the surroundings by the insulating part, the structure of cytochrome c can be regarded as a double tunneling junction for single electron tunneling. However, thin film of cytochrome c shows low conductivity, whereas, in vivo, single or several molecules derive electrons with high efficiency. For this reason, the measurement of the electrical conduction through single or several cyt.c molecules in solid state is a challenge to a critical stage towards the realization of bioelectronic devices using electron transfer proteins. Here, we demonstrate that cytochrome c molecules are electrically active on electrode surface modified with self-assembled monolayer. We also found that the strong influence of the variation of self-assembled monolayer on the conduction through cytochrome c. The gap-edge voltages observed are 0.5V for 2,2â?T-PySSPy and 1.3V for 4,4â?T-PySSPy. To confirm the participation of heme in the conduction through cytochrome c, the comparative experimenht for Zn cytochrome c, whose heme ion of Fe is replaced to Zn, was performed. In case of Zn cytochrome c, any detectable current has not been observed. This implies that the current goes through the ion in the reaction center of cytochrome c molecules suggesting that the conduction mechanism might be single electron tunneling. The SAM modification is also useful for nanogap electrode. The current through the molecule increases with increasing temperature suggesting the presence of thermal excitation.

10:40am **EM1-ThM8 Tunneling Transport through Benzoate on Cu(110)*, D.B. Dougherty*,** *P. Maksymovych, J.T. Yates Jr.,* University of Pittsburgh

The possible use of single molecules as devices in electronic circuits requires a fundamental understanding of the influence of the details of the linkage and charge transport to a macroscopic contact. Molecular orientation, chemical bond strength and location, and energetic location of molecular orbitals may all play a role in determining the possible use of a given molecule/contact system. Thus, detailed experimental studies of simple molecules in well-defined and reproducible configurations are necessary to supplement and guide more technologically relevant work. Significant progress has been made in understanding the transport properties through long chain molecules linked to Au surfaces by a thiolate group.@footnote 1@ These linkages are not the only potentially interesting candidates for electronics. In fact, the enormous chemical variety available is one of the great advantages of using organic molecules in devices. We have studied the electronic transport properties of benzoate molecules on a clean Cu surface which are linked by a carboxylate group instead of a thiolate.@footnote 2@ Such a linkage can be strong and surface-site specific and may therefore result in useful and reproducible electrical contact. More importantly, it provides a tool for addressing fundamental issues in single molecule transport. Using scanning tunneling spectroscopy, we have measured the I/V and conductance characteristics of differently oriented benzoate molecules chemisorbed on a Cu(110) surface. Benzoate molecules adsorbed with their plane perpendicular to the surface have a diminished conductivity in the low bias regime when compared to molecules with their plane parallel to the surface. The conductivity is found to be independent of temperature. *Supported by the W.M. Keck Foundation and a Japanese NEDO grant. @FootnoteText@ @footnote 1@ W. Wang et al., Rep. Prog. Phys. 68 (2005) 523.@footnote 2@ B.G. Frederick et al., Surf. Rev. Lett. 3 (1996) 1523.

11:00am **EM1-ThM9 Hopping Transport through Self-Assembled Monolayer on a GaAs Surface*, K. Lee*,** Purdue University

In organic solids, hopping transport is known to be a primary conduction mechanism. The prominent feature of hopping transport is its low mobility, which has been major limitation of utilizing organic solid as an active channel material. However, it has been known@footnote 1@ that, with efficient @pi@-@pi@ stacking of @pi@-conjugated molecules, the mobility of organic solids can be dramatically improved. To realize this idea, highly pure single crystals of organic molecules have been used to demonstrate much higher mobility,@footnote 2@ but it is questionable whether it would be feasible to fabricate a 3-terminal device with reasonable operating voltage. Another suggested solution is to use well-ordered self-assembled monolayer (SAM) of @pi@-conjugated molecules as an active channel component. In this study, a testbed for hopping transport through SAM has been fabricated using back-to-back schottky diode structure on semi-insulating GaAs. Before depositing molecules, pre-deposition current is less than 1nA. After forming SAM on GaAs surface, significant change in conductivity was observed in several molecules. For instance, thiophenol SAM increased conductivity by ~10 times, whereas ODT SAM suppressed bulk leakage current by one third. There are two possible conduction paths that can explain this conductivity increase: 1) hopping conduction through SAM 2) surface potential change due to the molecular dipole moments. However, it is not likely that the second possibility is a primary reason for enhanced conductivity because of the fact that ODT SAM, which has relatively strong molecular dipole moment but no @pi@-electrons, decreased conductivity. In addition, the dependence of mobility on temperature indicates that hopping transport is dominant. Finally, the application of the testbed to chemical sensors and organic transistors will be discussed. @FootnoteText@ @footnote 1@ J. L. Bredas, et al., PNAS, 99, 5084 (2002)@footnote 2@ Vikram C. Sundar, et al., Science, 303, 1644 (2004).

11:20am **EM1-ThM10 Charging and Discharging Nanoscale Domains in Thin Films of Arylamines Studied with Kelvin Probe Microscopy**, *J. Sun, S.C. Blackstock,* ***G.J. Szulczewski,*** University of Alabama

The work reported here was motivated to assess the feasibility of a non-volatile molecular memory based on charge storage in amorphous thin films. Toward that end, thin films of a series of redox-gradient arylamines were vapor deposited on oxidized p-type Si(100) wafers and subsequently charged in tapping mode with a voltage applied to a metal-coated AFM tip. The redox-gradient is designed to facilitate one-way electron transfer from the periphery of the molecule to its core. The concept is realized by synthesizing molecules with an easy to oxidize (i.e. ionize) moiety at the interior of molecule and surrounding it with harder to oxidize redox moieties.@footnote1@ In effect the gradient acts as a charge funnel toward the interior of the molecule. The extent of charging was measured with Kelvin probe microscopy (KPM). The charged domains have an apparent diameter of about 200 nm in the KPM image, which is larger than the real area due to the long-range interaction of the charge and the tip/cantilever. The charge half-life was proportional to the magnitude of the redox-gradient. For example, amines without a redox gradient discharged within 1 hour. In contrast, amines with a redox-gradient of ~0.8 eV could retain 50% of their initial charge after 10 hours. The charging is reversible. By applying a negative bias on the KPM tip the charged region could be neutralized. Although the charge is stable for many hours and can be neutralized, there is diffusion of charge in the films due to Coulombic repulsion. @FootnoteText@ @footnote1@ T. D. Shelby and S. C. Blackstock, "Preparation of a Redox-gradient Dendrimer. Polyamines

Designed for One-Way Electron Transfer and Charge Capture" J. Am. Chem. Soc. 1998, 120, 12155.

11:40am **EM1-ThM11 Observation of trans-to-cis in Azobenzene by Spatially Resolved Scanning Tunneling Spectroscopy*, B.-Y. Choi,*** Seoul National University, Korea*; S.-J. Kahng,* Korea University, Korea*; Y. Kuk,* Seoul National University, Korea

There have been serious efforts to apply various organic molecules to an organic based memory. These molecules change their configuration by a charge transfer between surrounding bonds or to reach an energy minimization state when a bias voltage is reached at a certain voltage. Similar but slightly different organic molecules, photo sensitive molecules, may be used for this application. Scanning tunneling microscopy/spectroscopy experiment was performed on azobenzene single molecule adsorbed on a Au(111) surface in UHV at 5K. Azobenzene has two stereoisomers; trans- and cis-azobenzene which can be transformed to each other by UV irradiation or thermal energy. We could induce the trans-to-cis transition of a single trans-azobenzene by injecting electric pulses by using STM tip and the electronic structure of them were observed in sub-atomic resolution. The tip bias for the trans-to-cis transition is ~1.5V and cis-azobenzene returned back under negative tip bias or in time at the adsorption site. The LUMO state of trans-azobenzene was confined mainly within the benzene segments which were lying parallel to gold substrate. The HOMO state was localized within the nitrogen. Cis-azobenzene shows several spectroscopy results depending on the molecule-surface configuration. We also observed an LDOS of azobenzene on NaCl layers deposited on Cu(111). Adsorbed on NaCl, the azobenzene shows an electronic states which are not coupled to that of the metal surface.

Electronic Materials and Processing
Room 310 - Session EM2-ThM
Heteroepitaxy and Low-Dimensional Structures

Moderator: R.S. Goldman, The University of Michigan

8:20am **EM2-ThM1 Materials Integration of III-V Heterostructures*, M. Goorsky,*** *S.L. Hayashi, A. Noori,* University of California, Los Angeles*; R.S. Sandhu,* University of California, Los Angeles and Northrop Grumman Space Technology*; A. Cavus, C. Monier, M. Lange, M. Wojtowicz, T. Block, A. Gutierrez-Aitken,* Northrop Grumman Space Technology **INVITED**

III-V wafer bonded structures satisfy requirements for electronic device structures that simultaneously possess a large surface lattice parameter (e.g., near that of InAs) and a high substrate resistivity. The objectives of the research are to address the fabrication of III-V composite wafer bonding with the ultimate goal of producing virtual substrates for advanced III-V devices. Graded buffer layers are one key technological step. Very thin InAlAs graded buffer layer structures were produced for virtual InAlAs substrate applications. The rapid kinetics of strain relaxation in In@sub x@Al@sub 1-x@As graded buffer layers (GBLs) was exploited to produce thin (0.21 µm - 0.90 µm) buffer layers graded from the InP substrate to 6.0 Å. GBL layers as thin as 0.21 µm showed full strain relaxation and GBL layers as thin as 0.45 µm showed similar growth mode, surface roughness, and strain relaxation as thicker GBL structures. The threading dislocation density was low (mid-10@super 6@ cm@super -2@) for the 0.45 µm and the 0.90 µm buffer layers but there was evidence of non-uniform threading dislocation distribution for the 0.21 µm buffer structures. The feasibility of aggressive grading for other III-V systems will also be addressed. For some applications, even a thin GBL - upon which device structures are grown - is not feasible for device applications. To address the issue of limited GBL thickness, hydrogen exfoliation ("Smart-Cut") has been assessed to transfer thin films of InP, InAs, or 6.0Å lattice parameter layers to high resistivity substrates. We have developed a strategy for implantation and exfoliation based on the nucleation and growth of mechanical cracks at the projected range of the implant. This method has led to reproducible exfoliation and successful transfer of a wide variety of semiconductor materials. Damage-free chemical-mechanical polishing (CMP) has also been developed to produce low roughness (< 1 nm r.m.s) surfaces for subsequent epitaxial deposition. Another issue associated with composite wafers is the coefficient of thermal expansion (CTE) differences between the bulk substrate and the transferred layer. We have incorporated the temperature-dependent CTE values into force-balance equations to determine the thermodynamic stability of heterostructures based on these materials. The stability criteria have been experimentally confirmed. Examples of device structures on graded buffer layers and transferred layers will be shown to demonstrate the feasibility of this approach for the integration of III-V heterostructures.

9:00am **EM2-ThM3 Interfacial Bond Formation in W-structured type-II IR Detectors as Revealed by Cross-Sectional Scanning Tunneling Microscopy*, J.C. Kim,*** *J.G. Tischler, I. Vurgaftman, J.R. Meyer, E.H. Aifer, L.J. Whitman,* Naval Research Laboratory*; C.L. Canedy, E.M. Jackson,* SFA Inc.

W-structured type-II superlattices (W-SLs) were originally developed to enhance the gain of mid-wave infrared lasers, but also have desirable properties for the design of infrared detectors. We are currently investigating ternary (and quaternary) W-SL structures composed of InAs, InGaSb (InGaAsSb), and AlInSb (AlInAsSb) layers for use in long-wave and very long-wave infrared photodiodes. Interfaces play a significant role in W-SLs because there are twice as many interfaces in each period than in a typical two-constituent SLs such as InAs/Ga(In)Sb, and therefore more options to engineer interfaces in order to compensate strain. We use x-ray diffraction to determine the overall strain in the W-SLs, and cross-sectional scanning tunneling microscopy (XSTM) to directly image the atomic-scale structure of the SLs, including the interfacial bonds, as a function of growth conditions. Differences in the local bond length of different interfaces (e.g., AlAs vs. InSb) result in specific contrast in XSTM images, making it possible to directly identify the interfacial bond types. We find that "unforced" AlSb/InAs interfaces, where both shutters are switched simultaneously with the intention of creating a neutral mix of interfacial bonds, actually consist predominantly of AlAs bonds, leading to undesirable strain. In contrast, InGaSb/InAs interfaces form as intended. We will discuss the surface science underlying the formation of these interfacial bonds, along with their effects on the optical properties and device characteristics.

9:20am **EM2-ThM4 Control of InAs/GaAs Quantum Dot Density and Positioning Using Modified Buffer Layers*, W. Ye,*** *S. Hanson, M. Reason, X. Weng, R.S. Goldman,* The University of Michigan

Recently, strain-induced self-assembled quantum dots (QDs) have enabled the development of high performance light-emitters and detectors. Further advances in optoelectronics and quantum computing will require a narrowing of the density of states and achievement of periodic charge distributions, both of which necessitate the fabrication of high density, nearly monodispersed, highly ordered QD arrays. Various efforts have been made to achieve high densities of laterally ordered InAs/GaAs QDs. However, the mechanisms of lateral ordering of QDs are the subject of continued debate. A significant remaining question concerns the effects of buffer layers on the QD density and lateral ordering. Therefore, we have examined the patterning effects of buffer layers during the growth of QD SLs. Our QD SLs consisted of 2.6 ML InAs and 5 nm GaAs grown by molecular beam epitaxy at 500°C. Prior to QD deposition, GaAs buffer layers were grown under several different conditions, involving growth and/or annealing at 580°C and 500°C. High temperature grown buffers consist of relatively flat surfaces, while lower temperature grown buffers contain "mound-like" features elongated along the [1-10] direction. Isotropic distributions of QDs are observed for QD growth on flat buffers. Interestingly, QD alignment along the [1-10] direction is observed for QD SL growth on buffers containing mounds. This anisotropic QD alignment is enhanced as the number of QD SL increases and is dependent on the density of mounds. For flat buffers, the density of QDs decreases with stacking, consistent with the model of Tersoff. However, for buffers containing mounds, this effect is compensated by an increase in QD density. We propose a new mechanism for QD nucleation, which is based upon patterning by undulated In-enriched GaAs spacer layers following the initials sets of QD SLs.

9:40am **EM2-ThM5 Implantation-Defect-Mediated Intermixing of InAs/InP Quantum Dot Layers*, C. Dion,*** École Polytechnique de Montréal, Canada*; S. Raymond, G. Ortner, P.J. Poole,* National Research Council of Canada, Canada*; F. Schiettekatte, M. Chicoine,* Université de Montréal, Canada*; P. Desjardins,* École Polytechnique de Montréal, Canada

The reduced dimensionality provided by quantum dots (QDs), which leads to atom-like discrete energy levels and @delta@-function-like density of states, offers possibilities for considerable improvements in optoelectronic device applications. However, the use of these nanostructures relies on achieving precise tunability of QDs luminescence emission through QDs size and composition. Since InAs/InP QDs growth is complicated by the rapid exchange of group V species at the InAs/InP interfaces, a post-growth method to fine tune the electronic properties of this particular system is of great relevance. We have investigated the effect of post-growth P implantation followed by rapid thermal annealing on the low-temperature photoluminescence (PL) spectra of self-assembled InAs/InP(001) QDs

grown by chemical beam epitaxy (CBE) and metal-organic vapor phase epitaxy (MOVPE). In untreated samples, threshold temperature for intermixing was found to be 725 °C with blueshifts of the PL peaks of up to 90 meV after RTA at 800 °C for 210 s, while preserving emission bandwidth. In order to obtain larger blueshifts, we studied the effect of introducing point defects into InP cap layers by implanting P at energies sufficiently low to insure that the InAs QDs were not damaged. Implantation with fluence as low as 10@super 12@ P/cm@super 2@ followed by annealing at 500 °C were sufficient to induce a 275 meV blueshift. These observations give important insights into the role of defects generated in InP-based structures on the As/P intermixing and reinforce the applicability of ion implantation for the fabrication of monolithically integrated devices. Implantation-defect-mediated intermixing for wavelength tuning of InAs/InP QDs-based laser structures was investigated.

10:00am **EM2-ThM6 Modeling of InAs/GaAs Self-Assembled Heterostructures: Quantum Dot to Quantum Ring Transformation***, **I. Filikhin,*** North Carolina Central University*; E. Deyneka,* North Carolina A&T State University*; B. Vlahovic,* North Carolina Central University

It is possible to directly observe discreet energy spectra of self-assembled quantum dots (QD) and quantum rings (QR) by means of capacitance-voltage (CV) spectroscopy.@footnote 1,2@ Related theoretical studies, however, had some difficulties interpreting the experiments. Acquired values of the electron effective mass in QD@footnote 1@ and QR@footnote 2,3@ were significantly larger than the bulk mass. Also, the value of the energy-gate-voltage conversion coefficient was in disagreement with experimental conditions.@footnote 2,3@ In presented work we use relatively simple single subband model for InAs/GaAs QD(QR) where the energy dependence of electron effective mass is defined by the Kane formula.@footnote 4@ Model assumptions lead to the non-linear Schrodinger equation in 3D space.@footnote 5@ Model geometrical parameters are based on the fabrication process for InAs/GaAs QD/QR,@footnote 6@ for which the experimental CV data is available.@footnote 1,2@ We assume that the QD to QR transformation occurs without the loss of InAs material. Energies of confinement states of QD(QR) are calculated. Obtained results for single energy levels are in good agreement with the CV spectroscopy.@footnote 1,2@ Our calculations reproduce experimental value for the energy-gate-voltage conversion coefficient as 7. Magnitude of the non-parabolic contribution to the electron effective mass is also evaluated. @FootnoteText@ @footnote 1@ B. T. Miller, et al., Phys. Rev. B 56, 6764 (1997).@footnote 2@ A. Lorke, et al., Phys. Rev. Lett. 84, 2223 (2000).@footnote 3@ A. Emperador, et al., Phys. Rev. B. 62, 4573 (2000).@footnote 3@ E. Kane, J. Physics and Chemistry of Solids 1 249 (1957).@footnote 4@ Li Y, et al., Journal Applied Physics 90 6416 (2002).@footnote 5@ I. Filikhin, E. Deyneka and B. Vlahovic, Model. Simul. Mater. Sci. Eng. 12, 1121 (2004).@footnote 6@ J.M. Garsia et al., Appl. Phys. Lett. 71, 2014 (1997).

10:20am **EM2-ThM7 Relaxed Coupling Conditions between Quantum Dots and Photonic Crystals***, **P. Petroff,*** University of California, Santa Barbara **INVITED**

The possibility of controling the photon emission directionality and enhancing their emission rate by using quantum dots (QDs) coupled to a high Q photonic crystal (PC) opens important technological applications e.g. single photon emitters and detectors. Hence, understanding and controling this coupling is essential if the weak or strong coupling regime is to be routinely achieved. Coupling conditions are however, very demanding, since both the position of the QD and its frequency must be tuned to the PC the mode location and the ultra sharp resonant frequency. We will demonstrate using the InAs/GaAs system a strategy which allows for the deterministic coupling of a single QD to an S1 PC. This technique is general and can be applied to other PC types.@footnote 1@ We report high Purcell factors and non-trivial relaxation dynamics for off resonance lines in all fabricated structures.. We will discuss the coupling of an L3 PC with a dilute InAs/GaAs QD system which shows an ultra low threshold stimulated emission. This "threshold-less" laser is realized even for off - resonance coupling conditions between the QDs and the L3-PC. This new body of experimental observations suggests a relaxation of the coupling conditions which is specific to the QDs. We will present evidence that the continuum of states associated with the wetting layer together with acoustic phonons are involved in these relaxed coupling conditions. Acknowledgments: This work has been carried out in collaboration with A. Badolato, K. Hennessy, S. Strauf, M. Atature, J. Dreiser, M. Rakher, L. Andreani, E.Hu, A. Imamoglu and D. Bouwmeester. The support of an NSF-NIRT no: 0304678 and DARPA no: 972-01-1-0027. @FootnoteText@@footnote 1@A.Badolato et al., Science 308, 1158 (2005).

11:00am **EM2-ThM9 Formation of Flat, Relaxed Si@sub 1-x@Ge@sub x@ Alloys on Si(001) Without the Use of Buffer Layers***, **S. Hong**, H.-W. Kim, D.K. Bae, S.C. Song, G.-D. Lee, E. Yoon,* Seoul National University, South Korea*; C.S. Kim,* Korea Research Institute of Standards and Science*; Y.L. Foo, J.E. Greene,* University of Illinois at Urbana-Champaign

Flat, fully-strained Si@sub 1-x@Ge@sub x@ layers with thicknesses ranging from 40 to 240 nm were grown on Si(001) at 450 @super o@C by ultrahigh vacuum chemical vapor deposition and subjected to furnace annealing at 1000 @super o@C for 20 min to induce relaxation. In order to suppress the thermally-activated surface adatom diffusion leading to surface roughening, while simultaneously promoting misfit dislocation formation, SiO@sub 2@ capping layers were deposited prior to annealing. The degree of strain relaxation R and the root-mean-square surface roughness w are determined as a function of layer thickness. For Si@sub 1-x@Ge@sub x@ layers annealed without SiO@sub 2@ cap layers, the primary relaxation mechanism is strain-induced roughening leading to the formation of a self-organized mound structure with high w and R. However, for capped layers, strain-relaxation occurs through the formation of misfit dislocations and surface roughening is controlled by the resulting cross-hatch. Detailed analysis using atomic force microscopy line scans show that the crosshatch patterns consist of slip steps produced by misfit dislocations at the Si@sub 0.77@Ge@sub 0.23@/Si(001) interface. The presence of oxide cap layers during annealing changes the mechanism of strain relaxation from strain-induced to misfit dislocation induced roughening and inhibits surface diffusion such that the evolution of crosshatch ridges from slip steps is limited. As a result, with oxide capped 240-nm-thick films, we obtain smooth, relaxed Si@sub 0.77@Ge@sub 0.23@ layers with w = 0.68 nm and R = 68% without the necessity of using several-µm-thick compositionally-graded buffer layers.

11:20am **EM2-ThM10 Formation of Epitaxial Ge Nanorings on Si by Self-assembled SiO@sub 2@ Particles and Touchdown of Ge Through a Thin Layer of SiO@sub 2@***, **Q. Li**, S.M. Han,* University of New Mexico

We demonstrate that hexagonally packed single-crystalline Ge rings can be grown around the contact region between self-assembled SiO@sub 2@ spheres and 1.2-nm-thick chemical SiO@sub 2@ on Si. When the oxide-covered Si substrate is pulled from a colloidal suspension of SiO@sub 2@ spheres, the SiO@sub 2@ spheres self-assemble into a hexagonally packed monolayer on the substrate. These SiO@sub 2@ spheres provide a surface diffusion path to guide the Ge adspecies to reach the substrate. We have previously determined that the Ge adspecies readily desorb from the bulk SiO@sub 2@ surface with a desorption activation energy of 42±3 kJ/mol. This low desorption activation energy gives rise to a low surface diffusion barrier, which in turn leads to a high diffusion length on the order of several micrometers, exceeding the dimension of the SiO@sub 2@ spheres. With a flux of Ge impinging at 45° from the surface normal, the Ge beam cannot directly impinge on the underlying substrate through the openings between SiO@sub 2@ spheres. The Ge adspecies diffuse around the SiO@sub 2@ spheres and "touchdown"[Li et al., APL, 85(11), 1928 (2004)] through the chemical SiO@sub 2@, forming epitaxial ring structures. The touchdown process anchors nanoscale Ge seed pads to the underlying Si substrate. The ring formation uniquely takes advantage of the SiO@sub 2@ sphere self-assembly; the weak interaction between Ge adspecies and SiO@sub 2@; and the touchdown where Ge densely nucleate on Si surface through the 1.2-nm-thick chemical oxide. We will also demonstrate that ring dimension and geometrical arrangement can be precisely controlled by the size of the SiO@sub 2@ spheres and by the artificially introduced surface corrugation, respectively.

11:40am **EM2-ThM11 Local Origins of Catalytic and Sensor Activity in 1D Oxide Nanostructures: From Spectromicroscopy to Device***, **A. Kolmakov,*** SIUC*; U. Lanke,* University of Saskatchewan, Canada*; S.V. Kalinin,* Oak Ridge National Laboratory

When nanowire radius (or nanobelt's thickness) is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire (nanobelts) drastically alters the bulk electron density inside the nanowire manifesting superior performance of nanostructure as a chemical sensor as an example. For the nanostructures which are functionalized with catalytic particles this appears to be an oversimplified picture. The sensing effect of such 1-D metal oxide chemiresistor or chemi-FET can have completely different origins like spillover effect from catalyst particles, gas induced barrier modulations of the local electroactive element (nanoparticles, defects etc)or transient

processes in the gate oxide. To explore the relative importance of these phenomena on catalytic and sensing performance of 1D nanostructures, adsorbate specific, microscopic techniques have to be developed. We have tested a range of imaging techniques to address local transport behavior in the working metal oxide nanostructure wired as chemiresitor and chemi-FET. In particular, we have developed the experimental techniques and preparative protocols for implementation of synchrotron radiation based spectro-microscopies (SPEM and X-PEEM) to individual 1D nanostructures. Using X-PEEM in NEXAFS mode we demonstrated the ability to reveal submicron lateral compositional and electronic (work function) inhomogeneouties in individual nanowire. We were also complemented our results with Scanning Impedance Microscopy (SIM) and Scanning Surface Potential Microscopy (SPPM) to acquire ac and dc potential distributions in an operating nanowire device. These results open new avenue to visualize the adsorption /desorption phenomena on the surfaces of the individual nanostructure both in real time and at nano- and mesoscopic level.

Electronic Materials and Processing
Room 309 - Session EM1-ThA

Organic and Molecular Optoelectronics

Moderator: A.V. Walker, Washington University in St. Louis

2:00pm **EM1-ThA1 Quantum Dot Light Emitting Devices for Pixelated Full Color Displays***, **V. Bulovic,*** MIT **INVITED**

Quantum Dot Light Emitting Devices (QD-LEDs) developed over the past three years demonstrate high external quantum efficiencies, saturated visible color emission, narrow-band infra-red emission, and a scalable fabrication technique. This recent development is a result of advancements in the chemistry of colloidal quantum dot synthesis and demonstrations of new fabrication methods for generating thin films of QDs. The talk will present the recent technical and physical highlights, and chart the way to the next generation of the QD-LED technology.

2:40pm **EM1-ThA3 Organometallic Approaches to Achieving High Efficiency Monochromatic and White Electroluminescence from OLEDs***, **M.E. Thompson,*** University of Southern California **INVITED**

There has been a great deal of interest in developing new materials for the fabrication of light emitting diodes, built from molecular and polymeric materials. A significant motivation for this work has been their potential for use in future flat panel displays. Our work has been focused on developing new emissive and charge transporting materials for these devices. Our materials have led to marked improvements in the efficiencies of these devices. In particular, we have efficiencies for LEDs close to 100%, by using phosphorescence based emitters. The phosphorescent dopants in these devices are heavy metal containing complexes (i.e. Pt, and Ir compounds). I will discuss the basic mechanism of electroluminescence in OLEDs, and then elaborate on the use of phosphorescent complexes to achieve high EL efficiencies in monochromatic OLEDs. In the discussion of electrophosphorescence I will highlight specifically how we tune emission color in both Pt and Ir based emitters by careful design of both the metal complexes and ligands. We have also demonstrated white light emitting OLEDs, using many of the same emissive materials. These devices emit simultaneously from monomer and dimer/aggregate states of Ir and Pt dopants. The result is an emission spectrum that covers the entire visible spectrum, giving true white illumination. We have recently prepared binuclear Pt complexes and can show that the low energy emissive species in the white OLEDs is most likely a ground state dimmer or aggregate. This aggregate state undergoes a structural change in the excited state, similar to an excimer. I will discuss the mechanism of electroluminescence in this system and describe our recent advances in achieving high efficiency white electroluminescence.

3:20pm **EM1-ThA5 Chemical Vapor Deposition of Thin Films of Electrically Conducting PEDOT***, **J.P. Lock**, J.L. Lutkenhaus, N.S. Zacharia, P.T. Hammond, K.K. Gleason,* MIT

Chemical vapor deposition (CVD) technology, vital to the fabrication of traditional semiconductor devices, is also desirable for next-generation organic devices, particularly for creating layers which are difficult to process by solution methods or for coating substrates which can not tolerate exposure to solvents. In this work, a CVD process has been demonstrated for the deposition of conducting poly-3,4-ethylenedioxythiophene (PEDOT). This CVD process eliminates the need for polystyrene sulfonate (PSS), which is used to disperse PEDOT in water, but has been identified as a possible source of corrosion in OLEDs leading to shortened device lifetimes. The CVD PEDOT films range from 50 nm to several microns in thickness. Fourier transform infrared spectroscopy confirms the similarity in chemical structure of PEDOT synthesized by CVD and solution techniques. An electrical conductivity as high as 4.37 S/cm has been achieved. The CVD process utilizes a modest stage temperature and results in conformal coatings of high surface area features like fibers and pores. This combination of characteristics has allowed PEDOT deposition onto paper and fabrics to be demonstrated. Conformal coating of microporous or fibrous materials by CVD PEDOT has the potential to lead to better efficiencies in organic devices with high effective surface areas including photovoltaics. Reversible electrochromic responses of CVD PEDOT have been observed as well. The light blue films in their as-deposited state turn darker blue upon electrochemical reduction. The maximum contrast to date is 16.5% with a switching speed of 27 msec for a film having a thickness of 50 nm.

3:40pm **EM1-ThA6 Molecular Level Alignment and the Role of the Charge Neutrality Level at Organic-Organic Heterojunctions***, **W. Zhao,*** Princeton University*; H. Vazquez, F. Flores,* Universidad Autonoma de Madrid, Spain*; A. Kahn,* Princeton University

The electronic structure of organic-organic (OO) interfaces is a key aspect of organic devices such as OLEDs and PV cells. Molecular level offsets at OO interfaces determine transport across devices, and directly affect their performance. This talk reports a recent investigation of the electronic structure of several OO interfaces between films of molecules such as tris(8-hydroxy-quinoline)aluminum (Alq@sub 3@), 1,4,5,8-naphthalenetetracarboxylicdianhydride (NTCDA), iridium-bis(4,6,-di-fluorophenyl-pyridinato-N,C@super 2@)-picolinate (FIrpic) or copper phthalocyanine (CuPc). The filled and empty states of these materials, their ionization energy (IE) and electron affinity (EA), and the interface molecular level alignment are determined via ultra-violet and inverse photoemission spectroscopy (UPS, IPES). Unlike many previously investigated OO heterojunctions,@footnote 1@ these are found not to follow vacuum level alignment and exhibit significant interface dipoles ranging from 0.2 to 0.5 eV. The analysis of these and previous results on OO heterojunctions is performed using the extension of the concept of charge neutrality level (CNL), developed for metal/organic interfaces,@footnote 2@ to the OO heterojunction.@footnote 3@ The energy-level alignment is driven by the alignment of the CNLs of the two organic semiconductors. The initial offset between the CNLs gives rise to a charge transfer across the interface, which induces an interface dipole and tends to align the CNLs. The initial CNL difference is reduced according to the screening factor S, a quantity related to the dielectric functions of the organic materials. Good quantitative agreement with experiment is found. This allows, for the first time, a semi-quantitative prediction of the electronic structure of OO heterojunctions. @FootnoteText@ @footnote 1@ I.G. Hill et al., Appl. Surf. Sci. 166, 354 (2000); @footnote 2@ H. Vazquez et al. EuroPhysics Lett. 65, 802 (2004); @footnote 3@ H. Vazquez et al. Phys. Rev B Rapid Comm. 71, 041306 (2005).

4:00pm **EM1-ThA7 New Device Functionalities and Materials***, **N. Tessler,*** Technion, Israel Institute of Technology **INVITED**

For certain device applications, semiconducting polymers can replace inorganic semiconductors at lower cost because they are more easily processed. Examples include the development of organic light emitting diodes (OLEDs), for full color screen applications, and of the development of field effect transistors (FETs) for smart circuit applications. These device applications make use of the semiconducting nature of conjugated polymer. However, by accounting for the organic (molecular) nature of these materials one can extend the material and device functionalities. In this contribution we highlight two approaches: a) the use of nano-composites b) the use of bio-inspired chemical modifications to produce libraries of functional materials. We will also address device properties and suitable methods for analysis.

4:40pm **EM1-ThA9 Photoelectron Spectroscopy of Phenylene Ethynylene versus Phenylene Vinylene Oligomers: a Search for Bond Alternation Effects***, **L.B. Picraux**, C.D. Zangmeister, S.W. Robey, R.D. van Zee,* NIST

Interest in factors controlling transport through conjugated molecular systems has lead to a significant experimental effort investigating conductivity in various configurations of metal-molecule junctions. One interesting result of these efforts was an investigation of the relative conductivity in junctions formed using crossed wire techniques containing phenylene ethynylene (OPE) or phenylene vinylene (OPV) oligomers. Vinylene-based oligomers were found to exhibit higher conductivity, a result that was attributed to an increased bandgap in phenylene ethynylene systems due to the larger impact of bond alternation effects in the triple bond containing system. We have used photoelectron spectroscopy to investigate the @pi@ electronic structure of these two systems, namely three-ring phenylene ethynylene oligomers with thiol bound to gold and the analogous three-ring OPV system, which were the compounds employed in the crossed-wire investigations. Spectra for the two oligomers are quite similar but the @pi@ levels in the OPV variant are approximately 0.2 eV closer to the Fermi level than in OPE, possibly consistent with the higher conductivity measured in crossed-wire junctions.@footnote 1@ While this could be construed as being consistent with a narrowing of the band gap in the OPV system, it appears to arise from a rigid shift of the levels. There is no evidence of increased dispersion within the @pi@ manifold as expected if reduced bond alternation were the cause. Finally, we will also discuss the potential impact of the self-assembled monolayer structure on transport measurements.

@FootnoteText@@footnote 1@Kushmerick JG, Hold DB, Pollack SK, et al., J. Am. Chem. Soc. 124(36): 10654-10655 2002.

5:00pm **EM1-ThA10 Monomolecular Insulator Film*, Y. Tai, H. Noda, A. Shaporenko, M. Grunze, M. Zharnikov,*** Universität Heidelberg, Germany

Progress in fabricating smaller and more efficient structures in electronic and spintronic devices depends on better dielectric materials for nanofabrication. A perspective nanoinsulator is a molecular thin organic film - self-assembled monolayer (SAM), which provide an alternative to commonly used oxide dielectrics such as e.g. SiO@sub 2@ or Al@sub 2@O@sub 3@. A so far unresolved technological problem for applications of SAMs in microelectronics and spintronics is the difficulty of fabricating stable metal layers on their surfaces, i.e. at the SAM-ambient interface. Such a film is generally leaky for metal adsorbates, which makes it impossible to integrate it into a multilayer assembly (e.g. in a tunnel junction magnetic memory cell) or to fabricate metal electrodes on its surface (e.g. in an organic thin film transistor). Using nickel as a test metal adsorbate and several different substituted and non-substituted SAMs as test substrates, we show that this difficulty can be overcome by the combination of a special design of the SAM constituents and their extensive cross-linking by low-energy electron irradiation. The properties of the SAM insulator and the metal overlayer were monitored by several complementary experimental techniques, including X-ray absorption spectroscopy and electrochemical measurements. The approach represents an important step toward the technological applications of monomolecular dielectric layers.

Electronic Materials and Processing
Room 310 - Session EM2-ThA
Dilute Nitrides and Small Bandgap Semiconductors

Moderator: R. Ahrenkiel, University of Denver

2:00pm **EM2-ThA1 Narrow Band Gap Group III-Nitrides*, W. Walukiewicz,*** Lawrence Berkeley National Laboratory **INVITED**

Incorporation of small amounts of N into group III-V semiconductors leads to a dramatic reduction of the band gap of resulting IIIN@sub x@V@sub 1-x@ alloys. This effect can be well described by the Band Anticrossing (BAC) model that considers the interaction between localized states of N and the extended conduction band states. The interaction splits the conduction band into two nonparabolic bands, resulting in large changes in the electrical and optical properties of these materials. The BAC model provides a consistent and quantitative description of experimentally observed data including the large band gap bowing, splitting of the conduction band, and increase of the electron effective mass. Comprehensive studies of the electronic structure and electrical and optical properties of InN and In-rich In@sub 1-x@Ga@sub x@N alloys will also be discussed. In addition to having a narrow gap (0.7 eV), InN also has an extremely high electron affinity of 5.8 eV, placing the conduction band edge of this material 0.9 eV below the average energy of dangling bond defects (Fermi level stabilization energy, E@sub FS@). This unusual band alignment has profound consequences for the behavior of dopants and defects and explains the extreme proclivity of InN and In-rich group III-nitride alloys for n-type conduction. As grown, undoped InN is always n-type with electron concentrations ranging from mid 10@super 17@ cm@super -3@ to as high as 10@super 21@ cm@super -3@. We show that similar range of electron concentrations can be achieved by irradiation of thin InN films with 2 MeV He@super +@ ions.

3:00pm **EM2-ThA4 Electronic Properties of GaAsN Quantum Wells*, S. Turcotte*,** *N. Shtinkov, J.-N. Beaudry,* École Polytechnique de Montréal, Canada*; G. Bentoumi,* Université de Montréal, Canada*; R.A. Masut,* École Polytechnique de Montréal, Canada*; R. Leonelli,* Université de Montréal, Canada*; P. Desjardins,* École Polytechnique de Montréal, Canada

Dilute semiconductor nitrides heterostructures are very promising for a variety of device applications including lasers and photovoltaic cells. The optimization of such devices relies on the understanding of the fundamental electronic properties of quantum well structures. Among these, optical transitions, quantum confinement, and band offsets need to be clarified. Using a combination of techniques including optical absorption and photoluminescence, we have studied GaAs@sub 1-x@N@sub x@ quantum wells in GaAs(001). Two series of samples grown by MOCVD were investigated. The first consists of 7-period, 10-nm-thick GaAs@sub 1-x@N@sub x@ multiple quantum wells (MQW) with x ranging from 0.001 to 0.02 as determined from high-resolution x-ray diffraction. A series of single quantum wells (SQW) was also fabricated to investigate the effect of well thickness, from 2.8 to 11.3 nm, for a nominal N content of x=0.01. The low-temperature (near 5K) PL spectra of the MQWs are characterized by a 10-20 meV wide emission peak at an energy decreasing from 1.5 eV to 1.3 eV with increasing N content. Annealing at 700°C for 2 min. resulted in more intense PL emission with negligible change in energy. Electronic structure calculations are carried out using a tight-binding model.@footnote 1,2@ We obtain an excellent agreement between experimental and numerical results for the case corresponding to perfectly aligned GaAs and GaAsN valence bands. The absorption edge measured at 6 K for the SQWs structures decreases from 1.45 to 1.35 eV with increasing thickness. By fitting these results to the tight-binding calculations, we deduce an electronic confinement of the order of 55 meV and 125 meV for the thickest and thinnest layers, respectively. @FootnoteText@ @footnote 1@ N. Shtinkov, P. Desjardins, and R. A. Masut, Phys. Rev. B 67, 081202(R) (2003)@footnote 2@ N. Shtinkov, S. Turcotte, J.-N. Beaudry, P. Desjardins, and R. A. Masut, J. Vac. Sci. Technol. A 22, 1606 (2004)

3:20pm **EM2-ThA5 High-Performance, Lattice-Mismatched GaInAs*, M.W. Wanlass,*** National Renewable Energy Laboratory **INVITED**

GaInAs is a pseudobinary III-V compound semiconductor that has a direct bandgap, and full miscibility, over its entire composition range. The room-temperature bandgap varies significantly, from 0.36 eV (InAs) to 1.42 eV (GaAs), between the binary endpoints. The above characteristics make GainAs particularly well suited to photovoltaic (PV) energy converter applications that require infrared-responsive components. Arbitrary bandgaps within the available range are achieved by considering epitaxial, lattice-mismatched (LMM) heterostructures grown on commercially available crystalline substrates (e.g., Ge, GaAs, and InP). We discuss structural approaches involving compositional grading that yield LMM materials with excellent minority-carrier parameters. A variety of characterization techniques are used to elucidate the microstructural and electronic properties. Specific PV device applications and results are also presented.

4:00pm **EM2-ThA7 Comparison of a Dominant Electron Trap in n-Type and p-Type GaNAs Using Deep-Level Transient Spectroscopy*, S.W. Johnston,*** *S.R. Kurtz,* National Renewable Energy Laboratory

Both p-type and n-type dilute-nitrogen GaNAs epitaxial layers grown by metal-organic chemical vapor deposition were characterized by deep-level transient spectroscopy (DLTS). For each case, the dominant DLTS signal corresponds to an electron trap having an activation energy of about 0.2 to 0.3 eV for p-type GaNAs and about 0.3 to 0.4 eV for n-type GaNAs. In p-type GaNAs, the electron traps fill slowly, as the DLTS signal reaches saturation using zero-bias filling pulses with widths on the order of 1 to 10 seconds. When applying a large range of filling-pulse widths, the activation energy tends to decrease from about 0.3 eV for short filling pulses to about 0.2 eV for longer filling pulses. In n-type GaNAs, the electron trap activation energy also tends to slightly decrease with increasing filling-pulse widths. For short pulse widths of microseconds to milliseconds, the activation energy is just below 0.4 eV, and for long pulse widths of seconds, the activation energy is just above 0.3 eV. The electron traps fill quickly in the n-type GaNAs, as the DLTS signal approaches saturation in microseconds. The capture cross-sections determined by the DLTS Arrhenius plots are typically about 10@super -13@ to 10@super -12@ cm@super 2@. The electron-trap densities range from 10@super 15@ to 10@super 16@ cm@super -3@ in mid-10@super 17@ cm@super -3@ n-type-doped GaNAs having a bandgap of 1.35 to 1.4 eV. These trap parameters give an estimated carrier lifetime of 1 ns or substantially shorter.

Thin Films
Room 306 - Session TF+EM-ThA
Transparent Conducting Oxides

Moderator: S. Gupta, The University of Alabama

2:00pm **TF+EM-ThA1 Transparent Conducting Oxides*, J.C.C. Fan,*** Kopin Corporation **INVITED**

Transparent Conducting Oxides (TCO) have enormous practical applications in energy-conserving heat mirrors, in solar-energy collectors, solar photovolactic and in electronic devices such as liquid crystal displays and light-emitting diodes. These oxides which are transparent in the visible spectrum are yet electrically conducting have been around for many decades. The most popular ones are In2O3-doped with Sn, and SnO2-doped with Sb. These two classes of TCOs have been extensively

researched for many years and their results and applications will be reviewed. In addition, there are newer TCOs in the fields, such as MoO3, ZnO, and others. Their status and potential will also be discussed.

3:00pm **TF+EM-ThA4 Study on Initial Growth Process of Transparent Conductive Oxide Films Deposited by dc Magnetron Sputtering***, **Y. Sato,** M. Taketomo, A. Miyamura, Y. Shigesato,* Aoyama Gakuin University, Japan

It has been noticed that surface defects such as spike or pinhole of transparent conductive oxide (TCO) films should cause the degradation on the performance of organic organic light emitting diode (OLED) displays as appearances of dark-spots. In order to improve their performances, the film surface morphology has been required to be extremely flat. Such surface morphology should be highly related to the initial growth processes of the thin film electrodes. In this study, we investigated the early stages of film growth of representative TCO films such as ITO (Tin doped Indium oxide), IZO (Indium Zinc oxide) and GZO (Gallium doped Zinc oxide) deposited by sputtering. These films with thickness of 5-200 nm were deposited on unheated non-alkali glass substrates by dc magnetron sputtering under a various total gas pressures of Ar/O@sub 2@ mixture gases. The surface morphology of the films was analyzed quantitatively by atomic force microscope (AFM). The average roughness (Ra) of ITO and GZO films with the nominal thickness of 5 nm, deposited under 1.0 Pa, reached maximum of 0.4 and 0.8 nm, respectively. Ra of the both films decreased and remained constant around 0.2 and 0.4 nm, respectively, with the farther increase in thickness larger than 25 nm. These trends implied that three dimensional (Volmer-Weber) growth occurs for the polycrystalline ITO or GZO films, i.e. after an initial nucleation, an island structure grew and coalesced with each other with increasing film thickness. This expectation is consistent with the electrical properties of these films. On the other hand, Ra for the amorphous IZO film remained constant with the increasing nominal thickness from 5 to 200 nm. It must be considered that a nucleation density of IZO film should be much higher than those of ITO or GZO films. This work was partially supported by a Grant-in-Aid for 21st COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

3:20pm **TF+EM-ThA5 Transparent Conducting Oxide Deposition using Closed Field Reactive Magnetron Sputtering***, **J.M. Walls,** D.R. Gibson, I. Brinkley, E.M. Waddell,* Applied Multilayers Ltd, UK

Magnetron Sputtering has many advantages for the deposition of optical coating materials. The sputtering process is "cold", making it suitable for use on the widest range of substrates including damage sensitive polymers. This paper will describe a "Closed Field" reactive sputtering process that allows high quality, transparent conducting oxide (TCO) thin films to be deposited at high rates. In contrast to previous reactive dc sputtering strategies the Closed Field process does not require a separate energetic ion or plasma source. The Closed Field automatically creates a magnetic confinement that extends electron mean free paths and leads to high ion current densities (>1mA.cm@super -2@). The combination of high current densities with ion energies in the range 15eV to 30eV creates optimum thin film growth conditions. As a result the films are dense, spectrally stable and exceptionally smooth (rms roughness

3:40pm **TF+EM-ThA6 Effect of Dendrimer Underlayers on Sputtered Indium-Tin Oxide Thin Film Microstructure, Morphology, Optical and Electrical Properties***, **R. Thunuguntla,** S. Gupta, S. Street,* The University of Alabama*; D. Loy,* The Army/ASUFlexible Display Center

Minimization of surface roughness is extremely important for sputtered indium-tin oxide (ITO) films used for organic light-emitting diode (OLED) applications. One of the techniques used to achieve smooth ITO films is the optimization of process parameters together with injection of cesium vapor into the plasma -- the recently-introduced negative sputter ion beam or NSIB process.@footnote 1@ We have investigated an alternative simpler approach -- the application of dendrimer monolayers by dip- or spin-coating techniques prior to ITO sputter deposition at ambient temperatures. The ITO films have been characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), and the film microstructure and morphology have been correlated with the optical and electronic properties such as transmission, resistivity, mobility and carrier concentration. The presence of the dendrimer underlayer appears to mediate the film roughness by grain size reduction and improved adhesion. The greatest effect is seen in films sputtered at low powers. This is expected, since a high level of ion bombardment is expected to damage or destroy the dendrimer underlayer. The observed improvement is most encouraging for flexible display applications, where good film properties and low surface roughness are required at low deposition temperatures. @FootnoteText@ @footnote 1@ M. H. Sohn et al., J. Vac. Sci. Technol. A21(4), 1347 (2003).

4:00pm **TF+EM-ThA7 Ferromagnetic Behavior in Indium Oxide Based Transparent Semiconductors***, **J. Moodera,*** Massachusetts Institute of Technology **INVITED**

Ferromagnetic semiconductors are expected to provide smooth transition for spin injection and transport needed for spin based technology leading to multifunctional devices of the future. Although the field of dilute magnetic semiconductors has been explored for a long time, in recent years there is increased activity due to the significant increase in the ferromagnetic ordering temperature (T@sub c@) of Ga@sub 1-x@Mn@sub x@As system and in various doped oxide systems, despite the existing skepticism in the latter area. We have observed ferromagnetism well above room temperature in Mn doped indium-tin oxide (ITO), Cr doped indium oxide (IO) as well as Mn doped zinc oxide films by reactive evaporation as well as sputtering. Films grown on sapphire (0001) and on silicon show excellent magnetic behavior with a moment ranging from 1 to 5µ@sub B@ for low concentrations of the dopant. Mn doped ITO and Cr doped IO are highly transparent as well as conducting. The electrical conduction is n-type with a carrier concentration in the range of 10@super 18@ to 10@super 20@ cm@super -3@. The charge carriers are seen to be spin polarized shown by the presence of anomalous Hall effect, revealing the magnetic interaction between itinerant electrons and localized Mn or Cr spins. What is interesting in these compounds is that the charge carriers can be independently varied independent of the dopant by the oxygen or the tin concentration in this transparent semiconductor for its easy integration into magneto-optoelectronic devices. In this talk the status of the field will be reviewed and compared with our work. Work carried out in collaboration with John Philip and Nikoleta Theodoropoulou. Supported by the CMI funds at MIT and NSF funds.

Electronic Materials and Processing
Room 309 - Session EM-FrM

Organic Electronic Devices

Moderator: A. Kahn, Princeton University

8:20am **EM-FrM1 Charge Transport in Amorphous Organic Semiconductors : Can We Describe a Wide Variety of Devices by a Single Model?*, Y. Roichman,*** Princeton University **INVITED**

During the last years we witnessed an improvement of organic electronic devices and emergence of new devices, as a homogenous PN junction. At the same time the theory of charge transport in organic semiconductors was reexamined, with an emphasis on application to devices realistic operation condition. In this talk I will review the recent experimental evidences and advances in theory of charge transport in amorphous organic semiconductors. I will demonstrate that taking into account non-linear effects and a reasonable shape density of states the electronic behavior different devices (PN homogenous diode, PV cell and FET) that operate at different conditions can be explained by a single theoretical model. The differences between the major theoretical approaches will be briefly discussed as well.

9:00am **EM-FrM3 Physical Mechanisms in Programmable Nanoscale Organic Nonvolatile Memory Devices*, T. Graves-Abe,*** *J.C. Sturm,* Princeton University

Great interest in novel, low-cost memory technologies has led to the development of a number of promising approaches based on organic thin films.@footnote 1@ We have recently reported memory devices based on 10-nm self-assembled films of 11-mercaptoundecanoic acid (MUA) sandwiched between gold electrodes.@footnote 2@ Devices can be placed into a high-conductance "ON" state by 3- to 4-V pulses and returned to a low-conductance "OFF" state with higher-voltage pulses. Devices have a number of desirable characteristics, including durability (more than 10@super 4@ write/erase cycles without degrading), nonvolatile memory states, fast programming times (<@micro@s), and large current densities (up to 10@super 5@ A/cm@super 2@ at 1 V) to minimize resistance-capacitance delays in large memory arrays for fast access times. Models based on charge-trapping or conducting-path formation have been proposed to describe similar results in other thin films,@footnote 3@ although in practice it is difficult to distinguish between the models. In this work, we report strong evidence that the programmable conductance of our devices is due to the formation and destruction of conductive paths. This evidence includes: i) the presence of multiple step-like increases in current during the transition from OFF to ON states, which are attributed to the formation of a small number (<10) of conducting paths leading to the ON state, ii) the exponential reduction in the time required to form these conductive paths with increased electric field, consistent with the field-assisted diffusion of metal ions into the organic layer to form the paths, iii) the dependence of electrical characteristics on choice of electrode material, and iv) the extremely thin nature of the films. @FootnoteText@ @footnote 1@ Y. Yang et al, MRS Bull. 29, 833 (2004).@footnote 2@ T. Graves-Abe and J. C. Sturm, Mat. Res. Soc. Symp. San Fran., CA, April 2005.@footnote 3@ G. Dearnaley et al, Rep. Prog. Phys. 33, 1129 (1970).

9:20am **EM-FrM4 Effect of Poly (3-hexylthiophene) Film Thickness on Organic Thin Film Transistor Properties*, H. Jia,*** *S Gowrisanker, G.K. Pant, R.M. Wallace, B.E. Gnade,* University of Texas at Dallas

We present the effect of poly (3-hexylthiophene) thickness on the performance of OTFTs. When the poly (3-hexylthiophen) film thickness varies from 3.8nm to 23.8nm, the drain current and the saturation mobility increase with the thickness because of the higher channel conductance. In contrast, the on/off ratio decreases with P3HT film thickness, primarily because of the higher off current. Gate leakage also becomes higher when the film thickness increases, also contributing to a lower on/off ratio. The threshold voltage is more sensitive to dielectric surface treatment than to the thickness of P3HT film thickness. The mobility increases and then saturates with gate voltage. For devices from thick P3HT films, increasing gate voltage further after saturation decreases the mobility. Short channel effects are observed for channel lengths of @<=@ 5 µm. We also present the channel length dependence of threshold voltage and mobility. The drive current, on/off ratio, and mobility of P3HT devices should be optimized based on the specific application. @Footnote Text@@footnote 1@ Jiyoul Lee, Kibum Kim, Jae Hoon Kim, Seongil Im, Duk-Young Jung, Appl. Phys. Lett. 82, 4169 (2003) @footnote 2@ Satoshi Hoshino, Toshihide Kamata, and Kiyoshi Yase, J. Appl. Phys. 6028 (2002) @footnote 3@ R. Schroeder, L. A. Majewski, and M. Grell, Appl. Phys. Lett. 83, 3201 (2003) @footnote 4@ Manabu Kiguchi, Manabu Nakayama, Kohei Fujiwara, Keiji Ueno, Toshihiro Shimada and Koichiro Saiki, Jpn. J. Appl. Phys. 42, L1408(2003)

9:40am **EM-FrM5 Vapor and Solution Deposited Organic Thin Film Semiconductor Transistors*, T.N. Jackson,*** Penn State University **INVITED**

Organic thin film transistor (OTFT) device performance now rivals or exceeds that of a-Si:H devices, and low OTFT process temperatures allow fabrication on a range of surfaces including cloth, paper, or polymeric substrates. However, it is still unclear whether OTFTs will find significant commercial application. To do so, OTFTs must demonstrate characteristics that differentiate them from other device technologies, especially a-Si:H TFTs. Potential advantages for OTFTs include the possibility of device and system fabrication on substrates not readily accessible to a-Si:H devices and also reduced cost manufacturing. For practical device and system use, OTFTs must demonstrate the uniformity, reproducibility, reliability, and integration with other devices, needed for realistic applications. As a candidate application we have considered the integration of vapor-deposited OTFTs with organic light emitting diodes (OLEDs). Working with Kodak we have fabricated small test displays that allow us to investigate device characteristics and passivation and isolation requirements for integrating these organic devices. Solution-deposited organic semiconductors may offer important advantages for low-cost processing. However, solution processed semiconductors typically lack the molecular-level order which may be important for good carrier transport and large field-effect transistor mobility. Working with J. Anthony (University of Kentucky) we have investigated functionalized pentacenes and pentacene derivatives. These materials use bulky molecular side groups to control molecular packing and allow solubility in a range of common solvents. Surprisingly, solution-deposited films of some of these materials show good molecular ordering and using these materials we have been able to fabricate OTFTs with mobility > 1.5 cm@super 2@/V-s.

10:20am **EM-FrM7 Optical and Electrical Properties of a New N-type Semiconductor: N, N@super '@-bis (3-phenoxy-3-phenoxy-phenoxy)-1,4,5,8-naphthalenetetracarboxylic diimide*, D.X. Yang,*** *R.P. Shrestha,* University of North Carolina-Chapel Hill*; T.J. Dingemans,* Delft University of Technology, The Netherlands*; E.T. Samulski, E.A. Irene,* University of North Carolina-Chapel Hill

Optical properties of N, N@super '@-bis (3-phenoxy-3-phenoxy-phenoxy)-1,4,5,8-naphthalenetetracarboxylic diimide (NDA-n2) thin film, a N-type organic semiconductor, were investigated using optical transmission and spectroscopic ellipsometry (SE) in the visible-near uv optical range. The dispersion in refractive index and extinction coefficient along with anisotropy, surface roughness and annealing results are reported. An oscillator model with one Tauc-Lorzentzian oscillator and four Gaussian oscillators was proposed to describe the dielectric function of NDA-n2. Vacuum annealing of the thin film was performed and monitored using in-situ SE. The films we stable up to 150 °C and no optical anisotropy was found for the films. Capacitance versus voltage (C-V) and current versus voltage (I-V) measurements were performed on capacitor and thin film transistor (TFT) structures, respectively. The C-V results indicate a value of about 3.4 for the static dielectric constant. The I-V yields TFT transfer characteristics that are used to optimize the film formation process and device performance of the thin film semiconductor for TFT@super '@s. The mobility of NDA-n2 was obtained from I-V results in a TFT structure.

10:40am **EM-FrM8 Growth and Chemical Structure of Crystalline Rubrene Films*, G. Witte,*** *D. Kaefer, Ch. Woell,* Ruhr-University Bochum, Germany

Rubrene single crystals have recently been demonstrated to exhibit remarkably high charge carrier mobilities@footnote 1@ which favors the use of this organic semiconductor material for molecular electronics applications e.g. organic field effect transistors. In contrast to other oligomer semiconductors such as pentacene the growth of crystalline thin films, however, has not been achieved for rubrene. Using x-ray absorption spectroscopy (NEXAFS) we have analyzed the initial stage of film growth on various substrates and demonstrate the importance of molecular conformation which involves a loss of chirality in case of rubrene. Whereas organic molecular beam deposition at room temperature only leads to rather amorphous layers, dendritic films are obtained at high substrate temperatures but the size of the crystallites is mainly limited by competing dewetting and desorption. An improved crystallite growth is achieved by using a modified "hot wall"-type deposition cell which allows operation

under UHV-conditions but at much higher vapor pressure. Moreover, by combining AFM and SEM with XPS and LDI-TOF mass spectroscopy the morphology of the films and the amount of rubrene-peroxide formed upon exposure to air was characterized. Large differences in the corresponding rubrene-peroxide concentrations and their depth profiles were found for the various films and crystals which is of great importance for applications in molecular electronics. @FootnoteText@@footnote 1@ V.C. Sundar et al. Science 303, 1644 (2004).

11:00am **EM-FrM9 Pentacene Wetting Layer Formation on SiO@sub 2@ Substrate***, C. Kim,* ***D. Jeon****,* Seoul National University, South Korea

We have applied in-situ ellipsometry to study the growth of pentacene film on the SiO@sub 2@ surface. As soon as the evaporation began, the intensity of ellipsometry spectrum decreased. Atomic force microscopy (AFM) images of the early stage of growth, however, did not show any pentacene-related morphology. The pentacene islands in the first layer appeared after a continued deposition. The immediate change of ellipsometry spectrum with the onset of deposition indicates that pentacene molecules accumulate on the SiO@sub 2@ surface from the beginning. However, the flat AFM image of the early stage indicates that pentacene initially forms an amorphous wetting layer before crystalline islands appear. The roughness of the SiO@sub 2@ surface decreased with the pentacene deposition, which is another indication of the amorphous wetting layer. Pentacene is known to form a wetting layer on a clean metal or semiconductor substrate. In other words, pentacene reacts with the surface before a crystalline film forms. Our result shows that pentacene forms a wetting layer on an inert substrate as well. The existence of an amorphous layer on an insulating substrate should affect the performance of the pentacene devices. To show this we will also present the result from the electrostatic force microscopy of the pentacene film. This work was supported by the Nano Systems Institute at Seoul National University.

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