Electronic Materials and Devices
Room: C-107 - Session EL+SC+MI-MoM

Semiconductors
Moderator: A. Rockett, University of Illinois

9:00am **EL+SC+MI-MoM3 Low-temperature Epitaxial Growth of the Wide Bandgap Semiconductor SiCAlN**, ***I.S.T. Tsong***, Arizona State University **INVITED**

Two compounds, SiC and AlN, normally insoluble in each other below 2000C, are synthesized as a single-phase solid solution thin film by molecular beam epitaxy (MBE) at 750C using a unimolecular precursor H3SiCN and Al atoms. The growth of epitaxial SiCAlN films with hexagonal structure takes place on 6H-SiC(0001) and Si(111) substrates. The surface morphology, microstructure, and composition of the films are analyzed by atomic force microscopy (AFM), cross-sectional transmission electron microscopy (XTEM), Rutherford backscattering spectrometry (RBS) and high-resolution electron energy loss spectroscopy (EELS). Two structural models for the hexagonal SiCAlN films are constructed based on first-principles total-energy density functional theory calculations, each showing agreement with experimental XTEM observations. The predicted fundamental bandgap is 3.2 eV for the stoichiometric SiCAlN, in good agreement with photoluminescence (PL) measurements. Bandgap engineering is a distinct possibility by varying the composition of the pseudo-binary (SiC)-(AlN) film.

9:40am **EL+SC+MI-MoM5 Evolution of Structure and Optical Properties of GaAsN Films Grown by Reactive Molecular Beam Epitaxy**, ***M.J. Reason***, *W. Ye, X. Weng, V. Rotberg, R.S. Goldman*, University of Michigan

Narrow gap nitride semiconductor alloys have shown significant promise for a wide range of electronic, optoelectronic and photovoltaic applications. At present, the ultimate limit of nitrogen solubility in GaAs, as well as the effects of growth conditions on stress relaxation and optical properties of narrow gap nitride films are not well understood. In this work, we have examined the evolution of nitrogen incorporation, strain relaxation, and optical properties of GaAsN films grown by solid-source molecular beam epitaxy using an N2-rf plasma source. The samples consisted of 500 nm buffer layers of GaAs grown at 580C and 20 nm layers of GaAs grown at 500C, both using a high arsenic flux; followed by 100-500 nm thick layers of GaAsN grown at 400C using a 10% N2/Ar gas mixture at a 0.15 sccm flow rate, with a variety of arsenic beam equivalent pressures (BEP). The structure and properties of the samples were investigated by reflection high energy electron diffraction (RHEED), multi-beam optical stress sensing (MOSS), high resolution x-ray rocking curves (XRC), nuclear reaction analysis (NRA), atomic force microscopy, and photoluminescence. For all of the arsenic fluxes studied, in-situ RHEED during the GaAsN layer growth reveals a pattern similar to that observed during the growth of the GaAs layers. As the arsenic BEP is increased, MOSS shows that the film stress decreases, indicating a lowering of the apparent nitrogen incorporation into GaAsN. Interestingly, variations in the absolute nitrogen concentrations determined from NRA analysis and a Vegard's law interpretation of XRC suggest significant nitrogen incorporation into interstitial sites. We will discuss the effects of arsenic flux on the stress relaxation and optical properties of a variety of GaAsN and InGaAsN films and heterostructures.

This work was supported in part by the DOE (Photovoltaics Beyond the Horizon Program), the Air Force Office of Scientific Research (MURI Program), and the TRW Foundation.

10:00am **EL+SC+MI-MoM6 Effects of LED Processing Steps on the Surface of Doped GaN Epilayers**, ***K.H.A. Bogart***, *D.D. Koleske, A.A. Allerman, A.J. Fischer, K.W. Fullmer, K.C. Cross, C.C. Mitchell*, Sandia National Laboratories

Gallium nitride (GaN)-based materials are critical for the creation of UV optoelectronic devices such as light-emitting diodes (LEDs). Ohmic contacts with low contact resistivities to p-type ($<1x10^{-3}\Omega cm^2$) and n-type ($<1x10^{-5}\Omega cm^2$) GaN are essential for improving optical device performance. Understanding the characteristics of p- and n-type GaN epitaxial layer surfaces and the interfaces formed with the contact metals is vital for optimization. Fabrication of an LED requires several processing steps including dicing, annealing, surface cleans (to remove native oxides), lithography, metal deposition, and plasma etching. The effects of processing steps on the surface morphology and electrical characteristics of the epitaxial materials and metal contacts have been investigated using scanning probe microscopies and the circular transmission line method (CTLM). One of the first LED processing steps is dicing a 50 mm wafer using photoresist for surface protection, which is later removed with solvents. For p-type GaN ($5x10^{17}cm^3$), AFM analysis showed that the surface roughness nearly doubled after photoresist exposure from an average of 0.24±0.05 nm to 0.50±0.10 nm. The source of the roughness increase was the formation of pits into the surface, ~1 nm in depth. In another LED processing step, n-type GaN is exposed by plasma etching a mesa structure into the p-type GaN overlayer. One half of a wafer with a 1.2µm n-type GaN ($1.7x10^{18}cm^3$) epitaxial film was plasma etched with chlorine-based chemistry. AFM analysis showed that the etched n-type GaN film (RMS=1.11±0.23nm) was not significantly more rough than non-etched n-type GaN film (RMS=1.70±0.59nm). However, after annealing ($500°C/N^2$), the plasma etched film had more Ohmic behavior by (CTLM) than did the non-etched film. More extensive experiments following the GaN epitaxial layers in processing will be presented and effects on contacts discussed.

10:20am **EL+SC+MI-MoM7 Hydrogen Removal Mechanisms from Gallium Nitride**, ***B.D. Thoms***, *Y. Yang, J. Lee*, Georgia State University **INVITED**

The reaction between hydrogen and GaN is important since hydrogen is often present (sometimes in abundance) during growth and processing and since it produces significant effects. For instance, the effect of hydrogen on the efficacy of Mg dopants has been widely reported and both annealing and electron exposures have been used to remove hydrogen. In addition, recombinative desorption of hydrogen is an important part of many dry etching processes. Removal of hydrogen requires both the transport of hydrogen to the surface and desorption from the surface. In this talk, the authors will discuss characterization of surface and subsurface hydrogen on GaN(0001) and its removal by annealing and by electron exposure.

11:00am **EL+SC+MI-MoM9 N-type Diamond Electronics With Nitrogen Doped Ultrananocrystalline Diamond**, ***J.E. Gerbi***, Argonne National Laboratory, *B.W. Alphenaar*, University of Louisville, *O. Auciello*, Argonne National Laboratory, *J. Birrell*, University of Illinois at Urbana-Champaign, *J.A. Carlisle, D.M. Gruen*, Argonne National Laboratory

Thin diamond films have extremely attractive properties for electronic device applications: high thermal conductivity, carrier mobility, and breakdown fields. However, efforts to create diamond based electronic devices have been hampered by the difficulty in incorporating dopants. Attempts to dope diamond films have resulted in low p-type carrier concentrations or unstable p-type surface layers. N-type doping has been even less successful, and it has not yet been possible to synthesize n-type diamond films with sufficiently high room-temperature conductivities. Ultra-nanocrystalline diamond (UNCD) is a fine-grained (3-5nm), phase-pure diamond material with atomically abrupt grain boundaries. Synthesized by microwave CVD using Ar-rich Ar/CH_4 plasmas, both the structure and electronic properties of UNCD can be tailored by doping with a controlled amount of N_2 in the plasma. As the N_2 content in the plasma increases to 20% , the grain size and grain boundary width of the UNCD films increase. This microstructural change correlates with a striking increase in room-temperature conductivity . Most importantly, nitrogen doped UNCD films are n-type with activation energies as low as 0.05 eV. This is striking, as traditional nitrogen substitutional doping of diamond produces a very deep state of 1.7eV, rendering the material useless for room-temperature applications. We use this material to demonstrate the first n-type diamond MESFET that can be operated at room temperature. We have characterized the films using Raman spectroscopy, NEXAFS, SIMS, Hall mobility measurements, and HRTEM, and measure device properties such as I-V curves and transconductance. The ohmic vs. Schottky behavior of various contacts to nitrogen doped UNCD as a function of growth chemistry has also been studied. A discussion of the microstructure-property relationship of nitrogen-doped UNCD films will be presented in the context of the UNCD-based MESFET performance.

11:20am **EL+SC+MI-MoM10 Electronic Structure and Spin-Polarization of Mn-containing Dilute Magnetic III-V Semiconductors**, ***L. Kronik***, *M. Jain, J.R. Chelikowsky*, University of Minnesota **INVITED**

The systematic use of electron spin, in addition to its charge, holds great promise for a new class of semiconductor devices with unprecedented functionality. Recently, Mn-containing, "dilute magnetic", III-V semiconductors have emerged as candidate materials for such a technology. They can potentially produce charge carriers with well-defined spin, yet are compatible with already existing semiconductor technologies. In order to assess the performance limits of such materials theoretically, we present first principles pseudopotential - density functional calculations for the electronic structure of the dilute magnetic semiconductors $Mn_xGa_{1-x}As$ and and $Mn_xGa_{1-x}N$, with an experimentally relevant realistic x=0.063, in their ordered ferromagnetic phase. We predict that both materials allow, in principle, for a theoretical limit of 100% spin-injection, and that spin-polarized transport can be attained in both materials in the context of a simple band picture. This is because in MnGaAs, hybridization of As 4p and Mn 3d orbitals splits the valence band, resulting in a ~0.5 eV energy range where holes have a well-defined spin and an effective mass comparable to that of GaAs. In MnGaN, the situation is even more favorable: hybridization of Mn 3d and N 2p orbitals results in the formation of a ~1.5 eV wide impurity band, which supports effective mass transport. We will discuss the technological impact of these findings and compare our results to pertinent experimental data.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+EL-MoM

Spintronic Materials and Hybrid Devices
Moderator: B.T. Jonker, Naval Research Laboratory

8:20am **MI+EL-MoM1 Spin-transport in Ferromagnet/Semiconductor Structures**, ***R. Jansen***, University of Twente, The Netherlands **INVITED**

Taking full advantage of electron spin in spin-electronics will eventually require an intimate integration of ferromagnetic and semiconductor materials. While device concepts are emerging, the understanding of spin transport in such hybrid ferromagnet/semiconductor structures is still at its infancy. We have focused on transport of non-equilibrium, hot-electron spins, for which spin currents can be controlled and manipulated via the electron energy and momentum. A particularly useful device for that purpose is the spin-valve transistor[1], consisting of a metallic spin-valve base, sandwiched between a semiconductor emitter and collector. Using the spin-valve transistor, we address the relative importance of interface, volume and thermal scattering of hot electron spins, and present new insight into the sources of spin-asymmetry in hot-electron transport.[2,3] From an application point of view, enhancing the output current of the transistor is desired. We demonstrate several routes to enhance the transfer ratio, culminating in an overall improvement by two orders of magnitude while preserving the low-field magnetic response above 200% at room temperature.[4] We also present transport in novel structures such as the magnetic tunnel transistor and the hot-electron spin-filter, and demonstrate that the latter allows room temperature injection of almost fully spin-polarized electrons into semiconductors.

[1] R. Jansen et al., J. Appl. Phys. 89, 7431 (2001).
[2] R. Jansen et al., Phys. Rev. Lett. 85, 3277 (2000).
[3] R. Vlutters et al., Phys. Rev. Lett. 88, 027202 (2002).
[4] O.M.J. van 't Erve et al., Appl. Phys. Lett. 80, to appear 20 may 2002.

9:00am **MI+EL-MoM3 Spin Dependent Electron Transport in Hybrid Ferromagnet/GaAs Structures at Room Temperature**, *S.J. Steinmuller, W.S. Cho, A. Hirohata, C.M. Guertler, G. Wastlbauer, T. Taniyama,* ***J.A.C. Bland***, University of Cambridge, UK

We report on the investigation of room temperature (RT) spin dependent electron transport in ferromagnet(FM)/GaAs hybrid Schottky barrier structures by photoexcitation. Spin accumulation in the GaAs was achieved by optical pumping with circularly polarised light. The photon helicity and the applied magnetic field were both introduced perpendicular to the plane of the film. Various FM materials were used (NiFe, Fe and Co) and investigated at different thicknesses (t=2.5nm, 5.0nm and 7.5nm). Furthermore an antiferromagnetic Cr sample was prepared as a reference. We measured the helicity-dependent photocurrent (PC), that is the difference in PC for illumination with right (i^+) and left circularly polarised light (i^-), for applied magnetic fields in the range from -2 T to 2 T as well as the spin polarisation $P=(i^+ - i^-)/(i^+ + i^-)$ of PC. NiFe and Fe showed a rather strong effect (P in the range 0.2-2%) increasing with film thickness, whereas almost no effect was observed in the Co. The magnetic field dependence of the helicity-dependent PC was in good agreement with polar MOKE measurements, proving that magnetic effects in the GaAs are negligible at RT. No field dependent effect was seen for the Cr as expected. Moreover we carried out measurements at different doping densities of the GaAs substrate (n- and p-type), showing the importance of the Schottky barrier in our experiment, and different photon energies. We also discuss the results of similar measurements on NiFe/Cu/Co spin valve structures. We show that our combined data provides strong support for our model of electron spin filtering at RT based on tunnelling of spin polarised electrons across the Schottky barrier followed by ballistic transport in the FM.

9:20am **MI+EL-MoM4 Tunneling Transport Across Reverse Biased Ag/Fe/Ag/GaAs Schottky Barriers**, ***D.A. Hite***, *S.E. Russek*, *D. P. Pappas*, National Institute of Standards and Technology

Electrical transport characteristics for the epitaxial Ag/Fe/Ag/GaAs(100) system have been studied under various growth conditions. The surfaces and structure of the multilayer were characterized by low energy electron diffraction and angle-resolved Auger electron diffraction at all steps of the fabrication. We have been able to prepare clean, well-ordered, epitaxial multilayers. The ultra-thin Ag buffer layer (~7 atomic layers) was prepared in a manner to create an ultra-thin layer to mediate the growth morphology of the Fe layer, to prevent the undesired intermixing associated with the Fe/GaAs system, and to create a tunneling barrier in reverse bias. In-situ conductance spectroscopy measurements were performed in order to characterize the rate of electron injection into the semiconductor as a function of bias voltage. We find that these multilayer diodes exhibit a reverse bias tunneling effect above 0.6 V. This is significant because it shows that we have been able to overcome the conductivity mismatch problem between the Fe and GaAs using an ultra-smooth, ultra-thin Ag buffer layer. The possibility of using these structures for direct spin injection from the Fe across the Ag/GaAs Schottky barrier will be discussed.

9:40am **MI+EL-MoM5 Modeling of Spin Injection into Disordered Semiconductors**, ***E.Y. Tsymbal***, University of Nebraska-Lincoln, *V.M. Burlakov*, University of Oxford, UK, *I.I. Oleinik*, University of South Florida **INVITED**

Spin injection into semiconductors is a topic of growing interest within the field of spin electronics. Developing a realistic model for spin injection is important both for the understanding of basic mechanisms that govern this phenomenon and for the application of spin injection in semiconductor devices. All the existing models so far either take into account a realistic band structure but neglect disorder within the semiconductor or consider phenomenologically defect scattering within a free-electron-type model. This talk will address the approach which combines an accurate description of the atomic structure, the electronic structure, and the conductance within a unique microscopic model. Within this approach the atomic structure is simulated using Metropolis MonteCarlo technique, the electronic structure is modeled using a multiband tight-binding approximation, and the conductance is calculated using the Landauer-Buttiker formalism including inelastic scattering. We will demonstrate results of the application of this model to amorphous silicon - a representative semiconducting material suitable for spin injection. We will discus decisive factors that control the efficiency of spin injection into disordered semiconductors.

10:20am **MI+EL-MoM7 Surface and Interface Properties of a Half-Metallic Alloy**, ***S.J. Jenkins***, *D.A. King*, University of Cambridge, UK **INVITED**

The ferrimagnetic semi-Heusler alloys have received considerable experimental and theoretical attention since the prediction in 1983 that they may show half-metallic behaviour (i.e. complete spin polarization at the Fermi level). Bulk properties of these alloys are now well understood. Nevertheless, application of these materials in practical situations is likely to be contingent upon the influence of their surface and interface properties, which have thus far been less thoroughly studied. This presentation will focus on recent calculations of the electronic structure of the NiMnSb(001) surface, with and without an Sb overlayer, carried out within the framework of density functional theory. Particular emphasis will be placed on the role of surface- and interface- localised electronic states in modulating the Fermi-level polarization.

11:00am **MI+EL-MoM9 Electrical Spin Injection from NiMnSb into GaAs**, ***W. Van Roy***, *P. Van Dorpe, V.F. Motsnyi, G. Borghs, J. De Boeck*, Imec, Belgium

We demonstrate electrical spin injection from NiMnSb into a GaAs light-emitting diode (LED). We compare single crystalline films grown epitaxially on GaAs(111)B with and without an additional AlAs tunnel barrier, and polycrystalline films grown on top of an AlO_x tunnel barrier on GaAs(001). The LEDs and NiMnSb films were grown by MBE in two chambers connected under vacuum. For the deposition of AlO_x tunnel barriers the samples were transported through air to a sputter system for the deposition of Al and oxidation in a controlled O_2 atmosphere. Spin injection was measured optically at T = 80 K. Electrons were injected with an in-plane spin-component. We used the oblique Hanle effect to transform this spin ensemble into an out-of-plane ensemble and used the circular polarization of the light emitted in the surface-normal direction as a measure of the electrical spin injection. The results were corrected for the out-of-plane tilting of the NiMnSb magnetization in the small oblique magnetic field, and for the MCD effect. We find electrical spin injection of up to 5% for polycrystalline NiMnSb films on top of an AlO_x barrier. The spin injection drops with increasing bias voltage. The low values indicate a strongly reduced spin polarization for the polycrystalline NiMnSb films. Epitaxial NiMnSb films, especially on (111)B interfaces, are expected to show a much larger spin polarization for the conduction carriers. However, we did not yet observe spin injection from these films. This is attributed to the low interface resistance of this configuration in combination with a NiMnSb surface polarization that, although larger than for the polycrystalline films, is still short of 100%.

11:20am **MI+EL-MoM10 Epitaxial Growth and Annealing Studies of Single Crystal, Ferromagnetic Co$_2$MnGa of GaAs (100)**, ***D.M. Carr****, *S. McKernan, F.M. Abdulle, J.W. Dong, C.J. Palmstrom*, University of Minnesota

Spintronic devices that use electron spin in semiconductor devices are promising candidates for the next generation of electronic devices. Ferromagnetic metals with high spin polarization may be required for successful implementation of these devices. The Heusler alloys are a promising family of metals because the material properties such as lattice parameter, saturation magnetization, Curie temperature, and spin polarization can be altered by changing the elemental composition. In addition, their lattice parameters span most of the lattice parameters of the compound semiconductors. Films of the Heusler alloy Co$_2$MnGa have been epitaxially grown on GaAs (100) using molecular beam epitaxy. In situ reflection high-energy electron diffraction patterns and ex situ x-ray diffraction patterns of 300 Å thick films indicate single crystal growth with an out-of-plane lattice constant of 5.94 Å, which suggests tetragonally distorted growth since the bulk lattice parameter is 5.77 Å. Variable temperature vibrating sample magnetometry measurements show the Co$_2$MnGa films to be ferromagnetic with in-plane magnetization and a Curie temperature close to the bulk value of approximately 690 K. Ex situ annealing at different temperatures from 300 to 450 degrees C reveals an increase in the saturation magnetization and reduced coercivity for anneal times as short as 5 minutes at 425 degrees C. Annealed films exhibit a smaller out-of-plane lattice constant suggesting relaxation of the strained films. Cross sectional transmission electron microscopy studies will be used to characterize the level of interfacial reaction before and after annealing.

11:40am **MI+EL-MoM11 Growth Temperature Controlled Magnetism in Molecular Beam Epitaxially Grown Ni$_2$MnAl Heusler Alloys**, ***X.Y. Dong***, *J.Q. Xie, J.W. Dong*, T.C. Shih, S. McKernan, C. Leighton, C.J. Palmstrom*, University of Minnesota

The Heusler alloy Ni$_2$MnAl is thought to be either antiferromagnetic or ferromagnetic depending on its crystal structure, B2 (disordered Mn-Al sublattice) or L2$_1$.[1] This suggests that a ferromagnet/antiferromagnet interface should be possible to be formed with Ni$_2$MnAl by controlling its crystal structure. Single crystal Ni$_2$MnAl thin films have been grown by MBE on GaAs (001) using Sc$_{0.3}$Er$_{0.7}$As interlayers. The effects of growth temperature on its structural and magnetic properties were studied. For all the films grown at different temperatures, streaky RHEED patterns were observed during the growth. The Ni$_2$MnAl / Sc$_{0.3}$Er$_{0.7}$As / GaAs (001) films were single crystals with cube on cube epitaxial relationship. The Rutherford backscattering spectrometry channeling minimum yield, χ_{min}, of ~ 5 %, confirms a relatively good quality crystal. XRD and TEM show that the Ni$_2$MnAl films have a tetragonally distorted structure with its c axis oriented along the growth direction. Higher growth temperature tends to result in ferromagnetic films suggesting a more L2$_1$-like structure, while lower temperature growth gives rise to non-ferromagnetic behavior, suggesting a more B2-like structure. For the ferromagnetic Ni$_2$MnAl film, the Curie temperature was determined to be approximately 220K. The exchange bias effect was observed for Co (70Å) / Ni$_2$MnAl (360Å, B2-like structure) bilayers, suggesting that the low temperature grown Ni$_2$MnAl is antiferromagnetically ordered. Therefore the self exchange biased Ni$_2$MnAl bilayers can be expected to be grown by varying the temperature during the growth. In this presentation, the effect of growth temperature on the structural and magnetic properties will be emphasized as well as the approaches of making self exchange biased structures will be reported.

[1] F. Gejima, Y. Sutou, R. Kainuma, and K. Ishida, Metal. Mater. Trans. A 30A, 2721 (1999).

***** Falicov Student Award Finalist

Electronic Materials and Devices
Room: C-107 - Session EL+SC+MI-MoA

Metal-Semiconductor Interfaces
Moderator: C.J. Palmstrom, University of Minnesota

2:00pm **EL+SC+MI-MoA1 Spin Transport in Ferromagnet-Semiconductor Schottky Diodes**, ***P.A. Crowell***, *A.F. Isakovic, B.D. Schultz, J. Strand, C.J. Palmstrom*, University of Minnesota **INVITED**

We have completed an investigation of spin injection in semiconductor heterostructures using a Schottky contact between Fe and n-$Al_{1-x}Ga_xAs$ as an injector and an $Al_{1-x}Ga_xAs/GaAs/Al_{1-x}Ga_xAs$ quantum well (QW) as the detector. The injector and detector are combined in a single device in which the QW is placed in the depletion region of a p-n junction. The Schottky contact is δ-doped, so that a tunneling current can be obtained under moderate reverse bias.[1] The injected electrons recombine in the QW with holes from the p-contact, and the polarization of the resulting electroluminescence (EL) is used to infer the spin state of the recombining carriers. We demonstrate that the doping profile chosen for the QW has a dramatic effect on the apparent spin-detection efficiency. EL polarizations over 10% are obtained in optimally biased devices in which the QW is intentionally p-doped. The field-dependence of the EL polarization closely matches the magnetization of the Fe electrode. However, the largest polarizations are not observed from ordinary ground-state recombination in the quantum well. The maximum polarization observed from ground-state recombination is approximately 4% and appears to be less sensitive to the doping profile. In contrast, the EL polarization in control samples is less than 2%, does not track the magnetization of the ferromagnetic electrode and depends only weakly on bias voltage. The interpretation of these measurements will rely on a thorough understanding of the QW spin detector and the identification of background contributions. For example, we show using optical pumping measurements that the spin detection efficiency of the QW is a function of the bias voltage, as is the background photoluminescence polarization. This work was supported by DARPA, ONR, and NSF (MRSEC).

[1] H.J. Zhu et al., Phys. Rev. Lett. 87, 016601 (2001); A.T. Hanbicki et al., Appl. Phys. Lett. 80, 1240 (2002).

2:40pm **EL+SC+MI-MoA3 Characterization of an Fe/AlGaAs Tunnel Barrier Interface for Electrical Spin Injection**, *A.T. Hanbicki*, ***R.M. Stroud***, *B.T. Jonker*, Naval Research Laboratory

Electrical injection of spin-polarized carriers from a contact into a semiconductor is essential for the success of spintronic devices. Ferromagnetic metals are attractive contact materials because of their ample supply of spin-polarized electrons, but the use of these materials has been limited by small injection efficiencies in the diffusive transport regime.[1] The use of a tunnel barrier between a metal and semiconductor.however. should facilitate usable spin currents.[2] Recent experiments reported spin injection from Fe into a AlGaAs/GaAs-based LED which produced an electron spin polarization of 15% in the GaAs quantum.[3] This was attributed to tunneling through the Schottky barrier. We have characterized the Fe/AlGaAs contact reported in reference 3 to verify the tunneling nature of the contact and to investigate the physical nature of the interface. Samples were grown by molecular beam epitaxy and were specifically engineered to utilize the Schottky barrier between the Fe and the semiconductor as a tunnel contact. Current vs voltage measurements were made through the structure at different temperatures. The conductance shows an asymmetric parabolic dependence on the voltage. Further, there is a weak insulating-like behavior of the zero-bias resistance as a function of temperature, a reliable indication that this is a tunneling process based on the Rowell criteria for tunneling.[4] High-resolution TEM measurements indicate an atomically abrupt interface between the metal and semiconductor. Current-in-plane measurements and the relation of bias voltage to spin polarization will also be discussed. This work was supported by the DARPA SpinS program and ONR.

[1] G. Schmidt, et al, Phys.Rev.B 62, R4790 (2000)
[2] E.I. Rashba, Phys.Rev.B 62, R16267 (2000)
[3] A.T. Hanbicki, et al., Appl.Phys.Lett. 80, 1240 (2002)
[4] B.J. Jönsson-Åkerman, et al., Appl.Phys.Lett. 77, (2000).

3:00pm **EL+SC+MI-MoA4 A Schottky Tunnel Barrier Contact for Electrical Spin Injection into a Semiconductor**, ***B.T. Jonker***, *A.T. Hanbicki, G. Kioseoglou*, Naval Research Laboratory, *G. Itskos, R. Mallory, A. Petrou*, SUNY at Buffalo

Electrical injection of spin polarized electrons into a semiconductor heterostructure is a critical issue for semiconductor-based spintronic devices. While very encouraging results have been obtained using magnetic semiconductors as injecting contacts,[1] the desire for room temperature operation at low magnetic fields leads one to consider other materials and avenues. Ferromagnetic (FM) metals offer high Curie temperatures and can be rapidly switched (~ 300 ps) at low applied fields. However, theory has indicated that only very small spin injection (~0.01%) can be expected for typical FM metals as diffusive contacts.[2] We report here electrical spin injection from an Fe Schottky contact into an AlGaAs/GaAs LED structure, with spin injection efficiencies above 34% which extend to room temperature. These robust effects are attributed to spin tunneling[3] through the tailored Schottky barrier contact. The samples are grown by MBE, and the width of the depletion region at the Fe/AlGaAs interface is controlled by the semiconductor doping profile. Under reverse bias, electrons tunnel from the Fe into the semiconductor, and radiatively recombine in the GaAs quantum well. The circular polarization of the surface emitted electroluminescence (Faraday geometry) provides a quantitative, model independent measure of the QW spin polarization, and hence the injection efficiency.[1] The spin tunnel current is dominated by minority spin carriers, in contrast to previous work using Al_2O_3 tunnel barriers and a superconducting film detector. The temperature dependence of the polarization will also be discussed. These results will be compared with previous work[4] and theoretical modeling of Schottky barrier injection. Work supported by the DARPA SpinS program and ONR.

[1] R. Fiederling, et al Nature (1999); B.T. Jonker et al, PRB (2000)
[2] G. Schmidt et al, PRB (2000)
[3] E.I. Rashba, PRB (2000)
[4] H.J. Zhu et al, PRL (2001).

3:20pm **EL+SC+MI-MoA5 Contact Metallurgy for the Antimonide Based Compound Semiconductors**, ***S.E. Mohney***, *W.E. Liu, H.S. Wang, J.A. Robinson*, Penn State University **INVITED**

Antimonide based compound semiconductors are promising candidates for both high frequency, low power electronic devices and optoelectronic devices, and the performance of electrical contacts to these semiconductors is critical for some of the devices currently under development, particularly the electronic devices. Control of the interfacial reactions between the contact metals and the semiconductors is necessary during device processing and packaging since interfacial reactions between the metals and semiconductors occur at very low temperatures. Therefore, we have examined the condensed phase equilibria in the metal-III-Sb systems to guide our selection of shallow, thermally stable contact metallizations. We have performed thermodynamic calculations to estimate ternary phase diagrams in the transition metal-Ga-Sb, transition metal-In-Sb and selected metal-Al-Sb systems. We find that W, Re, and Os are the only transition metals predicted to be in thermodynamic equilibrium with both GaSb and InSb under the conditions considered in our calculations, while W is the only transition metal predicted to be in equilibrium with AlSb. Finally, we give an example of our use of the information we have gathered for the design of a very shallow, thermally stable low resistance ohmic contact to p-type GaInSb. Since we have observed using transmission electron microscopy that Pd reacts uniformly with GaSb at low temperatures, we chose a very thin layer of Pd as the first metal in our contact. We then deposited W because of our prediction that it would be in thermodynamic equilibrium with both GaSb and InSb and that it could serve as a diffusion barrier between layers. Finally, we capped the films with Au, which was important for lowering the metal sheet resistance. A contact resistance of 3 x 10^{-7} ohm-cm^2 was measured with good stability at 250 °C for 100 h, as verified using contact resistance measurements and Auger depth profiles.

4:00pm **EL+SC+MI-MoA7 Electrical Contact Behavior of Ni/C60/4H-SiC**, ***W. Lu***, Fisk University, *W.C. Mitchel*, Air Force Research Laboratory, *J.R. Landis*, University of Dayton Research Institute, *T.R. Crenshaw*, Fisk University, *S.R. Smith*, University of Dayton Research Institute, *W.E. Collins*, Fisk University

Ohmic contact formation of Ni/C60 film on n-type 4H-SiC was investigated. A C60 interfacial layer between Ni film and SiC improves ohmic contact properties significantly. The C60 film was deposited by Langmuir-Blodgett method prior to the Ni film deposition on SiC using DC sputtering method. High quality ohmic contact of Ni/C60/4H-SiC is formed after annealing at 800°C in Ar for two hours with a specific resistance of 1.6

x 10^{-6} Ωcm^2 for the SiC with a doping concentration of 1.8 x 10^{19}cm^{-3}. Raman spectra reveal that the formation of graphitic carbons by Ni catalytic effects result in the formation of ohmic contact on SiC, and the nano-size graphitic flakes identified by Raman spectroscopy play a key role for ohmic contact formation on SiC. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) show a direct relationship between the graphitized morphological features on the film and ohmic contact behavior.

4:20pm **EL+SC+MI-MoA8 Electrical Characterization of AlN MIS/MIM-structures**, ***F. Engelmark***, *J. Westlinder, I.V. Katardjiev, J. Olsson, S. Berg*, University of Uppsala, Sweden

The electrical properties of insulating ceramic films such as AlN, Ta_2O_5, HfO_2, ZrO_2, Al_2O_3, etc. are of substantial interest for a number of microelectronic and electro-acoustic applications owing to their chemical stability in harsh environments along with some very interesting electrical properties. In this work, emphasis has been put on the electrical properties of Aluminum nitride (AlN) films. Thin AlN films have been deposited onto Si(100) and Mo/Si(100) substrates. The sputter deposited Mo is polycrystalline, showing a predominant (110) orientation. AlN film growth is performed using different process conditions in a reactive PVD (Physical Vapour Deposition). Both fully textured (0002) polycrystalline and XRD amorphous films have been grown and studied. MIS- and MIM-structures have been fabricated and electrical properties such as dielectric constant, leakage current as well as their high frequency behaviour are investigated. The measurements indicate that the dielectric constant does not vary with crystallinity of the films, and remains constant at a value of 10. Further, the high frequency behaviour of the dielectric constant have been studied in the range 100 MHz to 20 GHz. The leakage current mechanism is also similar for different films and is believed to be Poole-Frenkel controlled. C-V (Capacitance-Voltage) measurements for MIS structures revealed the presence of charges in the interface between the substrate and the dielectric layer. Trapped charge density was estimated to be $3.5*10^{10}$ cm^{-2}.

Electronic Materials and Devices
Room: C-107 - Session EL+SC-TuM

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

8:20am **EL+SC-TuM1 Epitaxial Growth and Characterization of CdS Layers Grown on InP (001) using Molecular Beam Epitaxy from Atomic Sulfur Beam and Thermally Evaporated Cd**, ***J.W. Choi***, *M.-A. Hasan, A. Bhupathiraju*, University of North Carolina at Charlotte

Recent progress in epi-ready InP(E_g=1.35 eV) wafer growth has prompted new applications of heterojunction devices and quantum structures based on closely lattice matched epitaxial films on InP. Cadmium sulfide (CdS), a direct bandgap material (E_g=2.5 eV), has a small lattice mismatch to InP (0.63%) that can facilitate optoelectronic integration on InP. In this work, growth of CdS on InP (001) substrates is investigated using modified molecular beam epitaxy (MBE). Two growth methods are investigated. In the first method, epitaxial growth is conducted by atomic sulfur (S) beam from an RF atomic source with H_2S as the source gas while Cd is supplied from a cracker cell. The RF source is operated at 13.56 MHz and produces an intense monoatomic sulfur beam (λ= 930.5 nm emission peak measured by plasma spectroscopy). In the second method, deposition is performed using CdS sublimation from a solid CdS using a conventional Knudsen cell. Rinsing by methanol is used to clean the epi-ready InP (001) substrates. Final substrate cleaning is achieved by thermal desorption (530-550°C) in vacuum. RHEED shows InP (001) 2x1 surface after thermal cleaning. In both methods, in-situ RHEED measurement indicates epitaxial growth of zincblende CdS; Auger electron spectroscopy (AES) shows stoichiometric CdS within the AES resolution limit. AES depth profiles also indicate an abrupt InP/CdS interface for all temperatures investigated. The growth rate of CdS is primarily governed by Cd flux as indicated by the activation energy measured from the flux-dependence of the growth rate. Atomic force microscopy (AFM) shows measurable dependence of surface roughness on growth method. For growth using an RF atomic source, average surface roughnesses of 1-2 nm is measured for all growth temperatures, layer thicknesses, and flux ratios with no evidence of island formation; higher roughness values (10-20nm) were typically measured for growth from solid CdS.

8:40am **EL+SC-TuM2 Structure of InAs/InP Interfaces Formed During Metalorganic Vapor-Phase Epitaxy**, ***D.C. Law***, *Y. Sun, C.H. Li*, University of California, Los Angeles, *S.B. Visbeck*, Siemens & Shell Solar Gmbh, *G. Chen, R.F. Hicks*, University of California, Los Angeles

We have studied the initial stages of heterojunction formation during the metalorganic vapor-phase epitaxy of indium arsenide on indium phosphide. Exposing an InP (001) film to 10 mTorr of tertiarybutylarsine below 500 °C results in the deposition of a thin InAs layer from 1.5 to 5.0 atomic layers thick (2.3 to 7.5 Å). The surface of this epilayer remains atomically smooth independent of arsenic exposure time. However, in an overpressure of tertiarybutylarsine at or above 500 °C, the arsenic atoms diffuse into the bulk, creating strained InAsP films. These films form three-dimensional island structures to relieve the built-up strain. The arsenic transport into InP can be described by a constant-source diffusion model with the arsenic number density given by: $N_{As} = 0.5\ N_T \mathrm{erfc}\ (x/2\sqrt{(D_{eff}t)})$. The activation energy and pre-exponential factor for arsenic diffusion into indium phosphide are: $D_o = 2.3\pm1.0\ x10^{-7}\ cm^2/s$ and $E_d = 1.7\pm0.2$ eV.

9:40am **EL+SC-TuM5 Device Quality III-V Compound Semiconductor Epitaxy on Si Via SiGe Interlayers**, ***S.A. Ringel***, *C.L. Andre, A. Khan, M. Gonzalez, M.K. Hudait,* Ohio State University, *E.A. Fitzgerald,* Massachusetts Institute of Technology, *J.A. Carlin, M.T. Currie, C.W. Leitz, T.A. Langdo,* AmberWave Systems Corporation **INVITED**

Integration of III-V compounds with Si using direct epitaxial approaches has been an area of intense interest for years. Achieving this would enable a complement of electronic and optoelectronic capabilities that would generate new circuit functions with higher speed, and potentially simpler architecture. There is also substantial interest in III-V/Si integration where the primary purpose for Si is as an alternative substrate for III-V solar cells, which are conventionally grown on Ge or GaAs substrates. Compared to Si, these substrates are expensive, brittle and heavy, which are issues for this application. For both of these directions, the materials issues of how to integrate III-V compounds with Si without degrading electronic properties due to the mismatch in structural, thermal and chemical properties so that high performance devices can be achieved are the same. Here we show that growth of compositionally graded SiGe interlayers to accommodate lattice strain between a Si wafer and III-V epitaxial structures, coupled with monolayer-scale control over the formation of the initial III-V/IV interface to eliminate anti-phase domain disorder and block interface diffusion, together yield high quality AlGaAs/GaAs and InGaP/GaAs layers, heterostructures and minority carrier devices. Time resolved photoluminescence measurements of III-V double heterostructures reveal record high minority carrier lifetimes for GaAs on Si in excess of 10 nanoseconds, which is attributed to the simultaneous elimination of anti-phase domains and reduction of residual threading dislocation densities to below $1x10^6$ cm^{-2}. SIMS and capacitance-voltage measurements show that autodoping is effectively eliminated for GaAs grown on Ge/SiGe/Si, with no additional background impurities detected in the GaAs layers grown on these substrates. Solar cells are used as examples of minority carrier devices to show that high performance comparable to similar devices grown on conventional substrates has been achieved, with record voltage output for III-V cells grown on Si.

10:20am **EL+SC-TuM7 Interdiffusion, Alloying, and Defect Formation at GaN-Sapphire Interfaces**, ***X.L. Sun***, *S.T. Bradley, G.H. Jessen, L.J. Brillson*, The Ohio State University

The chemical and electronic structure at GaN/sapphire interfaces has a major influence on the electronic quality of epitaxial GaN films. In particular, degenerate doping usually occur near hydride vapor phase epitaxy (HVPE) grown GaN/sapphire interfaces that can affect lateral transport in overgrown devices. Near the interface, impurity diffusion, alloying, and related defect formation can occur at the high (1150°C) growth temperatures that is important to understand and control. We have used Auger electron (AES) and cathodoluminescence (CLS) spectroscopies in a UHV scanning electron microscope (SEM) to probe the chemical and electronic features at the HVPE GaN/sapphire interface in cross section in a nanometer scale. Specimens were cleaved and Ar sputtered in UHV to prepare clean interfaces with well-defined AES, CLS, and secondary electron images. AES images reveal dramatic evidence for diffusion of O from sapphire typically decreasing exponentially ~ 1 µm into GaN from 60% to the detection limit of < 1% surface coverage. The AES O intensity line profile mirrors corresponding SIMS O depth profiles and a donor level CLS emission vs. depth normal to the interface found in similar samples. Conversely, N with plateau concentrations of ~5 % extend ~ 2 µm into the sapphire and correspond spatially to a 3.8 eV defect emission attributed to Al-N-O complexes. While Ga exhibits no strong diffusion, interface Al decreases from 10% to < 1% over ~1 µm into the GaN and support evidence for AlGaN alloy formation, based on ~3.6 eV CLS emission above the GaN band gap at the buried interface. Depending on surface pretreatment and growth conditions, such interfaces can be abrupt to < 200 nm or can exhibit interdiffusion on a micron scale. These results illustrate a new approach to probe chemical and electronic interactions at semiconductor heterojunctions and reveal that both interdiffusion and alloying can occur and lead to extrinsic electronic effects.

10:40am **EL+SC-TuM8 Growth and Characterization of Heterjunction Diode Made of AlN on Si(111)**, ***K. Sundaresan***, *M. Jenkins, M.-A. Hasan,* University of North Carolina, *M. Sardela Jr.*, University of Illinois

Single crystalline hexagonal AlN(001) was grown on Si(111) using surface-reconstruction induced epitaxy. The Si(111)7x7 surface, generated under thermal etching under UHV, was first passivated by deposition of ~0.3 monolayer (ML) of Al at 650-700 °C. Each Al atom bonds to 3 Si atoms on the surface, which give rise to the well-known Si(111)root3xroot3 surface. The well ordered, Al-passivated Si(111)root3xroot3 surface was then used as a template to initiate epitaxial growth of AlN on Si. The growth was conducted by using an atomic N flux from a RF atomic source and thermal Al evaporation. X-ray diffraction showed single crystalline hexagonal AlN(001) with a full width at half maximum (FWHM), measured from the layer peak, equal to that of the Si substrate indicating highly oriented AlN layer. Epitaxial growth was achieved over a wide range of Al/N flux ratio and growth temperatures extending from 350 to 850 °C. AlN/Si heterojunction diode, fabricated using this method showed a breakdown voltage in excess of 350 V and a leakage current below 100 nA indicating high quality interface.

11:00am **EL+SC-TuM9 Observation of a Long-range Strain Field under SiO$_2$/Si Interface by using Multi-wave X-ray Diffraction**, ***W. Yashiro***, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *K. Sumitani, T. Takahashi*, The University of Tokyo, Japan, *Y. Yoda*, Japan Synchrotoron Radiation Research Institute (JASRI), *K. Takahashi, T. Hattori*, Musashi Institute of Technology, Japan

In order to further improve the speed of VLSI circuits, new materials and device structures are being proposed in recent year. In particular there has been considerable interest in strained Si because it can lead to high-performance metal-semiconductor (MOS) devices. Transmission electron microscopy (TEM) is a technique to investigate local strains, e.g. around a dislocation at a phase boundary. In contrast with TEM, x-ray diffraction is powerful to investigate long-range ordered structures in crystals. In the present paper, we propose a new method that is sensitive to very small and long-range strains near surfaces of crystals by using multi-wave x-ray diffraction technique. To date, the Bragg reflection of x-ray diffraction is used to investigate such long-range strain fields. Recently Emoto et al. have indicated using the Bragg reflection that there exist very small strain fields on the side of the Si substrates if even ultra-thin layers are formed on them.[1] Our method is also a method using the Bragg reflection, but with the important distinction that we use a phenomenon, intensity modulation of the CTR scattering under a Bragg condition. This makes it possible to determine total displacements due to small lattice distortions, rather than local lattice spacing. The method was applied to a Si(001) wafer whose surface is covered with an oxide layer about 5 nm thick formed by microwave-excited high density Kr/O$_2$ plasma oxidation. We found that the total displacement of -0.18 Å in the direction normal to the surface exists under the interface between the oxide layer and the substrate.

[1] Emoto et al. Surf. Sci. 493 (2001) 221-226.

11:20am **EL+SC-TuM10 Measurement of Fermi Level Pinning Kinetics at Si-SiO$_2$ Interfaces: Implications for CMOS Transistor Manufacture**, ***K. Dev***, *M.Y.L. Jung, R. Gunawan, R.D. Braatz, E.G. Seebauer*, University of Illinois

Excessive transient enhanced diffusion (TED) of boron in silicon has been a major inhibitor to forming ultrashallow junctions for CMOS device applications. Current technology for junction formation relies on ion implantation into Si through SiO$_2$ to introduce dopants into the substrate, followed by rapid thermal annealing. We have investigated a previously unknown effect in this process sequence: charge build-up at the Si-SiO$_2$ interface and the resulting Fermi level pinning that can occur just after implant. Fundamentally, the charge build-up occurs in response to the ion-induced formation of dangling bonds that introduce energy states into the Si surface bandgap. The present work uses the optical technique of photoreflectance to demonstrate experimentally that these effects indeed exist and to measure their evolution kinetics. Photoreflectance is one of a class of modulation spectroscopies in which a semiconductor is periodically perturbed, and the resulting change in dielectric constant is detected by reflectance. The presence of a photoreflectance spectrum demonstrates unequivocally the existence of Fermi level pinning. The spectral amplitude scales linearly with the magnitude of built-in surface potential. Thus, we can deduce the pinning kinetics from the variation in amplitude. Our data demonstrate the existence of substantial pinning just after implant with 500 eV ions. Healing begins to occur in the vicinity of 400°C - within the temperature stabilization step in which interstitial clusters form. TED simulations using electrostatic boundary conditions derived from the photoreflectance experiments show that pinning deepens the pn junction significantly by transforming the Si-SiO$_2$ interface into a reflector of charged bulk interstitials.

11:40am **EL+SC-TuM11 Effects of Interface Properties on Degradation and Reliability of CMOS Devices with RPECVD Stacked Oxide/Nitride and Oxynitride Dielectrics**, *G. Lucovsky*, ***Y. Lee***, North Carolina State University, *Y. Wu*, Advanced Micro Devices, *C. Bae, J.G. Hong*, North Carolina State University

The effects of interface properties on device degradation and reliability of sub-2nm stacked oxide/nitride and oxynitride gate dielectrics prepared by the remote plasma enhanced CVD (RPECVD) technique under constant voltage stress (CVS) are investigated. Time evolutions of the transient SILC effect and threshold voltage (Vt) changes have been demonstrated to illustrate the breakdown behaviors and charge trapping during stress. More negative Vt shifts were observed for both P- and N-MOS devices, indicating the increases of hole trapping at the Si/SiO$_2$ interface. The p-channel transistors with stacked gate dielectrics received interface N$_2$/He nitridation and effectively suppress positive off-state leakage current, resulting in less device degradation as compared to the transistors without interface nitridation. This improvement is attributed to approximately one monolayer of N at the Si/SiO$_2$ interface which suppresses hole trapping. In addition, the influence of remote-plasma-assisted oxidation (RPAO) thickness on oxynitride device degradation and reliability is also studied. It is found that the devices with 0.6 nm RPAO exhibit improved C-V characteristics, lower post-breakdown current and higher TDDB reliability compared to the devices with 0.8 nm RPAO. The generation of interface states and the correlation between carrier conduction mechanism and TDDB are also discussed.

Magnetic Interfaces and Nanostructures
Room: C-205 - Session MI+EL+SC-TuM

Ferromagnetic Semiconductors
Moderator: B.T. Jonker, Naval Research Laboratory

8:20am **MI+EL+SC-TuM1 ab initio Magnetic Exchange Interactions in DMS and TiO$_2$**, ***M. van Schilfgaarde***, Arizona State University **INVITED**

The electronic structure of TM-doped TiO2 is studied within the ab initio local spin-density approximation and compared to more traditional TM-doped III-V DMS semiconductors. The conduction band of TiO2 consists mainly of Ti d character. Substituting a 3d TM for Ti, localized levels split off the conduction band; they are spin-split by an on-site exchange interaction and are responsible for the magnetism. The deepest level is of t2 symmetry and sweeps deeper in the gap in the series TM=V,Cr,Mn,Fe,Co. In the dilute alloy, the impurity level broadens into a narrow band. Thus the conductivity is expected to occur through a hopping mechanism, increasing with decreasing temperature as is observed in Co:TiO2. The character of this level is compared to TM d levels in the III-V DMS alloys (Cr,Mn,Fe):(Al,Ga,In)(N,P,As). Using a linear-response technique, the LSDA is mapped analytically onto a magnetic hamiltonian, which was used to investigate exchange interactions in random TM:TiO2 and (Cr,Mn):(Al,Ga,In)(N,P,As) alloys. Several novel phenomena will be described in the DMS case; for example Tc is predicted to increase monotonically with concentration for Cr:III-V, while for Mn:III-V Tc reaches a maximum at about 10% Mn concentration. The exchange interactions are found to have elements in common with both the carrier-mediated model and the double exchange/superexchange model, but also show important differences. For (V,Cr,Mn,Fe,Co):TiO2, the filling, magnetic moment and exchange interactions change systematically and are well described by a double exchange/superexchange model. However, for Tc to reach the observed RT in Co:TiO2, a source of holes is needed.

9:00am **MI+EL+SC-TuM3 Co$_x$Ti$_{1-x}$O$_2$ Anatase Heteroepitaxy on Si(001)**, ***T. Droubay***, Pacific Northwest National Laboratory, *A.C. Tuan*, University of Washington, *S.A. Chambers*, Pacific Northwest National Laboratory

With a Curie temperature above 700K, high remanence, and respectable coercivity, Co-doped TiO$_2$ anatase (Co$_x$Ti$_{1-x}$O$_2$) is one of the more magnetically robust dilute magnetic semiconductor (DMS) materials currently under investigation. The future of this material for near-term device use as a spin injector requires deposition on and compatibility with traditional semiconductors such as silicon. Successful growth of crystalline oxides on silicon without oxidizing the underlying substrate is a formidable challenge. Our goal in this work is to grow epitaxial Co$_x$Ti$_{1-x}$O$_2$ on Si(001) by using a suitable template layer, and then determine the resulting magnetic and electronic properties. We have previously shown that polycrystalline Co$_x$Ti$_{1-x}$O$_2$ grown on Si(001) with its native oxide is ferromagnetic at room temperature. We are now working on Co$_x$Ti$_{1-x}$O$_2$ heteroepitaxy on Si(001) using an ultrathin epitaxial SrTiO$_3$ buffer layer to prevent formation of titanium silicide and SiO$_2$ at the interface that result from a thermodynamic instability. An added benefit of the SrTiO$_3$ buffer layer is to generate a nearly zero conduction band offset to Si, which is essential for efficient n-type spin injection. A detailed analysis of the growth and properties of this heteroepitaxial system will be presented.

9:20am **MI+EL+SC-TuM4 Epitaxial Growth and Properties of Co-doped TiO$_2$ Anatase on LaAlO$_3$(001)**, ***S.A. Chambers***, *T. Droubay, C.M. Wang, S.M. Heald, S. Thevuthasan, A.S. Lea, C.F. Windisch, Jr.*, Pacific Northwest National Laboratory, *R.F.C. Farrow, L. Folks, J.-U. Thiele, M.G. Samant, R.F. Marks*, IBM Almaden Research Center

We are investigating Co-doped TiO$_2$ anatase heteroepitaxy on LaAlO$_3$(001) by oxygen plasma assisted molecular beam epitaxy. This material is of considerable interest because it is ferromagnetic well above room temperature. Thus, it may be a useful DMS for spintronics. The use of a higher growth rate (0.04 nm/sec) results in the nucleation of nanocrystals of rutile, the more stable form of TiO$_2$, within the continuous anatase film. The density of rutile nanocrytals increases as the quality of the substrate surface decreases. A lower growth rate (0.01 nm/sec) results in a much better film morphology, although a low density of smaller nanocrystals remains. Unlike the fast-grown films, these films show no evidence for any phase other than anatase. A number of techniques reveal that Co substitutes for Ti in the lattice and exhibits a +2 oxidation state; there is no evidence for elemental Co in any form. Each Co(II) substitution for Ti(IV) requires an O^{-2} anion vacancy in order to maintain charge neutrality, and evidence for such a vacancy is forthcoming from preliminary Co K-shell EXAFS. Such vacancies do not generate free carriers because they are uncharged. Hall effect and XPS measurements show that the films are n-type, the most likely cause being the presence of O atom vacancies that form during growth. These vacancies are independent of the presence of Co, and are negatively charged, thereby providing a source of free electrons from shallow donor states. The magnetization depends critically on free carrier concentration, as expected for a DMS. The exact Curie temperature is currently being determined, but appears to be in excess of 700K.

9:40am **MI+EL+SC-TuM5 Ferromagnetism in Mn-implanted Single Crystal Oxides**, ***D.P. Norton***, *S.J. Pearton, B.S. Jeong, Y.W. Heo, A.F. Hebard, N.A. Theodoropoulou,* University of Florida, *L.A. Boatner,* Oak Ridge National Laboratory, *Y.D. Park,* Seoul National University, Korea, *R.G. Wilson*, Consultant

Several semiconducting oxides, including ZnO, offer significant potential in providing spin-based functionality. Theoretical predictions suggest that room-temperature carrier-mediated ferromagnetism should be possible in Mn-doped p-type ZnO. In this paper, we report on the synthesis and properties of magnetically-doped semiconducting oxides, including ZnO. While previous efforts report no ferromagnetism in Mn-doped ZnO that is n-type due to group III impurities (consistent with theory), we find ferromagnetism in n-type ZnO that is co-doped with Mn and Sn. Hysteresis was observed in magnetization versus field curves for Mn-implanted n-type ZnO:Sn. Differences in zero field-cooled and field-cooled magnetizations persists up to ~ 150 K for Sn-doped ZnO crystals implanted with 3 at % Mn. These results indicate that ZnO doped with Mn and Sn may prove promising as a ferromagnetic semiconductor for spintronics.

10:00am **MI+EL+SC-TuM6 Self-compensation in Manganese-doped Ferromagnetic Semiconductors**, ***S.C. Erwin***, *A.G. Petukhov*, Naval Research Laboratory

We present theoretical evidence that the observed hole compensation in manganese-doped ferromagnetic semiconductors is due to interstitial manganese. We show that under the non-equilibrium conditions used during growth, interstitial Mn is readily formed near the surface by a simple low-energy adsorption pathway. In GaAs, isolated interstitial Mn impurities are electron donors, each compensating two substitutional Mn acceptors under p-type conditions. We show that partial compensation is a prerequisite for ferromagnetic order below the metal-insulator transition, and that the Curie temperature is highest when 1/6 of the Mn is interstitial.

10:20am **MI+EL+SC-TuM7 Ferromagnetic Semiconductor Heterostructures**[1], ***N. Samarth***, Penn State University **INVITED**

The molecular beam epitaxy (MBE) of ferromagnetic semiconductor heterostructures provides model systems for exploring fundamental issues in semiconductor spintronics. We provide an overview of heterostructures that combine the ferromagnetic semiconductor (Ga,Mn)As with conventional III-V and II-VI semiconductors, as well as with the metallic ferromagnet MnAs. After an introduction to the properties of MBE-grown (Ga,Mn)As, we discuss two classes of heterostructures: (a) hybrid ferromagnetic metal/semiconductor tunnel junctions that allow us to unambiguously probe spin injection into semiconductors using all-electrical techniques and (b) hybrid ferromagnetic/semiconductor photodiodes that serve as toy spintronic "devices" whose photo-response is magnetically controlled.

[1] This work is carried out in collaboration with S. H. Chun, K. C. Ku, S. J. Potashnik, and P. Schiffer, and is supported by grants from NSF, ONR and DARPA

11:00am **MI+EL+SC-TuM9 Epitaxial Growth of the Diluted Magnetic Semiconductor Cr_xGe_{1-x}**, ***G. Kioseoglou***, *A.T. Hanbicki,* Naval Research Laboratory, *Y.D. Park,* Seoul National University, Korea, *S.C. Erwin, B.T. Jonker*, Naval Research Laboratory

Ferromagnetic semiconductors (FMS) provide an opportunity to control spin-dependent behavior in semiconductor device heterostructures. Although much effort has focused on III-Mn-V materials such as GaMnAs , the mechanism of ferromagnetic order remains unclear; in particular the precise roles played by the dopant and the semiconductor host. We have explored this issue recently by developing a new Group-IV FMS, MnGe.[1] Here we report our work to develop an elemental FMS using a different dopant, Cr-doped Ge. This choice was motivated partly by our density-functional theory (DFT) calculations, which indicate that CrGe and MnGe should have comparable Curie temperatures. We report the epitaxial growth of Cr_xGe_{1-x} and describe the structural, magnetic and transport properties. The samples were grown on GaAs(001) substrates by molecular beam epitaxy at substrate temperatures of 40-500°C and the crystallinity was confirmed by the RHEED pattern. The Cr concentration used was 2-3% as determined from X-ray fluorescence. The RHEED pattern indicates single crystal growth for substrate temperatures above 200°C, with sharp 1x1 streaks. Growth at 40-70°C is initially single crystal, but the pattern becomes increasingly diffuse with film thickness. The samples are strongly p-type, and the hole density varies with the Cr concentration. SQUID measurements were performed on all samples to investigate the magnetic character of the Cr:Ge system. Samples grown at the higher growth temperatures exhibit only paramagnetic order. Co-doping with both Mn and Cr is also investigated. This work was supported by the DARPA SpinS program and ONR.

[1] Y.D. Park, et al., Science 295, 651 (2002).

11:20am **MI+EL+SC-TuM10 Cr-Doped III-V Ferromagnetic Semiconductors**, ***M.E. Overberg***, *G.T. Thaler, R.M. Frazier, C.R. Abernathy, S.J. Pearton, N.A. Theodoropoulou, A.F. Hebard,* University of Florida, *R.G. Wilson,* Private Consultant, *J.M. Zavada*, U.S. Army Research Office

Ferromagnetic semiconductors, consisting of a semiconductor host material doped with transition metal ions, are becoming increasingly prevalent in the literature as a candidate for incorporating the spin degree of freedom into device structures. To date, the vast majority of work in this area has centered on the incorporation of Mn into both II-VI and III-V materials by a variety of techniques. However, recent theoretical work has indicated that Cr may be a more suitable dopant for achieving room-temperature ferromagnetism within these materials.[1] In this paper, we will report on the preparation of GaCrN, GaCrP, and AlGaCrP by the direct implantation of Cr. The magnetic and magneto-transport (anomolous Hall Effect) properties of these films will be quantified both versus implantation dose (x=0.04, 0.06, 0.10) and versus post-implantation annealing, to identify an optimum combination of dose and annealing conditions. Analysis by SQUID magnetometry of the GaCrN with 6% Cr indicates the presence of a strong ferromagnetic phase with a Curie temperature above the 350 K limit of the magnetometer. High resolution x-ray diffraction (HRXRD) and transmission electron microscopy (TEM) results from the implanted films will also be presented to address the issue of the formation of second phases within these materials. HRXRD rocking curves of the implanted materials will also be used to trace the evolution of the implantation-induced lattice damage with annealing as well as strain-related effects due to the incorporation of Cr into substitutional lattice sites.

[1] K. Sato, and H. Katayama-Yoshida, Jap. J. Appl. Phys., Pt. 2, 40 (5B), p. L485 (2001).

11:40am **MI+EL+SC-TuM11 Suppression of Phase Segregation during MBE Growth of GaMnN Using Nitrogen-Hydrogen Plasma**, *Y. Cui,* ***L. Li***, University of Wisconsin-Milwaukee

Epitaxial growth of GaMnN by electron-cyclotron-resonance plasma-assisted molecular beam epitaxy using nitrogen-hydrogen plasma was studied by reflection high-energy electron diffraction, scanning electron microscopy, energy dispersive spectroscopy, and x-ray diffraction. The electron diffraction pattern changed from streaky to spotty when hydrogen was added to the nitrogen plasma, indicating that the effective N/Ga ratio was increased. Films grown with nitrogen plasma are phase segregated into GaN and manganese nitrides. In contrast, when nitrogen-hydrogen plasma was used, the films are single phase Ga1-xMnxN, with x can be as high as 0.06. These results indicate that phase segregation can be suppressed by adding hydrogen to the nitrogen plasma during growth.

Electronic Materials and Devices
Room: C-107 - Session EL+SC-TuA

Semiconductor Characterization
Moderator: P.H. Holloway, University of Florida

2:00pm **EL+SC-TuA1 Active-Device Scanning Voltage Microscopy Studies on a Forward and Reverse Biased InP pn Junction Sample**, ***ST.J. Dixon-Warren***, *R. Dworschak, G. Este, AJ. SpringThorpe, J.K. White,* Nortel Networks, Canada, *D. Ban, E.H. Sargent*, University of Toronto, Canada

Active-Device Scanning Voltage Microscopy (SVM) is a new Scanning Probe Microscopy (SPM) technique in which a two-dimensional voltage map is obtained on the cross-section of a biased semiconductor sample. The voltage is measured using a very high impedance voltmeter that is connected to a conductive doped-diamond coated SPM tip. Recently obtained results on a molecular beam epitaxy (MBE) grown InP pn junction sample will be reported, under both forward and reverse bias conditions. The results are compared to those obtained with Scanning Spreading Resistance Microscopy (SSRM) measurements under zero bias on the same sample. The SVM and SSRM results will be discussed in terms of the semi-classical model of the pn junction. The physics of the SVM measurement process will also be discussed. Finally, the results obtained on the simple pn junction sample will be compared with those obtained on more complex samples, such as InP based ridge waveguide and buried heterostructure laser samples under forward bias.

2:20pm **EL+SC-TuA2 Scanning Tunneling Microscopy Imaging of Charged Defects on Clean Si(100)-(2x1)**, ***G.W. Brown***, *H. Grube, M.E. Hawley,* Los Alamos National Laboratory, *S.R. Schofield, N.J. Curson, M.Y. Simmons, R.G. Clark*, University of New South Wales, Australia

We have used scanning tunneling microscopy (STM) to image charged defects on the clean Si(100)-(2x1) surface. In the absence of "C"-type defects, band bending can occur during STM imaging, allowing near surface charge to influence the state density contributing to the tunnel current. As in the case of cleavage faces of III-V semiconductor crystals, the charge-induced band bending produces long range enhancements superimposed on the periodic surface lattice. We observe this in empty-state STM images taken on n-type Si(100). No band bending signature is seen in the filled-state images. This can be understood by considering the band structure at the surface, which has surface states within the gap. The charged defects observed in this work are of the types commonly observed in clean Si(100)-(2x1) STM studies, however, not all defects of a given type appear charged. This would indicate subtle differences in defect structure or the influence of impurities. This work demonstrates the ability to observe charged features on the clean Si(100) surface, which will be important for current and future research focussed on producing atomic scale electronic structures. Predictions for signatures on p-type material will also be made.

2:40pm **EL+SC-TuA3 The Surface Photovoltage and Photoelectron Spectroscopy**, ***J.P. Long***, Naval Research Laboratory **INVITED**

Frequently, the surface of a semiconductor in equilibrium exhibits "band bending," an electrostatic shift of the surface relative to the bulk that arises from the built-in electric field associated with a surface depletion layer. When such a surface is illuminated, photogenerated electrons and holes move to screen the built-in field, thereby reducing the band bending and shifting the surface energy levels, an effect known as the surface photovoltage (SPV). Because the energy levels measured by photoelectron spectroscopy shift with the electrostatic potential of the surface, the technique is sensitive both to equilibrium band bending, a fact often exploited to characterize Schottky barrier heights, and to the SPV, which makes photoemission a useful SPV detector. However, under certain conditions, the ultraviolet or x-ray photoemission source itself can induce a sizable SPV that seriously hampers the measurement of equilibrium energy levels. This talk will introduce the SPV at a tutorial level, and will discuss the interplay between photoelectron spectroscopy and the SPV. Illustrations of photoemission as a SPV detector include the use of synchrotron radiation to characterize SPV decays in laser-excited Si and to detect, via SPV-induced band-flattening, inhomogeneous band bending on GaAs caused by Ga islands. In addition, the problem of SPV's induced by photoemission sources themselves will be addressed. Usually encountered below room temperature where the SPV is enhanced, source-induced SPV's become an important issue at and above room temperature in wide band-gap materials, which are acutely prone to a SPV when large equilibrium band bending is present. A striking example of current relevance is p-type GaN, which exhibits source-induced SPV's at room temperature exceeding a volt when examined by ordinary UPS and XPS laboratory sources.

3:20pm **EL+SC-TuA5 Direct Measurement of the Electrical Potentials in $GaInP_2$ Solar Cells**, ***C.-S. Jiang***, *H.R. Moutinho, J.F. Geisz, D.J. Friedman, M.M. Al-Jassim*, National Renewable Energy Laboratory

We report the application of electrostatic force microscopy (EFM) to photovoltaic devices. The built-in electric field plays a major role in photovoltaic devices, because it collects photo-excited carriers and is a key factor in determining the open-circuit voltages of solar cells. However, the measurement of the built-in potential has been limited to indirect ways such as the characteristics of current-voltage and capacitance-voltage. In these measurements, it is hard to distinguish the contributions from the multi-junctions or interfaces of a modern solar cell device. In this presentation, we report a direct measurement of the electric potential on cross-sectional planes of a $GaInP_2$ device both quantitatively and spatial-resolvedly, by using the Kelvin probe force model of the EFM technique. Two features on the potential profile are assigned respectively to the p-n junction of $GaInP_2$ and the band offset between the $GaInP_2$ base and the GaAs substrate materials. With varying the light intensities irradiated at the sample, we found that, in addition to the flattening of the p-n junction, two changes in the potential profile happened in the locations of the front window or the back surface field (BSF) layers under the condition of a lower or a higher light intensities, respectively. The two potential changes, together with the flattening of the p-n junction, contribute positively to the open-circuit voltage of the device, indicating the importance of the window and the BSF layers in solar cell designs. Furthermore, the potential change at the window layers is understood in terms of the band offset between the $AlInP_2$ window and the $GaInP_2$ emitter layers, and the potential change at the BSF layer is understood in terms of the total effect of the photo-induced flattening of the band bending and the band offset at the interface between the base and the BSF, respectively.

3:40pm **EL+SC-TuA6 Deep Level Defect Characterization of InGaAsN Layers Grown by Molecular-Beam Epitaxy**, ***S.W. Johnston***, *R.K. Ahrenkiel, A.J. Ptak*, National Renewable Energy Laboratory

The quaternary alloy $In_xGa_{1-x}As_{1-y}N_y$ can be grown lattice-matched to GaAs and can potentially be used as the 1-eV bandgap material in a four-junction, high-efficiency solar cell. We have characterized a series of $In_xGa_{1-x}As_{1-y}N_y$ samples with varying N content by measuring deep level transient spectroscopy (DLTS). The samples were grown by rf plasma-assisted molecular-beam epitaxy and contain N concentrations $0 \le y \le 0.02$. Our data show that each as-grown sample contains a hole trap whose peak occurs near 350 K for the 0.2-ms rate window. Analysis of these peaks indicates activation energies of 0.62, 0.62, and 0.75 eV for samples with y = 0.003, 0.013, and 0.02, respectively. Electron traps were also detected, even though the DLTS measurements were performed with Schottky contacts deposited on p-type material. This is attributed to a large Schottky barrier. For the sample with y = 0.003, an electron trap with an activation energy of 0.50 eV was detected. As N-content increased, the detected electron-trap activation energies decreased to 0.22 and 0.27 eV for the y = 0.013 sample, and to 0.13 eV for the y = 0.02 sample. We also show DLTS data correlating to varying growth conditions and the effects of annealing processes.

4:20pm **EL+SC-TuA8 Thermal Quenching and High Temperature Cathodoluminescent Degradation of Sulfide-Based Powder Phosphors**, ***B.L. Abrams***, *L.C. Williams, J.-S. Bang, P.H. Holloway*, University of Florida

Temperature effects on cathodoluminescent (CL)intensity, spectrum and degradation of ZnS:Ag,Cl powder phosphor have been investigated. Thermal quenching was studied by increasing the phosphor temperature without exposure to a continuous electron beam and measuring the decreased CL intensity. A characteristic thermal quenching temperature of 150^{o}C with an activation energy (E_a) of 0.87eV was observed for ZnS:Ag,Cl. Along with reduced CL intensity, the spectra shifted to longer wavelengths and changed shape at elevated temperature. The shift was dominated by band gap narrowing at high temperatures. Shape change was attributed to Cu contamination from the heater stage. The CL spectral distribution and intensity were 100% recoverable upon cooling back to room temperature when electron beam exposure was minimal ($<1C/cm^2$). With continuous electron beam exposure, CL intensity upon cooling to RT (after $24C/cm^2$, 2keV primary beam energy) was <40% of the original intensity before heating. The loss of CL intensity at high temperatures was less than at RT for the same primary beam energy and coulombic dose. This is consistent with the Electron Stimulated Surface Chemical Reaction

(ESSCR) Model of degradation which predicts that elevated temperatures will reduce the mean stay time of physisorbed gases, decreasing the rate of the surface reactions leading to CL degradation. Electron beam heating was calculated using a simple heat transfer model and was significant for powder samples. This is consistent with morphological erosion observed on the surface of the ZnS particles degraded at elevated temperatures or high power densities. It is speculated that at temperatures of about 300°C, surface chemical reactions in combination with heating leads to removal of S and evaporation of Zn. Work supported by DARPA Grant MDA 972-93-1-0030 through PTCOE.

4:40pm **EL+SC-TuA9 Analysis of Ion Implantation Damage in Silicon Wafers by a Contactless Microwave Diagnostic**, ***R.K. Ahrenkiel***, National Renewable Energy Laboratory, *B. Lojek*, Atmel Corporation

Rapid thermal annealing (RTA) of ion implantation damage is required to maintain the integrity of submicron integrated circuit devices. A quick, efficient, and contactless diagnostic of the implantation damage is highly desirable. The residual radiation damage drastically reduces the recombination lifetime in the implanted region. Here, we will demonstrate the use of resonance-coupled photoconductive decay (RCPCD) technique allows us to to probe this region in boron and arsenic-implanted silicon wafers. Using a tuneable optical excitation source, we excite electron-hole pairs in the implanted region only. We compare these recombination times with those of the non-implanted bulk of the crystal. The lifetime is independent of excitation wavelength for the as-grown, oxidized wafers with typical values larger than 50 ms in semiconductor-grade silicon. After ion implantation with either arsenic or boron, the near-surface (711 nm) lifetime drops more than two orders of magnitude because of recombination at implantation-produced defects. After an RTA process, the lifetimes increase and again approach the bulk lifetime. One first group of wafers was processed in a standard rapid thermal processing (RTP) system SHS 2000 with a Hotliner. A second set of wafers were exposed to constant wavelength irradiation with maximum photon energy of approximately 1.4 eV for about 5 seconds, which has been called a "spike anneal". Our studies showed that the latter process produces wafers of lower recombination center density that the standard process. We propose some possible models to explain the improved properties of the "spike-annealed" wafers.

5:00pm **EL+SC-TuA10 Gas-phase Nanoparticle Formation during AlGaN MOCVD**, ***J.R. Creighton***, *W.G. Breiland, M.E. Coltrin*, Sandia National Laboratories

The AlGaN MOCVD process is often plagued by parasitic chemical reactions that diminish the group-III deposition efficiency and make it difficult to control alloy composition. We have explored many possible mechanisms for the parasitic reactions using a variety of experimental techniques and complex reactive flow simulations. Results indicate that the reactions require high temperatures and occur in the boundary layer near the growing surface. These reactions ultimately lead to the formation of nanoparticles, which we have recently observed using in situ laser light scattering. Thermophoresis keeps the nanoparticles from reaching the surface, so the material tied-up in nanoparticles cannot participate in the thin film deposition process. In the case of AlN, the particle size was determined to be 48 nm, and the particle density was in the range of 10^{8-9} cm^{-3}. At these densities a significant fraction (20% or more) of the input Al is converted into nanoparticles. Analysis of the polarization dependence of the scattering from GaN nanoparticles indicates that they are non-spherical. This makes determination of their size and density more difficult, but they are in the range observed for AlN nanoparticles. For GaN and AlN nanoparticles the balance of thermophoretic and viscous forces results in a sharp height distribution centered at ~6 mm above the surface, which is in good agreement with the theoretical prediction.[1]

[1] 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.

Nanometer Structures
Room: C-207 - Session NS+EL-TuA

Quantum Dots
Moderator: J. Nogami, Michigan State University

2:00pm **NS+EL-TuA1 Peter Mark Memorial Award Address: Mechanisms of Semiconductor Nanostructure Formation**, ***R.S. Goldman****, University of Michigan **INVITED**

Recently, semiconductor nanostructures have shown significant promise for a wide range of electronic, optoelectronic, and magnetic applications. In this talk, I will discuss the formation mechanisms of a variety of semiconductor nanostructures, including phase separation-induced alloy nanostructures and strain-induced self-assembled quantum dots. I will show how we have used data from cross-sectional scanning tunneling microscopy, in conjunction with x-ray reciprocal space maps, to develop new models for self-ordering of InAs/GaAs quantum dot superlattices[1] and spontaneous lateral phase separation in InAlAs alloys.[2] I will also describe our recent investigations of the role of elastic anisotropy in semiconductor nanopatterning, towards the formation of three-dimensional quantum dot crystals. These mechanisms are likely to be applicable to a wide range of heteroepitaxial semiconductor nanostructures.

This work was supported in part by the National Science Foundation (CAREER Award and Nanoscale Exploratory Research Program) and the Army Research Office (MURI Program)

[1] B. Lita, R.S. Goldman, et al, Appl. Phys. Lett. 75, 2797 (1999); Surface Review and Letters 7, 539 (2000).

[2] B. Shin, A. Lin, K. Lappo, R.S. Goldman, et al Appl. Phys. Lett . 80, 3292 (2002).

2:40pm **NS+EL-TuA3 Strain Effects and Inter-Dot Coupling in Self-Assembled Quantum Dot Arrays**, ***H.T. Johnson***, *R. Bose*, University of Illinois at Urbana-Champaign, *B.B. Goldberg*, Boston University, *H.D. Robinson*, University of California at Los Angeles **INVITED**

A computational model is used to simulate optical properties of self-assembled InAlAs/AlGaAs quantum dot arrays. Array sections containing up to 30 dots of varying size, shape, and spacing are considered. Comparisons are made to experimental results for arrays characterized using near-field scanning optical microscopy (NSOM). The experimental and computational studies both measure emission/absorption spectra with energy resolution that shows the effects of individual dots in the array. In the computational approach, the optical properties are computed from the spectrum of electron and hole states found for the ensemble. The energies and wave functions in the spectrum are first computed using a strain-modified k-p Hamiltonian approach; the spectrum includes confined electron and hole states associated with individual dots in addition to some delocalized states associated with coupled dots as well as the wetting layer. By modeling the entire ensemble of dots simultaneously, it is possible to consider effects related to long range field interactions between dots, such as linear elastic fields and extended quantum mechanical states. Two key results are of interest. First, it is found that even minor contact between the optical fiber tip and the sample surface leads to indentation strain large enough to substantially shift emission wavelengths of individual dots in the array. Second, extended states in groups of neighboring quantum dots lead to sharp, well-defined resonances in the emission spectra for the arrays. Results of the simulations clearly show these effects that are also observed in the experimental data.

3:20pm **NS+EL-TuA5 Growth of Ge Quantum Dots on Si(100) Without a Wetting Layer** [1], *K. Yoo*, Oak Ridge National Laboratory, *F. Flack*, University of Wisconsin - Madison, *H.H. Weitering*, Oak Ridge National Laboratory, *M.G. Lagally*, University of Wisconsin - Madison, *Z. Zhang*, ***J.F. Wendelken***, Oak Ridge National Laboratory

When Ge atoms are deposited directly onto a Si(100) substrate, the growth follows the Stranski-Krastanov growth mode in which three-dimensional Ge islands, or quantum dots (QDs), are formed on top of three monolayer thick wetting layers. For many optical and electronic device applications, Ge QDs without the wetting layer may be highly preferred. Using a buffer-layer assisted growth approach,[2] we have achieved the formation of Ge QDs on Si(l00) without a wetting layer. These QDs are shown to possess a narrow size distribution and are also substantially smaller than the QD hut clusters that are formed with the nomal SK growth mode. Using the buffer layer approach, Ge QDs have been grown in a single layer and in multiple layers with silicon spacer layers as has been done with multilayers of conventionally grown Ge hut clusters. Due to the fact that growth in the buffer layer approach is well isolated from any stress effects associated with a preceding layer of QDs, it is not expected that the QDs in separate layers

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***** Peter Mark Memorial Award Winner

will exhibit any layer to layer alignment effects as observed for SK growth. However, the smaller size of the QDs obtained with the buffer layer approach may be expected to exhibit stronger quantum size effects. Initial tests with samples prepared by this approach show a strong photoluminescence signals in the IR that exhibit striking differences from PL results[3] obtained from Ge QDs grown by conventional means with a wetting layer.

[1] Work supported in part by the U. S. DOE at Oak Ridge National Laboratory, managed by UT-Battelle, LLC under Contract DE-AC05-00OR22725, and in part by the NSF at the University of Wisconsin through the MRSEC program.

[2] J. H. Weaver and G.D. Waddill, Science 251, 1444 (1991).

[3] M.W. Dashiell, U. Denker, and O.G. Schmidt, Appl. Phys. Lett. 79, 2262 (2001).

3:40pm **NS+EL-TuA6 Spontaneous Generation of Free-Standing Ge Quantum Dots on Silicon-on-Insulator**, ***E.A. Sutter***, *P.W. Sutter, P. Zahl*, Colorado School of Mines

The growth of heteroepitaxial materials on engineered composite substrates such as silicon-on-insulator (SOI) opens a new route for controlling the structural and electronic properties of materials at the nanoscale. Local lattice strain induced by Ge quantum dots grown coherently on SOI - a composite of an ultrathin monocrystalline Si template supported by amorphous SiO_2 on a conventional Si wafer, causes significant local distortion in the Si template and can be used as a tool for nanoscale band structure engineering of the Si substrate. The Ge islands themselves form on SOI initially as huts and then transform into domes, similar to the sequence of epitaxially constrained shapes they assume on bulk Si (100). While the shape sequence of epitaxial Ge islands on bulk Si ends here, we observe further dramatic morphological changes on ultrathin SOI: a spontaneous transformation to free-standing Ge islands accompanied by a breakup of the thin Si slab. We use a combination of atomic force microscopy (AFM) and transmission electron microscopy (TEM) to document the sequence of shape transformations of Ge islands on SOI. We investigate in detail the island shape evolution and redistribution of the substrate material between the islands both before and after the breakup of the ultrathin Si slab of the SOI substrate.

4:00pm **NS+EL-TuA7 Production and Structure of Gas-phase Prepared Germanium Nanocrystals**, ***C. Bostedt***, *T. van Buuren, T.M. Willey, J. Plitzko,* Lawrence Livermore National Laboratory*, T. Moller,* Hasylab at DESY, Germany*, L.J. Terminello*, Lawrence Livermore National Laboratory

Clusters and nanocrystals represent a new class of materials, which exhibits promising novel properties. Germanium nanoparticles are particularly interesting, as the cubic as well as the tetragonal crystal phases have been reported for particle sizes below 5 nm, depending on the production method. We have developed a gas-aggregation based production method for germanium nanoclusters, with which nanocrystals in the bulk-like cubic phase from 1 to 10 nm in size can be produced. The clusters are condensed out of supersaturated Germanium-vapor, which is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. The particle sizes and phases have been well characterized by transmission electron microscopy (TEM), x-ray diffraction (XRD) and atomic force microscopy (AFM). The crystal phase - production method relationship is discussed. Only little is know about the surface structure of nanocrystals. Information about the surface structure is difficult to obtain. No distinct particle boundaries can be imaged with TEM. Photoemission spectroscopy (PES) has been shown to be a powerful tool to investigate bulk-crystal semiconductor surfaces. PES experiments have been performed on Ge nanocrystal films and a disordered surface shell around a crystalline core is deduced for the nanoparticles. .

C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program, N. Franco from the Spanish Education and Culture Office. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

4:20pm **NS+EL-TuA8 Surface Passivation Effects of Deposited Ge-Nanocrystal Films Probed with Synchrotron Radiation**, *C. Bostedt*, ***T. van Buuren***, *T.M. Willey,* Lawrence Livermore National Laboratory*, T. Moller,* Hasylab at DESY, Germany*, L.J. Terminello*, Lawrence Livermore National Laboratory

Clusters and nanocrystals represent a new class of materials that exhibit promising novel properties. The production of these nanostructures in the gas phase gives control over not only the size of the nanoparticles, but also over surface passivation - often not possible in other growth modes. The clusters are condensed out of supersaturated Germanium-vapor which is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. Their surfaces can be subsequently passivated with different materials evaporated into the vacuum chamber. This approach allows us to probe in a controlled and dynamic fashion the effect of surface passivation on nanocluster properties. X-ray absorption spectroscopy (XAS) and photoemission (PES) were performed on thin films of Germanium (Ge) clusters. Clean Ge nanocrystal films are found to exhibit much stronger quantum confinement effects at the band edges than similar Si particle films. These findings are compared to recent electronic structure calculations. For passivated nanocluster films we find that the passivating agent strongly alters the electronic structure of the clusters. In general the absorption edge shifts to significantly higher energies compared to cluster films without surface passivation. These results will be discussed in terms of a reduction of the cluster-cluster interactions.

C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

4:40pm **NS+EL-TuA9 Growth and Properties of Si Compatible Nanostructures: Si Quantum Dots Grown on CaF_2/Si Films**, ***A. Klust***, *A.A. Bostwick, T. Ohta, Q. Yu, M.A. Olmstead*, University of Washington

Si/CaF_2 is a promising candidate for epitaxial semiconductor/insulator heterostructures for optoelectronic applications because of the low lattice mismatch (0.5%) and large band gap difference (12.4 eV for CaF_2 vs. 1.1 eV for Si). In addition, the strongly dissimilar ionic/covalent bonding character in the system CaF_2/Si allows it to serves as a model system both to study heteroepitaxy of two dissimilar materials and to study the influence of bonding character and electronic structure on scanning probe microscopy. Here, we present an investigation of ultra-thin (1-3 molecular layers) CaF_2 films and Si quantum dots grown on these films using both non-contact atomic force microscopy (ncAFM) and scanning tunneling microscopy (STM). On the one hand, the extremely large band-gap of CaF_2 makes STM measurements difficult; stable imaging is not possible for films thicker than 3-4 molecular layers. On the other hand, STM gives complementary information to that obtained with ncAFM. For instance, scanning tunneling spectroscopy is used to characterize the electronic properties of single Si QD. Furthermore, the contrast during STM imaging of the CaF_2 films depends strongly on the polarity of the bias voltage and the film thickness. Non-contact AFM is used to clarify this behavior to separate electronic and topographic contributions to the STM images. Atomically-resolved ncAFM images of the CaF/Si interface layer will be shown and compared with similar published data obtained from bulk CaF_2(111) crystals.[1] The atomic structure of the CaF/Si interface layer is practically identical to the surface structure of bulk CaF_2(111), while the electronic structure differs. We discuss the influence of the different electronic structure on atomic resolution ncAFM.

[1] A. S. Foster, C. Barth, A. L. Shluger, and M. Reichling, Phys. Rev. Lett. 86 (2001) 2373.

5:00pm **NS+EL-TuA10 Formation of Self-Assembled Copper-Oxide Nano-Dots on SrTiO3(100)**, ***I. Lyubinetsky***, Pacific Northwest National Laboratory

In addition to offering a wide range electrical, optical and magnetic properties, oxide nanostructures can be stable in a range of environments without needing to add protective layers. In this work, we have observed the formation of self-assembled oxidized-copper nanodots on the SrTiO3(100) substrate using oxygen plasma assisted molecular beam epitaxy. The composition and structure were examined by x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, x-ray diffraction, and scanning probe microscopy in a wide range of growth parameters (temperature, oxygen pressure, and Cu flux). Under different growth conditions different shapes and/or composition have been found: truncated dots, square pyramids, and multifaceted domes with composition to be Cu2O or containing Cu metal also. Since nanostructure composition changes with temperature, observation made by interrupting growth and cooling may not be adequate. Thus, in addition to scanning probe measurements in ambient conditions, XPS spectra have been acquired at elevated temperatures in step-by-step mode at different stages of nanodots formation. Observed correlations between structural and composition changes will be discussed. Understanding of the evolution of the dot shape, size and composition would allow us to optimize formation conditions to synthesize cooper oxide nanodots with desirable parameters.[1]

[1] This work has been conducted as part of the PNNL Nanoscience and Nanotechnology Initiative supported by the Office of Biological and Environmental Research, U. S. Department of Energy.

Organic Films and Devices
Room: C-102 - Session OF+SS+EL+SC-TuA

Organic Molecular Films
Moderator: H. Fairbrother, Johns Hopkins University

2:00pm **OF+SS+EL+SC-TuA1 Reactivity of Polymers Containing Nitrogen and Oxygen Functional Groups with Vapor Phase Metal Atoms**, ***A.J. Wagner***, *G. Wolfe, D.H. Fairbrother*, The Johns Hopkins University

The surface reactions during the initial stages of polymer metallization are crucial in determining bonding and adhesive characteristics with native and plasma treated polymers. In this study, we have compared the reactivity of different nitrogen and oxygen containing functional groups with a variety of vapor phase metal atoms during the initial stages of metallization. The reactivity of different nitrogen containing functional groups during the vapor deposition of Ti, Fe, Ni, Cu and Au on Nylon 6, containing an amide group (-NH-(C=O)-and nitrogen implanted Poly(ethylene) (N-PE) containing a mixture of C-N, C=N and CN groups was studied. In addition, the reactivity of vapor phase metal atoms with specific functional groups was also investigated using a nitrile (CN) terminated self-assembled monolayer (CN-SAM). For each of the metals studied except Au reaction with Nylon 6 and N-PE resulted in the formation of the metal-nitride (MN), although the extent of reaction increased in the order Ti > Fe > Ni ~ Cu, scaling with the M-N bond strength. Experimental evidence, however, indicated that the different nitrogen containing functional groups present in the nitrogen-modified PE were not equally reactive. Ti and Fe also reacted with the C=O functional group in Nylon 6 to form their respective oxides while Cu, Ni and Au were unreactive with the C=O functional group. Metal nitride formation was also observed during evaporation of Ti and Fe on the CN-SAM although Cu and Au were unreactive towards the CN functional group. In contrast, metal carbide production was only evidenced during reactions with Ti. Results from this investigation will be interpreted in terms of the relative bond strengths associated with specific functional groups within the polymer and potential product species (e.g. metal oxide, nitrides).

2:20pm **OF+SS+EL+SC-TuA2 A New Crystalline Form of Pentacene: pi-stacked Thin Films Grown on Au(111)**, ***J. Kang***, *X.-Y. Zhu*, University of Minnesota

The recent demonstration of pentacene and related molecules in high-mobility field effect transistors (FETs), including superconducting FETs, has attracted great interest in this class of organic semiconductors. Carrier mobility is known to depend intimately on crystalline quality. In order to establish a molecular level understanding of structure-property relationship, we have carried out a scanning tunneling microscopy (STM) and spectroscopy (STS) study of the growth of crystalline pentacene thin films on Au (111). The use of high bias voltage (~ 5 V) and low tunneling current (~ 1pA) has enabled us to image, with molecular resolution, the growth of a new crystalline phase of pentacene well beyond the first a few layers. High resolution imaging shows that pentacene molecules form a pi-stacked crystalline phase with their long-axis parallel to the surface. This is attributed to the strong molecule-surface interaction, which seeds the growth of this new crystalline phase.

2:40pm **OF+SS+EL+SC-TuA3 Vapor Deposition and Polymerization of Low-k Polycyanurate Films**, ***J.N. Russell, Jr.***, *V.J. Bellitto, B. Bartlett, MJ Brooks, P.G. Santangelo, A.W. Snow*, Naval Research Laboratory **INVITED**

Future microelectronics will require advanced materials and processes for smaller, faster and more robust devices. Polymers address these needs and range from ultra-low permittivity materials to molecular semiconductors. Developing and understanding solventless deposition processes such as vapor deposition polymerization is important for producing conformal, voidless polymer films. One class of low-k polymers, polycyanurates, shows promise as a vapor depositable material. Yet little is known about the surface chemistry of the cyanate functionality and the conditions required for surface polymerization. Initially the surface chemistry of key functionalities in the monomer and polymer are examined using model compounds such as phenyl cyanate and triazine on Al(111). Aluminum was chosen because it is used for interconnects in microelectronics. Then, the in situ vacuum deposition and polymerization chemistry of NCO-CH2(CF2)6 CH2-OCN (F6Cy) is studied on Al, Cu, and Si surfaces. The vapor deposited F6Cy monomer film undergoes a photo-induced cyclotrimerization process to form cross-linked cyanurate networks with a permittivity of 2.1 at 1 GHz.

3:20pm **OF+SS+EL+SC-TuA5 Formation of Chemically Patterned Surfaces using Gas-Phase Oxalyl Chloride**, ***M.C. Asplund***, *G. Husseini, M.R. Linford, E.T. Sevy*, Brigham Young University

Optical lithography is a common technique for the formation of electronic devices on semiconductor substrates. Here we show an analogous technique that allows the introduction of a reactive functional group (-COCl) onto an alkylated Si substrate, or onto any substrate that contains C-H groups. The importance of the -COCl group stems from its high reactivity with amino and hydroxyl groups. Our new method consists of exposing a C-H containing surface to a gaseous mixture of N2 and oxalyl chloride ($(COCl)_2$) and then illuminating with 355 nm light. The UV photons form free radicals from the oxalyl chloride that then react with the C-H containing surface. We have shown using wetting, XPS, elipsometry and FT-IR spectroscopies that we have been able to form acid chloride functional groups on surfaces. By using simple optical masks we have shown that this functionalization occurs only where the sample is exposed to light. The key step to understanding the reaction mechanism for the surface reaction is understanding the formation and subsequent reaction of the radicals formed from the oxalyl chloride. Previous liquid phase reaction studies of oxalyl chloride with adamantane led to the suggestion that at 266 Cl is the primary radical formed, while at 355 nm the primary radical is the COCl radical. We have looked at the formation of radicals as a function of wavelength to analyze dissociation mechanism, and product energy distributions as well as the effect of pressure on radical formation. The minimum feature size which can be made using this method is given by the diffusion length of the radical. Thus the quenching must be understood and optimized to have controlled patterning of surfaces.

3:40pm **OF+SS+EL+SC-TuA6 Characterization of Ultrathin Organic Films via Near-edge X-ray Absorption Fine Structure Spectroscopy**, ***T.M. Willey***, University of California Davis and Lawrence Livermore National Laboratory, *A.L. Vance, T. van Buuren, C. Bostedt, A.J. Nelson, L.J. Terminello*, Lawrence Livermore National Laboratory, *C.S. Fadley*, University of California Davis and Lawrence Berkeley National Laboratory

Self-assembled monolayers (SAMs) and other thiol compounds adsorbed on Au(111) surfaces have become increasingly important for achieving surface attachment and orientation of complex molecules. Surface-attached molecular species containing catenanes and rotaxanes promise to play a vital role in achieving molecular-scale electronics and other devices.[1] Only through a rigorous understanding of the structure and properties of such molecular monolayer species can a rational synthesis of these hybrid materials be realized. Orientation of chemical bonds and thus the orientation of molecules can be precisely determined with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. Here, we present NEXAFS results on the configuration of surface-attached fundamental building-blocks of such systems, including a simple surface-attached rotaxane and its constituents. This rotaxane consists of a crown ether ring, threaded by a molecule bound to the gold at one end and providing an athracene stopper at the other.[2] Investigating films of the stopper molecule only vs. the complete rotaxane we confirm the presence of the crown ether in the complete molecule. We present the orientation of the anthracene stopper and crown ether ring with respect to the surface by deconvoluting their respective features in the NEXAFS.

Acknowledgements: This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL; at the ALS under contract number DE-AC03-76SF00098 at LBNL; and at the SSRL under contract number DE-AC03-76SF00515 at SLAC.

[1] Collier et al., Science 289, 1172-5

[2] Kolchinski et al., Chem. Commun., 1998, 1437-8

4:00pm **OF+SS+EL+SC-TuA7 Interfaces with Evaporated Short Chain Polyaniline**, ***B. Xu****, *A.N. Caruso, M. Bai, Y. Ovchenkov, S. Ducharme, B. Doudin, P.A. Dowben*, University of Nebraska-Lincoln

The interface properties of evaporated short chain polyaniline (PANI) were investigated by X-ray photoemission spectroscopy (XPS), inverse photoemission spectroscopy (IPES), as well as angle integrated photoemission spectroscopy (UPS). With sodium doping, the valence bands, conduction bands as well as the characteristic core levels show consistent shifts to the higher binding energy. Sodium, as an electron donor, when added to the polyaniline system, results in increased electron populations in the polyaniline bands --- effectively filling the almost completely filled band. In the case of iodine doping, all the states shifted to lower binding energy. Iodine, as an electron acceptor, effectively depletes the electron population in the occupied bands polyaniline. There is no abrupt interface formed between sodium or iodine and polyaniline, as demonstrated by the angle-resolved XPS. By comparison, the interface between polyaniline and another polymer poly(vinylidene fluoride with trifluoroethylene) copolymer (PVDF-TrFE) is quite abrupt. A P-N diode

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***** Morton S. Traum Award Finalist

was made by evaporating PANI (p type) on the top of PVDF-TrFE (n type). The results presented here should apply to the problems associated with improving heterojunction polymer devices.

4:20pm **OF+SS+EL+SC-TuA8 Controlled p-Doping of Organic Molecular Films**, ***W. Gao***, *A. Kahn*, Princeton University

We investigate the controlled electrical p-doping of the hole-transport organic molecular material α-NPD with the strong electron acceptor tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) using ultraviolet and inverse photoelectron spectroscopies (UPS/IPES), and in-situ I-V measurements. We previously examined p-doping of ZnPc co-evaporated with F_4-TCNQ,[1] and found an excellent energy match between the ionization energy (IE) of ZnPc (5.28eV) and the electron affinity (EA) of F_4-TCNQ (5.24eV), demonstrating host HOMO-to-guest LUMO charge transfer. The ZnPc thickness dependence of I-V data further demonstrated a 7 orders of magnitude increase in hole current injected from Au due to tunneling through the doping-induced narrow depletion region at the metal/organic interface.[2] In the present study, we show that α-NPD (IE=5.52eV) is also efficiently doped with F_4-TCNQ. The hole injection current increases by almost 5 orders of magnitude when only the first 80Å of α-NPD away from the metal/organic interface is doped, and increases by another factor of 10 when the entire organic film is uniformly doped. However, the doping-induced movement of E_F toward the HOMO appears to be more restricted than in ZnPc. Having excluded extrinsic effects like surface photovoltage, we propose that the substantial (~0.2 eV) ionization-induced relaxation of molecular energy levels moves the "doped" α-NPD HOMO upwards, and thus pins E_F deeper into the gap than for ZnPc, which is a planar molecule with a negligible relaxation energy (< 0.05eV). This interpretation is further confirmed with UPS study of the host material growth on a film of the dopant molecules. We also show that molecular level alignment at organic/organic interfaces is controllable by doping-induced dipole. Work supported by the NSF (DMR-0097133).

[1] W. Gao and A. Kahn, Appl. Phys. Lett., 79, 4040 (2001)

[2] W. Gao and A. Kahn, Organic Electronics (in press).

4:40pm **OF+SS+EL+SC-TuA9 Processable Optically Transparent Thin Films of Conducting Polymers**, ***B.D. Martin***, *N. Nikolov*, *R. Shashidhar*, Naval Research Laboratory

A major problem in the area of electronically conducting polymers is that attempts to enhance their electrical conductivity by adding ionic dopants are always accompanied by a decrease of optical transparency. In this study we show how molecular self-assembly of small carbohydrate molecules can decouple the optical transparency and electrical conductance of conducting polymer films. When a carbohydrate such as glycerol, which is essentially a non-ionic hydrogen bonding dopant, is added to a commercially available conducting polymer suspension (Baytron P), the carbohydrate forms an intercalated, hydrogen bonded sandwich between the ionic pairs of the conducting oligomer unit and its supporting polymer suprastructure. This results in a pronounced increase of the distance between the ion pairs, and hence, to decreased electrostatic interaction. As a consequence there is an enhanced mobility of the ions and hence an increased conductivity without an accompanying increase in optical absorption. This behavior, which is in striking contrast to the normally observed trends in conducting polymers doped with traditional ionic dopants, is very important to the development of plastic liquid crystal displays (LCDs) and organic light emitting diode (OLED) displays.

5:00pm **OF+SS+EL+SC-TuA10 Optical Properties of Ordered Ultrathin Films of PTCDA**, ***R. Nitsche***, *H. Proehl*, *S. Mannsfeld*, *T. Dienel*, *T. Fritz*, TU Dresden, Germany

Research activity on molecular solids has gathered pace in recent years as these materials have a wide range of interesting properties, emerging industrial interest with real applications at the horizon, and possible future applications that will enable electronics to move into the nanoscale. High quality samples, precise structural data, and a detailed understanding of the physical properties is essential, with special emphasis on thin films and interfaces. In this respect, the use of highly controlled growth techniques like Organic Molecular Beam Epitaxy (OMBE) is becoming more and more important, aiming at high quality thin films with controlled crystal structure and morphology, therefore displaying well defined physical properties. In our contribution we will discuss the special optical properties of ultrathin films of an archetypal organic material, namely PTCDA (perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride). Highly ordered organic thin films on a gold single crystal have been prepared by means of OMBE with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode. Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy) both ex situ and in situ has been applied to measure the optical characteristics of those films. The results clearly show that ultrathin layers have different optical properties as compared to thicker films, which in turn match the results known for long from polycrystalline samples. The results are further compared to thin films grown on mica to discuss the influence of different substrates.

Organic Films and Devices
Room: C-102 - Session OF+EL+SS+SC-WeM

Metal-Organic Interfaces
Moderator: L.J. Guo, University of Michigan

8:20am **OF+EL+SS+SC-WeM1 Interfaces between Metals and Conjugated Organic Materials: From Physisorption to Covalent Bonding**, ***N. Koch***, Princeton University, *J. Ghijsen,* Facultes Universitaires Notre-Dame de la Paix, Belgium, *A. Rajagopal,* Rutgers University, *C. Chan,* Princeton University, *J.J. Pireaux,* Facultes Universitaires Notre-Dame de la Paix, Belgium, *J. Schwartz, A. Kahn*, Princeton University **INVITED**

The electronic properties of interfaces formed between conjugated organic materials (polymers and small molecules) and other organic and inorganic materials are of paramount importance in terms of the performance of organic-based devices (e.g., light emitting diodes, thin film transistors). The alignment of energy levels at such interfaces is a direct consequence of the physical and chemical interactions between the materials. Using mainly photoemission spectroscopy (PES), we show that the nature of interaction between low work function metals and phenylene-based electroluminescent oligomers and polymers covers the whole range from physisorption (aluminum and samarium) to chemical reduction (calcium), and to charge transfer reactions (alkali metals). Although PES is a very powerful experimental tool to determine electronic properties of interfaces, great care must be taken in the interpretation of the data when wide band-gap materials, such as conjugated organic materials, are being investigated. We demonstrate that the observation by PES of a finite density of occupied states at the Fermi-level on an organic film in which alkali metal atoms have been intercalated does not necessarily imply metallicity nor the presence of negative polarons (radical anions), as previously proposed. From a combination of ultraviolet PES and Kelvin probe measurements, evidence is obtained that the substrate and the surface of the organic film are not necessarily in thermodynamic equilibrium, leading to potential misinterpretations of the Fermi level position at the surface of organic films.

9:00am **OF+EL+SS+SC-WeM3 Structural and Electronic Properties of the Interfaces between Au(111) and the Organic Semiconductors Pentacene and p-sexiphenyl**, ***C.B. France***, *P.G. Schroeder, B.A. Parkinson*, Colorado State University

Thorough understanding of the interface between organic semiconductors and metal contacts is important because of charge transfer events that take place in new devices based on organic semiconductors. Transistors[1] and photovoltaic devices[2] have been fabricated using pentacene as the organic semiconductor. In the interest of understanding the structural and electronic environments of these interfaces we have investigated thin films of pentacene and p-sexiphenyl on the Au(111) surface in ultrahigh vacuum using multiple characterization techniques. The entergetics of these heterojunctions have been measured using photoemission spectroscopy. Large interfacial dipole barriers exist at the interface of both systems. Temperature programmed desorption has been used to investigate the binding environment of the organic semiconductors on the metal substrate. Two different binding environments have been uncovered for both molecular semiconductors on the Au(111) substrate. Scanning tunneling microscopy has been used to investigate the coverage dependant structures that are formed by thin films of semiconductor molecules on the Au(111) surface. Pentacene was found to generate many overlayer structures at differing film thickness. Structures found on low coverage, monolayer and multilayer films will be discussed.

[1] Schön, J. H.;Berg, S.;Kloc, C.;Batlogg, B. Science 2000, 287, 1022.

[2] Schön, J. H.;Kloc, C.;Bucher, E.;Batlogg, B. Nature 2000, 403, 408. .

9:20am **OF+EL+SS+SC-WeM4 Growth of Organic Molecules on Ferromagnetic Substrates for Hybrid Organo-metallic Spintronic Devices**, ***M.V. Tiba***, *O. Kurnosikov, B. Koopmans, J.T. Kohlhepp, C.F.J. Flipse, W.I.M. de Jonge, U.S. Schubert,* Eindhoven U. of Technology, CNM, The Netherlands

Motivated by the success of polymer based- and molecular electronics, a challenging new field is emerging. Recent work has demonstrated the feasibility of hybrid organo-metallic spintronics, in which the spin degree of freedom is explicitly being used. Application in future magnetic sensor and memory technology has been proposed. Improved characteristics of such devices require very clean interfaces, therefore deposition of organic molecules in UHV environment is desirable. A severe complication of growing ordered structures of organic molecules on transition metal ferromagnetic substrates is their high reactivity. In this work we investigate the influence of substrate passivation on the bonding to the substrate (and hence the molecular ordering) for different organic molecules. Selection of the molecules is based on their electronic properties as well as their tendency to form well ordered layers. In the particular case of PTCDA molecules deposited on a Ni(111) substrate we show that quarter monolayer of oxygen reduces enough the reactivity of Ni to enable the molecules to form an ordered structure.[1] Current activities aiming at the fabrication of organo-metallic hybrid magnetic tunnel junctions having polycrystalline Co electrodes and organic barriers will be addressed as well.

[1] M.V.Tiba et al. Surf. Sci. 498 (2002) 161.

9:40am **OF+EL+SS+SC-WeM5 Controlling Metallic Contacts to Molecular Electronic Devices**, ***A.V. Walker***, *T.B. Tighe, O. Cabarcos, B.C. Haynie, D.L. Allara, N. Winograd*, Pennsylvania State University

In the development and design of molecular electronic devices, it is vital to understand the nature of the metal-organic monolayer interaction. To fully characterize these interactions, we employ a multi-technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations. Using an unfunctionalized molecular wire (4-[4?-(phenylethynyl)-phenylethynyl]-benzenethiol) monolayer on Au, we demonstrate that the metal-monolayer contact can be varied from complete destruction of the monolayer to contact formation at the monolayer terminus to complete penetration through the layer. For example, we show that upon deposition of Cu or Ag, the Cu and Ag atoms simultaneously interact with the terminal phenyl ring and penetrate to the Au/S interface. In contrast, Au penetrates through the monolayer at all coverages studied. By using metals specifically tailored for the chemistry of the device molecule as well as for electronic states, the characteristics of the metal-molecule contact can also be controlled. These types of data provide a foundation for rational design of contacts in molecular electronic devices.

10:00am **OF+EL+SS+SC-WeM6 DLC Thin Film as Electron Injection Layer in Organic LEDs**, ***M. Cremona***, Pontificia Universidade Catolica do Rio de Janeiro, Brazil, *R. Reyes,* Universidad Nacional de Ingeniería, Perú, *C.A. Achete, P.I. Guimarães, S.S. Camargo, Jr.*, Universidade Federal do Rio de Janeiro, Brazil

Recently, there has been an increased interest in organic light emitting diodes (OLEDs) due of their potential applications to color flat panel displays and in new optoelectronic components. These devices are assembled using three organic molecular materials: an electron injection layer, the emitting one and finally the hole injection layer. However, in most cases the electron injection is more difficult to achieve than hole injection. In this work two different diamond like carbon (DLC) thin films cathode were used to decrease the electron injection barrier. The first kind were nitrogen-doped amorphous hydrogenated hard carbon films deposited by rf glow discharge from methane-nitrogen mixtures onto the TPD/Alq$_3$ layer structure thermally deposited. DLC films were obtained for different N_2 partial pressures (bias voltage V_b=â€“370 V and total pressure P=8 Pa). Next, amorphous carbon nitride thin films (a-CN$_x$) have been deposited using a rf diode sputtering system onto the same organic structure. In this case the DLC films were deposited in reactive nitrogen-argon atmospheres. The partial pressure of nitrogen ranged from 0% to 100% at two different deposition pressures (P = 2 Pa and P = 8 Pa). In both cases a thick (150 nm) aluminum electrode were deposited onto the whole structure. The deposition process for the organic compounds is performed in high vacuum environment (6x10^{-6} Torr) on glass substrates coated with an hole injecting ITO transparent layer. A preliminary investigation was conducted on the properties of the OLED device with the two DLC intermediate layers. The relationship between the properties of the DLC deposited films on the electroluminescent characteristics of the different devices are investigated. The refractive index of the DLC film deposited, their conductivity and optical absorption, the OLED I-V curves, a preliminary photoluminescent and electroluminescent OLED results are presented and discussed.

10:20am **OF+EL+SS+SC-WeM7 Self-assembly of Molecular 1D wires on Cu(110)**, ***Y. Naitoh***, *F. Rosei, P. Thostrup, M. Schunack, F. Besenbacher*, University of Aarhus, Denmark

The adsorption of a large organic $C_{90}H_{98}$ molecule, known as the Lander molecule, is studied by Scanning Tunneling Microscopy (STM) on a Cu(110) surface.[1] By exposing the surface to low doses of oxygen at elevated temperatures, we form a nanopattern of alternating bare Cu(110) regions and (2x1)-O reconstructed regions aligned parallel to the [001] direction. The oxygen-induced reconstruction reveals a long-range ordering of Cu-O rows 20-50 Å wide. When deposited on this template, Lander molecules adsorb preferentially on bare Cu regions. By tuning the oxygen dosing, thereby adjusting the lateral periodicity of the template, and by varying molecular coverage in a controlled manner we can form long 1D rows of molecular wires. This type of assembly opens new possibilities for ordering organic molecules on surfaces.

[1] F. Rosei et al., Science 296, 328 (2002).

10:40am **OF+EL+SS+SC-WeM8 Dip Pen Nanolithography on Insulating Substrates**, ***S.E. Kooi***, *P.E. Sheehan*, *L.J. Whitman*, Naval Research Laboratory

Methods of assembling nanoscale components at chosen locations on a surface are needed to produce nanoscale electronic and sensor devices. Dip pen nanolithography (DPN) has been successful in producing such features as small as ~10 nm wide and one monolayer thick in several different molecule - surface combinations. The most studied systems have been alkyl and aryl thiol depostion on gold surfaces; however, DPN has also been demonstrated for inorganic salts on silicon, biomolecules on gold, and silazanes on semiconductor surfaces. We explore the application of DPN to write functional molecules on a technologically important insulating surface, namely silicon oxide. We have written several different trichlorosilane molecules directly onto thermally-grown silicon oxide substrates. By choosing an appropriate trichlorosilane and post-deposition chemical modification of the written molecules, we can direct the deposition of other nanostructures (such as carbon nanotubes, semiconducting nanowires, or nanoparticles). For example, by writing 10-undecenyltrichlorosilane onto silicon oxide, we can create a terminal carboxylic acid group with a post-deposition chemical oxidation. Subsequent deprotonation of the patterned carboxylic acid groups produces a negative charge that directs the deposition of positively-charged nanostructures. The ability to place nanoscale components at chosen locations on a surface, in combination with traditional (e-beam) lithographic techniques, opens up the possibility of interfacing nanoscale components with traditional devices.

Dielectrics
Room: Exhibit Hall B2 - Session DI+EL-WeP

Poster Session

DI+EL-WeP2 Remote Plasma-assisted Cleaning, Oxidation and Oxidation/Nitridation of GaN for Low Defect Density GaN-SiO$_2$ Interfaces, ***C. Bae***, *G.B. Rayner, G. Lucovsky,* North Carolina State University

In previous studies, device quality Si-SiO$_2$ interfaces and dielectric bulk films (SiO$_2$) were prepared using a two-step process; i) remote plasma-assisted oxidation (RPAO) to form a superficially interfacial oxide (~0.6 nm) and ii) remote plasma enhanced chemical vapor deposition (RPECVD) to deposit the oxide film. The same approach has been applied to GaN-SiO$_2$ system. After a 300 °C remote N$_2$/He plasma treatment of the GaN surface, residual C and Cl were reduced below Auger electron spectroscopy (AES) detection, and the AES peak ratio of O KLL and N KLL was ~0.06 or ~0.1 monolayer of oxygen. RPAO of GaN surfaces using O$_2$, N$_2$O, and N$_2$O in N$_2$ source gases was investigated by AES and x-ray photoelectron spectroscopy (XPS) to determine the oxidation kinetics, chemical composition of the interfacial oxide and oxidation state of interfacial Ga. Without an RPAO step, subcutaneous oxidation of GaN takes place RPECVD deposition of SiO$_2$, and on-line AES indicate a ~0.6-0.8 nm subcutaneous oxide. Compared to single step SiO$_2$ deposition, significantly reduced defect state densities are obtained at the GaN-SiO$_2$ interface by independent control of GaN-GaO$_x$ interface formation by RPAO and SiO$_2$ deposition by RPECVD.

DI+EL-WeP3 Screen Printing of PMN-PT Thick Films on the Pt-coated Silicon Wafers, ***B.M. Park***, *Y.-S. Seo, G.S. Lee,* University of Texas at Dallas

Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) is one of the widely studied relax ferroelectrics with excellent piezoelectric and electrostrictive properties. Single crystals, ceramics, and thin films of PMN-PT have been investigated for various applications such as actuators, transducers, and etc. However, there have not been enough studies for thick film fabrication of PMN-PT and its applications. For a promising application of the mechanical actuating of PMN-PT in the silicon-based integrated processing, an easy and low-cost technique for the thick film fabrication should be developed. The screen printing is one of the well known techniques to make thick films easily. Thus, in this study, we investigated a screen printing of PMN-PT thick films for electronic applications. The two kinds of pastes with different ratios between 0.9PMN-0.1PT ceramic powders and vehicle such as 6:4 and 7:3 were used. Thick films were printed through 200 mesh or 325 mesh screens on the platinum coated silicon wafers. The printed films were burn out at 600°C then heat treated at various conditions for the sintering of ceramic powders. The films were characterized by using optical and scanning electron microscopes and X-ray diffraction. As the results, the uniform thick films of PMN-PT could be made and the thickness of a singly printed film was about 10µm after heat treatment. When the printed films were heat treated at higher temperatures and for longer times, it caused to form the pyrochlore phase. The pure perovskite PMN-PT film could be obtained when it was heat treated at 800°C for 1hour or less. To prevent the pyrochlore phase from being formed, the additions of small excess amount of PbO and MgO were studied also. The addition of excess PbO or MgO can be expected to retard the pyrochlore formation. Some electrical properties of these screen printed films will be discussed also here.

DI+EL-WeP4 Influence of Impurities on Attenuation of Acoustic Waves in LiNbO$_3$ Crystals, *F.R. Akhmedzhanov,* ***M.M. Akhmedjanova***, Samarkand State University, Uzbekistan

In present work the attenuation of longitudinal and transverse acoustic waves in pure LiNbO3 and Mg, Zn, Cu and Cr doped LiNbO3 crystals have been investigated in detail. The weight concentration of above-mentioned impurities in investigated samples was consisted 0.01-0.02 percents. The measurements of attenuation coefficient carried out by Bragg light scattering method at the temperatures 295 K and 480 K. Piezoelectric transducers of Lithium Niobate of appropriate cuts are used in order to excite the longitudinal and the transverse acoustic waves with the frequencies of 0.3-1.8 GHz. The values of attenuation coefficients were determined from the measurements of the dependence of the scattered light intensity from the distance to the piezotransducer along the direction of the acoustic wave propagation. The obtained values of the scattered light intensities have been used to calculate the quantity and frequency dependence of the attenuation coefficient of the acoustic wave. The velocities of all the investigated waves were with sufficient accuracy determined from the experimental data simultaneously. The results of measurements have shown that in crystals with impurities are observed the changes in the attenuation of acoustic waves. Also have shown that the impurity of Cr causes increase of the attenuation of longitudinal waves on 20-50% but at the same time decreases the attenuation of transverse waves almost in two times. At the same time impurities of Cu, Zn, Mg reduce the decrease of attenuation the longitudinal waves in 1,5-2 times and insignificantly increase of the attenuation of the transverse waves. The obtained results are interpreted in framework of various mechanisms of attenuation including the electron-phonon, Akhiezer and Landau-Khalatnikov mechanisms. The influence of dielectric losses on the attenuation of piezoactive acoustic waves in LiNbO3 crystals is also discussed.

DI+EL-WeP5 Study of Molecularly Templated Nanoporous Silica Dielectrics with an a-SiC:H Etch Stop Layer Deposited by High Density Plasma Chemical Vapor Deposition, *F.M. Pan,* ***B.W. Wu***, *A.T. Cho, T.G. Tsai, K.C. Tsai,* National Nano Device Laboratories, Taiwan, R.O.C., *C.M. Yang, K.J. Chao*, National Tsinghau University, Taiwan, R.O.C.

α-SiC:H thin films were deposited on nanoporous silica thin films as the etch stop layer by high-density plasma chemical vapor deposition (HDP-CVD) using trimethylsilane (3MS) as the precursor. The α-SiC:H thin film can effectively improve hydrophobicity of the nanoporous film during HDP-CVD deposition, and, therefore, improve the dielectric property of the nanoporous dielectric layer. Electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) depth profiles reveal that the methyl groups uniformly distribute in the nanoporous film after the α-SiC:H film deposition. After the α-SiC:H film deposition and hydrogen plasma treatment, the effective dielectric constant of the α-SiC:H/silica film can be as low as 1.65, and slowly rises to 1.98 after a 25 day storage in the cleanroom ambient. This study shows that hydrophobicity modification of the nanoporous silica film and the etch stop layer deposition can be completed at the same time during the α-SiC:H depostion. Moreover, calcination of the surfactant templated nanoporous film can be accomplished in the same HDP-CVD before the etch stop layer deposition. This obviously simplifies the integration steps of nanoporous silica materials in the dual-damascene interconnect technology.

DI+EL-WeP6 Degradation and Modification of Gate Dielectric in MOS Structures by High-field Multilevel Current Stress, ***G.G. Bondarenko***, Moscow Institute of Electronics and Mathematics, Russia, *V.V. Andreev, A.A. Stolyarov, V.E. Drach*, Bauman Moscow State Technical University, Russia

A new technique for the modification and the degradation analysis of gate dielectric in the MOS structures by means of high-field tunnel electron injection is proposed. It was found out that the injection treatment of the MOS structures by multilevel current stress allows to increase the charge-to-breakdown. The technique is proposed to be used for investigation of the gate dielectric degradation in the MOS structures during and after high-field stress. The proposed technique differs from an ordinary constant current stress technique in the additional measuring level of current, thus providing the possible to estimate the dielectric charge change. The additional measuring level of injection current allows to decrease significantly the error of positive charge density measurement in the dielectric. Disregarding of positive charge trapping during the initial part of injection of electrons into dielectric while stress mode is being established causes the error above. The technique allows right after high-field injection without sample re-switching to investigate both the generation and the relaxation of positive charge, created by injected electrons into MOS structure gate dielectric in wide range of electric fields. Using the technique proposed, the injection degradation of the MOS structures with thermal SiO$_2$ film was studied. Furthermore, the possibility of modifying the film above to increase the injection reliability was shown.

DI+EL-WeP7 Improvement of (Ba,Sr)TiO$_3$ Dielectric Properties by in-situ Formation of IrO$_2$ on Ir Electrodes, ***C.H. Lai***, *Y.C. Wu, W.C. Chen,* National Tsing Hua University, Taiwan, *S. Ma*, Applied Materials

The (Ba,Sr)TiO$_3$ (BST) thin films grown on Ir bottom electrodes have showed high dielectric constants and low leakage current density, which are generally attributed to the formation of IrO$_2$ at the BST/Ir interface. The IrO$_2$ can decrease the accumulation of the oxygen vacancies, and typically was formed during the post-annealing process. In this work, we use high working pressure (47 mtorr) during rf sputtering deposition to enhance the in-situ formation of IrO$_2$ without post-annealing. We verified that oxygen plasma bombardment on the Ir surface during the deposition of BST films was the dominant mechanism for IrO_2 formation under the condition of high working pressure. The as-deposited BST films of 100 nm grown at 500 C show a dielectric constant as large as 550 (at 10 kHz); however, the leakage current is relatively large (10^{-4} A/cm^2 at 200 kV/cm). The large leakage current resulted from rough interface due to formation of thick IrO_2. To reduce leakage current, the double-layer technology was used, in which a thin BST film (5 nm) was deposited with pure Ar, and followed by deposition of a thick film (95 nm) with mixture gas (Ar/O_2). The thin BST layer can significantly reduce the roughness of IrO_2, resulting in lower leakage current (10^{-6} A/cm^2); however, since this thin BST layer is oxygen-deficient, the dielectric constant is slightly reduced. When the total BST thickness decreased, the reduction of dielectric constant becomes significant in the double-layer structure. For 30 nm BST films, we applied a dc substrate bias (-100V) during BST deposition to manipulate the film structure. The substrate bias significantly increases the film density and grain size, and at the same time reduces the roughness. Consequently, a large dielectric constant (220 at 10KHz) and a quite low leakage current (10^{-9} A/cm^2) were obtained in 30 nm BST films.

DI+EL-WeP9 Medium to High Vacuum Metal Organic Chemical Vapor Deposition of Al_2O_3

Z. Song, *R.D. Geil, V. Parwar, D.W. Crunkleton, C.A. Hales, B.R. Rogers*, Vanderbilt University

Al_2O_3 is one of the most promising medium-k gate dielectric materials to replace SiO_2 in future high performance integrated circuits. Because of good interfacial properties of the Al_2O_3/Si system, the 2001 update of the ITRS indicates the possibility of using Al_2O_3 as an interfacial layer between silicon and high-k dielectrics that tend to form interfacial SiO_2 or silicate layers. This presentation reports results of our work on the deposition of Al_2O_3 onto cleaned silicon substrates. We have performed two types of deposition experiments. First, Al_2O_3 films were deposited on p-type Si(100) substrates by metal organic chemical vapor deposition from aluminum tri-s-butoxide. We used a temperature range of 300 - 450 °C and a pressure range in the medium to high vacuum regimes. Second, silicon surfaces were briefly exposed to the precursor gas at low temperatures in our one-of-a kind UHV-CVD system. The gas was then pumped out and the silicon substrate was heated to a preset temperature. The gases released during temperature ramping were analyzed by in-situ quadruple mass spectroscopy (QMS). The properties of the films were characterized by Spectroscopic Ellipsometry (SE), Time of Flight Medium Energy Back Scattering (ToF-MEBS), RBS, XPS, XRD and ATR FT-IR.

DI+EL-WeP10 N Composition and Chemical State Profiling in Thermally and Plasma Nitridated Silicon Oxide Films

Y.S. Chung, Samsung Advanced Institute of Technology, Korea, *H.S. Chang, D.W. Moon*, Korea Institute of Standards and Science

The composition and chemical state of N in thermally and plasma nitridated silicon oxide films were depth profiled by X-ray Photoelectron Spectroscop (XPS) using a chemical etching method with HF. The nitrogen profile of thermally nitridated film differs from plasma nitridated one. Nitrogen is rich at surface in plasma nitridated oxide films, while N is rich at interface in thermally nitridated film. The N depth profiles from XPS were compared with those from medium energy ion scattering spectroscopy in a good agreement. The N 1s core level of plasma nitridated oxide shows a main species with N?Si3 bonding and small amounts of defect nitrogens due to plasma treatment. The change of chemical composition with annealing to cure these defect also will be discussed.

DI+EL-WeP11 Study on Damage Recovery of Etched $(Ba_{0.6},Sr_{0.4})TiO_3$ Thin Films in Ar/CF_4 Plasma

P.S. Kang, *D.P. Kim, K.T. Kim, C.I. Kim*, Chung-Ang University, Korea, *T.H. Kim,* YIT, Korea, *S.J. Lee*, ETRI, Korea

In this study, $(Ba_{0.6},Sr_{0.4})TiO_3$ (BST) thin films on $Pt/Ti/SiO_2/Si$ substrates were deposited by a sol-gel method and the inductively coupled plasma (ICP) etching behavior of BST thin films had been investigated by a function of Ar/CF_4 gas mixing ratio. We also investigated the influence of etching damage in BST films during the ICP process. For analysis of the Ar/CF_4 plasma-induced damage in the Pt/BST/Pt capacitor, measurements of leakage current density and dielectric constant was carried out at different substrate bias voltage, ICP power and gas mixing ratio. The physical damage and structure of etched BST thin films were investigated by atomic force microscopy (AFM) and x-ray diffraction (XRD). The existence of contamination on the surface of the etched BST was measured using an x-ray photoelectron spectroscopy (XPS) analysis. Fluorine atoms definitely disappeared after O_2 annealing at 700°C. From the electrical property and structure analysis, the reduction and recover of etching damage by re-annealing was effective in the additive O_2 into Ar/CF_4 rather than additive O_2 into Ar/Cl_2 plasma.

Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2001-042-E00042).

DI+EL-WeP12 Etching Characteristics of $(Pb,Sr)TiO_3$ Thin Films Using Cl_2/Ar Inductively Coupled Plasma

G.H. Kim, *D.P. Kim, K.T. Kim, C.I. Kim*, Chung-Ang University, Korea

Recently, ferroelectric thin films have received great attention for the application to high density memory devices. Among the various ferroelectric films, the BST thin film was noticed as the most promising material due to its high dielectric constant and paraelectricity at normal operating temperature. Although BST possesses a satisfactorily high dielectric constant, it was known that a post heat treatment at a high temperature was essential to obtain good electrical property. The heat treatment at high temperature can cause deleterious effects on an electrode, barrier metal, and contact plug. Strontium titanate ($SrTiO_3$) is one of the few titanates which is cubic at room temperature. But, the dielectric constant is lower than BST. The addition of lead into strontium titanate makes its dielectric constant(ε_r=1377) higher and the temperature of crystallization lower. Therefore, PST thin film can be a promising material due to its high dielectric constant and paraelectricity at normal operating temperature. However, there is no report on the characteristics and mechanism of PST thin films during etching process. In this study, Inductively coupled plasma etching system was used for etching PST because of its high plasma density, low process pressure and easy control bias power. The etching characteristics of PST thin films were investigated in terms of etch rates and selectivity as a function of gas mixing ratio, rf power, dc bias voltage and chamber pressure. The Cl_2/Ar plasmas were characterized by optical emission spectroscopy and Langmuir probe analysis. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy and secondary ion mass spectrometry. Scanning electron microscopy was used to investigate the etching profile.

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DI+EL-WeP13 Etching Characteristics of $Bi_{4-x}Eu_xTi_3O_{12}$ Thin Films Using Inductively Coupled Plasma

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In recent years, some Bi-layered perovskite oxide such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_{4-x}La_xTi_3O_{12}$ (BLT) have been intensively studied for use in FRAMs because of its low leakage current, low coercive field, and fatigue-free with simple Pt electrode. The fatigue-free behavior of SBT and BLT thin film was due to the charge compensating effect of Bi_2O_2 layers resulting in the reduction of space charge and from domain wall unpinning that happens at least as rapidly as domain pinning. However, SBT and BLT thin films have a disadvantage of low remanent polarization for the high-density integration of FRAMs. From the viewpoint of the general formula of Aurivillius compounds, radii of Europium ion (0.95 Å), similar to Bi ion (0.93 Å) in the $Bi_4Ti_3O_{12}$(BIT), occupies the A site in the perovskite unit BIT. The europium-substituted BIT(BET) thin films resulted in a large 2Pr, whose value (60.99μmC/cm^2) is much larger than that of Sm-modified BIT thin film (2Pr = BSmT: 49μmC/cm^2) and BLT thin film (2Pr = 27μmC/cm^2) at an applied voltage of 10V. For this advantage, BET thin films have emerged as new ferroelectric materials. However, there is no report on etching BET thin films. Inductively coupled plasma source was used for etching BET because of its high plasma density, low process pressure and easy control bias power. BET thin films were etched with using CF_4/Ar plasma. The experiments were carried out with measuring etch rates and selectivities as a function of gas mixing ratio, rf power, dc bias voltage. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to investigate the surface morphology of BET thin films exposed in plasma and etching profile.

DI+EL-WeP14 Etching Characteristics of $YMnO_3$ Thin Films in Cl Based Inductively Coupled Plasma

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$YMnO_3$ thin films are excellent dielectric materials for high integrated FRAM because $YMnO_3$ have a relatively low permittivity (ε_r=20) and do not include volatile materials such as Pb and Bi which easy diffuse into the Si substrate and lead to point defects. To apply the $YMnO_3$ thin films on the highly integrated FRAMs, high-density plasma systems should utilized because it provides high degree of anisotropy and good selectivity. In this study, we etched $YMnO_3$ thin films in Cl based inductively coupled plasma (ICP). Etching characteristics of $YMnO_3$ thin films were investigated in terms of etch rate and selectivity as a function of gas mixing ratio, RF power, and substrate temperature. The diagnostics of the plasma were estimated using optical emission spectroscopy (OES). To investigate etching mechanisms of $YMnO_3$ thin film, chemical reactions on the etched surface of $YMnO_3$ thin films were investigated by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). Etching profile was investigated by scanning electron microscopy (SEM).

DI+EL-WeP15 The Effect of Cr Doping on the Microstructural and Dielectric Properties of $(Ba_{1-x},Sr_x)TiO_3$ Thin Films for Tunable Microwave Device Applications, ***C.I. Lee***, Ansan College of Technology, Korea, *K.T. Kim, C.I. Kim, D.H. Kang*, Chung-Ang University, Korea

$(Ba_{1-x}, Sr_x)TiO_3$ (BST) thin film is a very attractive material for the tunable microwave device applications such as electronically tunable mixers, delay lines, filters and phase shifters. We have investigated the structural, compositional and dielectric properties of BST thin film as a function of Cr dopant concentration from 0 to 15 mol% and analyzed using X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The dielectric constant of the 300 nm Cr-doped BST thin film decreased as the Cr concentration increased. The loss tangent of 15% Cr doped BST thin film was higher than that of the pure film, but the 1~10 mol% Cr doped thin film was lower than that of the undoped BST thin film.

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DI+EL-WeP16 Cyclic-CVD of Strontium Tantalate for Alterantive Gate Dielectric Applications, *H.S. Choi,* ***Y.M. Jang****, M.J. Kang, I.H. Choi*, Korea University

As gate oxide thickness in SiO_2-based MOS device decreases, new high-k dielectric materials are demanded to substitute for silicon dioxide. In this presentation, we will discuss our work on developing strontium tantalate for use as alternative gate dielectrics. We have grown strontium tantalate thin films on p-type Si substrate by cyclic chemical vapor deposition technique using $Sr[Ta(OC_2H_5)_5(OC_2H_4OCH_3)]_2$ as precursor. Our studies have included substrate temperatures between 250 and 400°C and post annealing temperatures 600 and 800°C. We have studied the surface and interface image, the structural properties and film compositions by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Rutherford Backscattering Spectrometry (RBS). Also we have investigated the applicability to MOS device through the capacitance voltage (C-V) measurement and leakage current measurement.

DI+EL-WeP17 Surface Preparation of Si (100) Substrates Prior to Deposition of High K Dielectrics, ***V. Pawar****, Z. Song, D.W. Crunkleton, B.R. Rogers*, Vanderbilt University

We have investigated different fluoride based reagents for etching of native oxide on silicon surfaces prior to chemical vapor deposition of high K dielectrics. We have also investigated different cleaning agents (water and organic based) to see the effect on the native oxide growth and surface cleanliness. The native oxide growth was monitored by spectroscopic ellipsometry and x ray photoelectron spectroscopy. We have shown that time logarithmic model can be used to model the data and useful information about the characteristic time (incubation time) can be obtained for different treatments.

DI+EL-WeP18 Comparison of Reactive Sputtered Oxide Films from Zr and Hf Metal Targets with Poly-Si or Poly-SiGe Gate, ***J.-H. Yoo***, Yonsei University, Korea, *S.-W. Nam*, Samsung Electronics Co., Ltd., Korea, *S. Nam, D.-H. Ko*, Yonsei University, Korea

As CMOS devices are being continuously scaled down, gate oxides with EOT < 15Ã… will be required. Key process issues in conventional SiO_2 scaling are with boron penetration, gate leakage for very thin gate oxides and depletion effects in the polysilicon electrodes. Therefore, dielectric materials with higher dielectric constant than SiO_2, possibly large band-gap, low interface state density, and good thermal stability have drawn a lot of attention as alternative gate dielectric materials. Recently, ZrO_2, HfO_2 and their silicates have been considered as promising alternative materials due to their high dielectric constant and good thermal stability with Si substrates. We investigated the microstructures and electrical properties of reactive sputtered ZrO_2 films and HfO_2 films on Si (100) substrate. And the thermal stabilities and compatibilities between the films with poly-Si gate electrode were compared. The films as a gate dielectric were deposited by reactive dc magnetron sputtering, followed by thermal annealing in N_2 gas ambient using furnace and subsequently the microstructures of the films were investigated by Ellipsometry, XRD, AFM, TEM and XPS. The interfaces with poly-Si or Si substrate were carefully observed by HR-TEM, XPS/AES and SIMS with annealing temperature. Also, the properties of the films with poly-SiGe as alternative gate electrode were investigated. The electrical properties were assessed and compared by C-V and I-V measurements of Metal-Oxide-Semiconductor capacitor structure.

DI+EL-WeP19 Mechanical and Optical Properties of Low Dielectric Constant Silicon Containing Fluorocarbon Films by Plasma Enhanced Chemical Vapor Deposition, ***Y.Y. Jin***, Louisiana State University, *G.S. Lee*, The University of Texas at Dallas

Silicon containing fluorocarbon (SiCF) film for use as low-k interlayer dielectrics (ILD) has been investigated on mechanical and optical properties. The preparation of SiCF films is carried out by plasma enhanced chemical vapor deposition (PECVD) using precursors 5% disilan in helium ($5\%Si_2H_6/He$) and tetrabluorocarbon (CF_4). Hardness and residual stress in the films subsequently measured using an atomic force microscopy (AFM) and the curvature method via Stoney's equation, respectively. The SiCF film samples were deposited on quartz plates to investigate the characteristics of optical transmission and optical energy gap. The optical transmission data were obtained in the wavelength range of 200 nm to 800 nm by the NIR-UV-VIS spectrophotometer at room temperature. The optical energy gaps of the films are calculated from a plot of Tauc extrapolations.

DI+EL-WeP20 Effect of Low Pressure Annealing for Low Temperature Crystallization of $SrBi_2Ta_2O_9$ Ferroelectric Thin Films, *H.S. Choi,* ***K. Lee****, G.S. Lim*, Korea University, *Y.T. Kim, S.I. Kim,* Korea Institute of Science and Technology*, I.H. Choi*, Korea University

A new low pressure annealing method for low temperature crystallization of $SrBi_2Ta_2O_9$ thin films is proposed. SBT films were prepared on IrO_2 bottom electrode by metalorganic decomposition (MOD) method and annealed under low oxygen pressure by a modified rapid thermal annealing process. Under an oxygen pressure as high as 30 torr, the crystallization temperature inducing the ferroelectric SBT phase can be lowered to 650°C. Those films processed at 650°C showed satisfactory ferroelectric properties, that is, the remanent polarization (P_r) and the coercive electric field (E_c) were 5.68 $\mu C/cm^2$ and 61 kV/cm at an applied voltage of 5 V, respectively. The films also showed fatigue-free characteristics: no fatigue was observed up to about 10^{10} switching cycles.

Electronic Materials and Devices
Room: Exhibit Hall B2 - Session EL+SC-WeP

Poster Session

EL+SC-WeP1 Mechanistic Aspects of SiC Oxidation, *C. Radtke,* ***F.C. Stedile****, I.J.R. Baumvol,* UFRGS, Brazil, *I.C. Vickridge, I. Trimaille, J.-J. Ganem, S. Rigo*, Universite de Paris 6 et 7, France

SiC is the material of choice in the field of high band-gap semiconductors used in high-power, high-frequency, high-voltage, and/or high temperature applications. The possibility of obtaining an oxide film with good electrical characteristics (SiO_2) by thermal oxidation is one of its major advantages. In order to develop an oxidation model, the knowledge of the oxidation mechanism is of great importance. We investigated the incorporation of oxygen in surface and interface regions during different stages of the oxidation process of the C-face of 6H-SiC(0001) wafers as well as its dependence with the gas pressure. Oxidations in natural ultra dry O_2 followed by oxidations using isotopically enriched oxygen ($^{18}O_2$) were performed. Different times of oxidation in the natural gas and chemical etching of grown oxides were used to obtain samples representing different starting conditions. Amounts of incorporated ^{18}O and depth profiles were determined using nuclear reactions in plateau and resonance regions of their cross-section curves, respectively. The results evidence that in the whole range of oxidation times studied, the oxidation process was limited by the reaction rate of diffusing oxygen with SiC. These results present a new dynamical mechanism with remarkable differences from the oxidation of Si.

EL+SC-WeP2 Comparison of the Decomposition of Metacarborane and Orthocarborane, ***A.N. Caruso****, P.A. Dowben*, University of Nebraska, Lincoln

It is now recognized that there are several different polytypes of B_5C (boron carbide) for which the electronic structure has remained obscure. We present a novel B_5C polytype that is radically different from previous polytypes in that it forms an n-type semiconductor. Decomposition of closo-1,7 dicarbadodecaborane (metacarborane) and closo-1,2 dicarbadodecaborane (orthocarborane) due to adsorption of photons (32eV soft x-rays) has been observed. We compare adsorption and decomposition for these molecules and attempt to address why molecules with the same basic structure create materials that are wildly different in their electronic (semiconducting) properties.

EL+SC-WeP3 Non Destructive Evaluation of Alternative Substrate Quality Using Glancing Incidence X-Ray Diffraction and Raman Spectroscopy, ***H.J. Haugan**, A.M. Cain, T.W. Haas, K.G. Eyink,* Air Force Research Laboratory, *C.J. Eiting,* Uniroyal Optoelectronics, *D.H. Tomich, L. Grazulis, J.D. Busbee*, Air Force Research Laboratory

Alternate substrate technology holds promise for the growth of high quality lattice mismatched epitaxial films. Unfortunately, the technology has been plagued by difficulties in reproducibility of results. Some of this problem resides in a lack of characterization of the thin, twist bonded layer used as the template for subsequent epitaxial growth. In this work, grazing incidence diffraction (GID) and micro-Raman spectroscopy were used to characterize the alternative substrate prior to growth. The 14 nm and 50 nm thin GaAs layers were bonded to (100) GaAs substrates and subsequently exposed by standard thinning and etching techniques. The crystalline quality of the thin bonded substrates was studied by GID. The full widths at half maximum (FWHM) of the 004 peaks were used to monitor optimum bonding condition. The measured FWHM varied from 29 to 601 arcseconds with smooth surfaces exhibiting the lowest values. The effect of bond pressures on template layers were studied for a series of 50 nm alternative substrates prepared using pressures ranging from 75 psi to 25 psi with a constant bonding temperature of 450 °C. All transferred template layers prepared within this pressure range showed poor quality (FWHM ranged from 324 to 601 arcseconds) when compared to the bulk-GaAs of 12 arcseconds. Micro-Raman measurements were also carried out on these samples. A transverse optical (TO) phonon line is seen and the intensity ratio of the TO to longitudinal optical phonon were much higher than that of GaAs substrate, confirming that the bonding process is causing damage to the thin template layer.

EL+SC-WeP4 Design and Simulation of AlGaN/GaN Heterojunction Bipolar Transistors, ***K.P. Lee**, S.J. Pearton, F. Ren,* University of Florida, *J.-I. Chyi,* National Central University, Taiwan, *A. Dabiran, P.P. Chow,* SVT Associates

The progress in developing AlGaN/GaN HBTs has been very limited compared to HEMT devices in the same materials system.HBTs would have advantages of better linearity,higher output power,better radiation resistance and more uniform threshold voltage compared to field effect transistors.To date,dc current gains in HBTs have been limited to <30 at room temperature and the rf performance is poor.The high base resistance is one of the limiting factors in npn structures.We have used a drift-diffusion model to simulate the dc characteristics of a variety of structures designed to improve the HBT performance.These include a superlattice base to enhance the hole concentration due to incomplete ionization of the Mg acceptors,base grading and a regrown base contact structure.The anisotropy in transport properties of the superlattice base have been taken into account.Base transport enhancement is predicted by the introduction of a quasi-electric field in the base layer.The minority carrier lifetime in the base is also a critical parameter determining the HBT performance.A comparison will be given of the relative strengths of the different device structures and their prospects for realizing a high gain,high speed,robust AlGaN/GaN HBT technology.

EL+SC-WeP6 Growth of Gallium Nitride on Silicon Substrate by MOCVD Using Multiple Buffer Layers, *M.A. Al-Tamimi, **D.A. Gulino***, Ohio University

An attempt has been made to improve the crystalline quality of MOCVD-grown gallium nitride on silicon (111) substrate by the insertion of a second aluminum nitride buffer layer. The conventional method for growing GaN on heterosubstrates has been to first grow a thin, low-temperature layer of typically aluminum or gallium nitride to act as a compliant, or "buffer," layer to reduce the degree of crystalline defects and threading dislocations in the subsequently-grown GaN epilayer. In the work reported here, a second, low-temperature AlN buffer layer was grown on top of the first GaN epilayer, and this was followed by a second GaN epilayer. We have found improvement in the crystalline quality of the second GaN epilayer as measured by x-ray diffraction rocking curves. We also experimented with ramping the temperature during growth of both the first and second AlN buffer layers, and we discovered that the best quality GaN film obtained in this work occurred when the first buffer layer was grown as the temperature was ramped from 800 to 1060°C and the second buffer layer grown at a fixed temperature of 800°C.

EL+SC-WeP7 Edge Termination Design and Simulation for Bulk GaN Rectifiers, ***K.H. Baik***, University of Florida, *Y. Irokawa*, Toyota Central Research Laboratories

GaN bulk rectifiers show excellent on-state resistances (in the milli-ohm.cm-2 range) forward turn-on voltages of ~1.8V and reverse-recovery times of <50ns. A key requirement is to develop effective edge termination techniques in order to prevent premature surface-induced breakdown. We have performed a simulation study of the effects of varying the dielectric passivation material(SiO2,SiNX,AlN,Sc2O3 or MgO),the thickness of the this material, the extent of metal overlap onto the dielectric and the ramp oxide angle on the resulting reverse breakdown voltage(VB) of bulk rectifiers. We find that SiO2 produces the highest VB of the materials investigated, that there is an optimum metal overlap distance for a given oxide thickness and small oxide ramp angles produce the highest VB. Initial experimental results on small-area devices show good agreement with the trends identified by the simulations. The dc characteristics are still dominated by the defect density in the substrate for large-area rectifiers.

EL+SC-WeP8 Photoelectrochemical Oxidation of GaN and Fabrication of Metal-oxide-semiconductor Structures using Ga-oxide Dielectrics, ***D.J. Fu**, T.W. Kang*, Dongguk University, Korea

GaN metal-oxide-semiconductor (MOS) capacitors were fabricated by using Ga oxide formed by photoelectrochemical oxidation of GaN. The electrical properties of the MOS structures as characterized by capacitance-voltage measurement were found to be dependent on the oxidation time and post-treatment. Positive flatband voltage was observed in devices with thin oxide layers indicating the existence of negative oxide charge. Very thin oxide exhibits high capacitance and reverse leakage, which can be reduced by rapid thermal annealing. Passivation of the interface by the annealing is partially responsible for the improvement. Thicker oxide layers exhibit improved electrical properties. Low density of interface states was obtained in the Ga-oxide/GaN structure grown under optimized conditions.

EL+SC-WeP9 Relating Interfacial Structure and Composition of Pt/CdZnTe to Radiation Detector Device Performance, ***D.J. Gaspar**, M.H. Engelhard, V. Shutthanandan, S. Thevuthasan,* Pacific Northwest National Laboratory, *A.A. Rouse, C. Szeles, J.-O. Ndap, S.A. Soldner*, eV PRODUCTS

The interfacial structure and composition of platinum/CdZnTe interfaces was examined to establish correlations between surface and interfacial stoichiometry and radiation detector device performance. X-ray photoelectron spectroscopy (XPS), including depth profiling, and Rutherford backscattering spectroscopy (RBS) were used to determine surface and Pt/CdZnTe interfacial composition. The ^{57}Co spectral response of five CdZnTe detector devices formed by deposition of Pt contacts on a CdZnTe crystal was correlated to the interfacial stoichiometry and the ideality factor. Non-ideal contact behavior was correlated to interfacial oxidation and to the bulk series resistance of the diode. XPS depth profiling revealed differences in the formation of the rectifying contacts, which correlated to device electrical performance.

Organic Films and Devices
Room: Exhibit Hall B2 - Session OF+EL-WeP

Organic Films and Devices

OF+EL-WeP1 Cycloaddition of Silyl-disila-cyclopentene on Si(001) Surface, ***B.-Y. Choi**, Y.-J. Song, Y. Kuk,* Seoul National University, South Korea

It is known that π bonds of unsaturated organic molecules can easily react with Si=Si dimers of the reconstructed Si(001)-2x1 surface, resulting in two new Si-C σ bonds. Through such a cycloaddition, densely-packed molecules on hybridized Si(001) surface are highly ordered both translationally and rotationally over macroscopic length scale. However, in spite of much effort, the mechanism of cycloaddition on surface is not known clearly. We investigated the reaction of 2-silyl-1,3-disilacyclopent-4-ene (SDC) with the Si(001) surface using scanning tunneling microscopy. STM images show that the SDC molecules are slightly elongated parallel to the dimer direction, suggesting that the molecules bond in a manner of typical [2+2] cycloaddition. It can be noted that there exists a preferred bonding site of SDC molecule. However, the analysis of the observed structure suggests that there is more than one way for SDC to bond to the Si(001) surface. Some molecules place perpendicular to dimer direction and even complex absorbates are shown. We suggest that the several reactions occur nearly as frequently.

OF+EL-WeP2 Nanolithography Technique Based on Dynamic Mode Atomic Force Microscopy and Organosilane Self-Assembled Monolayers, ***K. Hayashi**, N. Saito, H. Sugimura, O. Takai,* Nagoya University, Japan

Organosilane self-assembled monolayer (SAM) is a candidate for resist material in future nanolithography techniques. Although several techniques have been applied to patterning of the SAMs, scanning probe lithography using an atomic force microscope (AFM) is promising since the method has a high potential in archiving nanometer scale resolution. However, there has been a serious problem, that is, damages of the AFM-tip, when the AFM is operated in the contact mode. Here we report on nanopatterning of organosilane SAMs using a dynamic mode AFM in which tip damages are expected to be reduced. We observe AFM-tip induced chemical changes on the SAM surfaces by Kelvin-probe force microscopy (KFM) working in the dynamic mode as well. Onto cleaned silicon (Si) substrates covered with native oxide (SiO_2), a SAM was formed from n-octadecyltrimethoxysilane [ODS: $CH_3(CH_2)_{17}Si(OCH_3)_3$]. Thickness of this ODS-SAM was ca. 1.8 nm. While scanning a AFM-tip (Au coated Si tip), operated in the dynamic mode, on an ODS-SAM/Si sample, a DC bias voltage was applied between the conductive tip and the sample. After the patterning, the sample surface was characterized by KFM. Due to electrochemical reactions induced by the injected current, the modified region where current had been injected from the tip was found to show a more positive surface potential than the surrounding unmodified region. Through the surface potential images acquired by KFM, chemical changes of ODS-SAM could be detected, while such changes could hardly be confirmed in topographic images. KFM is a powerful means to characterize nanoscale patterns on the SAMs drawn by scanning probe lithography.

OF+EL-WeP3 Photoemission Study of Dodecanthiol on Au (111), *H. Geisler, S. Sales,* Xavier University of Louisiana, ***J.M. Burst****, S.N. Thornburg, C.A. Ventrice Jr.,* University of New Orleans, *Y. Losovyj, P.T. Sprunger*, Louisiana State University

The adsorption of alkanethiols on various single-crystal metal surfaces results in the formation of self-assembled monolayers (SAMs). Typically, SAMs are grown on surfaces that are immersed in aqueous solutions, and adsorption times of 15 hours or more are necessary to obtain well-ordered, defect free structures. In this study, 1-dodecanethiol was vapor deposited on Au (111) in ultra high vacuum, which produces a SAM in a period of only a few minutes. Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) was used to determine the orientation and the electronic structure of the thiol. Deposition at room temperature gave no signature of thiol adsorption at the surface with either ARUPS or low energy electron diffraction (LEED). Deposition at ~100 K resulted in an ordered monolayer, as indicated by the dispersion of the thiol valence band emissions. A comparison between clean gold and the SAM spectra indicate that the 1-dodecanethiol adsorbs upright at a 20° angle to the surface normal. Deposition of multilayers of thiol at ~100 K produced a disordered overlayer with no dispersion of the valence band emissions. The onset of emission from the thiol valence band for the multilayer films was measured to be 3.5 eV below the Fermi level.

OF+EL-WeP4 XPS Studies of Brilliant Green Doped Conducting Polymer Polythiophene Films, ***H.K. Kato****, S.T. Takemura, M.H. Hirayama,* Kanto Gakuin University, Japan, *H.M. Makihara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecule brilliant green (BG) prepared by electrochemical doping and diffuse injection methods were investigated by XPS. Polymeric structure, charge transfer and interaction between the dye molecule and PT backbone in the hybrid films were closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. XPS core-level analysis of N 1s showed that BG molecules were injected into polymer matrix in the hybrid films prepared by electrochemically reduced method and BG diffused method. S 2p lines were observed split indicates simultaneous doping of BG cation and HSO4-. The higher binding energy peak corresponds to HSO4- while lower binding energy peak can be assigned to the S sites of polymer backbone. Synthesized film samples were categorized into two types, A-type and B-type by the difference of S 2p core-level energy shift. In the sample of A-type, the energy shift of the lower peak of S 2p suggest the charge transfer between BG molecules and polymer backbone creating a n-type polymer backbone state. In the case of electrochemically as-grown films, both BG and HSO4- doping were not observed because S 2p line was single and no N 1s signal was observed.

OF+EL-WeP5 XPS Studies of Initial Stage of Conducting Polymer Film Growth on Si Substrate, *H.K. Kato,* ***S.T. Takemura****,* Kanto Gakuin University, Japan, *H.M. Makihara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) film growth on Si substrate was investigated by XPS. PT/Si interface fabricated by electrochemical method was closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. At the initial stage of electrochemical polymer growth, affinity between a deposited polymer PT film and Si substrate was strong compared with the case of PT film growth on ITO substrate expecting bondings between polymer chains and Si substrate layers. Spectral profiles of Si core-level spectra showed that both Si 2s and 2p spectra were basically composed of different Gaussian components correspond to different valence states of Si in contrast to the core-level spectra of non-deposited Si substrate. The lower binding energy peaks (LS1 and LS2) observed in Si 2p spectra of PT/Si correspond to the Si states with strong interaction between Si and PT. The peak height of LS1 slightly increases and LS2 drastically grows in the case of PT polymer growth on Si substrate. The C 1s core-level spectrum was composed of a higher energy component and a lower energy component originated from the polymer backbone and oxidized Si layers, respectively. Strong affinity between a deposited polymer PT film and Si substrate and variation of the XPS spectral profile suggest that Si-C and Si-F bondings are created at the PT/Si interface.

OF+EL-WeP6 Formation and Characterization of Ferrocene and Porphyrin Monolayers on Si and Ge Surfaces : Towards a Hybrid Molecular/CMOS Electronic Device, ***A.A. Yasseri****, Z. Liu, R. Dabke,* University of California Riverside, *V. Malinovskii, K.H. Schweikart, J.S. Lindsey,* North Carolina State University, *W.G. Kuhr, D.F. Bocian, K.M. Roth*, University of California Riverside

Construction of a novel hybrid molecular based device may provide the most tractable approach in bridging the gap between modern day semiconductor materials and molecular based devices. Toward this goal, we have examined functionalized monolayers of ferrocene and porphyrin terminated alcohols and thiols covalently linked to mono-crystalline Si and Ge (100) and (111). Electrochemical communication with the surface immobilized molecules was achieved through a covalently anchored Si-O, Si-S or Ge-O and Ge-S tether to photlolithographically patterned surfaces. Silicon microelectrodes were fabricated on heavily doped silicon masked with a thermally grown oxide to define the active electrode area for monolayer assembly. Surfaces were activated via a two-step process. Chemically stable hydride-terminated surfaces, using HF or ammonium fluoride, were reacted with a solution of iodine yielding an iodide functionalized surface. XPS measurements confirm the mechanism for the displacement of surface iodine atoms via a base catalyzed reaction with alcohol terminated iron and zinc-centered ferrocene and porphyrin respectively. Iodide derivitization prior to film deposition chemically facilitates the formation of more densely packed monolayer of porphyrins. Fast scan voltammetry performed on monolayers demonstrate the chemical stability of the films over millions of cycles in an inert atmosphere. Modified AC voltammetry was used to probe the redox kinetics of the semiconductor film junction in order to measure the rate for film oxidation and reduction under an applied potential. Monolayers formed from solution phase assembly reactions were further characterized using scanning probe microscopy.

OF+EL-WeP7 Characterization of OLED Degradation by Emission Microscope, ***N. Miura****, Y. Luo, K. Takagi,* ITES Co. Ltd., Japan

The purpose of this study is to investigate how an emission microscope has been applied to evaluation for the degradation mechanism of organic light-emitting devices (OLED). One of the most effective ways to characterize OLED degradation is to study a physical and chemical phenomenon that occurs with an exact point of interest. The problem, however, is one of isolating the exact point of degradation. Thickness of a luminescent layer is around 0.1 microns. Consequently, a less-than-0.1-micron foreign matter can become a cause of an electrical short failure. On the other hand, a size of a pixel is the approximately one hundred microns. Therefore pinpoint detection of a failure location is extremely difficult. In order to solve this problem, an emission microscope used for a failure analysis of Si-based LSIs has been applied to detect a degradation point in plane luminescent devices. An emission microscope is a tool to detect a faint light emitting at a failure point with PMT or CCD camera and to find out a point of interest by adding an optical image and a detected one. This study describes a method for applying emission microscope in the failure analysis of OLED and demonstrates the effectiveness of this method. It is confirmed that an observation under sub-threshold bias condition is effective to find out a failure point. Although no electro-luminescence is observed under this condition with an optical microscope, an emission microscope can get detect a photon emission at a failure location. Some case studies are described to demonstrate the effectiveness of this method. Cross sectional TEM observations of defects located with this technique are also included.

OF+EL-WeP8 Polyatomic Ion Deposition of Thiophenic Thin Films, ***Y. Choi****, E.R. Fuoco, L. Hanley,* University of Illinois at Chicago

Oligo- and polythiophenes are utilized as conducting polymers in many applications. Polyatomic ion deposition at ion impact energies below 200 eV is an effective method for the growth of thin organic films on polymer, metal, and semiconductor surfaces.[1] We demonstrate here the growth of thiophenic thin films on aluminum and silicon substrates by mass-selected <200 eV $C_4H_4S^+$ ion beams. Thiophenic films are also grown by non-mass selected ion beams containing <200 eV $C_4H_4S^+$ and fragment ions. Our non-mass selected ion deposition method permits rapid film growth over wide substrate areas and it is described here for the first time. X-ray photoelectron spectroscopy and atomic force microscopy are used to compare the film chemistry and morphology for the two methods. Oxidation of the films during aging in air is observed.

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OF+EL-WeP9 Mg-Phthalocyanine Thin Films with High Sensitivity for Chlorine Gas, ***T. Miyata***, *S. Kawaguchi*, *T. Minami*, Kanazawa Institute of Technology, Japan

There has been considerable interest in the study of organic substances such as phthalocyanines in thin film form for use as the active layer in gas sensor devices. In particular, the electronic properties of metal phthalocyanine (MPc) thin films are known to be affected by the presence of a foreign gas. Recently, we have demonstrated newly developed high-sensitivity chlorine (Cl_2) gas sensors using Cu-phthalocyanine (CuPc) thin films. However, these CuPc thin film gas sensors still have several unsolved problems such as low sensitivity at operating temperatures above 150°C and the necessity of a heat treatment process for repeated operation. In this paper, we introduce newly developed chlorine gas sensors that can be operated at high temperatures using Mg-phthalocyanine (MgPc) thin films. The Mg-phthalocyanine thin films (thickness from 30 to 180 nm) were evaporated onto substrates; Au thin films were deposited as electrodes. The substrate temperature was varied from RT to 180°C. Gas sensitivity is defined as ratio $(I-I_0)/I_0$. Here, I_0 and I are the currents through the sensors before and after gas introduction, respectively. The sensor resistance decreased when exposed to chlorine gas; MgPc thin film gas sensors exhibited high sensitivity at the operating temperatures as high as 230°C. The characteristics of MgPc thin film sensors were strongly dependent on the preparation conditions of the MgPc thin films. For example, sensitivity increased as the substrate temperature of the MgPc thin films was increased from RT to 180°C: maximum sensitivity at a thin film deposition temperature of 180°C. At an operating temperature of 200°C, the sensitivity of the optimized MgPc thin film gas sensor linearly increased with the Cl_2 gas concentration in the range of 0.35 to 35 ppm.

OF+EL-WeP10 The Surface Stress under Ion Irradiation on Si and SAM-coated Si, ***A.N. Itakura***, *M. Kitajima,* Institute for Materials Science, Japan, *R. Berger*, IBM Deutschland Speichersysteme GmbH, Germany

Evaluation of stress in the Si stencil mask is very important for ion projection patterning or ion lithography technology, because the stresses would cause a deformation of the projected patterns. Ar ion irradiation makes a compressive stress on Si(001) surfaces.[1] Stencil masks often become folded during the ion projection patternings, which should be owing to this ion induced compressive stress. In this paper, we have studied the stress evolution of Si membranes under ion irradiation. Bare Si and alkanethiol-coated-Si were examined during ion irradiation from ion energies of 5 to 50eV. The stresses were in-situ real-time monitored by using a microcantilever sensor technique combined with ion irradiation system in UHV. Self-assembled monolayers (SAM) such as alkanethiol, $HS-(CH_2)_{n-1}-CH_3$ for n=4,6,8,12, on gold induced compressive stresses.[2] In contrast to the compressive stress during SAM growth, a strong tensile surface stress of about -0.7 N/m was found when the sensor is exposed to Ar ions. This value is 3-4 times larger than the compressive stress. The constant value of the tensile stress for an Ar-ion dose higher than 4×10^{14} ions/cm^2 indicates that a stable monolayer forms during Ar-ion irradiation. Stable protective monolayers featuring tensile stress can play a key role in micro-machining and as protective overlayers for silicon mask lithography.

[1] T.Narushima, A.N.Itakura and M.Kitajima, Appl.Phys.Lett.79, 605-607 (2001),

[2] A.N.Itakura, R.Berger, T.Narushima and M.Kitajima, Appl.Phys.Lett.(2002), in printing.

OF+EL-WeP11 Controlled Growth of Ultrathin Molecular Films, ***E.J. Kintzel, Jr.***, Florida State University, *D.-M. Smilgies,* Cornell High Energy Synchrotron Source, Cornell University, *J.G. Skofronick, S.A. Safron, D.H. Van Winkle*, Florida State University

Controlled growth of the aromatic p-phenylene oligomer molecules adsorbed onto KBr(001), KCl(001), NaCl(001), and NaF(001), has been investigated by x-ray diffraction (XRD) and atomic force microscopy (AFM). XRD analysis provides evidence that the substrate temperature during deposition, substrate lattice constant, and molecular length affects the molecular orientations within these ultrathin films. AFM images contribute independent evidence for a surface microstructure evolution that is consistent with the XRD results. Oriented films can therefore be grown with the desired molecular orientations by careful selection of an appropriate combination of the above deposition parameters.

OF+EL-WeP12 Current Sensing AFM Study on Electric Property of Organic Monolayer Formed on Hydrogen Terminated Si(111) via Si-C Bond, *K. Uosaki*, ***J.-W. Zhao***, Hokkaido University, Japan

Current Sensing AFM was used to measure the conductivity of alkyl monolayer of various chain length formed on hydrogen terminated Si(111) via Si-C Bond. Conductance was dependent on chain length, bias and force. The current increased exponentially with the bias. Based on the chain length dependence of the Log(current) - bias relation, the conduction mechanism is discussed. The force dependence of the conductance at a given bias was well explained by the bending of the monolayer and the chain length dependence of the mechanical property of the monolayer will be discussed.

OF+EL-WeP13 Surface Structure and Surface Properties of Organosilane Monolayers Selectively Assembled on the Si-wafer Substrate, ***A. Takahara***, *T. Koga, M. Morita, H. Otsuka*, Kyushu University, Japan

Three-component micropatterned organosilane monolayers were successfully fabricated on Si-wafer substrate by stepwise vacuum ultraviolet-ray (VUV) photolithography technique with a rotation of line-type photomask. The introduction of different organosilanes was confirmed by X-ray photoelectron spectroscopy (XPS). Atomic force microscopic and lateral force microscopic observations revealed that the line-widths of micropatterned surface corresponded to those of photomask. Micropatterning of the surface functional groups influenced the magnitudes of surface free energy.

Electronic Materials and Devices
Room: C-107 - Session EL+SS+SC-WeA

Semiconductor Film Growth and Oxidation
Moderator: R.K. Ahrenkiel, National Renewable Energy Laboratory

2:00pm **EL+SS+SC-WeA1 Scanning Tunneling Microscopy and Spectroscopy of Gallium Oxide and Indium Oxide Deposition on GaAs(001)-(2x4)**, ***M.J. Hale***, *J.Z. Sexton,* University of California, San Diego, *S.I. Yi,* Applied Materials, *D.L. Winn, A.C. Kummel*, University of California, San Diego

The surface structures formed upon deposition of Ga$_2$O and In$_2$O onto the technologically important As-rich GaAs(001)-(2x4) surface have been studied using scanning tunneling microscopy (STM) and spectroscopy (STS), low energy electron diffraction (LEED), and density functional theory (DFT) calculations. At submonolayer coverage, the initial bonding sites are different for Ga$_2$O and In$_2$O adsorptions due to the different activation barriers for the two oxides to chemisorb at various sites onto the surface. In$_2$O initially bonds in the trough between the arsenic dimer rows, whereas Ga$_2$O first inserts into the top layer arsenic dimer rows. Conversely, at elevated surface temperatures, both Ga$_2$O and In$_2$O form a crystalline monolayer. Both oxides form crystalline (2x1) surface reconstructions that are electronically unpinned: there are no states within the band gap. Although both oxides form a (2x1) surface reconstruction, the surface structures differ. At monolayer coverage the Ga$_2$O/GaAs surface has a much larger step density while the In$_2$O/GaAs surface shows a broad distribution of row oxide spacing. The DFT calculations confirm the observed surface structures and show that both oxides form unpinned surfaces because the bonding to these oxides restore the charge on the first and second layer As and Ga atoms to near bulk values.

2:20pm **EL+SS+SC-WeA2 Structure-Sensitive Oxidation of the Indium Phosphide (001) Surface**, ***G. Chen***, University of California, Los Angeles, *S.B. Visbeck,* Siemens & Shell Solar Gmbh, Germany, *D.C. Law*, University of California, Los Angeles, *R.F. Hicks*, University of California, Los Angeles; AVS fellow

Abstract The properties of oxide/semiconductor interfaces significantly affect the performance of indium phosphide-based electronic and photonic devices. In this study, indium phosphide films were grown on InP (001) substrates by metalorganic chemical vapor deposition (MOCVD). Then the samples were transferred to an ultrahigh vacuum system, and annealed at 623 and 723 K to produce the (2x1) and delta(2x4) reconstructions with phosphorus coverages of 1.0 and 0.125 ML, respectively. These structures were exposed to unexcited molecular oxygen, and the reaction characterized by X-ray photoelectron spectroscopy (XPS), reflectance difference spectroscopy (RDS) and low energy electron diffraction (LEED). At 298 K and above, the In-rich InP (001) surface rapidly oxidizes upon exposure to O2. The oxygen dissociatively chemisorbs onto the delta (2x4), inserting into the In-P back bonds and the In-In dimer bonds. By contrast, the P-rich (2x1) reconstruction does not absorb O2 up to 500,000 L at 298 K. Above 453 K, the (2x1) becomes reactive with oxygen inserting into both the In-P back bonds and the phosphorus dimer bonds. Based on these results, we conclude that the oxidation of indium phosphide (001) is highly structure sensitive. This means that the oxide/semiconductor interface formed on InP devices can vary widely depending on the process history.

2:40pm **EL+SS+SC-WeA3 The Addition of Sb and Bi 'Surfactants' during GaN Growth by Metal Organic Vapor Phase Epitaxy**, ***T.F. Kuech***, *L. Zhang, H.F. Tang, J. Schieke, M. Mavrikakis*, University of Wisconsin - Madison **INVITED**

The addition of certain impurities has been shown to modify the growth behavior of several lattice-mismatched epitaxial semiconductor systems, most notably SiGe-Si. Of the many impurities studied, antimony and bismuth have been shown to act as 'surfactants' during SiGe epitaxy altering the critical thickness and surface morphology. Such impurities have not been studied in detail in other systems, such as GaN and related materials. We present data on the role and effect of isoelectronic centers, Sb and Bi, on the structure and properties of GaN epilayers during metal organic vapor phase epitaxy. The Sb addition slightly improved the optical and structural properties of GaN epilayer at a low level of Sb incorporation. The addition of Sb resulted in changes in the GaN surface morphology, which was further explored by the lateral overgrowth epitaxy technique through the changes in the growth rates and the facet formation. The presence of Sb in the gas phase greatly enhanced the lateral overgrowth rate and altered the formation of the dominant facets. While Sb altered the growth facet present during LEO, only a small amount of Sb was incorporated into the GaN, suggesting that Sb may be acting as a 'surfactant' during the GaN MOVPE growth. Sb addition produces surface conditions characteristic of a Ga-rich surface stoichiometry indicating both a possible change in the reactivity of NH$_3$ and/or enhanced surface diffusion of Ga adatom species. Other changes in the surface chemistry and transport were studied by the use of state-of-the-art periodic self-consistent DFT calculations. Bismuth has also been studied as a surfactant to alter the surface chemistry and defect structure during the GaN growth. Bi addition resulted in a decrease in surface roughness as measured by atomic force microscopy while no significant Bi was incorporated over a broad range of gas phase concentrations.

3:20pm **EL+SS+SC-WeA5 Surface Reaction Study of Tungsten Nitride Precursors Decomposition on Si(100)-(2 x 1)**, ***Y.-W. Yang***, Synchrotron Radiation Research Center, Taiwan, *J.-B. Wu, Y.-F. Lin, H.-T. Chiu,* National Chiao-Tung University, Taiwan

Reaching an atomic-scale understanding of the surface reaction pathways followed by precursors during MOCVD thin-film growth is a daunting task. We have been studying the transition metal nitride growth on both Cu and Si surfaces. Here, we report a thermal decomposition study of WN precursor on Si(100)-(2 x 1) using TDS and synchrotron-based XPS techniques. The studied precursors are (t-BuN)$_2$W(NHBu-t)$_2$ and (t-BuN)$_2$W(NEt$_2$)$_2$ and their structural characteristics consist of the presence of both W-N and W=N bonds and either the presence or the absence of β-H that influences the thermolysis of the precursors. XPS data show that the metallic tungsten already forms for a submonolayer dose of the precursors at room temperature, suggesting the complete abstraction of the amine ligands by the dangling bonds on Si(100) surface. The evolution of hydrocarbon and amine species during the pyrolysis are followed by the TDS and the results suggests the similarity to the amine adsorption on Si(100). High temperature annealing produces silicon carbides and silicon nitrides. In stark contrast, no metallic tungsten is ever formed during the pyrolysis of the same precursors on Cu(111) and the formation of tungsten nitride is secured through the gradual loss of excessive amine ligands. Based on these results, possible surface reaction mechanism and the structural effect of the precursor are to be discussed.

3:40pm **EL+SS+SC-WeA6 Thermal Decomposition and Desorption Study of Tetrakis(diethylamido)zirconium(TDEAZr) on Si(100) for MOCVD and ALD of ZrO$_2$**, ***K. Yong***, *J. Jeong, S. Lim*, Pohang University of Science and Technology, Korea

Tetrakis(diethylamido)zirconium (TDEAZr) is used as a zirconium-precursor to deposit zirconium oxide by metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD). Surface reaction study of precursors can aid in describing the kinetics of MOCVD and ALD. Surface reaction and desorption of TDEAZr (Zr(N(C$_2$H$_5$)$_2$)$_4$) on Si(100) were studied using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). During TPD, ethylethyleneimine, diethylamine, acetonitrile, ethylene and hydrogen desorbed as main decomposition products of diethylamido, which was chemisorbed on Si(100) through the scission of zirconium-diethylamido bond in TDEAZr. The formation of silicon-carbide and silicon-nitride was observed on the surface after TPD runs. These results indicated that a complete decomposition of diethylamido also proceeded. A reaction pathway model of TDEAZr/Si(100) was proposed. Also, the coadsorption of TDEAZr with water on Si(100) was studied.

4:00pm **EL+SS+SC-WeA7 Reactions of Organosulfur Compounds with Si(100) for Chemically Controlled Epitaxy of II-VI Semiconductors on Si(100)**, *Z. Zhu, A. Srivastava,* ***R.M. Osgood Jr.***, Columbia University

The growth of silicon-based quantum devices requires precise control of ultrathin Si/wide-bandgap-semiconductor/Si heterostructures. We have investigated the initial stages of chemistry-based low-temperature epitaxy using organosulfur precursors. The approach uses the chemical insight gained from organic functionalization of Si.[1] Thus we have studied the reaction of (CH$_3$S)$_2$, CH$_3$SH, (CH$_3$)$_2$S with Si(100) at room temperature, under UHV conditions for atomic layer growth of functional-group-terminated sulfur on Si(100). This reaction is the first step in the layer by layer self-limiting epitaxy of ZnS, for example, on Si(100). AES studies indicate that each of these organosulfur compounds have different reaction kinetics with the Si(100) surface and reach different levels of sulfur saturation coverage. The differences observed for (CH$_3$S)$_2$ and (CH$_3$)$_2$S reactions have been shown to be explained by the relative bond strengths and the number of sulfur atoms present in the adsorbate molecule. Our TPD studies from 25-825°C show no sulfur-related desorption. Instead AES studies confirm that sulfur atoms remain on surface until ~ 525°C and then diffuse into the Si(100) substrate upon further annealing. TPD studies also indicate evolution of H_2 at temperatures similar to those obtained for H_2 desorption from saturated atomic H on Si(100). In our studies methyl desorption also occur at T > 650° C, temperatures higher than that of H_2 desorption. The amount of m/e = 15,16 fragments is dependent on the organosulfur compound examined. Chemical strategies are now being explored to grow layers of Zn on methyl-terminated sulfur layer as shown in the epitaxy using sequential H_2S/dimethyl cadmium dosing on ZnSe.[2]

[1] Bent SF, J Phys Chem B, 106(11): 2830-2842, 2002.

[2] Luo Y, Han M, Slater DA, Osgood RM, J Vac Sci Tecnol A 18(2): 438-449, 2000.

4:20pm **EL+SS+SC-WeA8 Kinetics and Mechanism of Adsorption and Ultrathin Oxide Growth by Ozone on Si(100)2x1 and Si(111)7x7**, ***K. Nakamura***, *A. Kurokawa, H. Nonaka, S. Ichimura*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Ozone is one of the promising oxidants to synthesize an ultrathin oxide film on silicon surfaces for the near-future MOSFET because of rapid oxidation rate at low substrate temperature, negligible thickness of structural transition layers in the oxide film, etc.[1] However, to control the thickness of an oxide film precisely and accurately,[2] kinetics and mechanism of initial oxide growth must be clarified. Thus, in this paper, we discuss chemistry of adsorption and ultrathin oxide growth by ozone on silicon surfaces. Si(100)2x1 and Si(111)7x7 were exposed to highly concentrated (>80%) ozone gas and monitored by x-ray photoelectron spectroscopy (XPS) and second harmonic generation (SHG). Kinetic analysis has suggested that initial dissociative adsorption of ozone on Si(100)2x1 and Si(111)7x7 proceed with the mechanism of leaving only one oxygen atom on the surface and of desorbing the other two, possibly, as a molecular oxygen. This adsorption, in contrast to that of oxygen, was featured with structure-insensitive kinetics, no activation barrier for the dissociation, and high sticking probability close to unity. After the adsorption was completed, first three oxide layers were synthesized by random adsorption of oxidant species on each layer in the consecutive manner. The formation of three layers led to the further growth of an oxide film with ozone with linear growth kinetics, but not with molecular oxygen. Each of these initial ozone-oxide layers has distinctively different activation energy for its growth: they were estimated 0 eV, 0.34 eV, 0.68 eV, and 0 eV for first, second, third, and above fourth layers on Si(100), respectively, enabling accurate control of the thickness of an oxide film.

[1] K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, J. Vac. Sci. Technol. A 17 (1999) 1275.

[2] K. Nakamura, A. Kurokawa, and S. Ichimura, Jpn. J. Appl. Phys. 39 (2000) L357.

4:40pm **EL+SS+SC-WeA9 Stress-induced Dissociative Chemisorption of Oxygen on Si(001)**, ***M. Yata***, *Y. Uesugi-Saitow*, National Institute for Materials Science, Japan

We have investigated the role of surface stress in dissociative adsorption process of O_2 on Si(001)-2x1by supersonic molecular beam technique. The tensile stress was externally applied on the surface along[110] direction. The Si(001)-2x1surface reconstructs by dimerization of atoms in adjacent rows. In areas of the surface separated by an odd number of monoatomic steps the orientation of the dimer bonds is rotated by 90° giving 2x1 and 1x2 orientational domains. Their domain populations are changed to relax the stress at the surface and the kinetics of the change depend on the surface temperature.[1] Below room temperature, the domain populations were almost equal during the molecular beam experiments. Two co-existing dissociation channels are seen, a trapping-dissociation channel at low translational energy of incident O_2 and a direct activated channel at high translational energy.[2] In case of the trapping-dissociation, O_2 molecule is trapped to a precursor state and undergoes a kinetic competition between desorption and dissociation. We have estimated a difference in activation barrier heights between desorption and dissociation at 30 meV. The initial dissociative sticking probability for low translational energy of incidence increases as the tensile stress increases. This indicates that trapping-mediated dissociation is enhanced by the stress. We have found that the difference in the activation barrier heights between desorption and dissociation decreases as the stress increases. We will discuss the change of dissociation dynamics with the tensile stress in detail.

[1] F. K. Men, W.E. Packard and M. B. Webb, Phys. Rev. Lett. 61(1988) 2469.

[2] B. A. Ferguson, C. T. Reeves and C. B. Mullins, J. Chem. Phys.110(1999)11574.

5:00pm **EL+SS+SC-WeA10 Direct Detection of D_2O and D_2 on D/Si(111) Surfaces under O Atom Exposures**, ***F. Rahman***, *F. Khanom, A. Aoki, S. Inanaga, A. Namiki*, Kyushu Institute of Technology, Japan

Initial oxidation stage of D/Si(111) surfaces by atomic oxygen (O) have been studied from the absorption point of view. O/D/Si(111) co-adsorbed surfaces were prepared by various O exposure on 1.25ML D/Si(111). TPD measurement shows nearly 50% reduction of D adatoms from the surface for 2 min O exposure indicating the D adatoms abstraction by incident O atoms. Measurement of desorbing species have been done with a QMS during O exposures on the 1ML D/Si(111) surface for various surface temperatures (T_S). D_2O as well as D_2 molecules were observed. Rate curves of both species show an initial rate jump and then a gradual increase having a peak, which is followed by a nearly exponential decay with exposure time. Both D_2O and D_2 rates vs. T_S curves show similar line shape to the similar plot of D_2 rates vs. T_S curve obtained for the reaction system of H + D/Si(111) --> D_2. In a previous work, the later reaction was understood as due to the so-called β_2 TPD desorption arising from a dideuteride phase. Therefore, we consider that the O induced D_2 formation proceeds along the same mechanism as for the β_2-channel TPD. Regarding D_2O formation, it is significant and interesting since the reaction takes place as a result of picking up two D adatoms by single O atom upon collision. We will propose a possible mechanism to explain the O-induced D_2O formation on the D/Si(111) surfaces.

Nanometer Structures
Room: C-207 - Session NS+EL-WeA

Nanolithography & Self Assembly
Moderator: P.S. Weiss, The Pennsylvania State University

2:00pm **NS+EL-WeA1 Recent Development in Nanoimprinting Lithography**, ***L.J. Guo***, University of Michigan **INVITED**

Nanoimprinting lithography is an emerging technology that promises ultra-high resolution, high throughput and low cost. Unlike soft contact printing that uses an elastomer stamp, nanoimprinting uses a hard mold to create nanoscale features by directly imprinting into the polymer film at a temperature higher than its glass transition temperature (T_g). Sub-10 nm resolution and large area patterning have already been demonstrated in the past. This talk will present some recent development in nanoimprinting lithography, including imprinting at reduced temperature by using low T_g polymer materials; a reversed imprinting technique that enables "inking" of polymer materials onto a substrate, and patterning on non-flat surfaces without planarization, as well as the creation of simple 3D structures. This reversal nanoimprinting method also offers a unique advantage by allowing imprinting onto a flexible substrate that is otherwise difficult to spin-coat with polymer film, and we have demonstrated this by imprinting on a 50 mm thick flexible polyimide film. Nanoimprinting not only has the ability to pattern nanoscale features, but also it is compatible with polymer material processing. Based on these characteristics, we have applied it to two new applications. The first one is polymer micro-ring resonator photonic device fabricated by nanoimprinting, which is in the form of a micro-ring closely coupled to a waveguide, and offers unique properties such as narrow bandwidth filtering, high quality factor, compactness, and could find important applications in integrated photonic circuits. The second application is in organic polymer light emitting diodes (OP-LEDs), where we have developed a simple method based on nanoimprinting to define the OP-LEDs with pixel size ranging from nano- to micron-scale. The demonstration of those small size OP-LEDs indicates the possibility of fabricating ultra-high resolution OP-LEDs for applications such as micro-displays.

3:00pm **NS+EL-WeA4 Fabrication of Molecular Nanostructures by Scanning Near-Field Optical Lithography**, ***K.S.L. Chong***, *S. Sun, G.J. Leggett*, University of Sheffield, UK

Nanoscale patterns of self-assembled monolayers (SAMs) on gold and silver can be fabricated by a new technique called scanning near-field photolithography (SNP).[1] In SNP, a 244 nm laser coupled to a scanning near-field optical microscope is used to carry out nanometre scale photopatterning of SAMs. The photooxidised SAMs can be dipped into a solution of a different thiol, which displaces the oxidised material and adsorbs at the surface. Chemical patterns with linewidths of 40 nm were routinely obtained though patterns as small as 25 nm have been observed by friction force microscopy. The oxidised pattern can also be transferred to the underlying substrate by wet etching where linewidths of 80 nm have been obtained on gold substrates. Because of the ease by which SAMs can be patterned by this method, SNP can be routinely used to create nanoscale molecular patterns. Nanoscale patterns in SAMs can be used as templates for the attachment of biomolecules offering another approach to the miniaturisation of biological devices. Preliminary data have shown that proteins may be successfully immobilised to micron-scale patterned monolayers created using similar photochemistry. These methods are currently being combined with SNP in order to create biological nanostructures.

[1] Shuqing Sun, Karen S.L. Chong and Graham J.Leggett, J.Am.Chem.Soc, 2002, 124, 2414.

3:20pm **NS+EL-WeA5 Photoinduced Anisotropy of Second-Harmonic Generation from Azobenzene-Modified Alkylsiloxane Monolayers**, *Y.W. Yi, **T.E. Furtak***, Colorado School of Mines, *M.J. Farrow, D.M. Walba*, University of Colorado

Non-contact alignment of substrates in liquid crystal displays offers the advantage of reduced contamination and minimal surface charging. This approach also provides a means of reversible alignment after a device has been assembled. With this objective we have synthesized self-assembled monolayers based on dimethylaminoazobenzene units covalently attached to a glass surface by means of a short alkylsiloxane anchor (azo-SAM). The resulting architecture favors an orientation in which the axis of the azobenzene group should be nearly parallel to the surface with an isotropic azimuthal distribution. Under illumination with polarized UV light the trans-cis isomerization and subsequent relaxation serves to wiggle the molecule into an orientation perpendicular to the UV optical field. We have tested this scenario using optical second harmonic generation. We are able to identify a surface order parameter that characterizes the photoalignment of the azobenzene group. These data correlate with the recently reported behavior of nematic liquid crystal cells containing one substrate treated with the same azo-SAM.[1] This work is supported by NSF MRSEC grant DMR-9809555.

[1] "Liquid Crystal Alignment by Photo-Buffing Azo-SAMs", G. Fang, N. A. Clark, J. E. Mcclennan, M. Farrow, D. Walba, March Meeting of the American Physical Society, Indianapolis (3/20/20002).

3:40pm **NS+EL-WeA6 Nanostructuring of Hydrogenated Silicon Surfaces by Electron Beam Irradiation of Self-assembled Hydroxybiphenyl Monolayers**, *A. Küller, W. Geyer, V. Stadler*, Universität Heidelberg, Germany, *T. Weimann*, Physikalisch Technische Bundesanstalt, Germany, *W. Eck, **A. Gölzhäuser***, Universität Heidelberg, Germany

A new species of aromatic self assembled monolayers, hydroxy biphenyl, are formed on hydrogen terminated silicon and used as a negative tone electron beam resist. The formation of the monolayer and the electron induced modifications are observed by X-ray photoelectron spectroscopy. Nanometer patterns in the molecular layer were defined by low energy electron proximity printing as well as via conventional e-beam lithography. The patterns are transferred into silicon by a wet chemical etching process in KOH. The fabrication of patterns with lateral dimensions below 20 nm is demonstrated.

4:00pm **NS+EL-WeA7 Electrode Modification by Electron-induced Patterning of Self-assembled Monolayers**, ***B. Völkel**, G. Kaltenpoth, T. Felgenhauer, W. Geyer, H.T. Rong*, Universität Heidelberg, Germany, *M. Buck*, University of St Andrews, UK, *A. Gölzhäuser*, Universität Heidelberg, Germany

Nanopatterns on electrode surfaces control the electrochemical deposition. An example is the formation of nanoscale dots or wires via the preferred nucleation at defects and step edges.[1] We present a method to artificially fabricate such electrochemical templates via coating of electrodes with self-assembled monolayers (SAMs) and subsequent patterning by electron beams. SAMs provide a flexible route to modify electrode surface properties via their molecular structure, ranging from inert alkane chains, which exhibit a blocking behavior, to redox active moieties. The e-beam patterning offers perspectives to generate arrays of microelectrodes with specific functionality. We coated gold electrodes with SAMs of w-(4'-methyl-biphenyl-4-yl)-dodecylthiol (BP12) and hexadecanethiol (HDT) and patterned them by electron beam lithography. The subsequent copper deposition in an electrochemical cell revealed that the e-beam patterned alkanethiol behaves opposite than e-beam patterned biphenyl. Similar to the behavior of these materials as resists,[2] HDT acts as a "positive template" leading to copper deposition only on the irradiated parts. BP12 acts as a "negative template", where the irradiated biphenyl layer is cross linked and exhibits a blocking behavior,[3] hence copper is only deposited on the non-irradiated parts. By using these effects well defined Cu nanostructures could be generated.

[1] M. P. Zach, K.H. Ng, R.G.Penner, Science 290, 2120 (2000).

[2] A. Gölzhäuser, W. Geyer, V. Stadler, W. Eck, M. Grunze, K. Edinger, T. Weimann, P. Hinze, J. Vac. Sci. Technol B 18, 3414 (2000).

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4:20pm **NS+EL-WeA8 Electrochemically Controlled Film Formation of Self-assembled Monolayers of Biphenyl-based Thiols**, *I. Thom, B.J. Livesay*, StAndrews University, UK, ***P. Cyganik***, Jagiellonian University, Poland, *M. Buck*, StAndrews University, UK

Usually self-assembled monolayers (SAMs) of thiols are prepared by mere immersion of the substrate in a solution containing the respective thiol. Whereas a number of preparation parameters such as the thiol concentration, temperature, immersion time, or solvent type have been investigated in some detail, no systematic studies have been performed on how the substrate potential affects the kinetics of film formation and the resulting SAM structure. Since the potential controls the bonding of a thiol to the substrate, i.e. its stability, the rate of adsorption/desorption and the mobility of the thiols are affected and, consequently, a pronounced influence of the potential can be expected. Using thiols which are characterized by a biphenyl unit and an alkane spacer chain between the aromatic moiety and the SH group we have studied the kinetics of film formation using nonlinear optical spectroscopies and scanning tunneling microscopy. Both the kinetics of film formation and the final film structure undergo significant changes ranging the potential from values near the reductive desorption of thiols to values around zero volts.

4:40pm **NS+EL-WeA9 Modification of Self-assembled Monolayers by Free Radical-dominant Plasma: The Effect of the Chain Length and the Substrate**, *M. Zharnikov, S. Frey, **M. Grunze***, Universität Heidelberg, Germany, *M.-C. Wang, J.-D. Liao, C.-C. Weng*, Chung Yuan Christian University, Taiwan (ROC), *R. Klauser*, Synchrotron Radiation Research Center, Taiwan (ROC)

Synchrotron-based high-resolution photoelectron spectroscopy was applied to study the modification of aliphatic and aromatic thiol-derived self-assembled monolayers (SAMs) on (111) gold and silver substrates by a nitrogen-oxygen downstream microwave plasma. It was found that the plasma treatment does not result in a "soft" modification of SAMs, but in their massive damage and disordering. Contrary to the electron beam treatment, both the aliphatic and aromatic films became modified and damaged in a similar way, with the extent of the changes depending on the length of the molecular chains and, above all, on the substrate. For SAMs on Au a profound desorption of the entire SAM constituents and a complete fragmentation of the residual hydrocarbons is observed. For the SAMs on Ag only partial desorption and oxidation took place and, for short treatment times, the films remained practically intact. The desorption of molecular species was preceded by the oxidation of the pristine thiolates to weakly-bonded sulfones, which occurred after the penetration of chemically active oxygen species into the S/substrate interface via defect sites. Such a mechanism clearly explains the observed dependence of damage extent on the SAM thickness and emphasizes the importance of the strength of the thiolate-substrate bond. Thus, a stronger thiolate-substrate bond can be suggested for Ag as compared to the Au substrate. In addition, considering the similarity of the plasma-induced processes and UV-photooxidation, one can extend the major conclusions obtained for the plasma treatment to UV-photooxidation.

Organic Films and Devices
Room: C-102 - Session OF+EL+SC-WeA

Molecular and Organic Films and Devices
Moderator: N. Koch, Princeton University

2:00pm **OF+EL+SC-WeA1 Recent Developments in Organic Optoelectronics**, ***S.R. Forrest***, Princeton University **INVITED**

The interest in organic materials for optoelectronic device applications has undergone explosive growth in the last several years. This growth has been propelled by advances in organic thin films for displays, and for low cost electronic circuits. With a few successful product introductions employing active electronic organic devices, it is possible that the "age of organic optoelectronics" has finally arrived. This talk discusses some of the recent progress in organic device technology, with an eye to the future which may include making active electronic devices with a single molecule. In particular, we discuss extremely high external emission efficiency organic light emitting devices used for displays and lighting applications. Also, similar progress in high bandwidth, high efficiency of organic photodiodes, and efficient thin film photovoltaic cells are discussed. For example, multilayer organic nanostructure photodetectors are found to have very high frequency response with detection sensitivity in the visible spectral range. Finally, we present some new ideas on organic device fabrication enabling patterning of structures on the nanometer scale in both the vertical and horizontal directions.

3:00pm **OF+EL+SC-WeA4 Electron Transport in Platinum Complex Molecules: An Approach to Molecular Electronics**, *T.L. Schull, J.G. Kushmerick,* ***R. Shashidhar***, Naval Research Laboratory

Molecules that are highly conducting and which can be attached to metal on both sides via a functional chemical group form the basic elements of a molecular electronic device. Electron transport across different types of organic molecules are being actively investigated using different types of measuring test beds. In this paper, we present results of our electron conduction studies across a family of organo metallic molecules using a new cross-wire test bed developed recently.[1] We show that trans-platinum-bis-acetylides show good electron transport across their molecular length that are even better than the properties of the corresponding π-conjugated oligo(phenyleneethynylene) studied by several groups. The dependence of the metal ligands on the electron transport properties of materials is discussed. We have also used a simple extended Huckel Theory coupled with a Green Function approach to calculate the current voltage characteristics of these molecules. These theoretical calculations are compared with experiments.

1. J.G. Kushmerick, D.B. Holt, J.C. Yang, J. Naciri, M.H. Moore and R. Shashidhar, to be published.

3:20pm **OF+EL+SC-WeA5 Organic Light-Emitting Diodes and Solar Cells with Electrically Doped Transport Layers**, ***K. Leo***, TU Dresden, Germany **INVITED**

In classical semiconductor technology, controlled n- and p-type doping has always been a standard technique. In contrast, organic materials for devices such as organic light-emitting diodes (OLED) are usually prepared in a nominally undoped form. We discuss results of a comprehensive study of controlled electrical doping of various thin-film molecular organic materials. The layers are prepared by co-evaporation of matrix materials with acceptor molecules and characterized by several electrical techniques. UPS and XPS measurements directly show the Fermi level shift and the reduction of space charge layer width due to increasing doping.[1] We further show that these electrical doping concepts can be successfully applied in devices. The concept of molecular doping is applicable for amorphous wide-gap hole transporting materials and allows for realizing devices with the lowest operating voltages reported so far for small-molecule devices.[2] The concept of controlled doping has also enabled us to prepare a semitransparent inverted OLED with outstanding performance. It features an inverted layer sequence with ITO efficiently injecting electrons into a highly n-doped layer, despite a very large energy barrier of around 1.8eV. The devices reaches display brightness of 100Cd/m2 at 3.4V, which is far below any other literature result. We will also present first results on doped phosphorescent OLEDs which show that the concept of electrical doping can be extended to high-efficiency emitters. Finally, we will discuss the application of doped transport layers in solar cells. (Work done in collaboration with M. Pfeiffer, J. Blochwitz-Nimoth, X. Zhou, J. Huang, D. Qin, B. Maennig, D. Gebeyehu, A. Werner, J. Drechsel.)

[1] J. Blochwitz et al., Organic Electronics, 2 , 97 (2001)

[2] J. Huang et al., Appl.Phys. Lett. 80, 139 (2002).

4:00pm **OF+EL+SC-WeA7 Understanding Charge Transport Across Metal-Molecule-Metal Junctions**, ***J.G. Kushmerick***, *R. Shashidhar*, Naval Research Laboratory

Charge transport across a metal-molecule-metal junction is regulated by three factors 1) the structure of the molecule 2) the nature of the metal-molecule contacts and 3) the choice of metal electrode. We use an experimentally simple crossed-wire tunnel junction to interrogate how each of these three factors influences the current-voltage characteristics of a molecular junction. Results on symmetric and asymmetric junctions demonstrate that a specific molecular core can act either as a molecular wire or a molecular rectifier depending on its coupling to the metal electrodes. We will also show that the experimentally measured conductance of a molecular wire can be directly related to how well it's π-conjugated backbone mimics an ideal one-dimensional metal.

4:20pm **OF+EL+SC-WeA8 Zero-bias Anomaly in Molecular Monolayer Tunneling**, ***D.R. Stewart***, *D.A.A. Ohlberg, P.A. Beck, R.S. Williams*, Hewlett-Packard Laboratories

Electron tunneling is the dominant transport mechanism in nearly all proposed molecular electronic devices. Standard tunneling theory is normally used to predict device behavior, yet few experimental investigations of molecular tunneling exist due to the difficulty in constructing high quality molecular monolayer films. We describe detailed electronic transport characterization of several planar electrode / Langmuir-Blodgett (LB) molecular monolayer / electrode systems that show a large zero-bias anomaly and an anomalous exponential temperature dependence. Single-species LB monolayers of C_{22}, C_{20}, C_{18}, C_{16} and C_{14} carboxylic acid alkanes were sandwiched between upper and lower platinum electrodes, with active device areas of 7-200μm^2. Current and differential conductance were measured as a function of voltage ±1V and temperature 2-300K. Below 40K, device characteristics were constant. Surprisingly, from 40-300K device currents were exponential in temperature. A very wide ±150mV dip in conductance was also present and temperature activated. Both results contradict standard tunnel theory, indicating that the electronic transport is not yet understood even in this simplest symmetric alkane monolayer system.

4:40pm **OF+EL+SC-WeA9 Lateral Confinement of Interfacial Electrons by a Surface Dipole Lattice**, ***X.-Y. Zhu***, *G. Dutton*, University of Minnesota

Interface formation between molecules and a solid substrate often involves charge redistribution, the extent of which can influence a wide range of physical and chemical phenomena. In high mobility field effect transistors (FETs) based on organic single crystals, charge transport is believed to occur in one to two layers of molecules at the organic-dielectric interface. Such an interface may involve charge redistribution and dipole formation. The presence of surface dipoles may significantly alter lateral charge transport in the thin organic layer. When the interface is disordered, these surface dipoles are scattering centers for band transport. On the other hand, if the interface is ordered, there is essentially a two-dimensional lattice of dipoles. Such a surface dipole lattice should give rise to an electrostatic potential which provides periodic confinement of valence and conduction band electrons. We demonstrate this effect for image electrons on C60 thin film covered Cu(111) using angle resolved two-photon photoemission spectroscopy. Metal-to-molecule electron transfer within the first layer creates a (4x4) superlattice of surface dipoles. Such a surface dipole lattice provides lateral confinement of image electron wavefunction, effectively eliminating parallel dispersion for the n=1 image state on one monolayer C60 covered Cu(111). This is in contrast to the significant dispersion observed at higher coverages. The electrostatic potential from the surface dipole lattice is screened by additional layers of C60 molecules, thus, restoring the expected free electron behavior (parallel to the surface) for image states. Quantum mechanical simulation reproduces experimental findings and reveals the extent of wavefunction localization by the surface dipole lattice.

5:00pm **OF+EL+SC-WeA10 Measurement of the Site Specific PDOS of Organic Electronic Materials via Soft X-ray Emission Spectroscopy[1]**, ***J.E. Downes***, *C. McGuinness, P. Sheridan, K.E. Smith,* Boston University, *J.A. Schlueter, U. Geiser,* Argonne National Laboratory, *G. Gard*, Portland State University

Recent advances in the technique of soft x-ray emission spectroscopy (XES) have produced a method to directly measure the bulk elementally and, in certain cases chemically, specific partial density of states of materials. While the detailed measurement of the valence band electronic structure of solids has traditionally been the realm of photoemission spectroscopies several problems have been encountered with the application of these techniques to organic materials. The principal issue is photon induced damage to the compound that modifies the electronic structure as it is being measured. Another is the fact that photoemission measurements probe the surface electronic structure of a material, which may or may not be representative of the bulk. We will show that the use of XES can avoid both of these problems and allows the detailed valence band electronic structure of recently developed organic electronic compounds to be measured. An overview of the technique of XES and its advantages for studying these organic compounds will be followed by specific results from several organic electronic compounds of current interest in the fields of molecular organic semiconductors, (TDATA, Alq_3, TPD, Cu-Pc etc.), and ET based conducting organic charge transfer salts, (β-$(ET)_2SF_5CH_2CF_2SO_3$).

[1] Work supported in part by the DOE under DEFG0298ER45680; the SXE spectrometer was funded by the U.S. ARO under DAAH04950014. The experiments were performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.

Dielectrics
Room: C-107 - Session DI+EL-ThM

Issues for Gate Dielectrics
Moderator: D.P. Norton, University of Florida

8:20am **DI+EL-ThM1 Epitaxial Oxides on Silicon for Alternative Gate Dielectrics and More**, ***D.G. Schlom***, Penn State University **INVITED**

The epitaxial growth of oxides on silicon presents opportunities to harness the full spectrum of electronic, optical, and magnetic behavior available in oxides, while simultaneously exploiting the properties of the underlying semiconductor. One key application for epitaxial oxides on silicon, which will be the focus of this talk, is to produce a viable gate dielectric alternative to SiO$_2$ for silicon MOSFETs with higher dielectric constant (K). As a first step in the identification of such an alternative gate dielectric, we used tabulated thermodynamic data to comprehensively assess the thermodynamic stability of binary oxides and nitrides in contact with silicon at temperatures from 300 to 1600 K. Sufficient data exist to conclude that the vast majority of binary oxides and nitrides are thermodynamically unstable in contact with silicon. The dielectrics that remain are candidate materials for alternative gate dielectrics. Of these remaining candidates, the oxides have significantly higher K than the nitrides. We then extended this thermodynamic approach to multicomponent oxides comprised of candidate binary oxides. The result is 13 silicon-compatible gate dielectric materials with $K > 20$, of which at least six have an optical bandgap ≥ 5 eV. Having identified promising candidate materials with high K, high optical bandgap, and the likelihood for thermodynamic stability in contact with silicon, we have been using MBE to epitaxially integrate the candidate materials having the best lattice match with silicon. High-resolution cross-sectional TEM analysis of the epitaxial interface between silicon and epitaxial oxides will be shown. Some of these interfaces were formed by growing silicon on the dielectric; others were formed by growing the dielectric on silicon. Achieving the former interface is easier as it involves the deposition of a single component material (Si) in a vacuum environment. In contrast, the latter involves multiple components, and as one of these components is oxygen, the possibility of oxidizing the silicon surface and not only losing the epitaxial template, but also forming an undesired SiO$_2$ layer. Over the last two decades, three strategies have been used to grow epitaxial oxides on silicon: (1) to grow with no excess oxidant, (2) to grow with excess oxidant at high substrate temperatures, and (3) to grow with excess oxidant at low substrate temperatures. The overarching goal of all three strategies is to avoid the formation of an amorphous SiO$_2$ layer that would result in the loss of the substrate's crystalline template before the oxide has a chance to nucleate on it. Most reports of the epitaxial growth of oxides on silicon fall into the high temperature / excess oxidant regime. Although successful for the nucleation of an epitaxial oxide layer, these growth conditions typically lead to the growth of an SiO$_2$ layer at the silicon interface. To avoid this layer, whose replacement is the purpose of the alternative gate dielectric, we have studied the last of the three regimes-the low temperature / excess oxidant regime. In this regime the oxidation of silicon by the oxidant is limited by kinetics. However, kinetic barriers to the oxidation of the constituents of the desired oxide at these low temperatures can also occur. We have performed in situ oxidation studies to assess the low temperature oxidation of various elements. Examples illustrating oxides that can be grown epitaxially on silicon in the low temperature / excess oxidant regime will be presented, as well as epitaxial oxide / silicon heterostructures that make use of the integration of the overlying epitaxial oxide layers and the underlying silicon.

9:00am **DI+EL-ThM3 Electrical and Material Properties of 10 nm Thick Hf-Doped Tantalum Oxide High k Dielectrics**, ***J. Lu***, *J.Y. Tweg, Y. Kuo*, Texas A&M University, *P.C. Liu,* AMD, *B.W. Schueler*, Physical Electronics

A high k gate dielectric material that replaces the nm thick SiO$_2$ is necessary for sub 100 nm ULSICs for many practical reasons.[1] Metal oxides such as Ta$_2$O$_5$, HfO$_2$, ZrO$_2$ and Al$_2$O$_3$, are promising candidates and have been intensively investigated. However, they suffer from problems such as the high leakage current and high interface states. It was reported that by adding a third element into the metal oxide, some of the dielectric properties could be improved.[2,3] In this paper, we studied the Hf-doped Ta$_2$O$_5$ thin films deposited by reactive magnetron sputtering. Electrical properties of the 10 nm thick films, such as the k value and leakage current, were measured. Compositions, microstructures, and interfacial properties of the film were probed with ESCA, TEM and SIMS. Compared with the undoped film, the doping process reduced the leakage current, improved the k value, and lowered the fixed charge density. Influences of the post-deposition annealing process parameters, such as temperature and time, to high k properties were also studied. We are going to present these experimental results and to compare them with literature reports. This project is supported by the Texas Higher Education Coordination Board ATP program (project # 0005120003-1999).

[1] International Technology Roadmap for Semiconductors, 1999 edition, SIA.

[2] Y. Kuo, J. Y. Tewg, J. P. Donnelly, and J. Lu, ECS Procs. Intl. Semi. Technol. Conf., 2001-17, 324, 2001.

[3] Y. Kuo, J. Y. Tewg, and J. P. Donnelly, ECS Meeting Abstract, 2001-1, No. 232, 2001.

9:20am **DI+EL-ThM4 The Effect of N$_2$ Annealing on Al$_x$Zr$_y$O$_z$ Oxide**, ***J. Pétry***, *O. Richard, W. Vandervorst, T. Conard,* IMEC, Belgium, *J. Chen, V. Cosnier*, International Sematech c/o IMEC, Belgium

In the path to the introduction of high-k dielectric into IC components, a large number of challenges have to be solved. One of these concerns the stability of high-k oxides to high temperature annealing. Indeed annealing will most likely be necessary to improve the electrical characteristics of the high-k layer itself and the high-k stack will be submitted to annealing in further processing. In this study, we investigated the effect of annealing of ALCVD AlZrO layers in N$_2$ from 700 to 900C by XPS, TOFSIMS, TEM and FTIR. The effect of the Si surface preparation (HF-last, 0.5 nm RTO, Al$_2$O$_3$) on the modification of high-k oxide and interfacial layer upon annealing was also analyzed. We first studied the compositional changes of the mixed oxide upon annealing. For all temperature and surface preparation considered, we observed a segregation of the mixed oxide with the Al oxide at the surface. We also observed an increase of the Si concentration in the high-k film itself, with a diffusion profile towards the surface of the film. On the other hand, the modification of the interfacial layer is strongly dependent on the system considered. In the case of mixed oxide grown on 0.5 nm RTO, no changes are observed between the as-deposited layer and the layer annealed at 700C. At 800C, radical change appears: the initial RTO layer seems to be converted to a mixed layer composed of the initial SiO$_2$ and AlO coming from the mixed oxide, without forming an Al-silicate layer. This remains for annealing at 900C. When grown on 1.5 nm Al$_2$O$_3$ on 0.5 nm RTO, the only difference from the previous system is the observation of an Al-silicate fraction in the interfacial layer for the as-deposited and 700C annealed samples, which disappears at higher temperatures. Finally, when grown on HF-dipped Si, we observe a slight increase of the interfacial thickness after annealing at 700C and no further changes for higher annealing temperature.

9:40am **DI+EL-ThM5 Pulsed Plasma Enhanced MOCVD of High k Y$_2$O$_3$ Layers for Gate Dielectric Applications**, ***C. Durand***, *B. Pelissier, C. Vallee, M. Bonvalot, L. Vallier, O. Joubert*, CNRS/LTM, France, *C. Dubourdieu*, CNRS/LMGP, France

CMOS transistor scaling is rapidly reaching its limits with traditional SiO@sub2@ gate oxide due to increasing tunneling currents. Rare earth oxides, as high k materials to replace SiO@sub2@, have shown promising results. Here, we focus on the elaboration of Y@sub2@O@sub3@ thin films by an innovative technique, namely pulsed injection Plasma Enhanced Metal Organic Chemical Vapor Deposition (PE-MOCVD). In this technique, dissolved Y(thd)@sub3@ precursors are sequentially injected into an evaporator, which allows perfect reproducibility of the amount of precursors delivered to the plasma chamber and then onto the SiO@sub2@ (8 @Ao@)/Si substrate heated at 350@degree@C. An Ar/O@sub2@ plasma is applied to favor precursor decomposition and surface reactivity. Preliminary experiments have shown that no Y@sub2@O@sub3@ film is deposited on substrates heated at 350@degree@C by pulsed MOCVD only, whereas stoichiometric layers (typ. 5 nm thick) are obtained with the plasma. The plasma induces a lower deposition temperature compared to MOCVD. Based on X-rays Photoelectron Spectroscopy (XPS) and infrared spectroscopy studies of the initial stages of the thin film formation, it seems that metallic yttrium atoms react with SiO@sub2@ to form silicate compounds. The thickness of the initial SiO@sub2@ layer gradually changes leading to silicate layer formation. The SiO@sub2@ underlayer can be fully consumed. Y@sub2@Osub3@ thin films have been annealed at a temperature of 600@degree@C under several atmospheres. Subsequent XPS analyses indicate that carbon contamination can be reduced by half, independent of the annealing atmosphere Ar or O@sub2@, thereby suggesting densification of the layer. Further experiments are under way to determine optimum annealing conditions leading to fully oxidized Y@sub2@O@sub3@ layers without carbon atoms. Simultaneously, the behavior of the silicate interface during this annealing treatment will be carefully analyzed.

10:00am **DI+EL-ThM6 Plasma Enhanced MOCVD of Hafnium Oxide and Hafnium Silicate Thin Films**, *V. Rangarajan*, ***H. Bhandari***, *T.M. Klein*, University of Alabama

Hafnium oxide films were deposited by Metal Organic Chemical Vapor Deposition (MOCVD) on Si using hafnium t-butoxide as the metal organic precursor. X-ray diffraction data show a monoclinic crystal structure when films were deposited at 400°C. Films were subjected to ex-situ furnace anneal and compared with as deposited films using XPS that showed a significant interfacial silicon dioxide growth. Hafnium silicate films were deposited by both thermal and plasma enhanced MOCVD using SiH_4 as the Si precursor. Plasma excitation improved Si incorporation resulting as much as 21.5 at.% Si. The films were subjected to furnace anneals up to 1100°C in oxygen and XPS analysis was done to confirm the silicate formation, composition and stability. Surface and bulk film morphology was studied using AFM and XRD respectively. Thermally grown Hf silicates had a measured 1.1 nm rms roughness, while plasma deposited films had 5.2 nm rms roughness. Both thermal and plasma deposited Hf silicates are amorphous as deposited, however thermal films exhibit crystallinity after a 30 min 1100°C furnace anneal in oxygen while plasma deposited films remained amorphous after the same treatment. Reflection FTIR measurements were performed and results show no evidence of bulk carbon incorporation. In-situ anneals in Ar ambient were done on thin films of HfO_2 and silicates and their change in chemical state was studied using XPS.

10:20am **DI+EL-ThM7 UHV-CVD of Al_2O_3 for Gate Dielectric Applications**, ***B.R. Rogers***, *Z. Song, R.D. Geil, V. Pawar, D.W. Crunkleton, R.A. Weller*, Vanderbilt University

Successful replacement of silicon dioxide-based MOSFET gate dielectrics by a high-permittivity (high-k) dielectric is a critical step in the continued drive to build the smaller, faster, lower-power, more-integrated circuits that society is demanding. Our goal toward this effort is to develop a thermodynamically and microstructurally stable, amorphous material system, having no interfacial silicon dioxide formation. In this presentation I will briefly discuss the need for an alternative gate dielectric and a "wish list" of characteristics for this material. I will then discuss our work on developing alumina/zirconia alloys as a potential gate dielectric. We have begun this effort by studying the deposition of alumina films in an ultra-high-vacuum chemical vapor deposition (UHV-CVD) system. I will present our findings to date in relation to the CVD process. In addition I will discuss the characterization of these films using spectroscopic ellipsometry and time-of-flight medium energy backscattering (ToF-MEBS), a characterization capability unique to Vanderbilt University.[1]

[1] This work is supported by the National Science Foundation grant # CTS-0092792.

10:40am **DI+EL-ThM8 Hafnium Oxide As an Alternative Gate Dielectric in MOSCAP and MOSFET Application**, ***Y. Lin***, *R. Puthenkovilakam, J.P. Chang*, University of California, Los Angeles

HfO_2 is investigated in this study to replace SiO_2 as the gate dielectric material in metal-oxide-semiconductor devices. HfO_2 films were deposited on P-type Si (100) wafers by an atomic layer chemical vapor deposition (AL-CVD) process using hafnium (IV) t-butoxide $Hf(OC_4H_9)_4$ as the precursor and oxygen as the oxidant. The two chemistries were introduced sequentially into the reactor with purging and evacuation in between. The deposited films were stoichiometric and uniform based on X-ray photoemission spectroscopic and ellipsometry. The X-ray diffraction analysis indicated the deposited film was amorphous, however, it showed an interfacial layer formation at on the silicon substrate based on the chemical etching resistance experiment. This interfacial layer will be examined by the high-resolution transmission electron and medium energy ion scattering analysis. The step coverage will also be examined by depositing HfO_2 on 200 nm features with an aspect ratio of 4. The thermal stability of HfO_2 thin film on silicon was examined by Synchrotron radiation x-ray photoemission spectroscopy. The HfO_2 thin films were thermally stable up to 950° C in vacuum. In-situ Infrared analysis and ellipsometer measurement are underway to enhance our ability to understand the surface reactions. Isotope labeling of oxygen will be perform to study the effect of the oxidation/annealing processes on film composition. The dielectric constant of HfO_2 was 18 from the C-V measurement, which was slightly lower than the bulk HfO_2 . In the C-V measurement a small hysteresis and the interface state density was approximately $5.22x10^{11}$ cm^{-2} eV^{-1} are observed. The leakage current is 2~3 order magnitude lower than SiO_2 at the same equivalent oxide thickness. NMOS transistors will be fabricating to exam the applicability of HfO_2 for MOSFET application.

11:00am **DI+EL-ThM9 Hafnium Silicate and Nitrided Hafnium Silicate as Gate Dielectric Candidates for SiGe-based CMOS Technology**, ***S. Addepalli***, *P. Sivasubramani, H. Zhang, M. El-Bouanani, M.J. Kim, B.E. Gnade, R.M. Wallace*, University of North Texas

Strained epitaxial Si_xGe_{1-x} layers on Si have attracted considerable technological interest due to the enhancement in hole mobility, as well as ease of integration with existing Si CMOS technology. One of the major drawbacks, however, is the inability to produce a high-quality gate oxide in direct contact with Si_xGe_{1-x}, while maintaining the integrity of the oxide-Si_xGe_{1-x} interface. The introduction of a stable high-κ dielectric provides the prospect of simultaneously enhancing the capacitance of the gate stack and reducing leakage current for high performance SiGe devices. We have investigated hafnium silicate and nitrided hafnium silicate as viable candidates for SiGe-based CMOS technology. Hafnium silicide and nitrided hafnium silicide films were sputter deposited directly on Si_xGe_{1-x}. These films were subsequently converted to hafnium silicate and nitrided hafnium silicate respectively by employing a room temperature UV-ozone assisted oxidation approach in order to preserve the pseudomorphic nature of the Si_xGe_{1-x} layers. The bonding and composition of these films were characterized by X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), and Rutherford Backscattering Spectrometry (RBS). The deposition and post-deposition processing parameters were optimized using XPS, High-resolution transmission electron microscopy (HRTEM), and FTIR. The electrical performance of the films was evaluated from capacitance-voltage (C-V) and current-voltage (I-V) measurements. The effects of various post-deposition annealing treatments on the electrical performance of the films were also studied. This work is supported by DARPA through SPAWAR Grant No. N66001-00-1-8928, and the Texas Advanced Technology Program.

11:20am **DI+EL-ThM10 XPS Study of Chemical Phase Separation in Amorphous Zr Silicate High-k Dielectrics**, ***G.B. Rayner***, *D.H. Kang, G. Lucovsky*, North Carolina State University

X-ray photoelectron spectroscopy (XPS) was used to investigate chemical phase separation in pseudo-binary Zr silicate alloys, $(ZrO_2)_x(SiO_2)_{1-x}$, deposited at 300C on Si substrates as a function of alloy composition, film thickness and subsequent annealing temperature. Based on previous infrared (IR) and x-ray diffraction (XRD) studies, it been shown that a chemical phase separation in (a) ZrO_2 and (b) SiO_2 with up to about 5 atomic percent ZrO_2 occurs in Zr silicate alloys when annealed at 900C in a non-oxidizing ambient such as Ar.. This separation is not accompanied by crystallization for silicate alloys with $x \sim 0.25$, but crystallization of the ZrO_2 phase occurs for $x > \sim 0.5$. For Zr silicate films ~30 nm thick and $x < \sim 0.6$ the XPS O1s core level peak shapes are essentially unchanged for annealing temperatures to 500C. However, for annealing at 900C, the O1s core level peak splits into a distinct doublet with binding energies independent of alloy composition for $0.35 < x < 0.6$. The peak at low binding energy, assigned to O^{2-} ions in the ZrO_2 phase, scales approximately linearly with composition. These results indicate a transition from silicate bonding, characterized by Si-O-Zr alloy bonds, into bonding characteristic of the end-member oxide phases, SiO_2 and ZrO_2. The XPS results presented here provide additional insights into local bonding that are complementary to what has been revealed previously in IR studies, as well as confirming the chemical phase separation that occurs for annealing temperatures > 900C in inert ambients. Included also are the results of a parallel study on the effect of chemical phase separation on the electrical performance of metal oxide semiconductor capacitors.

11:40am **DI+EL-ThM11 Electrical Properties of SiO_2 Films Grown by Si(100) Reactions with Oxygen, Wet-oxygen and Wet-hydrogen**, ***Y. Liu***, *J. Hebb*, Axcelis Technologies, Inc.

The oxidation of Si(100) by oxygen (O_2), wet-oxygen (H_2O+O_2) and wet-hydrogen (H_2O+H_2) is of great importance for silicon oxide (SiO_2) dielectric film formation in the advanced CMOS devices. At the atmospheric pressure and high temperatures (>1100°C), 20 to 100 Å SiO_2 films have been grown on Si(100) wafers (dia.=200 mm) using a hot-wall rapid thermal processor (Summit 200, Axcelis) enhanced with a small volume (3-liter) quartz reactor for rapid gas switching. Wet-oxygen and wet-hydrogen with controlled compositions are produced using a hydrogen-rich and an oxygen-rich catalytic water vapor generator (WVG), respectively, and are monitored in real-time with a residual gas analyzer (RGA). Kinetic equations for Si(100) reactions with oxygen and water vapor are used to control oxidation temperature, oxidant fractional pressure and time to achieve desired oxide thickness. To grow a thermal oxide film, a Si(100) wafer is rapidly heated to a desired temperature in nitrogen or hydrogen. Rapid gas sequencing is carried out to expose the wafer to oxygen, wet-oxygen or wet-hydrogen for oxidation, and back to nitrogen or hydrogen for annealing and cooling. Critical electrical properties of the thermal oxide films grown under various conditions are measured and compared systematically using a powerful and non-contact Corona Oxide Characterization of Semiconductor (COCOS) tool (FAaST, SDI). These properties include equivalent oxide thickness (EOT), oxide capacitance, flat band voltage, effective oxide charge, interface trapped charge, interface trap density, and interface trap density spectrum. Gate oxide integrity (GOI) of these films is quantified by leakage current versus voltage (I-V) and stress-induced leakage current (SILC) measurements. Correlation between growth conditions and oxide qualities will be made.

Surface Science
Room: C-112 - Session SS+EL+OF-ThM

Reactions and Patterning of Organics on Silicon
Moderator: S.F. Bent, Stanford University

8:20am **SS+EL+OF-ThM1 Fixation of Alkyl Groups on Si(111) Surface through C-Si Single Covalent Bond formed by Reaction of Grignard Reagent and H:Si(111)**, ***T. Yamada***, *T. Inoue, K. Yamada, N. Takano, T. Osaka,* Waseda University, Japan, *H. Harada, K. Nishiyama, I. Taniguchi*, Kumamoto University, Japan

Alkyl adsorbates that are directly bonded to the outermost atoms of silicon wafer surfaces have prospective properties for application in nanometer-scale fabrication and surface functionalization.[1] Several methods have been proposed to deposit alkyl groups on hydrogen-terminated H:Si(111).[2] The conversion of the H-Si bonds in H:Si(111) into C-Si bonds caused by chemical processes is an important issue in preparing the organic adlayers. In this work, high-resolution electron energy loss spectroscopy (HREELS) was utilized to prove the formation of single covalent bonds between Si(111) surface atoms and alkyl groups by the chemical reaction of a Grignard reagent and hydrogen-terminated H:Si(111)(1x1).[2] The reaction was performed by heating a piece of H:Si(111) in 1M tetrahydrofuran (at 65°C) or diethylether solution (at 30°C) of desired alkylmagnesium halide for 18 hours under Ar atmosphere. By this reaction condition, somewhat 20% of the product surface were still covered with residual hydrogen. The bending vibration mode of the residual hydrogen (630 cm^{-1}) obscured the alkyl signals in the range of 600 - 700 cm^{-1}. By using deuterium-terminated D:Si(111), the vibration at 680 cm^{-1}, assigned to the C-Si bond, was isolated within the spectrum of CH_3-. The CH_3 groups were thermally stable at temperatures below 600 K. Similar features were observed for C_2H_5-, phenyl- and so on. The C-Si bonds are essential for enhancing the stability and lowering the mobility of alkyl moieties. Such properties of alkyl moieties of will lead to a new prospective science and technology in nanometer-scale fabrication.

[1] T. Yamada, N. Takano, K. Yamada, S. Yoshitomi, T. Inoue, and T. Osaka, Jpn. J. Appl. Phys. 40 (2001) 4845.

[2] R. Boukherroub, S. Morin, F. Bensebaa and D. D. M. Wayner, Langmuir 15 (1999) 3831.

8:40am **SS+EL+OF-ThM2 Chemomechanical Production of Sub-Micron Edge Width, Functionalized, ~20 Micron Features on Silicon**, ***M.R. Linford***, *Y.-Y. Lua, T.L. Niederhauser, B.A. Wacaser,* Brigham Young University, *I.A. Mowat,* Charles Evans & Associates, *A.T. Woolley, R.C. Davis,* Brigham Young University, *H.A. Fishman,* Stanford University Medical School

We have recently reported that monolayers on silicon can be formed, and silicon substrates concomitantly patterned, when native oxide-terminated silicon is scribed with a diamond-tipped instrument in the presence of 1-alkenes,[1,2] 1-alkynes,[1,2] alkyl halides (chlorides, bromides, and iodides),[2,3] and alcohols.[3,4] Monolayers were prepared in the open laboratory with reagents that had not been degassed.[1-4] However, while this method is particularly facile, the features produced using a diamond scribe are coarse and irregular.[1] The high degree of edge and surface roughness in these features will no doubt limit the utility of our earlier work in some circumstances. Here we describe a substantial improvement in our earlier method by showing the production of sharp, well-defined, functionalized features on silicon that are invisible to the naked eye and very shallow. In contrast to the earlier procedure that used oxide-terminated silicon and a diamond-tipped scribe,[1-4] this new method consists of 1) cleaning and drying a silicon shard, 2) immersing the silicon in a fluoride ion etch to remove its native oxide and produce hydrogen-terminated silicon, 3) wetting the dry, H-terminated silicon surface with a reactive liquid, and 4) scribing the surface with a small tungsten carbide ball. Both Si(100) and Si(111) were successfully patterned and functionalized with this new method.

[1] Niederhauser, T. L.; Jiang, G.; Lua, Y.-Y.; Dorff, M. J.; Woolley, A. T.; Asplund, M. C.; Berges, D. A.; Linford, M. R. Langmuir 2001, 19, 5889-5900.

[2] Lua, Y.-Y.; Niederhauser, T. L.; Matheson, R.; Bristol, C.; Mowat, I. A.; Asplund, M. C.; Linford, M. R. In Press Langmuir 2002.

[3] Niederhauser, T. L.; Lua, Y.-Y.; Sun, Y.; Jiang, G.; Strossman, G. S.; Pianetta, P.; Linford, M. R. Chem.Mater. 2002, 14, 27-29.

[4] Niederhauser, T. L.; Lua, Y.-Y.; Jiang, G.; Davis, S. D.; Matheson, R.; Hess, D. A.; Mowat, I. A.; Linford, M. R. In press Angewandte Chemie 2002.

9:00am **SS+EL+OF-ThM3 Formation of Nanoscale Organic and Inorganic Features on Semiconductor Surfaces**, ***J.M. Buriak***, Purdue University **INVITED**

Integration of molecular devices and nanoscale materials with semiconductors, including silicon and germanium, is an area of intense interest, due to the potential for interfacing nanomaterials with the macroworld. We have developed a number of wet chemical routes which allow for covalent attachment of both organic functionalities, including molecular wires, and inorganic nanoparticles. For instance, a cathodic electrografting reaction between alkynes and hydride-terminated silicon surfaces results in alkynyl moieties bound directly through Si-C bonds, with no intervening oxide layer. The surfaces are air and water stable, and can withstand boiling pH 12 solutions. In order to pattern these alkynyl groups on the silicon surface in nanoscale regions, conducting probe lithography has been utilized to write the organic monolayers, with feature sizes as small as 30 nm. For inorganic structure patterning, electroless deposition has been combined with microcontact printing, dip pen nanolithography (DPN), and UV-mediated hydrometallation to produce nano- and micron-scale features. These approaches and others will be described.

9:40am **SS+EL+OF-ThM5 Structures, Dynamics, and Chemical Reactivity of Si (001) at Finite Temperatures: A First Principles Study**, *D. Pillay, Y. Wang,* ***G.S. Hwang***, The University of Texas at Austin

Imparting organic functions onto a well-defined functionality of semiconductor surfaces with atomic-scale precision provides an enormous opportunity to develop new molecular devices including chemical and biological sensors and molecular electronic devices. For semiconductor systems, the rates and pathways of chemical reactions are strongly influenced by local electronic structures determined by surface reconstructions and defects. Due to such complex structural effects, chemical dynamics on semiconductor surfaces has not been fully understood. To gain molecular-level control, therefore, first we must develop a detailed understanding of structures, dynamics, and chemical reactivity of clean, defective, or modified (with various adsorbates) surfaces at finite temperatures, along with the structures and bonding of organic compounds onto the surfaces. In this talk we will present first principles quantum mechanics [Density Functional Theory with plane-wave basis sets and pseudopotentials] simulations for structures, dynamics, and chemical reactivity (towards organic species) of (001)-faced Si and Ge surfaces at finite temperatures. This includes the dynamics of buckled dimers on clean and defective surfaces and their effects on adsorption dynamics of various organic molecules.

10:00am **SS+EL+OF-ThM6 Superexchange Interactions in STM-Organic-Semiconductor Systems**, ***L.C. Teague***, *J.J. Boland,* University of North Carolina at Chapel Hill

The incorporation of organic layers and individual molecules into existing semiconductor technologies requires a thorough understanding of surface/molecule reactions. Although numerous studies have focused on the reaction of individual molecules with the Si(100) surface, the specific reaction mechanisms remain poorly understood. The similarity of the Si(100)-2 x 1 surface chemistry with that of C=C systems opens up the possibility of a wide range of organic chemistry reactions. Here, a combination of Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) calculations are used to study and interpret the reaction of 1,3-cyclohexadiene (1,3-CHD) with the bare Si(100)-2 x 1 surface. Because STM probes the local density of states (LDOS), the local bonding geometry of 1,3-CHD can be inferred from the location of the π bond in the adsorbed molecule. Other groups have reported similar observations.[1,2] However, DFT calculations indicate the π^* orbital is located several eV above the Fermi Energy and should be energetically inaccessible under typical bias conditions. Here, we show that these images can be understood by considering the interaction between the STM tip and the molecule-surface system. The superexchange mixing of the tip dangling bond state with the filled π state on the molecule produces a new state within the tunneling window. This state is responsible for the observed image contrast and suggests superexchange effects of this type may be important in understanding the charge transfer that occurs through these molecular systems.

[1] Hamaguchi, K.; Machida, S.; Nagao, M.; Yasui, F.; Mukai, K.; Yamashita, Y.; Yoshinobu, J.; Kato, H. S.; Okuyama, H.; Kawai, M.; Sato, T.; Iwatsuki, M. J. Phys. Chem. B 2001, 105, 3718.

[2] Hovis, J. S.; Liu, H.; Hamers, R. J. J. Phys. Chem. B, 1998, 102, 6873.

10:20am **SS+EL+OF-ThM7 Modifying the Semiconductor Interface with Organonitriles**, ***M.A. Filler***, *C. Mui, C.B. Musgrave, S.F. Bent*, Stanford University

Organic functionalization of group-IV semiconductor surfaces has recently garnered considerable attention and applications in the areas of molecular electronics, biological recognition, and reagentless micropatterning have been proposed. If these and other concepts are to become technologically feasible, however, the creation of an ordered and selectively grown layer as well as the ability to successively attach additional organic monolayers will be necessary. Organonitrile compounds were studied as potential candidates for first and subsequent layer surface reactions on Si(100)-2x1 and Ge(100)-2x1. Bonding is investigated experimentally with infrared spectroscopy and theoretically with density functional theory. We find that acetonitrile does not react on the Ge(100)-2x1 surface at room temperature and explain this result with kinetic and thermodynamic arguments. A [4+2] cycloaddition product through the conjugated π system and a [2+2] C=C cycloaddition product through the alkene are found to be the dominant surface adducts for the multifunctional molecule 2-propenenitrile. While the non-conjugated molecules 3-butenenitrile and 4-pentenenitrile are not expected to form a [4+2] cycloaddition product, both show vibrational modes characteristic of this adduct and we propose the possibility of a surface catalyzed reaction. Pathways directly involving only the nitrile functional group are thermodynamically unfavorable at room temperature on Ge(100)-2x1 and the conversion of the remaining nitrile functionality as well as its use in additional surface reactions will also be presented.

10:40am **SS+EL+OF-ThM8 Adsorption and Reaction of Allyl- and Ethyl-amine on Germanium and Silicon Surfaces**, *P. Prayongpan*, ***C.M. Greenlief***, University of Missouri-Columbia

The adsorption and reaction of allyl- and ethyl-amine with the Ge(100) and Si(100) surfaces is examined. These processes are followed by a variety of surface sensitive techniques including ultraviolet photoelectron spectroscopy and temperature programmed desorption. Possible adsorption structures are also examined by theoretical methods. Density functional theory calculations are used to help interpret the photoelectron spectroscopy data. The calculated molecular orbital energies (within Koopmans' approximation) are used to help identify adsorbed molecular species, as well as, reaction intermediates. The interaction of these nitrogen-containing molecules with surface dimmer bonds and ordering of the resulting surface layers will be discussed.

11:00am **SS+EL+OF-ThM9 Adsorption Chemistry of Cyanogen Bromide and Iodide on Silicon (100)**, ***N.F. Materer***, *P. Rajasekar, E.B. Kadossov*, Oklahoma State University

The adsorption of cyanogen iodide (ICN) and bromide (BrCN)on a silicon (100) surface is studied by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and thermal desorption spectroscopy (TPD). After submonolayer exposures, XPS indicates that the CN triple bond of both ICN and BrCN emains intact upon adsorption at 100K. The UPS spectrum of these molecules contains two peaks assigned to the pi electrons in the CN triple bond. The splitting of these levels, due to the interaction between the pi electrons on the cyanogen and the halide, show that some portion of the initially adsorbed cyanogens halide also remains intact upon low temperatures adsorption. In contrast, the UPS spectrum of ICN and BrCN adsorbed at room temperature on Si(100) contains only one peak due to the pi electrons in the carbon nitrogen triple bond. The lack of splitting in the room temperature UPS spectrum is a result of XC (X=Br, I) bond dissociation. Thus, the XC bonds breaks while the CN bond remains intact during room temperature adsorption on Si(100). Upon annealing the Si(100) surface to higher temperatures, the UPS spectra indicates that the C-N triple bond remains intact until approximately 700 K. Simultaneous changes in the C 1s photoelectron peak are consistent with the idea that C-N bond cleavage in the cyanogen halides is correlated with silicon carbide formation.

11:20am **SS+EL+OF-ThM10 Theoretical Adsorption Studies of ICN on the Si(100) Surface**, ***E.B. Kadossov***, *P. Rajasekar, N.F. Materer*, Oklahoma State University

Ab initio quantum calculations have been used to study the adsorption and surface reactions of ICN on the Si(100) surface represented by Si_2H_{12} single-dimer cluster. At low temperatures, experiments show that some faction of the initially exposed ICN is molecularly absorbed to the surface. Calculations of the molecularly absorbed species support the formation of end-on configuration with the N forming a dative bond with the lone pair on the Si(100) surface. Upon annealing, experiments reveal that the remaining molecular adsorbed ICN species dissociate to produce I and CN species on the surface. Calculations show that this process can take place directly or through a stable side-on adsorption intermediate. The transition barrier to form the side-on intermediate species is slightly lower than for the direct reaction (12.82 vs. 17.26 kJ/mol). After dissociation, the CN is bound to the silicon surface through either the C or the N ends. The C bound species possesses the lowest energy and is consistent with experimental XPS results. In addition, these two possible structures are separated by an activation barrier of 107.39 kJ/mol, easily overcome by the excess adsorption energy. An alternate pathway for the ICN side-on species is to isomerize into an INC structure through a 212.26 kJ/mol activation barrier. However, the activation barrier between this new species and the dissociated state is 5.53 kJ/mol. This transition barrier is even lower than the 84.05 kJ/mol barrier between side-on ICN surface species and the dissociated state.

11:40am **SS+EL+OF-ThM11 Infrared Study of Adsorption of C_6H_6 onto Si(100)(2x1)**, *M. Shinohara, H. Watanabe, Y. Kimura, H. Ishii*, ***M. Niwano***, Tohoku University, Japan

The interaction of benzene with the (100) and (111) surfaces of silicon has proven to be an interesting model system for molecular adsorption on semiconductor surfaces. The adsorption of benzene on the Si(100)(2x1) surface has been expensively studied in recent years both experimentally and theoretically. Previous elaborate theoretical calculations predicted that adsorption of benzene onto the Si(100)(2x1) surface leads to two different adsorption structures: One corresponds to benzene adsorbed on top of a dimer row between two adjacent Si dimers. This structure has four C atoms of benzene bonded to four Si atoms from two adjacent dimers. The other corresponds to the benzene molecule that sticks on top of the dimer row and has two of its C atoms bonded to two Si atoms of a single surface dimer. However, there still is a controversy regarding which structure is more favored. In this study, we have investigated the adsorption of benzene C_2H_6 on the Si(100)(2x1) surface using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR) and the so-called hybrid density-functional theory (DFT) to determine the most preferred adsorption structure of benzene on Si(100)(2x1) at room temperature. IRAS-MIR provides us with valuable information about the hydrogen bonding configurations on semiconductor surfaces. We analyzed IRAS spectra in the C-H stretching vibration region to determine the detailed adsorption structure of benzene. The central result is that benzene adsorbs in different manners depending on the surface coverage of benzene: at low coverage the molecule adsorb on the surface to favor the formation of benzene adsorbed on two adjacent dimers. On the other hand, at high coverage the molecule adsorb on the Si surface to generate benzene adsorbed on a single dimer. We also discuss the reason why the adsorption structure depends on surface coverage.

Surface Science
Room: C-110 - Session SS+EL-ThM

Structure of Semiconductor Surfaces & Interfaces
Moderator: C.J. Palmstrom, University of Minnesota

8:20am **SS+EL-ThM1 Strain Control of the Ge(105) Surface via Hydrogen Adsorption**, ***Y. Fujikawa***, *M. Kawashima, T. Nagao, T. Sakurai*, Tohoku University, Japan, *M.G. Lagally*, University of Wisconsin-Madison

Controlling the size and shape of Ge quantum dots formed on the Si(001) substrate is of great technological importance for their potential application in future semiconductor devices. Surfactant effects on this system are regarded as a promising method to achieve the controlled growth of quantum dots. Among them, hydrogen adsorption, which has been studied intensively, is known to suppress the formation of Ge "huts", pyramidal nanocrystals bounded by four Ge{105} facets.[1] We have investigated hydrogen adsorption on a Ge(105) surface formed on a Si(105) substrate using STM to elucidate the role of surface strain on the stability of Ge(105) under hydrogen-adsorption conditions. The STM images of Ge(105) surfaces with adsorbed hydrogen atoms are understood based on the newly-established atomic structure of Ge(105).[2] We observe the stability of hydrogen-covered Ge(105) for different amounts of Ge initially deposited on the Si(105) surface. We find that hydrogen adsorption on Ge(105) surfaces formed from deposited amounts of Ge less than 1.5 ML makes the surface remarkably unstable and results in the formation of local defects. This fact indicates that hydrogen adsorption on Ge(105) increases the surface strain by arresting the strain-relief mechanism that would ordinarily occur on clean Ge(105) with the formation of sp^2-hybridized dimers. Thus, the formation of Ge(105) will be unfavorable and suppressed in the presence of adsorbed hydrogen. This work is supported by NSF.

[1] Kahng et al., Phys. Rev. Lett. 80, 4931 (1998).

[2] Fujikawa et al., Phys. Rev. Lett. 88, 176101 (2001).

8:40am **SS+EL-ThM2 A LEEM Study of the Ge(001)-(2x1)-(1x1) Phase Transition; Domain Wall Proliferation and Dimer Break-up**, *E. van Vroonhoven, H.J.W. Zandvliet*, ***B. Poelsema***, University of Twente, The Netherlands

The Ge(001) surface exhibits two phase transitions. At low temperatures it is c(4x2) reconstructed, evolving with increasing temperature into (2x1). The origin of the reconstruction is dimerization of the surface: the number of dangling bonds is reduced from two per surface atom, for a bulk terminated surface, to only one. In the c(4x2) phase the dimers are buckled in an anti-symmetric way; in the (2x1) phase the dimers rapidly switch between the two buckled orientations and appear symmetric. Due to the diamond structure of Ge, the dimer rows on neighboring terraces are rotated by 90°. At high temperature the (2x1) phase disappears and the (1x1) phase emerges. Two conflicting models have been proposed in literature. One model suggests that this phase transition is driven by vacancy pair creation and dimer break-up on the Ge(001) surface. The other claims that the phase transition involves (2x1) domain wall (step) proliferation rather than dimer break-up. Our results demonstrate that domain wall proliferation sets in around 950 K, leading to a complete loss of contrast in LEEM around 1050 K. The dimers, however, remain clearly visible up to about 1130 K. The dimer concentration is a strong function of the substrate temperature between 1030 and 1130 K. Our combined microscopy and diffraction data are only consistent with the first model. It is even possible for the first time to directly extract the free energy gain of dimerization, being 1.6 eV per pair. This value compares perfectly with calculations performed for silicon after scaling with the melting temperature. We estimate the temperature to be accurate with ± 25 K and thus the dimerization energy with ± 5%.

9:00am **SS+EL-ThM3 Encapsulation of SiGe Quantum Wells and Quantum Dots**, ***G.G. Jernigan***, *P.E. Thompson*, US Naval Research Laboratory

Semiconductor device characteristics are dependent on the chemical and structural properties of the electrical interface. As such, we are interested in SiGe quantum wells and quantum dots grown in Si. Heterojunctions between Si / SiGe / Si are chemically smeared due to Ge segregation, but little is known about the structural nature of the heterojunctions. We will present an STM study of the encapsulation of a $Si_{0.8}Ge_{0.2}$ alloy grown in Si at 500, 650, and 800 °C. Alloy deposition induces a rougher morphology than the inital Si surface. Intermixing of Ge from the alloy with the Si substrate is observed to happen immediately to produce a rough surface. The amount of intermixing increases with increasing growth temperature, and at 800 °C the surface roughness exceeds the thickness of deposited alloy. After intermixing, Ge segregates out from the alloy, and the surface Ge leads to an island growth mechanism, which further increases the surface roughness. At 500, 650, and 800 °C the alloy surfaces obtain a steady-state value for surface roughness, which has been characterized as 2D planar, rippled, and hutted, respectively. Encapsulation of the alloy layer with Si attempts to restore a smooth morphology. At 800 °C where the height of the huts are ~40 nm, a 5 nm Si layer reduced the hut height to ~10 nm, and after 20 nm of Si, the huts are gone. Remnants of the underlying alloy morphology can still be seen on the surface in the form of square pits where material did not fill in between the huts. For lower growth temperatures, less Si is needed to reduce the surface roughness, and square pits are still observed from the underlying alloy. The square pits arise from Ge segregation modifying the S_A and S_B step-edge sticking coefficient of Si to produce equal sized S_A and S_B terraces. A structural model for the heterointerfaces based on the STM observations will be presented.

9:20am **SS+EL-ThM4 First Atomic-Resolution Ultrahigh Vacuum Scanning Tunneling Microscopy Study of GaSe/Si(111) Ultrathin Films**, ***T. Ohta***, *A. Klust, J.A. Adams, Q. Yu, M.A. Olmstead, F.S. Ohuchi*, University of Washington

Gallium-selenide thin films deposited on Si(111) are of increasing interest for applications, both in their own right as optoelectronic structures, and as non-reactive, low surface energy, high band gap buffer layers for subsequent nanostructure formation. Gallium selenide crystallizes into two crystal structures, layered GaSe and cubic Ga_2Se_3 with bandgaps of 2.0 and 2.6eV, respectively. Crystal structure and stoichiometry of the deposited Ga_xSe_y can be controlled by the substrate temperature during deposition. We present the first atomic-resolution ultrahigh vacuum scanning probe microscopy study of GaSe/Si(111) ultrathin films. When GaSe thin films are deposited at substrate temperature 520°C, atomically flat surfaces consisting of a single molecular layer of GaSe with altered step structures of 7*7-Si(111) were observed. These surfaces have no dangling bonds to react with residual gases, or to provide nucleation sites for subsequent growth. We also observed occasional point defects causing long-range alterations of the local band bending, but no sharp states revealed by the tunneling spectroscopy. At lower substrate temperatures, Ga_xSe_y multilayers with flat surface and triangle features with 3-4nm sides were formed. Height difference of the atomic steps suggests that the multilayers have a cubic structure. These triangles are likely associated with Ga or Se vacancies in the Ga_2Se_3.

This work was partially supported by the M. J. Murdock Charitable Trust and NSF Grant DMR 0102427.

9:40am **SS+EL-ThM5 Electronic and Structural Properties of Aluminum Selenide Ultrathin Film on Si(111)**, ***J.A. Adams***, *A.A. Bostwick, T. Ohta, A. Klust,* University of Washington, *E. Rotenberg,* Advanced Light Source, *F.S. Ohuchi, M.A. Olmstead*, University of Washington

The wide band gaps of aluminum selenide and gallium selenide make them appealing candidates for blue-green opto-electronics, and they are closely lattice matched to silicon making them compatible in silicon-based structures and devices. However, very little is known about the properties of aluminum selenide heteroepitaxial films. Bulk aluminum selenide, a defected wurtzite structure, has a 3.1 eV band gap, and its hexagonal lattice constant is about 1.3% larger than Si(111). Unlike gallium selenide, which is stable in both layered GaSe and defected zincblende Ga_2Se_3 structures, layered AlSe has not been reported in either bulk or thin film form. We investigated varying thicknesses of ultrathin films of aluminum selenide grown epitaxially on Si(111) including sub-monolayer growth, a single bilayer, and the subsequent initial stages of growth on the bilayer. The AlSe/Si interface forms a bilayer structure similar to GaSe-terminated Si, although the temperatures for bilayer formation and for Se-evaporation from the film are higher for AlSe than for GaSe. The reactivity of the AlSe terminated Si(111) surface with both residual gases and for subsequent film growth is much higher than that of GaSe. Further deposition of aluminum selenide produces films that resemble the bulk stochiometry Al_2Se_3. Electronic band-structure for AlSe/Si was investigated using angle resolved photoelectron spectroscopy (ARPES). Unlike GaSe/Si, the AlSe bilayer appears to have a true surface state. Si-Al bond lengths and Al-Se bond lengths were measured by energy dependent photoelectron diffraction (EDPD). Initial results indicate that the Al-Si bond is 8% larger that in Al/Si(111)-(√3x√3). Heterostructures of AlSe/GaSe on Si(111) will also be discussed. Funded by NSF Grant DMR-0102427.

10:00am **SS+EL-ThM6 Ga Surface Segregation in ErAs (100)/GaAs (100)**, ***H.K. Jeong***, *T. Komesu, C.-S. Yang, P.A. Dowben,* University of Nebraska-Lincoln, *B.D. Schultz, C.J. Palmstrom*, University of Minnesota

Surface segregation has now been characterized by angle resolved x-ray photoemission for NiMnSb, a variety of perovskites, and a number of binary alloys. Using angle-resolved x-ray photoemission spectroscopy (ARXPS), the surface composition of the sample can be roughly established since the effective probing depth is shorter at large emission angles with respect to the surface normal. Epitaxial thin films of the rare earth pnictide ErAs(100) can be grown on GaAs(100), but at elevated temperatures the ErAs film degrades. Ga segregation through the ErAs to the surface has been identified by angle-resolved X-ray photoemission spectroscopy, following extensive annealing. The angle-resolved XPS data indicates that the segregation of Ga is extensive throughout the ErAs thin film and is not restricted just to the surface layer.

10:20am **SS+EL-ThM7 Absolute Orientation-Dependent TiN(001) Step Energies from Two-Dimensional Equilibrium Island Shape and Coarsening Measurements on Epitaxial TiN(001) Layers**, ***S. Kodambaka***, *S.V. Khare, V. Petrova,* University of Illinois, *A. Vailionis,* Stanford University, *I. Petrov, J.E. Greene*, University of Illinois

In situ high-temperature (1030-1185 K) scanning tunneling microscopy was used to determine the equilibrium shapes of two-dimensional TiN vacancy islands on atomically-smooth terraces of epitaxial TiN(001) layers. Inverse Legendre transformations of the equilibrium island shapes yield relative step energies as a function of step orientation within an orientation-independent scale factor λ, the equilibrium chemical potential of the island per unit TiN molecular area. We then use quantitative TiN(001) adatom island coarsening measurements to determine λ and, hence, absolute orientation-dependent step energies β and step stiffnesses b̆eta. For <110> and <100> steps on TiN(001), we obtain: β_{110} = 0.21±0.05 eV/Å, β_{100} = 0.25±0.05 eV/Å, b̆eta$_{110}$ = 0.9±0.2 eV/Å, and b̆eta$_{100}$ = 0.07±0.02 eV/Å. From the b̆eta values, we calculate kink formation energies ε_{110} = 0.40±0.2 eV and ε_{100} = 0.11±0.1 eV based on the unrestricted terrace-step-kink model.

10:40am **SS+EL-ThM8 Scanning Force Microscopy Measurements on Ionic Crystals at Low Temperatures and Comparison to Atomistic Simulations**, ***R. Hoffmann***, *M.A. Lantz*, University of Basel, Switzerland, *L.N. Kantorovich*, University College London, UK, *A. Baratoff, H.J. Hug*, University of Basel, Switzerland, *A.L. Shluger*, University College London, UK, *H.-J. Güntherodt*, University of Basel, Switzerland

Alkali halide surfaces were the first insulating materials to be imaged by scanning force microscopy (SFM) with true atomic resolution. Although atomic resolution images on alkali halides have been obtained by several groups, the tip-sample interaction above specific sites has so far been studied only theoretically.[1] Knowing this interaction force provides insight into atomic resolution image mechanisms and allows to study bonding interactions on a surface on the atomic scale. Recently, site-specific force-distance experiments have been performed for the first time at low temperatures on the Si(111) 7x7 surface.[2] Here we report similar measurements on the KBr (001) and the NaCl (001) surface in which we study the interaction forces and the imaging mechanism. The short-range forces have been calculated using atomistic simulations. The magnitude of the calculated forces agrees well with the experimental data, although for KBr the calculated corrugation is larger than the measured one even when the long-range forces are included. For NaCl also the corrugation is in good agreement to the experiment.

[1] L. N. Kantorovich et al. Surf. Sci. 445, 283 (2000)

[2] M. A. Lantz et al. Science 291, 2580 (2001)

11:00am **SS+EL-ThM9 Core-level Spectroscopy Study of the Clean c(4x2) and the Hydrogenated 2x1-H Phases on the 3C-SiC(001) Surface**, ***L.S.O. Johansson***, *S.M. Widstrand, K.O. Magnusson, M.I. Larsson*, Karlstad University, Sweden, *H.W. Yeom*, Yonsei University, Korea, *S. Hara, S. Yoshida*, AIST, Japan

We report a core-level spectroscopy investigation of the clean Si-terminated 3C-SiC(001)-c(4x2) surface and the hydrogenated 3C-SiC(001)2x1-H surface. The 2x1-H surface was formed by exposing the clean c(4x2) surface to excited hydrogen gas. Desorption of the hydrogen at 900° C led to the restoration of the c(4x2) periodicity. Higher hydrogen exposures led to the formation of diffuse 1x1 and mixed 3x1/2x1 phases, as observed by low-energy electron diffraction (LEED). This behaviour is remarkably similar to hydrogen adsorption on the Si(001)2x1 surface. Si 2p core-level spectra from the clean c(4x2) surface displayed the characteristic surface peak shifted by 1.4 eV to lower binding energy, which in previous studies has been attributed to Si adatoms on top of a Si-terminated surface.[1,2] The formation of the 2x1-H surface lead to dramatic changes in the Si 2p lineshape, where the main surface components now appeared closer to the bulk peak. Detailed decompositions of the spectra are presented and are discussed in relation to the suggested structural models for the c(4x2) surface[3,4] and to previous core-level studies.[1,5].

[1] M.L. Shek, Surf. Sci. 349, 317 (1996).

[2] A. Catellani, G. Galli, and F. Gygi, Appl. Phys. Lett. 72, 1902 (1998).

[3] P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli, and C. Joachim, Phys. Rev. Lett. 78, 907 (1997).

[4] W. Lu, P. KrÃ¼ger, J. Pollmann, Phys. Rev. Lett. 81, 2292 (1998).

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11:20am **SS+EL-ThM10 The Anomalous Effective Surface Debye Temperature of ErAs(100)**, ***T. Komesu***, *H.K. Jeong, P.A. Dowben*, University of Nebraska-Lincoln, *B.D. Schultz, C.J. Palmstrom*, University of Minnesota

We have recently explored the surface electronic structure of ErAs(100), as well as the compositionally stability, but the vibrational modes are a key contribution to both electronic structure and compositional stability. Consistent with a surface electronic structure different from the bulk, here we show that the surface vibrational modes are different from the bulk from our estimates of surface and bulk Debye temperature using LEED (low energy electron diffraction) and XPS (X-ray photoemission spectroscopy). This could contribute to the very large temperatures dependence of transport effects across ErAs interfaces.

11:40am **SS+EL-ThM11 CRN Models of Covalent Amorphous Materials and Their Interfaces**, ***D. Yu***, *G.S. Hwang*, The University of Texas at Austin

Understanding the structural properties of covalent amorphous (semiconductor and dielectric) materials and their interfaces as well as defect-dopant dynamics in the disordered systems is an outstanding problem of great importance for microelectronic and optoelectronic applications. Significant advances in Continuous Random Network (CRN) models have made it possible to generate the amorphous and interface structures that are in good agreement with experiments. This further allows us to address the behaviors of defects and dopants in the disordered structures. In this talk we will present our newly developed CRN models and some recent results on i) the diffusion and clustering dynamics of vacancies and self-interstitials in a-Si and the amorphous-crystalline interface, ii) the structures of a very thin amorphous SiO_2 layer and its interfaces with Si, and iii) thermal stability of Si/Ge nanoclusters in SiO_2.

Thursday Afternoon, November 7, 2002

Dielectrics
Room: C-107 - Session DI+EL-ThA

Processing and Properties of Dielectric Materials
Moderator: C.J. Palmstrom, University of Minnesota

2:00pm **DI+EL-ThA1 Plasma Etch Processes for Ferroelectric Memory Integration**, ***F.G. Celii***, *M. Thakre, S. Summerfelt, S. Aggarwal, J.S. Martin, K.R. Udayakumar, T.S. Moise*, Texas Instruments

Embedded ferroelectric memory has the potential to enable increased functionality, reduced power, and potentially lower cost for portable electronics applications. In recent years, several companies have demonstrated lateral scaling of ferroelectric capacitors needed to realize high-density capacitor arrays consistent with low-cost requirements. In this paper, we summarize our current status towards integration of FeRAM capacitors into a CMOS flow, with emphasis on the etch processes. We review the various schemes for FeRAM integration and highlight our selected multi-height Via approach. In this approach, we define the Ir / PZT / Ir capacitors by a combination of hardmask and capacitor stack etches. Following encapsulation and interlevel dielectric deposition, the Via-0 pattern is applied and etched, utilizing a high-selectivity oxide etch to give the bi-level Via-0 etch profile. Electrical results from integrated and non-integrated capacitors will be presented.

2:20pm **DI+EL-ThA2 Electrical Properties of the $Bi_{4-x}La_xTi_3O_{12}$ Films Etched in Cl_2/Ar Inductively**, ***D.P. Kim***, *C.I. Kim, K.T. Kim*, Chung-Ang University, Korea, *A.M. Efremov*, Ivanovo State University of Chemistry and Technology, Russia

For last decade, Bi-layered perovskites materials including $SrBi_2Ti_2O_9$ and $Bi_{4-x}La_xTi_3O_{12}$ (BLT) show high resistance to polarization fatigue due to Bi_2O_2 layers, which reduce space charges and the unpinning of domain walls. The BLT of 200 nm was spun-coated on the Pt/Ti/SiO_2/Si substrate by MOD. Pt thin films, which used as not only the top electrode but also as physical mask, were deposited on the BLT films. However, there is no report on the electrical characteristics of BLT thin films after etching process. BLT thins films were etched in Cl_2/Ar using ICP due to easy control bias power. The etch rates and selectivity of BLT thin films were investigated as a function of gas mixing ratio, rf power and dc-bias voltage. With adding 20 % Cl_2 in Ar plasma, increasing rf power and dc bias voltage and lowering pressure, the etch rate of BLT increased. To understand the effects of etching parameters on the etch rates of BLT thin films, the atoms of Cl and the ions of Ar were investigated in Cl_2/Ar plasma using optical emission spectroscopy and Langmuir probe. The surface of the etched BLT was investigated with x-ray photoelectron spectroscopy. To estimate electrical properties of BLT after etching process, the etched species were characterized with measuring leakage current using semiconductor parameter analyzer [HP4145B] and P-E loops of Pt/BLT/Pt capacitor using precision work station. According to our experiment, the etch rate of BLT highly depends on removing etch-product ($LaCl_2$: Tm = 2700 °C) effectively. After etching process, we obtained low remnant polarization value and high leakage current density compared with virgin sample. The degraded electrical properties of BLT were recovered after annealing at 800 °C for 1 hour.

Acknowledgement This work was supported by grant No. R01-2001-00268 from the Korea Science & Engineering Foundation.

2:40pm **DI+EL-ThA3 Formation of Al Oxynitride Alloys by Low-temperature Remote Plasma Nitridation**, ***C. Hinkle***, *G. Lucovsky*, North Carolina State University

Remote rf plasma nitridation of plasma deposited Al_2O_3 films was studied. Online Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and nuclear resonance profiling (NRP) are used to characterize the composition and spatial distribution of the resultant films. Al_2O_3 films were deposited by remote plasma enhanced chemical vapor deposition (RPECVD). Nitridation was carried out using 30 W rf power and a substrate temperature of 300 C. Nitrogen was introduced upstream diluted with Helium in a 60:160 ratio, and the process pressure was varied from 0.0325 Torr to 0.3 Torr. Nitridation at lower process pressures allows the plasma to extend into the processing chamber and results in greater nitrogen incorporation. Previous studies of nitrided SiO_2 have shown different fundamental nitridation mechanisms depending on process pressure and identified through different nitridation kinetics. In those experiments, low pressure nitridation in the plasma glow resulted in top surface nitridation by N_2^+ ions while high pressure nitridation with the plasma confined in the generation tube produced uniform nitridation throughout the film via N atoms. A kinetics study of the plasma-nitrided Al_2O_3 films shows the data to fit an expression of the form, $[N] = A \{1-exp(-Bt_N)\}$, where A increases inversely and exponentially with process pressure, B is a time constant that remains constant (within 10%) as process pressure changes, and t_N is the nitridation time in minutes. The fact that the time constant remains constant suggests that there is a single mechanism for the nitridation of Al_2O_3 that is associated with the N_2^+ ions that impinge on the oxide film.

3:00pm **DI+EL-ThA4 Heterostructured Cu-Based Electrode for High-Dielectric Constant Oxide Thin Film Devices**, ***W. Fan***, Northwestern University, *O. Auciello, S. Saha, J.A. Carlisle, D.M. Gruen*, Argonne National Laboratory, *R.P.H. Chang*, Northwestern University, *R. Ramesh*, University of Maryland

Copper (Cu) has recently been introduced as an interconnect material in integrated sub-micron circuit technology, due to its low resistivity and high electro- and stress-migration resistance. The main problems inhibiting its application as an electrode material in high-dielectric constant (k) thin film capacitors are the Cu oxidation and diffusion during the growth of the high-k layer at relatively high temperature in an oxygen environment. To overcome these problems, heterostructured Ti-Al/Cu/Ta multilayers were fabricated on SiO2/Si substrates using ion beam sputtering deposition. The Ta layer acts a diffusion barrier to prevent high temperature-induced diffusion of Cu into the Si substrate, while the amorphous Ti-Al alloy layer provides the protection against oxidation of the Cu film during growth of the high-k materials. The diffusion and oxidation resistance of the Cu-based heterostructured electrode layer was investigated using a variety of complementary characterization techniques, including x-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and four-point probe sheet resistance measurements. Analytical results showed that the Cu/Ta heterostructure remained intact through the annealing in 6 mTorr oxygen up to 600 °C. A thin oxide layer, formed on the Ti-Al surface, effectively prevented the oxygen penetration toward underneath layers. To test the feasibility of the proposed heterostructured electrode integrated with high-k thin films, complex oxide $(Ba_xSr_{1-x})TiO_3$ (BST) layers were then deposited on Ti-Al/Cu/Ta by magnetron sputtering. Polycrystalline BST film was obtained at 500 °C and 600 °C, and the measured permittivity and leakage current density were 170 ~ 330 (at zero bias) and 10^{-6} ~ 10^{-9} A/cm^2 (at 100 kV/cm) respectively.

3:20pm **DI+EL-ThA5 Investigation of the Interfacial Region of $(Ba,Sr)TiO_3$ Thin Films Deposited on Pt Substrates by MOCVD**, ***T.C. Kaspar***, University of Washington, *L.V. Saraf, C.L. Aardahl, J.W. Rogers, Jr.*, Pacific Northwest National Laboratory, *T.S. Dory*, Intel Corporation

Thin films of $(Ba,Sr)TiO_3$ (BST) have been extensively investigated as high-permittivity materials for microelectronics applications such as dynamic random access memory (DRAM) and advanced packaging components. By controlling the bottom electrode composition, electrode/film interface, and film stoichiometry and structure, the dielectric properties of the film can be tailored. In this study, BST thin films are deposited by MOCVD at low temperatures (500-575°C) using liquid delivery of metalorganic β-diketonate precursors on Pt/Ti/Si(100), Pt/Cr/Si(100), and MgO(100) substrates. A $(Ba,Sr)TiO_3$ film deposited on Pt/Ti/Si with a bulk composition of (Ba+Sr)/Ti = 57 / 43 forms a thick titanium-rich interfacial region at the platinum interface, with a composition of (Ba+Sr)/Ti = 36 / 64, which adversely affects the dielectric properties of the film ($\varepsilon_r = 84$). Since titanium enrichment is not observed in deposition on MgO substrates, the unique precursor chemistry that occurs on the platinum surface plays a role in the formation of the interfacial region. To better understand the effect of titanium non-stoichiometry on the dielectric properties, a BST film was deposited with a titanium-rich composition of (Ba+Sr)/Ti = 35 / 65. After annealing at 750°C, the film exhibited a low dielectric permittivity of $\varepsilon_r = 92$ and a leakage current density of $J_L = 8.7x10^{-5}$ A/cm^2. The mechanisms of excess titanium incorporation in the interfacial region, its effect on the dielectric properties, and its reduction or elimination are discussed.

3:40pm **DI+EL-ThA6 Reduction of the k Value of the Low k Polyimide Film by Plasma Hydrogenation**, ***Y. Kuo***, *T. Chung*, Texas A&M University

For advanced VLSICs, the multi-level interconnection structure requires two types of materials: a low k dielectric and copper metal. Polyimide is one of the few dielectrics that have a low k value, e.g., < 3, and can stand a high annealing temperature, e.g., > 350°C. Previous, it was reported that when a polymer thin film was exposed to a hydrogen plasma, its material properties were drastically changed.[1] The hydrogenated film can be applied to many new areas. In this paper, authors report a plasma hydrogenation method that improves the dielectric characteristics of a low k polyimide thin film. We investigated the influence of the plasma process parameters to physical properties, such as the k value, the leakage current, and morphology, and chemical structure, such as the composition and bonding states, of a fluorinated polyimide film. The result shows that the k value was lowered from 2.7 to 2.3 after the hydrogenation process while the leakage current was still low, e.g., 10^{-9} Amp. Hydorgenation is an effective method in improving the dielectric characterists of the low k polyimide film. The process is compatible with current semiconductor processes.

[1] Y. Kuo, "Plasma Swelling of Photoresist," Jpn. J. Appl. Phys., 32(1), 1AB, L126, 1993.

4:00pm **DI+EL-ThA7 Materials Transformation and Kinetics in the Formation of Porous Low-K Polymer Dielectrics for Advanced Interconnect Technology**, ***P. Lazzeri***, *L. Vanzetti, M. Bersani, M. Anderle,* ITC-irst, Italy, *J.J. Park, Z. Lin, G.Y. Yang, R.M. Briber, G.W. Rubloff,* University of Maryland, *R.D. Miller,* IBM Research

The advance of Si ULSI technology requires the integration of very low K materials (i.e., low dielectric constant) into Cu Damascene interconnect schemes. To produce such low-K materials spin-casting and curing of multi-component polymeric precursor materials to form nanoporous films through selective degradation of one of the components (termed the porogen) is an attractive option, but process reproducibility and control, microstructure, and sensitivity to contaminating ambients during processing all present serious manufacturability challenges. We have used time-of-flight SIMS (ToF-SIMS) and XPS to investigate the chemical composition of a leading low-K candidate, polymethylsilsesquioxane (PMSSQ), and porous versions of PMSSQ, as a function of curing treatment to characterize reaction kinetics which accompanies formation of the low-K matrix and evolution of the volatile porogen to form a nanoporous microstructure. The PMSSQ matrix, with an average composition of Si(CH3)O1.5, shows only small changes in chemical composition upon curing. The formation of the nanoporous PMSSQ involves the degradation of the added porogen, poly(methylmethacrylate-co-dimethylaminoethylmethacrylate) (PMMA-co-DMAEMA) at elevated temperatures. The degradation products of the porogen are also evaluated by means of ToF-SIMS. The loss of the porogen and the evolution of the contaminants upon curing are observed to primarily occur in the range 125-450°C. These results show that such surface analysis methods may reveal the kinetics of critical materials transformations in these complex inorganic-organic hybrid systems, which are required for establishing the manufacturability of porous low-K dielectrics.

4:20pm **DI+EL-ThA8 Fluorinated Amorphous Carbon Films Prepared by Plasma Enhanced Chemical Vapor Deposition for Solar Cell Applications**, ***L. Valentini***, University of Perugia, Italy, *V. Salerni,* University of L'Aquila, Italy, *I. Armentano, J.M. Kenny,* University of Perugia, Italy, *L. Lozzi, S. Santucci*, University of L'Aquila, Italy

Amorphous carbon a-C or a-C:H and/or diamond-like-carbon (DLC), has attracted attention as an environmentally benign and economically viable optoelectronic device material over others such as amorphous silicon (a-Si and/or a-Si:H) due to various advantage and therefore possibility to replace the existing technology based on the a-Si/a-Si:H.[1] Heterojunction diodes fabricated by plasma enhanced chemical vapor deposition of n-type fluorine-doped amorphous carbon (a-C:H:F) on p-type silicon are analyzed in terms of their electronic and photoresponse properties. The nature of heterojunction is confirmed by the rectifying current-voltage characteristic of a-C:H:F/p-Si junction. The photovoltaic behavior of the junction is presented as a function of both fluorine incorporation and thermal treatment of the a-C:H:F films after the deposition. The diodes made show a behavior dependent on the amount of the fluorine content. A better photovoltaic effects was observed from annealed a-C:H:F heterojunction structures. The optical and structural characterization performed by Raman spectroscopy and UV-VIS transmittance on films after the thermal treatment indicates that this behaviour is most likely due to an extended graphitization.

[1] H. A. Yu, Y. Kaneko, S. Yoshimura, and S. Otani, Appl. Phys. Lett. 68 (1996) 547.

4:40pm **DI+EL-ThA9 Dopant Penetration Studies in Hf Based Gate Dielectrics from Doped Polysilicon Films: Effect of Nitrogen in Penetration Robustness**, ***M.A. Quevedo-Lopez***, *H. Zhang, M.J. Kim, M. El-Bouanani, B.E. Gnade, R.M. Wallace,* University of North Texas, *M.R. Visokay, A. Li-Fateau, J.J. Chambers, A.L.P. Rotondaro, L. Colombo,* Texas Instruments Inc.

As the aggressively scaling of CMOS technology continues, high-κ gate dielectrics become one of the solutions in providing increased capacitance without remarkable increase in gate leakage current. However, issues such as thermal stability[1] and dopant penetration still require further study. Hf based films have been proposed as suitable candidates for advanced gate dielectric applications.[2] However, dopant penetration (B, As, P) following dopant activation annealing needs to be investigated. Recently, nitrogen incorporation in $HfSi_xO_y$ has been shown to be an efficient way to improve the thermal stability of Hf-silicate films, without compromising the electrical performance.[3] Dopant penetration studies (experimental and modeling) of boron, arsenic, and phosphorous from doped poly-crystalline silicon (poly-Si) through 4-5 nm thick $HfSi_xO_y$ and $HfSi_xO_yN_z$ into Si after aggressive annealing will be presented. XPS, HRTEM, RBS, and DSIMS results are presented. Dopant diffusivities in the dielectric films are calculated by fitting the dopant profile in the Si substrate to a reported model.[4] Implications for the use of these films as high-κ gate dielectrics on CMOS processing are also discussed. This work was supported by the Texas Advanced Technology Program, the Semiconductor Research Corporation, Texas Instruments, and DARPA.

[1] M. Quevedo-Lopez, M. El-Bouanani, S. Addepalli, J. L.Duggan, B. E. Gnade R. M. Wallace M.R.Visokay, M. Douglas, M.J. Bevan, and L. ColomboAppl. Phys. Lett. 79 (2001) 2958.

[2] For a review, see: G.D. Wilk, R.M. Wallace, and J. M. Anthony. J. Appl. Phys. 89, 5243 (2001).

[3] M.R. Visokay, J.J. Chambers, A.L.P. Rotondaro, A. Shanware, and L. Colombo, Appl.. Phys. Lett. 80, 3183 (2002).

[4] C. T. Sah, H. Sello, and D. A. Tremere, J. Phys.:Condens. Matter. 11, 288 (1959).

5:00pm **DI+EL-ThA10 Nanoporous MSSQ Films Characterised by Surface Acoustic Wave Spectroscopy and Brillouin Light Scattering**, ***C.M. Flannery***, Colorado School of Mines, *T. Wittkowski, K. Jung, B. Hillebrands,* Universitaet Kaiserslautern, Germany, *M.R. Baklanov*, IMEC, Belgium, *D.C. Hurley*, National Institute of Standards and Technology

Nanoporous methylsilsesquioxane films are a leading candidate for low dielectric constant (low-κ.) materials for microelectronic interconnect. However, mechanical strength reduces rapidly with lower density.(increasing porosity), yet there is a lack of techniques to characterize these properties in the κ~2 range. This work reports application of surface acoustic wave spectroscopy and Brillouin light scattering to characterization of the density/porosity and Young's modulus for a range of methylsilsesquioxane films from different manufacturers. Dispersion of laser-generated surface acoustic waves detected by both piezoelectric and optical methods yields density and stiffness measurements which are independently verified by specular X-ray reflectivity, ellipsometric porosimetry and Brillouin spectroscopy. Brillouin results also show that attenuation is related to pore size. Nanoindentation measurements consistently overestimate stiffness and we discuss why this is so. The behaviour of 3 sets of films show different stiffness-porosity relationships, the initially stiffer materials declining more rapidly with increasing porosity than the softer materials. This has important consequences for stiffness properties in the κ<2 region.

Surface Science
Room: C-112 - Session SS+EL-ThA

Growth & Etching on Semiconductor Surfaces

Moderator: A.C. Kummel, University of California, San Diego

2:00pm **SS+EL-ThA1 Epitaxial Growth Dynamics of Semiconductor Quantum Dot Structures**, ***S.R. Leone***, University of California and Lawrence Berkeley National Laboratory **INVITED**

The formation of Ge nanodots on Si(100) occurs by strain-induced mechanisms (Ge is 4% larger than Si) and obeys the Stranski-Krastanov (SK) growth mode: a wetting layer (3-5 layers) is followed by the formation of three-dimensional (3D) Ge structures. Quantitative studies of Ge island size distributions and their shape transformations, including huts, pyramids, domes, and superdomes, and shape changes due to annealing of the islands under the influence of surfactants, such as arsenic, are studied by molecular beam epitaxial growth and atomic force microscopy (AFM) post-analysis. For device applications, it is important to attain control over the size and spatial distributions of self-assembled nanostructures. The Ge growth experiments are also carried out on patterned silicon substrates (mesas formed by electron beam lithography followed by etching), for specific positioning of the dots. A 'one island on one mesa' relationship is achieved. The density of islands is higher than can normally be produced on unpatterned silicon, where island coalescence would usually occur well before this density is possible. Preferential growth on the tops of the mesas most likely occurs because the Si mesa tops are deformable, fulfilling a strain relaxation condition. In this work, pyramid-type islands as small as 25 nm are also aligned on the mesa tops, and no limit to the size reduction of the islands is apparent, being controlled mainly by the size of the etched features that can be introduced.

2:40pm **SS+EL-ThA3 Si Deposition on H-terminated Si(100) Surfaces***, ***J.-Y. Ji***, *T.T. Barus, T.-C. Shen*, Utah State University, *G. Qian*, University of Illinois at Urbana-Champaign, *X. Luo*, National Renewable Energy Laboratory, *S. Ren*, Illinois State University, *S. Zhang*, National Renewable Energy Laboratory, *Y.C. Chang*, University of Illinois at Urbana-Champaign

The presence of H has long been considered adverse to Si homoepitaxy. Copel and Tromp[1] reported that while no apparent effect on epitaxy was observed at H coverage <1 ML and H segregates at growth temperature >400 K, a drastic epitaxial temperature increase was required at H coverage >1 ML. We will present the results of our STM, and first principle molecular dynamics studies on Si monohydride and dihydride effect in Si epitaxy. We confirmed that at growth temperatures ~ 500 K, H stays on the growth front on monohydride surfaces and epitaxy can be achieved but the domain sizes are much smaller than those grown on the bare Si. Continuous rebonding apparently is responsible for the epitaxial growth on Si monohydride surfaces. The diffusion barrier for the Si adatom along the Si monohydride dimer rows is calculated to be 1.1 eV which is significantly higher than the corresponding 0.6 eV barrier on the bare Si(100)-2x1 surface. To account for the H segregation, a mechanism to exchange H atoms between a surface Si atom and the incident Si atom is proposed. The experimental and theoretical result on the dihydride effect will be discussed.

*This work is supported by NSF-DMR9875129, ARDA/ARO DAAD 19-00-1-0407 and DARPA-QuIST DAAD 19-01-1-0324.

[1] M. Copel and R. M. Tromp, Phys. Rev. Lett. 72, 1236 (1994).

3:00pm **SS+EL-ThA4 An Atom-Resolved Study of Vacancy Dynamics and Surface Roughening on Bromine-Etched Si(100) Surfaces**, ***C.F. Herrmann****, *J.J. Boland*, University of North Carolina, Chapel Hill

Halogen etching of Si(100) surfaces has long been considered to involve the selective removal of atoms from an essentially static surface. However, our high temperature scanning tunneling microscopy (STM) study reveals that halogen-covered surfaces are highly unstable. This instability stems from the inherent steric repulsions between halogen adatoms on the surface. At high temperatures, repulsive interactions are relieved by vacancy formation, diffusion and surface roughening, each of which is directly observed in real-time by STM. Together, these dynamical processes result in surface features identical to those found after high temperature etching. These results demonstrate that diffusion and roughening must be considered in any model of halogen etching. Moreover, steric repulsions and the instability they create place fundamental limits on the ability to achieve atomically smooth morphologies using halogen etching.

3:20pm **SS+EL-ThA5 Dynamics of Si(100)-(2x1) Surface Modification with Cl**, ***G. Xu***, *E. Graugnard, V. Petrova, K.S. Nakayama, J.H. Weaver*, University of Illinois at Urbana-Champaign

The etching dynamics of Cl-Si(100)-(2x1) at elevated temperature have been studied with variable temperature scanning tunneling microscopy. Clean samples were exposed to Cl_2 at room temperature to near saturation and then heated to 700 K for over 20 hours. By scanning the same area of the sample, we observed pit creation, diffusion, incorporation and annihilation. Pit annihilation has not been reported previously under conditions of steady state etching and surface saturation. We also observed regrowth islands creation, growth and decay. Surface reactions at 700 K produced single Si adatoms, which were bonded to Cl-free Si dimers. Single Si adatoms diffused through these Cl-free Si dimer sites, but adatom diffusion was restricted by the high Cl concentration. The adatoms could form regrowth dimers when they met or they could be accommodated at the ends of regrowth structures. The adatoms could also be released from the regrowth dimer rows with the assistance of bare dimers. We have also observed (3x2) and (5x2) surface structures and, for the first time, the phase transition between (3x2) and (5x2) structures and dimer vacancy lines.

3:40pm **SS+EL-ThA6 Surface Modification without Desorption: Recycling of Cl on Si(100)-(2x1)**, ***K.S. Nakayama***, *E. Graugnard, J.H. Weaver*, University of Illinois at Urbana-Champaign

We demonstrate the structural consequences of thermally activated reactions of Cl on Si(100)-(2x1). We used scanning tunneling microscopy at room temperature to obtain atomic-resolution images of the surface before and after thermal processing. We show surface modification under conditions where Cl is recycled rather than desorbed as $SiCl_2$. In this unexpected reaction, the surface roughens as dimer vacancies are produced. First, a dimer with 2 Cl atoms, 2SiCl, converts to $SiCl_2$ + Si. This allows the destabilized, bare Si atom to escape onto the terrace. At temperatures where the desorption is negligible, the $SiCl_2$ unit decays as the Cl atoms can move to other active sites of the Si surface, allowing the second Si atom to escape. The result is a dimer vacancy, Si atoms on the terrace that can form self-organized regrowth structures, and Cl that is able to participate in another pitting event. Access to this unexpected roughening pathway is controlled by the Cl concentration and temperature. This previously overlooked process represents an important component of Si(100) surface processing.

4:00pm **SS+EL-ThA7 Spontaneous Roughening -- Fundamental Limits in Si(100) Halogen Etch Processing**, ***D. Chen***, *J.J. Boland*, University of North Carolina at Chapel Hill

A dynamical Scanning Tunneling Microscopy and Density Functional Theory study of the thermodynamic stability of halogen-terminated Si(100) surfaces is presented. Defects-free halogen-covered Si(100) surfaces are shown to be intrinsically unstable and prone to spontaneous roughening. This instability is the result of steric effects and is observed for all halogens except fluorine (which is already known to yield rough surfaces). These results demonstrate that an atomically smooth Si(100) morphology cannot be realized using halogen etch processing which sets a lower bound on the atomic scale perfection that can be achieved using such processing.

4:20pm **SS+EL-ThA8 Preparation of Atomically Flat Si(100) Surface by Ion Etching**, ***J. Kim***, *J.-Y. Ji, T.-C. Shen*, Utah State University, *J.S. Kline, J.R. Tucker*, University of Illinois

Preparation of atomically flat Si(100) surface under limited thermal budget has been one of the challenging processes in the research of atom-scale electronic device fabrication. While atomically flat monohydride surfaces can be obtained by aqueous NH_4F etching on Si(111) surfaces,[1] wet-chemical process has yet to produce an atomically flat Si(100) hydride surface at a scale of more than a few nanometers. Ion irradiation effects on Si surfaces have been investigated extensively from mid-70s to early 90s as a surface cleaning process prior to Si epitaxy. Recent atomistic studies of ion sputtering on pristine Si and metal surfaces were more focused on the dynamics of ion-induced defects.[2] We are currently using STM to investigate the surface morphologies during ion etching of oxide or wet-chemically prepared Si(100) surfaces by 0.4 - 1.5 keV Ar and Xe ions. We will delineate the effects of ion energy, ion fluence and substrate temperature, and assess the possibility of achieving atomically flat Si(100) surfaces by optimizing these parameters. This work is supported by NSF-DMR9875129, ARDA/ARO DAAD 19-00-1-0407 and DARPA-QuIST DAAD 19-01-1-0324.

[1] G. S. Higashi et al., Appl. Phys. Lett. 56, 656 (1990).

[2] P. Bedrossian, Surf. Sci. 301, 223 (1994) and references therein.

4:40pm **SS+EL-ThA9 Probing the Chemistry of Impurities with STM: The Profound Effect of Dissolved Oxygen on Silicon Etching**, ***S.P. Garcia***, *H. Bao, M.A. Hines*, Cornell University

A new technique has been developed to quantify the surface reactivity of impurities, which combines the exquisite defect sensitivity of scanning tunneling microscopy (STM) and the analytical capabilities of atomistic kinetic Monte Carlo (KMC) simulations. This technique exploits kinetic competition between the impurity and a reference etchant to produce impurity-concentration-dependent changes in nanoscale etch morphology. These changes are then quantified using STM measurements and KMC simulations. We used this technique to measure the site-specific reactivity of dissolved O_2 -- a ubiquitous impurity in aqueous solutions -- with H-terminated Si(111) surfaces. The site-specific reactivity of O_2(aq) is surprisingly anisotropic. Oxidation of the highly strained dihydride step site is four times faster than oxidation of the relatively unstrained monohydride step site. Both steps are 10^4 times more reactive than terrace sites. FTIR measurements of the Si-H stretch vibration showed that dissolved O_2 inserts O atoms into surface Si-Si backbonds without removing the H-termination. Dissolved O_2 does not attack Si-H bonds, since neither Si-H consumption nor silanol production is observed.

***** Morton S. Traum Award Finalist

Authors Index

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