Applied Surface Science
Room: C2 - Session AS+EM+MS+TF-MoM

Spectroscopic Ellipsometry I
Moderator: M.S. Wagner, Proctor and Gamble

8:20am **AS+EM+MS+TF-MoM1 Optical Properties of Bulk GaSe and InSe Single Crystals**, ***S.G. Choi***, National Renewable Energy Laboratory, *C. Martinez-Tomas, V. Munoz Sanjose,* Universitat de Valencia, Spain, *D.H. Levi*, National Renewable Energy Laboratory

III-VI compounds generally crystallize in layered-structures characterized by strong covalent interactions *within* the layers but weak Van der Waals binding *between* the layers. This unique structural characteristic has made III-VI compounds attractive for their potential applications in nonlinear optics. Among these compounds, in particular, InSe has been considered as a promising candidate for thin film photovoltaic (PV) material owing to its energy bandgap, optical and transport properties. Recently, high-quality epitaxial InSe thin films have been grown on GaSe substrates, and PV device structures containing *n*-InSe and *p*-GaSe have been successfully fabricated [1].

In order to design and optimize a high-performance PV device structure, knowledge of optical properties of constituent materials over a wide spectral range is required. However, large discrepancies were found in the properties of GaSe and InSe available in the literature, which have been measured mostly by reflectance methods with the Kramers-Kronig transformation employed to obtain the dielectric functions. Here, we present ellipsometrically determined pseudodielectric function $\langle\varepsilon\rangle=\langle\varepsilon_1\rangle+i\langle\varepsilon_2\rangle$ spectra from 0.73 to 6.45 eV of bulk GaSe (ε-phase) and InSe (γ-phase) single-crystals grown by a vertical Bridgman method. The surfaces with minimum overlayers were obtained by peeling off the top few layers from the sample surface and ellipsometric measurements were immediately followed under flowing N_2 environment, which yields good approximations to the intrinsic dielectric responses. The measured spectra exhibited a number of interband-transition critical-point structures, and their energy values were obtained precisely from numerically calculated second-energy-derivatives of $\langle\varepsilon\rangle$ assuming the parabolic-band critical-point model.

Data obtained in this work can be used to model PV device structures utilizing GaSe and InSe, and the critical-point energies determined will be useful for theoreticians to perform fine band structure calculations of III-VI compounds.

The work done at Universitat de València was supported in part by the Spanish Project MAT2007-06841. This abstract is subject to U.S. government rights.

[1] J.F. Sánchez-Royo, J. Appl. Phys. 90, 2818 (2001).

8:40am **AS+EM+MS+TF-MoM2 Ellipsometric Porosimetry for the Microstructure Characterization of Plasma-Deposited SiO_2-Like Films**, ***M. Creatore***, *N.M. Terlinden, G. Aresta, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

SiO_2 layers have been deposited from Ar/O_2/hexamethyldisiloxane mixtures in a remote expanding thermal plasma setup enabling a good control of both the ion flux (by changing the deposition chemistry and the arc plasma parameters) as well as the ion energy. This latter is achieved by an additional rf substrate biasing or a tailored ion biasing technique, i.e. a low frequency pulse-shaped bias. The role of the ion energy and ion-to-growth flux ratio on the film microstructure and densification at low substrate temperature (100ºC) has been investigated by means of ellipsometric porosimetry. This technique monitors the refractive index change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the SiO_2 layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity in the layer can be determined. It is found that both biasing techniques lead to densification of the deposited layer, which experiences a transition from micro-/ mesoporosity to microporosity and eventually non-porosity, as function of the increasing ion energy. Although both biasing techniques lead to a comparable critical ion energy value per deposited SiO_2 unit (about 100 eV), the ion-to-growth flux ratio and ion energy are not found to be interchangeable parameters. In fact, in the case of the rf bias, the meso- and large micropores are first affected leading to a quantitative decrease of porosity, i.e. from 11% to 3% at an ion energy less than 20 eV. A further increase in ion energy eventually reduces the presence of smaller micropores leading to non porous films at energy of 45 eV. When the pulse-shaped biasing technique is adopted, the micro- and mesopores are simultaneously affected over the whole range of available ion energy, leading to a non porous layer only at very high energy values, i.e. 240 eV. This difference is attributed to the increasing ion-to-growth flux ratio accompanying the rf biasing, as a consequence of the rf plasma generation in front of the substrate.

9:00am **AS+EM+MS+TF-MoM3 Industrial Applications of Spectroscopic Ellipsometry**, ***J.A. Woollam***, J.A. Woollam Company, Inc., *J.N. Hilfiker, P. He*, J.A. Woollam Company Inc. **INVITED**

Spectroscopic Ellipsometry (SE) has been used for decades for basic research on surfaces and thin films. Hundreds of articles, review papers, and books describe SE use in physics, chemistry and surface and materials engineering. Far less is available describing industrial applications because companies gain competitive advantage using SE and are not motivated to publish.

Without revealing anyone's proprietary information, this talk reviews examples of SE use in industry. This involves both production quality control (QC), and product development. Best known is SE for QC in integrated circuit manufacturing. Others include integrated circuit critical dimension (CD) metrology, read-write heads, display technologies, optoelectronics, photovoltaics (crystalline and thin film), optical coatings, web-coaters, wear surfaces, and protective coatings. Industrial SE applications include ex-situ, in-situ, and in-line metrology.

9:40am **AS+EM+MS+TF-MoM5 Spectroscopic Ellipsometry Studies of Sputtered Vanadium Oxide Thin Films**, ***N.J. Podraza***, *B.D. Gauntt, M.A. Motyka, E.C. Dickey, M.W. Horn*, The Pennsylvania State University

Vanadium oxide (VO_x) thin films have been used for the last twenty years as the imaging material in uncooled infrared imaging devices. The important material properties for this application are a high thermal coefficient of resistance (TCR), controllable resistivity (ρ), low electrical noise and process compatibility with standard IC fabrication. However, vanadium can adopt many different oxidation states, yielding a number of stable metal oxides, which can lead to difficulties in reliable and consistent device fabrication. In this work, VO_x thin films were fabricated via pulsed-DC magnetron sputtering in an argon and oxygen atmosphere under variable total pressure and oxygen-to-argon ratio deposition conditions in order to investigate the variability in desired material properties. In situ real time spectroscopic ellipsometry (RTSE) has been applied to stuffy films prepared under variable deposition conditions in order to evaluate the microstructural evolution of VO_x during film growth and changes occurring to the surface and bulk material upon initial exposure to atmosphere. These films were characterized ex situ using a number of complementary techniques including, Rutherford backscattering spectroscopy (RBS) in order to obtain the oxygen content, x; transmission electron microscopy (TEM) to determine film crystallinity; glancing incidence X-ray diffraction (GIXRD) was used to ensure localized measurements from the TEM were representative of the entire film; and I-V curve measurements as a function of temperature were used to determine the film resistivity and TCR. By varying deposition conditions, the film resistivity was varied over seven orders of magnitude from $\sim10^{-3}$ to 10^4 Ω-cm and the TCR spanned from -0.1 to -3.5 %/K. The growth evolution, complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), and structure are correlated to these electrical properties. Films produced at low oxygen-to-argon ratios exhibit nanocrystalline V, V_2O, and VO phase material dependent on the specific deposition conditions, while films produced at higher oxygen-to argon ratios are amorphous. In both the nanocrystalline and amorphous phases, features in e obtained from spectroscopic ellipsometry have been shown to correlate with the oxygen content and resistivity and RTSE studies have been used to monitor changes occurring at the film / ambient interface after the vanadium oxide is exposed to air. This array of techniques were used to establish the roles deposition parameters play in the final structure and composition of each film, as well as to determine the resulting effects of these characteristics on the electronic transport and optical properties.

10:00am **AS+EM+MS+TF-MoM6 Real Time Spectroscopic Ellipsometry Studies of Si:H and Ge:H Thin Films for Microbolometer Applications**, ***D. Saint John***, *E.C. Dickey, N.J. Podraza*, The Pennsylvania State University

Thin film hydrogenated silicon (Si:H) and germanium (Ge:H) have been of wide interest as thin film semiconducting materials, and are now of growing interest for use in infrared sensing uncooled microbolometers, although the impact of the growth evolution and structure on device performance is only beginning to be determined. Ideal properties for incorporation of these layers in microbolometers include: a high temperature coefficient of resistance (TCR); controllable resistivity (ρ); low 1/f noise within frequencies of interest; and process compatibility with standard IC fabrication. In this work, n- and p-type doped Si:H and undoped Ge:H thin films have been prepared by plasma enhanced chemical vapor deposition (PECVD) with resulting resistivities ranging from 1.5 to 2500 Ω cm and TCR ranging from –0.8 to –4.0 %/K and studied using real time spectroscopic ellipsometry (RTSE). These films, monitored in situ during growth by RTSE, have been shown to exhibit changes in microstructure as a function of deposition conditions. For example, films prepared at low hydrogen dilution may remain amorphous throughout growth (a-Si:H), while films prepared at higher dilution may initially grow as amorphous until a bulk layer thickness where microcrystallites nucleate and eventually coalesce into a single-phase microcrystalline layer (μc-Si:H). A combination of in-situ RTSE, transmission electron microscopy (TEM), and electrical measurements (ρ, TCR, 1/f noise) have been used to study the effects of deposition conditions on the resulting microstructure during film growth and the dependence of the electrical properties on this microstructure. Studies of p-type a-Si:H have shown that both TCR and ρ increase with hydrogen dilution for fixed doping gas-to-silane ratio, which suggests that optimizing the TCR for a film of a given resistivity may potentially be obtained by varying both the hydrogen and doping gas dilutions. n-type a-Si:H and mc-Si:H films were evaluated in order to quantify changes in TCR and r resulting from microstructural differences (a-Si:H: ρ= 250 Ω cm, TCR = –3.8 %/K; μc-Si:H: ρ = 1.5 Ω cm, TCR = –0.8 %/K). Growth evolution studies of undoped Ge:H films prepared under variable hydrogen dilution conditions show transitions from amorphous to microcrystalline material at higher hydrogen dilution and relatively high TCR values ranging from –2.2 to –3.6 %/K as dilution is increased within the amorphous growth regime.

10:40am **AS+EM+MS+TF-MoM8 Non-destructive Determination of Spatial Distributions of Free-Charge-Carriers in Low Doped Semiconductors using THz Ellipsometry**, ***T. Hofmann***, University of Nebraska-Lincoln, *C.M. Herzinger*, J. A. Woollam Co. Inc., *M. Schubert*, University of Nebraska - Lincoln

The non-contact and non-destructive optical determination of spatial distributions of free-charge-carriers in low doped semiconductor homo- and heterojunctions addresses fundamental physical properties of device related structures. However, the optical characterization of low density free-charge-carriers, particularly for hole densities with their intrinsically lower mobility parameters than electron densities is very challenging. For low carrier densities the plasma frequencies are located at within the terahertz (THz) spectral region and measurements of plasma frequency properties in a at THz frequencies have been used for the determination of free-charge-carrier properties in single crystals (e.g. [1,2]). The characterization of free-charge-carrier properties in low-doped homo- and heterostructures remains a challenge.

Here we report on the non-invasive optical measurement of hole diffusion profile in a p-p$^+$ Silicon homojunction by spectroscopic ellipsometry in the terahertz (0.2 to 1.5 THz) and mid-infrared (9 to 50 THz) spectral regions. In the terahertz region a surface guided wave resonance with transverse-electrical polarization is observed at the boundary of the p-p$^+$ homojunction, and which is found to be extremely sensitive to the low-doped p-type carrier concentration as well as to the hole diffusion profile within the p-p$^+$ homojunction. Effective mass approximations allow determination of homojunction hole concentrations as p=2.9x10^{15} cm^{-3}, p^+=5.6x10^{18} cm^{-3}, and diffusion time constant D_t = 7.7x10^{-3} μm^2, in agreement with previous electrical investigations.

[1] D. Grischkowsky, Soren Keiding, Martin van Exter, and Ch. Fattinger, J. Opt. Soc. Am. B **7**, 2006 (1990).

[2] M. Herrmann, M. Tani, K. Sakai, and R. Fukasawa, J. Appl. Phys. **91**, 1247 (2002).

11:00am **AS+EM+MS+TF-MoM9 Ellipsometric Depth Profiling of Polymer-Blend Films for Organic Electronics and Photovoltaics**, ***L.J. Richter***, *D.S. Germack, D.M. DeLongchamp, D.A. Fischer, V.M. Prabhu, D.J. Gundlach,* National Institute of Standards and Technology, *J.E. Anthony,* University of Kentucky, *N. Shin, D. Yoon*, Seoul National University, Korea

Interest has emerged in the development of devices based on organic materials and low energy, low cost, roll-to-roll fabrication techniques. Two specific target applications have received particular attention: organic transistors to enable macroelectronics (large area displays, RFID tags, etc.) and organic photovoltaics. Common to both applications is the development of optimal inks: for macroelectronics, small crystallizable molecules in an inert polymer binder, for photovoltaics, fullerene based acceptors blended in an active polymer donor. Critical to a proper understanding of the device performance is an understanding of the vertical profile of the fabricated film. For thin film transistors, segregation of the small molecule semiconductor to the interfaces is essential. For PV, segregation of the fullerene can be both advantageous (if at the cathode) and deleterious (if at the anode). Spectroscopic ellipsometry studies of the vertical profile are daunting, as the systems are in general anisotropic with individual component spectra that are strongly dependent on the local order. We present SE studies of both TFTs and OPV devices using a multiple sample approach to remove correlations in the resultant models. The optical depth profiles are compared to both NEXAFS studies of the interface composition and neutron reflectivity studies of similar processed films. We find good agreement between the SE and less model dependent techniques. The studies illuminate general principles of the influence of interfacial free energy on the resultant segregation of the species.

11:20am **AS+EM+MS+TF-MoM10 Thickness Variations Determined by Spectroscopic Ellipsometry in Organometallic Chemical Vapor Deposition: Connection to Growth Processes**, ***X. Liu***, *D.E. Aspnes*, North Carolina State University

Lateral thickness variations are commonly observed for films deposited by organometallic chemical vapor deposition (OMCVD). The variations are typically systematic near boundaries between growth and adjacent surfaces, for example masks. We use spectroscopic ellipsometry to study thickness variations for the heteroepitaxy of GaP by OMCVD on (001) GaAs, thermally generated SiO$_2$, (001) Si, and nanoscopically roughened Si surfaces using trimethylgallium (TMG) and phosphine (PH$_3$) sources, showing that the variations provide information about details of OMCVD growth that would be difficult to obtain in any other way. Our reference surface is the polycrystalline GaP inadvertently deposited on the Mo susceptor that surrounds the 2 in. wafers. We find that the thicknesses of the deposited GaP films increase or decrease accurately exponentially toward the edge. Using an analytic Green-function approach based on the one-dimensional diffusion equation, we show that for our growth conditions (4 Torr chamber pressure), the exponential thickness variations are due to differences in chemical reactivities of the various surfaces, especially on the different catalytic effects that they exert on PH$_3$ decomposition. The results show directly that different parts of the surface, including the susceptor, are in constant contact with each other through lateral gas-phase diffusion. The data are explained by assuming that growth occurs via a precursor that is formed by heterogeneous catalysis, largely desorbs, and involves both Ga and P, for example the H-P=Ga-CH$_3$ dimer adduct. To distinguish this process from selective area growth (SAG), which takes place with a similar configuration, we also solve the SAG problem analytically, in this case using a conformal map. For SAG the thickness near mask edges is found to vary as $r^{-1/2}$, where r is the lateral distance away from the edge. The distinctive differences in these thickness dependences indicate that SAG growth occurs via a different mechanism.

11:40am **AS+EM+MS+TF-MoM11 Optical Anisotropy Induced by Oblique Incidence Ion Bombardment of Ag(001)**, ***H. Wormeester***, *F. Everts, B. Poelsema*, University of Twente, The Netherlands

Oblique incidence ion sputtering has become a widely used method for the creation of highly regular patterns of lines and dots. On a Ag(001) surface oblique incidence sputtering creates a ripple pattern that exhibits plasmonic features. The photon energy of this plasmonic feature depends on the ripple periodicity. The development of these anisotropic features was measured in-situ with the optical technique Reflection Anisotropy Spectroscopy (RAS).

The ion induced nanopatterning was done with 2 keV Ar ions with a flux of a few mA/cm2 in a temperature range of 300 - 420K. With RAS, a periodicity of ripples above 200 nm is measured by a shift in photon energy of the plasmon resonance. Features with a smaller periodicity show a plasmon resonance around 3.65 eV. For very grazing incidence sputtering, 80o polar angle of incidence, only a resonance feature around 3.65 eV is observed. High resolution LEED measurements after sputtering confirm the formation of 1D nanoripples.

For a polar angle of incidence of the ion beam of 70o a shift in the maximum of the plasmon resonance feature is observed. These spectra can be well described within the Rayleigh-Rice description for scattering from a slightly rough surface. The formation of nanoripples, i.e. a roughening of the surface perpendicular to the direction of the ion beam in one direction suffices to describe the measured optical data. The evolution of the rms, wavelength and wavelength distribution of the ion induced nanoripples is obtained from the in-situ measurements. For a polar angle of the ion beam of 61o we find that also the roughening in the direction along the nanorippels has to be taken into account to describe the optical spectra.

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Room: C2 - Session AS+EM+MS+TF-MoA

Spectroscopic Ellipsometry II
Moderator: M. Creatore, Eindhoven University of Technology, The Netherlands

2:00pm **AS+EM+MS+TF-MoA1 Spectroscopic Ellipsometry on Protein Layers: Characterization and Sensor Applications**, ***H. Arwin***, Linköping University, Sweden **INVITED**

Ellipsometry is very attractive for studies of biolayers including protein layers. First, its thickness resolution is well below 1 nm which is perfect for protein layers as they typically are composed of nm-sized molecules. Second, ellipsometry can be used in any transparent medium, so it can be applied to solid-liquid interfaces where many bioreactions take place. Third, molecules do not have to be labeled, as required for techniques based on fluorescence or radioactivity. One drawback is that it is not analytic if operated in the visible spectral range and in simple applications one primarily measures the optical mass on a surface. However, with high precision spectroscopic ellipsometry, structural information in protein monolayers can be obtained in some cases and chemical analysis can be performed with infrared ellipsometry.

In this report, the use of various types of ellipsometry for studies of protein layers at air/solid and liquid /solid interfaces are reviewed. Among the methods included are spectroscopic, dynamic, internal reflection and imaging ellipsometry. Two examples of methodology for analysis are discussed in some detail. First we observe that *in situ* studies allow monitoring of the dynamics of protein layer growth. Modeling of layer structure by separation of refractive index and thickness from such *in situ* data recorded during adsorption of fibrinogen layers is presented as well as strategies for evaluation of surface mass density.

In a second example, a model dielectric function (MDF) concept for protein layers in the UV-VIS-IR spectral range is presented. The MDF contains model parameters like resonance energies and broadenings of vibrational structures, e.g. in the amide bands. Changes in these parameters can be monitored and used to assess the conformational state in the protein layer. As an example, studies of thermally induced degradation of fibrinogen layers are presented.

Finally potential sensor applications based on imaging and dynamic ellipsometry utilizing sub-nm thickness resolution are reviewed. The use of surface-plasmon resonance enhancement to increase resolution of internal reflection ellipsometry to pm in thickness will be discussed.

2:40pm **AS+EM+MS+TF-MoA3 Anisotropic Optical and Magneto-Optical Properties of Sculptured Thin Films**, ***D. Schmidt***, *T. Hofmann, A. Kjerstad, E. Schubert, M. Schubert*, University of Nebraska-Lincoln

Three-dimensional structure design on the nanoscale is in the focus of modern material science and engineering because intriguing applications are foreseen for such nanostructured films in various fields ranging from optics, electromechanics or electromagnetics. We utilize glancing angle electron-beam deposition, where physical shadowing and varying particle incidence azimuth are exploited for fabrication of three-dimensional individual nanostructures arranged in sculptured thin films with different morphologies. We will present the anisotropic (structure-related) optical and magneto-optical properties of sculptured thin films from cobalt. Generalized spectroscopic ellipsometry is employed to determine the anisotropic principal optical constants of slanted columnar and chiral nanocoil thin films in the spectral range from 400 to 1650 nm. These thin films show strong form birefringence and large dichroism and are distinctly different from their bulk material. We will also discuss why slanted columnar thin films have monoclinic optical properties [1]. Magneto-optic Kerr effect measurements in the polar configuration lead to the determination of the magneto-optical Q-values (Voigt parameters) of such highly anisotropic ferromagnetic sculptured thin films.

[1] D. Schmidt, A. C. Kjerstad, T. Hofmann, R. Skomski, E. Schubert, and M. Schubert, J. Appl. Phys. **105**, XXX (2009).

3:00pm **AS+EM+MS+TF-MoA4 Development of Hybrid Quartz Crystal Microbalance / Ellipsometric Porosimetry for the Characterization of Anisotropic Optical Materials**, ***R.A. May***, *D.W. Flaherty, C.B. Mullins, K.J. Stevenson*, University of Texas at Austin

Ellipsometric porosimetry (EP) relies on monitoring the change in optical properties during vapor adsorption/desorption and has been successfully applied to an array of materials using a variety of adsorbates both in vacuum and at ambient pressures. However, these studies typically avoid the analysis of optically complex systems with strong absorbance or optical anisotropy. Towards this end, a hybrid quartz crystal microbalance/ ellipsometric porosimetry (QCM/EP) technique is being developed to facilitate the study of more complex optical materials and to quantitatively estimate parameters such as porosity, pore size distribution, and surface area. To highlight the power of this hybrid approach thin films of TiO_2 and TiC, have been deposited using reactive ballistic deposition (RBD). RBD provides control over film parameters such as surface area, porosity, pore size, and birefringence through variation of the deposition angle. Combined with the QCM/EP technique these films provide a platform for understanding both novel material properties and the requirements for extracting valid optical constants from anisotropic optical materials.

3:40pm **AS+EM+MS+TF-MoA6 Multichannel Ellipsometry for Thin Film Photovoltaics Applications: From Materials to Solar Cells**, ***R.W. Collins***, *J. Li, M.N. Sestak, J.A. Stoke, L.R. Dahal*, University of Toledo **INVITED**

Second generation or thin film photovoltaics (PV) technologies have achieved the lowest manufacturing costs in the PV industry. These technologies benefit from multichannel ellipsometric analysis for characterization of multilayered thin film materials and deposition processes, specifically for determination of component layer thicknesses and dielectric functions. From such results, predictions of the maximum achievable quantum efficiency of multilayered PV device structures are possible. In this presentation, the current applications and future prospects of multichannel spectroscopic ellipsometry (SE) will be discussed for optical characterization of PV materials and devices during fabrication in the research laboratory as well as for on-line and off-line evaluation in PV module production. First, this review will address the advances in instrumentation for multichannel SE. Second, this review will provide examples of the analysis of real time SE data acquired during film growth to obtain structural parameters and dielectric functions, as well as the subsequent analysis of the resulting dielectric functions in terms of parameterized models to deduce useful information on thin film materials properties. Recent applications to be discussed in this presentation involve (i) the analysis of grain size, strain, and void profiles from the dielectric functions of polycrystalline CdS and CdTe thin films used as heterojunctions in efficient solar cells; (ii) the analysis of amorphous and nanocrystalline volume fraction profiles from the dielectric functions of mixed-phase hydrogenated Si (Si:H) thin films also used in efficient solar cells; and (iii) the determination of interface dielectric functions and losses associated with Ag/ZnO structures used as back-reflectors in efficient thin film Si:H PV devices. In the latter studies, the optical features of confined plasmon resonances can be identified. Methods for dealing with microscopic (sub-wavelength order) and macroscopic (wavelength order) surface and interface roughness will be treated, as will its impact on prospects for analyzing PV device structures on-line during module manufacturing. The ability to extract polarization, depolarization, and irradiance information from the reflected beam by multichannel SE is advantageous in many such PV applications.

4:20pm **AS+EM+MS+TF-MoA8 Universal Behavior of Light Scattering from Self-Affine Fractal Surfaces: A Quantitative Relationship between Roughness and EMA Models**, ***A. Yanguas-Gil***, *B.A. Sperling,* University of Illinois at Urbana-Champaign*, J.R. Abelson*, University of Illinois, Urbana-Champaign

The effective medium approximation (EMA) is typically used to model the influence of roughness on the optical response of a surface or buried interface as measured by ellipsometry. Although the standard assumption of 50% material - 50% void provides useful results, the relationship between the EMA layer thickness and the surface topography is not fully understood. For example, in thin film deposition many authors have found a good correlation between the thickness of the EMA layer and the rms surface roughness measured by AFM, while others have found significant discrepancies between the time evolution of these two parameters.

Using first principles scattering models, we have analyzed the ellipsometric response of surfaces that exhibit a self-affine dependence of surface topography on the lateral scale of measurement. This type of surface roughness is found for a wide variety of real surfaces, including many deposited thin films. The calculations show that when the surface correlation length evaluated from the height-height correlation function or the power spectral density is much smaller than the incident wavelength, a universal behavior is found in the ellipsometric response. Both the amplitude of the reflected fields in the p- and s-polarizations, and the thickness of the EMA layer, depend on the product of the *rms* surface roughness times the average surface slope. Therefore, the linearity between roughness and the thickness of the EMA layer holds only as long as the average surface slope remains constant. That is the case when the growth obeys the predictions of dynamic scaling theory, i.e., the *rms* roughness and the correlation length change with time as $\sigma \sim t^{\beta}$ and $\xi \sim t^{\beta/\alpha}$, where α and β are the roughness and the growth exponents, respectively. Results are presented for different materials whose optical properties cover a broad range from metals to dielectrics. An important consequence of this universality is that the ellipsometric response is mathematically separable into two independent functions, one depending only on the optical properties of the film and the other only on the surface topography.

4:40pm **AS+EM+MS+TF-MoA9 Numerical Ellipsometry: Thin Absorbing Films Deposited on Opaque Substrates**, ***F.K. Urban**, D. Barton,* Florida International University*, T.E. Tiwald*, J A Woollam Co.

A major challenge for those utilizing ellipsometry is numerical processing of the measured data. The transcendental, multivalued equations arising from the physics of simple reflection are problematic for the least-squares numerical methods in common use. These early numerical methods require fairly accurate initial estimates, bounding to avoid local minima, and only find solutions at the bottom of a relatively flat numerical topography. Previously we have applied Complex Analysis in the n-k plane to improve visualization of the mathematics and this has led to a growing array of new numerical methods avoiding these difficulties. The work presented here extends these new numerical methods for use beyond transparent substrates to include absorbing substrates. Results show that reflection ellipsometry alone can be sufficient for determination of thin absorbing film thickness and optical properties without the need for additional kinds of measurements.

Numerical processing considering surface layers such as air-formed oxides will also be presented.

5:00pm **AS+EM+MS+TF-MoA10 *In situ* Spectroscopic Ellipsometry As a Versatile Tool to Study Atomic Layer Deposition**, ***E. Langereis**, H.C.M. Knoops, W. Keuning, A.J.M. Mackus, N. Leick, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is considered as one of the primary candidates for the deposition of ultrathin and conformal films with precise growth control. In this contribution, the merits of using *in situ* spectroscopic ellipsometry (SE) to address various aspects of ALD will be discussed. In particular, the versatility of this all-optical diagnostic will be demonstrated by results obtained on metal oxide (Al2O3, HfO2, Er2O3, TiO2, Ta2O5, and SrTiO3), metal nitride (TiN and TaN*x*), and metal (Pt and Ru) films with thicknesses ranging from 0.1 to 100 nm [1]. By acquiring SE data within a combined photon energy range of 0.75-6.5 eV in between the ALD (half-)cycles and by analyzing the film thickness and the energy dispersion of the optical constants of the films, the layer-by-layer growth and material properties of the films can be studied in detail. It will be shown that the growth rate per cycle and the ALD saturation curves can be determined directly by monitoring the film thickness as a function of the number of cycles, while also the nucleation behavior of the films on various substrates can be probed. Furthermore, it is demonstrated that the energy dispersion relation can provide information on the optical properties, the crystalline phase, and the material composition of the films. For metallic films, electrical properties can be calculated from the Drude absorption yielding insight into the electrical resistivity and electron scattering effects in ultrathin films.

[1] E. Langereis et al., J. Phys. D: Appl. Phys. 42, 073001 (2009).

5:20pm **AS+EM+MS+TF-MoA11 Mueller-Matrix Ellipsometry Studies of Optically Active Structures in Scarab Beetles**, ***K. Järrendahl**, J. Landin, H. Arwin*, Linköping University, Sweden

Ellipsometry is a valuable tool for general materials characterization but also for optical investigations of complex structures including multilayers, photonic crystals, metamaterials and other artificial materials. The complexity of these kind of structures has during the years promoted the use of spectroscopic, variable angle, generalized and Muller-matrix ellipsometry. In parallel more complex optical models and analysis algorithms have come into use. Naturally occurring structures may show even higher complexity than artifical structures but with a more narrow range of constituent materials, mainly chitin and various proteins. Many interesting structures are found in insects, especially in butterflies and beetles. Fascinating reflection properties result from intricate photonic structures in their wing scales and cuticles. Currently there is a large interest to explore such functional supramolecular architectures for exploitation in nanotechnology.

Even though the optical properties of natural structures are frequently investigated, ellipsometry rarely has been used to reveal structural and optical properties. In this study, Mueller-matrix spectroscopic ellipsometry is applied in the spectral range of 300 to 1700 nm to investigate structures in the cuticle of Scarab beetles, primarily *Cetonia aurata* (the rose chafer). The cuticle of *Cetonia aurata* is green with a metallic look and reflects circular polarized light. It has been suggested that the circular polarization of this metallic gloss is caused by a helical structure in the chitinous cuticle. We find that the circular polarization effect is limited to the narrow spectral range 470-550 nm and for shorter or longer wavelengths the reflection properties are similar to those from a near-dielectric material. Furthermore, the light reflected from *Cetonia aurata* is left-handed circularly polarized and the beetle thus appears black if viewed through a right-handed circular polarizer. In addition to Mueller-matrix spectroscopic ellipsometry, reflectance and scattering measurements are used to characterize the cuticle of *Cetonia aurata*. Model calculations and parameterization of the nanostructure employing a heliocoidal structure are discussed.

Surface Science
Room: M - Session SS1+EM-MoA

Semiconductor Surfaces and Interfaces I: Ge and III-V's
Moderator: M. Losurdo, IMIP-CNR, Italy

2:00pm **SS1+EM-MoA1 III-V MOS Device Performance Enhancement by Detection and Control of Individual Surface Oxidation States**, ***C.L. Hinkle**, M. Milojevic, A.M. Sonnet, E.M. Vogel, R.M. Wallace*, University of Texas at Dallas **INVITED**

Field effect transistors (FETs) remain at the heart of integrated circuit technology, and are forecasted to do so for at least the next decade. Silicon has been the material of choice for this purpose, but appears to be reaching significant performance limitations with further device dimension shrinking. As a result, the use of alternative semiconductor materials has again become of interest for FE T s. However, the native oxides (As-O and Ga-O) of these materials have been shown for more than thirty years to be of poor quality for metal-oxide-semiconductor (MOS) device performance. Furthermore, deposition of any gate oxide onto a clean III-V surface results in the oxidation of the substrate to detrimental effects. Despite the extensive research of III-V materials, there is still much to be understood about these oxides. In particular, the individual oxidation states of As (5+ and 3+) and Ga (3+ and 1+) are rarely considered despite evidence that they are quite different in forming defect states.

Recent work [1,2,3] will be presented on the detection and control of each of these surface oxidations states through carefully managed interfacial reactions and depositions on GaAs and InGaAs. The fabrication of MOS capacitors and FETs with these studied interfaces has led to a correlation between the spectroscopy and electrical measurements. An emphasis on controlling or eliminating each oxidation state through a variety of techniques has allowed for a detailed understanding of these native oxides and how each one affects device performance. The presence of the Ga 1+ oxidation state is spectroscopically detected for the first time at these interfaces and a dramatic increase in device performance is demonstrated by controlling the Ga 3+ surface concentration. This work is supported by the FCRP Materials, Structures, and Devices (MSD) Center, SEMATECH, FUSION funded by System IC 2010 (COSAR), The Texas Enterprise Fund, and NIST, Semiconductor Electronics Division.

[1] Hinkle et al., APL **94**, 162101 (2009).

[2] Sonnet et al., APL. **93** 122109 (2008).

[3] Hinkle et al., IEEE EDL **30**, 316 (2009).

2:40pm **SS1+EM-MoA3 Unpinning of $In_xGa_{1-x}As(001)-(4x2)/c(8x2)$ via Oxide Deposition for III-V MOSFETs**, ***J.B. Clemens**, S.R. Bishop, A.C. Kummel*, University of California, San Diego

The formation of a semi-ordered oxide passivation layer between hafnium oxide and $In_{0.53}Ga_{0.47}As(001)$-(4x2)/*c*(8x2) and InAs(001)-(4x2)/*c*(8x2) was studied using scanning tunneling microscopy/spectroscopy (STM/STS), and density functional theory (DFT) calculations. A passivation layer is needed to protect the surface from disruption during bulk amorphous oxide deposition for a high-κ gate insulator. Two methods of forming low coverage of HfO_2 were investigated: reactive oxidation of the e-beam deposited Hf metal and e-beam deposition from an HfO_2 target. STM results show that Hf atoms must cluster to be reactive to O_2. DFT suggests there is a high tendency for Hf to displace substrate atoms, which is undesirable. Direct deposition of the oxide is a better method. At submonolayer coverage, STM has identified individual bonding sites for the HfO_2 molecule; the HfO_2 forms small structures of mostly monolayer height with a high nucleation density. Density functional theory (DFT) calculations have been employed to assign the bonding structure. The DFT simulations show that for HfO_2/InAs(001)-(4x2), the most likely sites are stable by about -4.5 eV and the calculated density of states (DOS) shows no evidence of Fermi level pinning (no mid-gap states). At submonolayer coverage, the HfO_2 molecule bonds via group III-oxygen bonds and group V-hafnium bonds. STS measurements of clean InGaAs(001)-(4x2) reveal that the surface has significant band bending, showing p-type character for both n-type and p-type samples. Deposition of > 1 ML of HfO_2 is enough to move the Fermi level towards the conduction band for n-type InGaAs(001)-(4x2), as shown in results of STS vs. HfO_2 coverage. For p-type material, the Fermi level remains near the valence band after deposition of HfO_2. These results are consistent with the Fermi level remaining unpinned. In addition, annealing effects are studied. At temperatures of 300 °C and above, ordered oxide structures are seen in STM which form rows in the [-110] direction. However, lower annealing temperatures of 200 °C and below are preferable for good STS results. Hafnium oxide, evaporated via electron beam deposition, likely creates some O_2 and HfO, which may react in an undesirable way with the semiconductor surface. For this reason, a method is also proposed to protect the surface during e-beam deposition via a CO_2 protecting layer at low temperature (90 K), which does not appear to perturb the surface.

3:00pm **SS1+EM-MoA4 Formation and Structure of Alkaline Earth Template Layers for Oxide Epitaxy on Semiconductor (100) Surfaces**, *B. Lukanov, K. Garrity, J. Reiner, F.J. Walker, C.H. Ahn, S. Ismail-Beigi,* ***E.I. Altman***, Yale University

The finding that alkaline earth titanates can be epitaxially grown on Si and Ge(100) surfaces with atomically abrupt interfaces without oxidizing the semiconductor has spurred research into exploiting these materials for high k gate dielectrics, and for integrating new functionality into semiconductor devices. Attempts to epitaxially grow other oxides with similarly abrupt interfaces have thus far failed. It has been suggested that the initial interfacial layer formed by the reaction between the alkaline earths and Si and Ge is key to the success achieved with the alkaline earth titanates; therefore, we have been studying the interaction Sr and Ba with Ge and Si(100) with scanning tunneling microscopy (STM), complemented by density functional theory (DFT). At elevated temperatures, both Sr and Ba cause massive restructuring, indicative of surface alloy formation. Initial deposition causes an apparent etching away of the substrate dimers leading to dimer chains and islands on the surface. For Sr on Ge(100), increasing the coverage leads to an apparent c(4x4) structure decorated by bright spots that order only locally; the density of these bright spots decreases with increasing Sr coverage. The apparent c(4x4) structure ultimately gives way to a (3x2) structure that is characterized by periodic arrays of islands and trenches when it completely covers the surface. Electron diffraction data shows that continuing to raise the coverage causes a structural transformation to a (2x1) structure. On the atomic scale, STM images of the apparent c(4x4) and (3x2) structures vary dramatically with imaging bias; in particular changing the polarity of the bias voltage causes a contrast reversal where bright features in filled state images appear dim in empty state images and vice versa. Based on the observed bias dependence for Sr adatoms deposited at 300 K and simulated images derived from DFT calculations, a model of the (3x2) structure was developed in which Sr atoms replace every third row of Ge atoms on the surface. The striking periodic island and trench morphology is then associated stress relief of the the (3x2) structure. The results clearly show that at elevated temperatures the template layer does not form through simple surface adsorption.

3:40pm **SS1+EM-MoA6 STS and KPFM Investigation of InAs Pinning and Unpinning**, ***W. Melitz****, J. Shen, S. Lee, A.C. Kummel*, University of California, San Diego

A combined scanning tunneling spectroscopy (STS) and Kelvin probe force microscopy (KPFM) study was performed on InAs(001)-(4×2) to elucidate the surface electronic properties since this surface is a leading candidate for III-V MOSFETs. KPFM provides higher energy resolution than STS, which is critical for studies of materials like InAs which have small band gaps (Eg=0.354 eV). Amplitude modulation (AM) mode KPFM provides especially high energy resolution (10 meV) and is free of tip induced band bending because of the low applied voltage (70 meV). STS spectra of InAs(001)-(4×2) consistently show pinning, with the surface Fermi level near the conduction band for both n-type and p-type samples even on nearly defect free surfaces. Using KPFM, the work functions for both n-type and p-type clean InAs(001)-(4×2) surfaces is 4.3 eV consistent with surface pinning. Using the electron counting rule, indium dimers in the trough are sp^2 hybridized having a completely empty dangling bond. However the indium dimer atoms are positioned in a sp^3 tetrahedral configuration; these strained bonding sites might be responsible for the pinning. If the pinning is solely due to the (4×2) reconstruction, it is expected that other reconstructions without indium dimers would be unpinned. KPFM was also performed on cross-sectional InAs, which is defect free and has no indium dimers. These results were consistent with the bulk values with a work function difference between n-type and p-type of 0.49 eV. By eliminate the buckled indium dimer states with a passivation layer the InAs(001)-(4×2) surface could become unpinned.

4:00pm **SS1+EM-MoA7 Doping of InP Nanowires Studied by STM and X-ray PhotoEmission Electron Microscopy**, ***M. Hjort****, A.A. Zakharov, M.T. Borgström, E. Hilner, R. Timm, A. Fian, J.N. Andersen, E. Lundgren, L. Samuelson, A. Mikkelsen*, Lund University, Sweden

Self-assembled III-V nanowire heterostructures could be key components in many future optoelectronic devices [1], for example solar cells [2]. To realize photovoltaics from these structures variable p- and n-type doping along the nanowires are a fundamental prerequisite. The active component in solar cells, the pn-junction, has been grown axially in InP nanowires with different p- and n-type doping levels. However determining specific doping levels, effects of the nanowire surfaces and junction abruptness and band alignment across the interface with any precision is very difficult. Recently we have shown that scanning tunneling spectroscopy on nanowires with high resolution is possible [3] and we are now combining this with synchrotron based photoemission methods.

We have examined InP nanowires with up to two axial pn-junctions with Spectroscopic PhotoEmission and Low Energy Electron Microscopy (SPELEEM), X-ray Photoelectron Spectroscopy (XPS) as well as Scanning Tunneling Microscopy/Spectroscopy (STM/S). These techniques have given us the possibility to probe not only the structure of the nanowires but also the electrical properties (such as doping level) with high lateral resolution.

With our different setups we can probe the local density of states, atomic scale structure and work function differences along the wires. We can clearly distinguish between the different n- and p-type parts of the nanowires with both the scanning probe as well as with the synchrotron radiation based techniques. Both surface and the inner regions of the wires can to some extent be probed by varying photon energies in SPELEEM or modifying the surface for STM. This gives us the opportunity to understand the device at many different levels and improve its future quality.

[1]. L. Samuelson et al., *Physica E* **2004**, 21, 560-567

[2]. M. T. Borgström et al., *Nanotechnology* **2008**, 19, 445602

[3]. E. Hilner et al., *Nano Letters* **2008**, 8 (11), 3978-3982

4:20pm **SS1+EM-MoA8 Direct Atomic Scale Imaging and Spectroscopy of the Interior and Exterior of III-V Nanowires**, ***A. Mikkelsen***, Lund University, Sweden **INVITED**

Free-standing III-V nanowires and nanotubes are likely to become central components in future electronics and photonics with applications in IT, life-science and energy[1]. A very wide variety of III-V materials and dopants can be self-assembled into complex axial and radial heterostructures - precisely tailoring their structure down to the atomic scale.

We have used Scanning Tunneling Microscopy /Spectroscopy (STM/STS) and X-ray PhotoEmission and Low Energy Electron Microscopy (XPEEM/LEEM) to study nanowires and nanowire surfaces. Previously we have developed the means to directly study the interior of III-V semiconductor nanowires by STM[2], and now we have also developed direct methods for studying also the exterior nanowire surfaces to the atomic scale with STM[3].

We describe several significant results on the fundamental limits to atomic scale interface precision in AlGaAs/GaAs nanowires heterostructures, STS measurements on the interior of these wires and new insights into the influence of the growth substrate. We present atomically resolved STM images of the outside surface of InAs nanowires with InP segments along with STS measurements on the clean surfaces. The imaged surfaces of InAs nanowires are quite intriguing as the wires grow in the wurtzite crystal phase, in contrast to the zincblende bulk phase. Further we present STM images and STS measurements of InP nanowire pn-junctions. Using XPEEM and XPS we have characterized III-V nanowire surface chemistry and electronic properties and investigated the influence of various ultra-thin dielectrics to reduce surface band-bending effects.

The structure and morphology of semiconductor nanowire surfaces down to the single atom level are significant in determining both growth and function of the wires. Diffusion and nucleation on the nanowire surfaces will directly influence the final appearance of the wires, and it has been shown that transport and optical properties of semiconductor nanowires are to a considerable extent governed by their surfaces. Scanning Tunneling Microscopy is a great tool for imaging both geometric and electronic structure with high resolution, however direct atomically resolved STM studies of nanowire surfaces is very difficult. Still having overcome these problems (as in the present study) and by also applying synchrotron based spectroscopy/microscopy we obtain fascinating new insights into the interplay between nanowire growth, structure and function.

[1] C.M. Lieber and Z.L. Wang, MRS Bull. 32, (2007) 99

[2] A. Mikkelsen et al, Nature Mater. 3 (2004) 519 ; L. Ouattara et al, Nano Lett. 7 (2007) 2859

[3] E. Hilner, et al, Nano Lett., 8 (2008) 3978

5:00pm **SS1+EM-MoA10 Passivation of Ge(100) Surface Studied by Scanning Tunneling Microscopy and Spectroscopy**, ***J.S. Lee***, *S.R. Bishop, A.C. Kummel*, University of California, San Diego

Finding a good passivant for Ge surface is critical for fabricating a Ge-based MOSFET device. Recent studies have shown that GeON or GeO_2 interfacial layers can partially passivate the Ge/high-k dielectric interface and improve the electrical properties of the device. Introducing N (GeO_xN_y or Ge_3N_4) suppresses the Ge outdiffusion from the passivation layer into the high-k oxide layer at elevated temperatures, thereby reducing the post annealing density of interface states between Ge and high-k gate oxide. To minimize the density of interface states, the GeO_xN_y or Ge_3N_4 must be formed with a minimal dangling bond density, which is challenging in a thermal oxidation or nitridation process. To investigate the bonding and electronic structures of Ge-N and Ge-O surface species, in-situ scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) experiments were performed after oxidation and nitridation. Direct nitridation was carried out on Ge(100) using an electron cyclotron resonance plasma source, both at room temperature and at 500^{o}C. The nitridation at room temperature generated nitride sites, O sites (from trace water) and Ge adatoms which pin the surface Fermi level. The Ge adatoms are created because both O and N displace Ge surface atoms in order to bond at high coordination sites. These Ge adatoms can be removed by high temperature annealing. Nitridation at 500^{o}C produced a highly ordered Ge-N structure on the surface without O sites or Ge adatoms, but the Fermi level of the n-type surface was still pinned near the valence band probably due to the surface defects caused by plasma damage. Oxidation of Ge(100) was studied using a differentially pumped H_2O dosing system and the results were compared with our previous study on O_2 dosing of Ge(100). The H_2O dosed surface showed dark –OH adsorption sites with very few Ge adatoms, while the O_2 dosed surface had the equal densities of Ge adatoms and O sites. Annealing the H_2O/Ge(100) surface to 300^{o}C induces formation of bright Ge oxide sites which are slightly taller than Ge adatoms. However, both H_2O and O_2 dosing form GeO sites which are observed in STS to pin the Fermi Level. DFT calculations are being performed to determine the ordered nitride structure. In addition, the e-beam or ALD deposition of Ge_3N_4 or GeO_2 are being studied since they may form passivation layers without Ge displacement, plasma damage, and GeO, thereby unpinning the Fermi level.

5:20pm **SS1+EM-MoA11 Surface-driven Method for Incorporation of Mn into Ge Quantum Dots**, ***C.A. Nolph***, *K.R. Simov, P. Reinke*, University of Virginia

Magnetically doped nanostructures and quantum dots are important building blocks in future spintronic devices. We study the feasibility of magnetic doping of Ge quantum dots with Mn, an element with a large magnetic moment. A surface-driven route for Mn incorporation in Ge quantum dots promises superb control of the doping process. The Ge quantum dots are known to grow by strain-driven self-assembly (Stranski-Krastanov growth). Two pathways for Mn-doping have been identified: firstly, trapping of Mn at the Si-Ge interface and incorporation during quantum dot growth, and secondly, the deposition of Mn on the Ge quantum dot surface and dissolution of Mn during an annealing process. The first route requires a precise control of the Mn-bonding state at the Si(100) 2x1 substrate prior to the growth of quantum dots. Mn was deposited on Si(100) 2x1 and the surface phase diagram was determined across several temperature regimes and monitored with scanning tunneling microscopy. Mn-wire structures which formed at room temperature degrade and agglomerate to form Mn-clusters (115 - 270°C ± 30°C), then Mn moves into subsurface sites (316°C ± 38°C), and the onset of Mn-silicide formation is observed at about 342 - 416°C. This sequence is driven by the kinetics of the surface reaction between Mn and Si. A photoelectron spectroscopy study of the Si-Mn and the Si-Mn-Ge interface yields further insight into the bonding at the respective interfaces. The second route to dope quantum dots, namely the room-temperature deposition of Mn on Ge quantum dots, reveals the formation of Mn clusters, whose position is defined by the reconstruction of the Ge{105} facets. The diffusion of Mn on Ge(100) and Ge{105} facets, and into the Ge quantum dots is observed with STM during the annealing process. Our observations offer a comprehensive understanding of the Mn-interaction with all surfaces of relevance in the Si-Ge quantum dot system. The feasibility of the surface-driven route for Mn doping of Ge quantum dots will be discussed.

Electronic Materials and Processing
Room: A8 - Session EM1+PV-TuM

High Efficiency and Quantum Structure Photovoltaics
Moderator: C.S. Ferekides, University of South Florida

8:00am **EM1+PV-TuM1 Enhancement of the Thermoelectric Figure of Merit in Bulk Semiconductors at the Atomic Level**, ***J.P. Heremans***, The Ohio State University **INVITED**

Recently, several thermoelectric semiconductor systems have been developed with double the thermoelectric figure of merit, zT, of conventional materials. Almost all the progress comes from achieving reductions in thermal conductivity using nanotechnologies or structural disorder. Because the lattice thermal conductivity has a lower limit, the amorphous limit, further progress must come from an enhancement of the electrical properties, in particular the thermoelectric power or Seebeck coefficient. We present a new technique to achieve that, based on creating distortions of the density-of-states by doping with resonant impurities, resulting in a doubling of the zT of PbTe, a semiconductor used for power generation applications near 500 ^{o}C. We will also review current progress with this technique in Bi_2Te_3, the other classical thermoelectric, which we study because the commercial materials used for Peltier cooling are $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ alloys. The theory behind this approach will be outlined, and its applicability to a wide variety of thermoelectric semiconductors discussed.

8:40am **EM1+PV-TuM3 Synthesis of PbTe Nanowires by Lithographically Patterned Nanowire Electrodeposition (LPNE) and Their Thermoelectric Properties**, ***Y. Yang***, *D.K. Taggart, R.M. Penner, S.C. Kung, F. Yang, C.X. Xiang, M.A. Brown, J.C. Hemminger*, University of California, Irvine

Thermoelectric materials have received renewed interest in the past decade stemming from theoretical calculations that one-dimensional thermoelectric materials (i.e., nanowires) should show a remarkable enhancement in the dimensionless figure of merit—ZT caused by enhanced Seebeck coefficients, electrical conductivities and/or depressed thermal conductivities relative to their bulk counterparts. The prediction has been verified recently on silicon single-crystalline nanowire-arrays that showed almost one hundred times of enhancement of ZT. In contrast, there has not been anydemonstration of a similar effect on PbTe nanowires—one of the best thermoelectric materials in bulk. This presentation reports a synthesismethod called lithographically patterned nanowire electrodeposition (LPNE) for making PbTe nanowires and characterization of their thermoelectricproperties. The nanowires are semi-rectangular in cross-section with width and height independently controlled from 60 to 500 nm and from 10 to 100nm respectively, and they are electrically continuous up to millimeters. The structure and chemical composition of the nanowires are characterizedwith X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The electrical conductivity and Seebeck coefficient are measured at variable temperatures. A method for making suspended nanowires cross an air gap is also developed, which iscrucial for measurement of thermal conductivity. Ag-doped PbTe nanowires synthesized by the same method demonstrate tunable thermoelectric

properties due to the modification of the carrier type and concentration.

9:00am **EM1+PV-TuM4 PbSe Quantum-Dot Solar Cells**, *K.S. Leschkies, T.J. Beatty, M.S. Kang, D.J. Norris,* ***E.S. Aydil***, University of Minnesota

Quantum confinement of electrons and holes in nanometer size crystals (quantum dots or QDs), endows them with properties that may be advantageous for efficient solar-to-electric energy conversion. First, electronic energy levels and optical absorption in QDs can be manipulated by changing their size. This allows the optimization of their optical absorption for maximum overlap with the solar spectrum. Second, the ability to manipulate energy levels through size raises the possibility to make inexpensive multijunction solar cells by judiciously layering different size QDs. Third, it has been suggested that quantum confinement may slow energy dissipative electron and hole relaxation rates such that two new physical processes, multiple exciton generation and hot electron extraction may now compete with relaxation and lead to higher photocurrents or higher photovoltages, respectively. Finally, QDs can be prepared in large quantities as stable colloidal solutions under mild conditions and deposited on surfaces of various planar or nanostructured substrates as thin films through inexpensive high-throughput coating processes to form photovoltaic devices. For these reasons, solar cells based on QDs may have the potential to achieve high power conversion efficiencies at low cost and are promising candidates for third generation photovoltaic devices. We report a new type of solar cell based on heterojunctions between PbSe QDs and thin ZnO films. We find that the photovoltage depends on the QD size and increases linearly with the QD effective band gap energy. Thus, our solar cells resemble traditional photovoltaic devices based on a semiconductor-semiconductor heterojunction but with the important difference that changing the size of the QDs can vary the band gap of one of the semiconductors and hence the cell's photovoltage. Under simulated 100 mW/cm2 AM1.5 illumination, these QD solar cells exhibit short-circuit currents as high as 15 mA/cm2 and open-circuit voltages up to 0.45 V. Overall power conversion efficiency of the best device to date is 1.6% but may be increased further using nanostructured interfaces between PbSe QDs and ZnO. Moreover, we show evidence that this new solar cell may be operating like an excitonic solar cell rather than a traditional p-n junction solar cell.

9:20am **EM1+PV-TuM5 Phosphonate Self-Assembled Monolayers as Organic Linkers in Quantum Dot Sensitized Solar Cells**, ***P. Ardalan***, *T.P. Brennan, S.F. Bent*, Stanford University

Narrow band gap nanostructures such as cadmium sulfide quantum dots (QDs) are known to show size quantization effects as well as multiple exciton generation. They are therefore beneficial for absorption of light in the visible and near infrared region of the solar spectrum and can be used to fabricate photovoltaic devices with high theoretical efficiencies. In quantum dot sensitized solar cells (QDSSCs), these QDs can be engineered to transfer the electron to a wide band gap semiconductor such as titanium dioxide (TiO_2). However, performance in such devices is reduced by charge recombination at the TiO_2 surface and hence use of organic linkers and electron conductors such as self-assembled monolayers (SAMs) on these devices could provide a means of eliminating recombination sites and lead to increased efficiency. In this study, we investigated the effects of different aliphatic and aromatic SAMs with phosphonic acid headgroups and varied tailgroups on the bonding and performance of cadmium sulfide (CdS) QDSSCs. Our studies focus on bonding of the CdS QDs on both planar and nanoporous TiO_2 with or without the SAM linkers. To study the SAM/QD growth on planar surfaces, TiO_2 was deposited on Piranha-cleaned Si or microscope glass via atomic layer deposition (ALD) and the resulting surfaces were characterized by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Next, different SAMs were attached to the TiO_2 substrates from solution, where the effects of chain length, aromaticity, tailgroup, solvent, and dip time on the quality of the SAMs were investigated by the same techniques as well as infrared (IR) spectroscopy, water contact angle (WCA) measurements, and ellipsometry. Finally, CdS QDs were grown on the SAM-passivated TiO_2 surfaces by the successive ionic layer adsorption and reaction (SILAR) process, and the bonding and performance of the resulting materials were evaluated by UV-visible and other spectroscopic techniques. The results were compared to the case of QDs grown on the non-passivated TiO_2 surfaces. Our results show promising differences in the bonding of the CdS QDs at the TiO_2 surfaces with the SAM linkers. We will also present results on the dependence of solar cell performance on the properties of the SAM.

10:40am **EM1+PV-TuM9 High Efficiency Multijunction Solar Cells – Present Status and Future Directions**, ***P. Sharps***, Emcore Corporation **INVITED**

Multi-junction solar cells based on the $GaInP_2$/GaAs/Ge triple junction architecture have achieved the highest efficiency of any photovoltaic device, for either space or terrestrial applications. However, the cost of these cells is high compared to other photovoltaic devices. For space applications (i.e., satellite power) the higher efficiencies are more critical than cell cost, and on a system level, including launch and deployment costs, the multi-junction cells are actually lower on a $/watt basis than Si solar cells. The high efficiency multi-junction cell is now widely used on satellites. For terrestrial applications, the high efficiency cells must be used in high concentration systems where the high cell cost is offset by the lower costs of lenses, mirrors, and structure metal. The cell becomes such a small part of the system cost that a doubling of cell cost has a small effect on the cost of power generation. However, the efficiency of the cell may have a much larger effect on the cost of power generated. So for either space or terrestrial applications the efficiency of the photovoltaic device is very important.

Multi-junction solar cells offer a performance advantage over single junction solar cells because of the reduction in carrier thermallization losses. Different parts of the solar spectrum are absorbed by different band gap materials. III-V materials are able to achieve very high performance on a single junction basis, and when appropriately combined provide an even higher performance advantage. Fortunately, $GaInP_2$, GaAs, and Ge junctions can be combined in a lattice matched configuration, making a monolithic device with a good combination of junctions for converting the solar spectrum into power. Appropriate modifications can be made to the device to optimize it for either space or terrestrial applications.

To achieve even higher efficiencies, more junctions need to be added and/or the junctions need to be better matched to the solar spectrum. A number of approaches have been studied, including novel materials (e.g., InGaAsN, $ZnGeAs_2$, etc.), mechanically stacked devices, and metamorphic devices. With metamorphic devices junctions are grown lattice mismatched on one another to achieve the optimal set of band gaps in a complete device. One metamorphic approach, the inverted metamorphic multi-junction (IMM) solar cell, has demonstrated significant performance improvements over the lattice matched triple junction device.

We report on these improvements, describing how the IMM approach is enabling for both space and terrestrial power generation.

11:20am **EM1+PV-TuM11 GaAs Integration on High-Quality Ge on Si for Multijunction Solar Cells**, ***D. Leonhardt***, *J. Sheng,* University of New Mexico, *J.G. Cederberg, M.S. Carroll,* Sandia National Laboratories, *S.M. Han*, University of New Mexico

In an effort to reduce the cost of multijunction solar cells, we have scaled up a process to produce low-defect-density Ge films on 2-inch-diameter Si substrates. These engineered substrates could replace Ge wafers that are currently used in multijunction solar cell fabrication if the Ge film quality on engineered substrates can match that of commercially available epi-ready Ge wafers. We will present results for the scaled up process of engineered Ge on Si substrates, including key aspects of nucleation, defect formation, and defect reduction/elimination, using a variety of characterization techniques. For ensuing GaAs growth, we polish the Ge surface, using a slurry-free H_2O_2 based chemical-mechanical planarization (CMP) process. This CMP technique results in a root mean square (RMS) roughness less than 1 nanometer as revealed by atomic force microscopy. However, stacking faults in the Ge film that terminate at the film surface show up as raised lines after polishing. We have found that thermal annealing at a very early stage of Ge film growth largely eliminates these stacking faults and produces much smoother films than those grown without the annealing step. We have used a combination of atomic force microscopy and transmission electron microscopy (TEM) to investigate the effect of annealing on eliminating the stacking faults and on the initial Ge island morphology. In addition to defect reduction, we have developed a process for cleaning and passivating the Ge surface in preparation for GaAs growth. GaAs films grown on our engineered substrates have an RMS value of 3.6 nm and show integrated photoluminescence intensity that matches GaAs grown on commercially available off-cut Ge substrates. Future work and directions will be discussed in light of our findings.

11:40am **EM1+PV-TuM12 Investigation of Rare Earth - Doped Silicon Nitride Layers for Solar Cell Applications**, ***M.C. Petcu***, *A. Sarkar, M. Creatore, H.T. Hintzen, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Nowadays the application of thin SiN_x layers as bulk passivating and antireflection coatings for Si-based solar cells applications is considered to be a successful solution for the increase in efficiency[1]. A new concept to further increase the efficiency of the solar cell is based on the light conversion mechanism: according to this approach the solar spectrum can be efficiently modified by shifting the photons towards a wavelength range where the solar cell has a better or higher response[2].

Recently, a novel class of rare earth (RE)- doped SiN_x layers has been demonstrated to be a highly promising red-emitting conversion phosphor for white-LED applications. These materials have allowed the shifting of the emission wavelength by tuning the concentration of a specific RE element in a SiN_x based crystalline matrix[3]. The investigation of RE-doped amorphous silicon nitride (SiN_x) compounds, where the electronic properties of Si are combined with the optical properties of RE^{3+} ions, have been shown already potential in optoelectronics[4]. Therefore, parallel studies on the incorporation of a RE material in amorphous SiN_x host lattices, which could be implemented in solar cells to increase the efficiency, are considered to be presently a challenge.

In this contribution the properties of europium- and samarium- doped amorphous SiN_x layers are investigated. The RE-doped SiN_x layers are deposited using a remote PECVD expanding thermal plasma fed with $Ar/SiH_4/NH_3$ mixtures in combination with a RE magnetron sputtering source implemented in the proximity of the substrate holder. Growth rates of the RE doped layers obtained from Spectroscopic Ellipsometry (SE) measurements were in the range 0.6-2.2 nm/s. The successful incorporation of RE in the SiNx matrix has been demonstrated by means of Rutherford Back Scattering (RBS) and X-ray Photoelectron Spectroscopy (XPS) analysis, i.e. up to 2%. Preliminary photoluminescence results point out a broad band emission in the region of 500-800 nm when excitation wavelengths of 270 nm and 320 nm have been used. The emission band observed can be attributed to Sm^{2+}.

[1] J. Hong et *al*., J. Vac. Sci. Technol. B. 21 (5).

[2] C. Strümpel et *al*., Sol. Energ. Mat. Sol. C. 91 (2007) 238 – 249.

[3] Y. Q. Li et al., J. Alloys. and Comp. 417, 273 – 279.

[4] A. R. Zanatta, et *al*., J. Phys.:Condens. Matter 19 (2007) 436230.

Electronic Materials and Processing
Room: B1 - Session EM2-TuM

Complex and Multifunctional Oxides
Moderator: J.D. Phillips, The University of Michigan

8:00am **EM2-TuM1 Electrical Properties of HfO_2 Thin Films Made by RF Sputtering**, ***B. Aguirre***, *R.S. Vemuri, D. Zubia,* University of Texas at El Paso, *W. Jiang, M.H. Engelhard, V. Shutthanandan,* Pacific Northwest National Laboratory, *C.V. Ramana*, University of Texas at El Paso

Hafnium oxide (HfO_2), which exhibits a very high dielectric constant (*k*) and large bandgap, is considered as a next-generation high-*k* material for application in complementary metal-oxide-semiconductor (CMOS) technology. However, growth of high-quality HfO_2 layers on Si without the formation of interfacial compounds poses a significant challenging problem. The objective of the present work was to optimize the conditions to grow high-quality HfO_2 nanolayered films on Si(100). In our work, HfO_2 films were grown by RF sputtering of HfO_2 ceramic target at various substrate temperatures (T_s= 30-500 ^oC) and studied their structure and electrical properties. $Al/HfO_2/Si$ capacitive structures were fabricated to obtain a metal-oxide-semiconductor (MOS) configuration to mimic the gate stack of CMOS technology and study the electrical properties. Grazing incidence x-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS) measurements indicate that the effect of T_s is significant on the microstructure. HfO_2 films grown at T_s<200 ^oC are amorphous. An amorphous-to-crystalline transition occurs at T_s=200 ^oC. Nanocrystalline HfO_2 films crystallized in a monoclinic structure with a particle size ~20 nm. XPS measurements indicate the high chemical quality of HfO_2 films grown at T_s=30-500 ^oC. The capacitance-voltage characteristics of the $Al/HfO_2/Si$ devices indicate that HfO_2 films grown (or post-deposition annealed) at 400 ^oC exhibit the expected monoclinic-HfO_2 characteristics. HfO_2 films exhibit a direct correlation with the microstructure. The results obtained are presented and discussed in detail.

8:20am **EM2-TuM2 XPS Characterization of Hf-based High-k Oxide/SiO_2/Si Films Stacks**, ***E. Bersch***, *M. Di,* University at Albany, *S. Consiglio, R. Clark, G. Leusink,* TEL Technology Center, America, LLC, *A.C Diebold*, University at Albany

As the MOSFET SiO_2-based gate dielectric layer approaches its fundamental physical limits, the investigation of high-k oxides is ongoing in order to determine which oxides can best continue the scaling of the MOSFET. HfO_2, hafnium silicates and nitrided hafnium silicates are leading candidates due to their relatively large band gaps, thermal stability in proximity to Si and relatively high dielectric constants.

The band offsets between the high-k oxide layers and Si in high-k/SiO_2/Si films stacks are important parameters in that the gate leakage current depends strongly on them. Recent studies by various groups have also shown that the threshold voltage in MOSFETs with high-k gate oxides can be altered by the presence of an additional oxide layer such as La_2O_3 or Al_2O_3.[1-3] In the case of a La_2O_3 interface layer, the flatband voltage shift has been correlated with a shift in the energy level alignment in the high-k gate stack.[4]

We have used a combination of x-ray photoemission spectroscopy (XPS) and spectroscopic ellipsometry (SE) to measure the valence and conduction band offsets (VBO and CBO, respectively) between high-k layers and Si substrates. We will report VBO and CBO values for HfO_2, hafnium silicate and nitrided hafnium silicate films with Si. In addition, we will report measurements of the HfO_2-Si band offsets from $HfO_2/La_2O_3/SiO_2/Si$ film stacks, noting the effect of the La_2O_3 layer.

Analysis of XPS spectra of the Si 2p spectra from $HfO_2/SiO_2/Si$ film stacks will also be reported, which shows that the composition of the SiO_2 layer and the energy level alignment between the SiO_2 and Si layers were affected by the growth of the HfO_2 layer and the annealing of the film stack. These results will be discussed with respect to the band offset measurements for HfO_2 film stacks.

Finally, using angle resolved XPS (ARXPS) data we constructed non-destructive compositional depth profiles using a maximum entropy algorithm. A comparison between thickness values extracted from these depth profiles and thicknesses measured with SE will be presented.

References:

1. P. D. Kirsch *et al*., *Appl. Phys. Lett.*, **92**, 092901 (2008).
2. V. Narayanan *et al.*, *Symp. VLSI Tech.*, 178 (2006)
3 K. Iwamoto *et al., Appl. Phys. Lett.,* **92,** 132907 (2008)
4. K. Kakushima *et al*., *Appl. Surf. Sci*., **254**, 6106 (2008).

8:40am **EM2-TuM3 Enhanced Dielectric Polarizability of Ge Doped HfO$_2$ Films on Si and Ge***, **L. Miotti**, K.P. Bastos, G. Lucovsky,* North Carolina State University*, D. Nordlund*, Stanford Synchrotron Research Lightsource

The use high dielectric constant materials (high-κ) as gate dielectric in complementary metal-oxide-semiconductor devices based on Si and other higher carrier mobility semiconductors has been focus of intense research. So far, hafnium oxide is among the high-κ dielectrics with higher dielectric constant and higher technologic interest. The most common phase of HfO$_2$ thin films after deposition and processing is monoclinic with a dielectric constant of κ~ 16-20. However, its dielectric constant can be improved by increasing it in its tetragonal (κ~ 30-35) or cubic phase (κ~ 20-25), which are its thermodynamic equilibrium phases at higher temperatures

We report here on the investigation of Ge doping HfO$_2$ films and its role in stabilizing the tetragonal phase of hafnium oxide phase. The films were deposited by remote plasma enhanced chemical vapor deposition on both Si(001) and Ge(001) substrates. Hf-t-butoxide and GeH$_4$ were used as source for Hf and Ge, while O$_2$ as the oxidizing agent. Germanium concentration in the films was determined by Auger electron spectroscopy. Interface reaction was hindered by nitridation of the substrates before the deposition of the films. Conventional x-ray diffraction analysis is not suited to investigate the crystallographic order in very thin films (< 10 nm), as well as those of interest for device applications. Therefore, we probed the local symmetries by x-ray absorption spectroscopy using the beam line 10 in SSRL.

The x-ray absorption spectra for 2 and 5 nm thick HfO$_2$ films deposited on Si with 0, 5, or 15 at.% Ge, as well as the second derivative of these spectra was studied. Based on previous studies of HfO$_2$ films on Si, the shape of the transitions to the E$_g$ and T$_{2g}$ states of the 5 nm thick film without Ge doping corresponds to a monoclinic phase with a different Jahn-Teller distortion than the trigonal. A significant change in these features is observed when the film is doped with 5 at.% Ge. In this case the E$_g$ and T$_{2g}$ transitions correspond to a tetragonal symmetry. Higher germanium doping leads to a mixture of monoclinic and tetragonal phases causing a broadening of the absorption spectra. There is not significant difference in the absorption spectra for the 2 nm thick films with different doping, indicating that the Ge stabilization of a tetragonal phase can only be achieved above a critical thickness.

The mechanism that stabilizes the tetragonal phase of HfO$_2$ using a tetravalent dopant is significantly different from that associated with trivalent impurities as yttrium, which involves oxygen vacancies. This mechanism results in decrease of the c/a ratio with no vacancies involved.

9:00am **EM2-TuM4 Correlated Oxide Heterostructures**, ***R. Ramesh***, The University of California, Berkeley **INVITED**

Complex perovskite oxides exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. The basic materials physics of such materials provide the ideal playground for interdisciplinary scientific exploration. Over the past decade we have been exploring the science of such materials (for example, colossal magnetoresistance, ferroelectricity, etc) in thin film form by creating epitaxial heterostructures and nanostructures. Among the large number of materials systems, there exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics. Using our work in the field of ferroelectric and ferromagnetic oxides as the background, we are now exploring such materials, as epitaxial thin films as well as nanostructures. Specifically, we are studying the role of thin film growth, heteroepitaxy and processing on the basic properties as well as magnitude of the coupling between the order parameters. In this talk I will describe to you some aspects of such materials as well as the scientific and technological excitement in this field.

9:40am **EM2-TuM6 Polarization-dependent Electron Tunneling Into Ferroelectric Surfaces*, P. Maksymovych*,** *S. Jesse,* Oak Ridge National Laboratory*, P. Yu, R. Ramesh,* University of California, Berkeley*, A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Electron tunneling underlies numerous devices relevant to information technology and has been proposed in future energy harvesting and quantum computing applications. Replacing a conventional insulator in the tunnel junction with an electronically correlated material can yield new types of electronic functionality. In one such concept, dubbed ferroelectric tunneling, the tunneling barrier height is controlled by the polarization of a ferroelectric oxide, enabling non-volatile conduction states that can be switched with electric field. Although ferroelectric tunneling has been thoroughly theorized, a convincing experimental demonstration of this phenomenon is still lacking. The key challenge is to find a material system that simultaneously satisfies the dimensional constraints for tunneling and ferroelectricity, as well as to assure that the conductance is not dominated by extrinsic effects of charge injection and filamentary conduction, which is ubiquitous in complex oxides.

In this talk we will demonstrate a highly reproducible polarization control of local electron transport through epitaxial Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ films. Despite being 30-50 nm thick, conductive atomic force microscopy revealed that the films possessed spatially and temporally reproducible local conductivity in the regime of Fowler-Nordheim electron tunneling. This is likely due to a strong electric field in the sub-surface region (excess of 10^6 V/cm) created by the relatively sharp metal tip. Local I-V characteristics exhibited strong hysteretic behavior across the surface. By combining conducting atomic force microscopy with piezoresponse force microscopy, we have, for the first time, directly correlated local events of ferroelectric and resistive switching [1]. The large spontaneous polarization of PZT produced as strong as 500-fold enhancement of FN-tunneling conductance upon ferroelectric switching, sufficient to demonstrate a local non-volatile memory function. The physical mechanism of the observed effect was traced to the polarization-dependence of the height and possibly width of the metal-ferroelectric Schottky barrier.

By observing the role of inherent disorder in ferroelectrics and comparing films grown on different electrode materials, we have shown that the switching voltage and the magnitude of conductance hysteresis are subject to electrostatic control via ferroelectric switching. Variable-temperature measurements and local effects due to dielectric non-linearities will also be discussed.

[1] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, S. V. Kalinin, Science (2009) *in press*.

10:40am **EM2-TuM9 XAS and XPES Studies of Strongly Correlated Ti d-states in Gd(Sc$_{1-x}$Ti$_x$)O$_3$*, G. Lucovsky*,** North Carolina State University*, C. Adamo,* Penn State University*, D.L. Schlom,* Cornell University*, K.B. Chung*, North Carolina State University

There is considerable interest in complex oxides comprised of transition metal, TM, and lanthanide rare earth, LRE, atoms with room temperature magnetic properties that can modulated by electrical input. Ferro- and ferri-magnetic properties require strongly correlated spin sub-bands derived from TM(LRE) d(f)-states, and have been reported in elemental oxides: CrO$_2$ and Fe$_3$O$_4$, and EuO$_2$. Strongly correlated bands are created by a double exchange mechanism requiring a transition to a metallic state. The incorporation of tetravalent Ti into a d^0 complex oxide with trivalent Gd and Sc, requires that Ti be in a formal trivalent valence state, Ti^{3+}. Alloying with Ti then introduces a d^1 occupied state into the complex oxide host in direct proportion to the Ti content.

Gd(Sc$_{1-x}$Ti$_x$)O$_3$ alloys > 5 nm thick with x = 0.0, 0.01, 0.05, 0.18 and 0.25 were deposited at room temperature in an UHV system onto (i) LaAlO$_3$ substrates for epitaxial growth, and (ii) superficially oxidized Si(001) to produce nano-grain films. As-deposited nano-grain dimensions are 2-2.5 nm, and are too small for Jahn-Teller distortions and spin ordering of Ti alloy atoms. The correlation exchange energy for spin correlated bands is obtained from room temperature films on Si is approximately equal to the energy difference between the localized Ti impurity state energy and Sc band edge d-state.

A compositionally dependent insulator/metal transition is reported for the first time in Gd(Sc$_{1-x}$Ti$_x$)O$_3$ alloys for x > 0.16, and is attributed with a correlated Ti d-state band. This insulator to metal transition is identified by X-ray absorption spectroscopy, XAS, extending into the pre-edge regime for X-ray energies <530 eV. Annealing at 900°C in Ar increases grain size enabling Jahn-Teller distortions, and results in an insulator to metal transition evidenced by opening of a gap between oppositely directed Ti spin states. This insulator to metal transition is also observed in as-deposited epitaxial films as well, and consistent with percolation theory, only if the Ti concentration exceeds a critical concentration of ~16.5 %, as in the 18 and 25 % alloys. Differentiation of XAS spectra indicates ferrimagnetism, with a second partially occupied spin band. As predicted by theory, the separation of these spin bands is the same as the correlation exchange energy obtained from the Ti impurity band energy.

This transition is also observed in X-ray photoemission spectroscopy, XPES. The dominant correlated spin band is below the $Gd(Sc_{1-x}Ti_x)O_3$ alloy Fermi level energy in the XPES spectra, and the oppositely directed spin band is at the Fermi level energy.

11:00am **EM2-TuM10 $ZnO/LiNbO_3$ Heterojunctions: A Candidate System For Multifunctional Oxides**, ***E. Cagin***, *J.D. Phillips*, University of Michigan, Ann Arbor

Ferroelectric/semiconductor heterostructures are desirable for multifunctional devices using the charge of a ferroelectric material to manipulate the conductivity of a semiconductor. The quality of the ferroelectric/semiconductor interface is critical for maintaining a significant ferroelectric polarization charge density, and coupling this charge density into the semiconductor. Therefore, materials must have excellent chemical and structural compatibility. ZnO and $LiNbO_3$ may provide the desired characteristics based on the crystalline compatibility of the materials, excellent semiconducting properties of ZnO, and excellent ferroelectric properties of $LiNbO_3$. In this work, the structural and electrical characteristics of ZnO thin films deposited on z-cut $LiNbO_3$ substrates by pulsed laser deposition will be presented and compared to ZnO thin films on c-plane sapphire substrates. In all experiments, preferentially-oriented c-plane ZnO thin films were obtained based on x-ray diffraction measurements.

Hall effect measurements demonstrate a background carrier concentration in ZnO of $n=2.\ 6x10^{17}cm^{-3}$ for $ZnO/LiNbO_3$, and an order of magnitude decrease of $n=3.0x10^{18}cm^{-3}$ for ZnO/sapphire. Similarly, an improved electron mobility of $\mu=36\ cm^2/Vs$ is observed for $ZnO/LiNbO_3$ in comparison to $\mu=21\ cm^2/Vs$ for ZnO/sapphire. The reduced carrier concentration and improved mobility are attributed to a depletion layer at the $ZnO/LiNbO_3$ interface induced by polarization charge. The temperature dependence of electron transport in ZnO thin films will also be presented to examine the influence of polarization charge induced by the pyroelectric effect in $LiNbO_3$.

11:20am **EM2-TuM11 The Study of Electrical and Structural Properties of SiO_2 Film Containing Metal oxide using Organosiloxane-based Silica Precursor**, ***K. Watanuki***, *A. Inokuchi*, Tohoku University, Japan, *A. Banba, H. Suzuki, T. Koike, T. Adachi*, Ube-Nittou Kasei Co., Ltd., Japan, *A. Teramoto, Y. Shirai, S. Sugawa, T. Ohmi*, Tohoku University, Japan

High quality SiO_2 film formation is important for many applications as electrical insulator films, protective films for semiconductor, alkali-dissolution barrier films and antireflection films on the glass. In some of applications, the electrical property of the films plays an important role. Various techniques have been used thus far in preparing SiO_2 films. Especially, in various techniques, sol-gel technique has significant advantage compared with other techniques with uniformity of thickness, damage free, easy coating of large surfaces, homogeneous multi-component oxide films, controllability of compositions, and potential industrial application. So, in this work, we have evaluated the electrical and structural characteristics of SiO_2 film using organosiloxane-based silica precursor. And we have evaluated the influence of additives to organosiloxane-based silica precursor, such as TiO_2, HfO_2, Ta_2O_5, ZrO_2 and several kinds of metal oxide components on the electrical and structural property of these SiO_2 base insulator films.

The organosiloxane-based sol-gel material investigated here is derived from the mixture of tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS) by changing the molar ratio of TEOS/MTMS. In the case of the addition of metal oxide to SiO_2 matrix, such as TiO_2, HfO_2, Ta_2O_5, ZrO_2 and several kinds of metal oxide, metal alkoxides such as tetraisopropoxytitanate (TPOT) were added in the concentration ranging from 1 to 15 mol %. In order to evaluate the electrical property of films, we fabricated MOS (Metal-Oxide-Silicon) devices.

By controlling mixing molar ratio between TEOS and MTMS in the sol-gel precursor, the dielectric constant of films can be controlled. This sol-gel precursor was prepared not only of perfect silica film but also a dense film through optimized conditions such as the pre-baking for 5 min at 130˚C, N_2 ambience low pressure gas removing process continuously increasing the temperature up to 900˚C, and oxidation process using O_2/H_2O at 900˚C. In this study, the influence of additives to the sol-gel precursor was examined on the structural and electrical property of the SiO_2 based films derived from the sol-gel precursor. The breakdown voltages of the resultant films were effectively improved by adding a small amount of metal oxide such as TiO_2, HfO_2, Ta_2O_5 and ZrO_2. It was found that the SiO_2 based film derived from the sol-gel precursor added with metal oxide components, such as TiO_2, HfO_2, Ta_2O_5 and ZrO_2, had excellent uniformly-structured Si-O-Metal bond and that the electrical insulation property of the film was improved by the concentration of metal oxide additives.

Graphene Topical Conference
Room: C3 - Session GR+EM+MS-TuM

Graphene and Carbon-based Electronics
Moderator: J.E. Rowe, North Carolina State University

8:00am **GR+EM+MS-TuM1 Graphene: Quantum Transport in a 2D Membrane**, ***C.N. Lau***, University of California, Riverside **INVITED**

Graphene, a two - dimensional single atomic layer of carbon, has recently emerged as a promising candidate for electronic materials, as well as a new model system for condensed matter physics. It also has the double identity of an extraordinary conductor and the thinnest isolated membrane. In this talk I will present our results on both of these aspects: (1) our observation of novel transport phenomena in graphene, including coherent interference of multply-reflected charge waves and properties of p-n-p junctions in zero and high magnetic fields; and (2) our work on ripple formation and manipulation on suspneded graphene sheets. I will conclude the talk with a brief discussion on the fascinating prospect of strain-based graphene engineering.

8:40am **GR+EM+MS-TuM3 Air Induced Suppression of n-Type Conduction in Field-Effect Transistors**, ***P. Levesque***, Université de Montréal, Canada, *C.M. Aguirre*, École Polytechnique de Montréal, Canada, *M. Paillet, F. Lapointe*, Université de Montréal, Canada, *B.C. St-Antoine, P. Desjardins*, École Polytechnique de Montréal, Canada, *R. Martel*, Université de Montréal, Canada

Carbon nanotube, graphene, and organic semiconductor based devices share common features when exposed to atmospheric environment. For carbon nanotube field-effect transistors (FET), the effect is an almost exclusive p-type character in air. N-type conduction can only be observed under certain conditions, for instance when the devices are annealed in vacuum. By performing experiment under controlled atmosphere, we investigated the impact of the chemical nature of the substrate and of gas adsorbates on the field-effect switching behavior of both nanoscale and thin-film nanotube FETs. Our study revealed that the intrinsic material properties are modified and lead to the reduction of n-type conduction when an adsorbed water layer containing solvated oxygen is present on the SiO_2 surface. This finding demonstrates that an electrochemical charge transfer reaction between the semiconducting channel and the aqueous oxygen redox couple is the underlying phenomenon behind the suppression of electron conduction in nanotube devices. The impact of this redox couple on graphene FET explored in this context will also be discussed. We forecast that these redox active species generally influence the transport properties of transistors operating in air and propose a general mechanism that explains behaviors observed in many material systems on SiO_2/Si substrates, also including nanowires, polymers and organic materials.

9:00am **GR+EM+MS-TuM4 Epitaxial Graphene Device Technology**, ***D.K. Gaskill***, U.S. Naval Research Laboratory, *J. Moon*, HRL Laboratories, LLC, *J.L. Tedesco*, U.S. Naval Research Laboratory, *J.A. Robinson*, The Pennsylvania State University, *A.L. Friedman, P.M. Campbell, G.G. Jernigan, J.K. Hite, R.L. Myers-Ward, C.R. Eddy, Jr.*, U.S. Naval Research Laboratory, *M.A. Fanton*, The Pennsylvania State University

Recently, the world's first graphene RF field effect transistors (FETs) have been fabricated using photolithography on epitaxial graphene (EG) grown on 50 mm SiC semi-insulating wafers. The RF FETs had f_{max} of 14 GHz at 5 V_{ds} for 2 μm gate widths and results are expected to improve as gate widths are scaled down. Continued research addressing key materials issues is needed to push the performance metrics for devices fabricated on wafer-scale EG significantly higher. Some of these key materials issues are morphology and thickness control, enhanced mobility, uniformity of sheet carrier density and resistivity, and optimizing atomic layer deposition (ALD) of high dielectric constant oxides on EG. In this presentation, we will present details on our approach using Si sublimation from SiC substrates for growing EG on 50.8 and 76.2 mm diameter SiC wafers and discuss the impact of key material issues on RF device performance.

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Epitaxial graphene was synthesized using a commercial Aixtron VP508 SiC epitaxial growth reactor on the Si- and C-faces of 4H- and 6H-SiC semi-insulating 0° oriented substrates at temperatures from approximately 1225 to 1700°C and for times ranging from 10 to 300 min. Substrates were 16 x 16 mm^2 coupons and 50.8 and 76.2 mm diameter wafers. Both *in-vacuo* (10^{-6} to 10^{-4} mbar) and Ar ambient (50-200 mbar) Si sublimation synthesis conditions were investigated. Dielectrics were deposited using a Cambridge NanoTech Savannah 200 ALD system. EG was characterized by a wide array of tools including atomic force, Nomarksi and scanning tunneling microscopies, Raman spectroscopy, Hall effect, and Lehighton contactless resistivity and mobility wafer probe.

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The growth of EG on 50.8 mm Si-face wafers using the *in-vacuo* process was optimized and excellent relative resistivity uniformity of 2.8% and record 300 K Hall mobilities up to 2700 cm^{2}V^{-1}s^{-1} were found. Raman spectroscopy mapping of the 2D peak on the wafers determined: (1) the majority of the film was monolayer EG, (2) two layers of EG could be found at step edges and (3) the EG was continuous across the wafer. RF FETs fabricated using the latest optimized wafer-scale EG exhibited state-of-the-art ambipolar behavior, I_{on}/I_{off} ratios and peak transconductances. Frequency performance metrics were established for these devices such as f_T●L_g products of 10 GHz●µm and f_{max} of 14 GHz. To our knowledge, the highest field effect mobilities reported to-date have been measured using these devices. We will discuss the impact of key material parameters associated with EG for these record results as well as the impact of Ar ambient controlled graphenization on future RF devices.

9:20am **GR+EM+MS-TuM5 Hydrogen Adsorption at Surfaces of the Epitaxial Graphene on the 6H-SiC(0001)**, *Y. Aoki,* ***H. Hirayama***, Tokyo Institute of Technology, Japan

Recently, adsorption of a small amount of atomic hydrogen was reported to transform the exfoliated graphene from highly conductive semimetal into an insulator [1]. In this case, the C-atom is only the site for hydrogen adsorption. However, at the epitaxial graphene on the SiC(0001) substrate, hydrogen could adsorb on both C- and Si-site. Furthermore, the surface structure changes by stages from Si-rich 3x3, $\sqrt{3}x\sqrt{3}$ to C-rich $6\sqrt{3}x6\sqrt{3}$ phase in the epitaxial growth of graphene on SiC substrates [2]. In this study, we investigated the hydrogen adsorption at these surfaces appeared in the way of epitaxial growth of graphene on the Si-terminated 6H-SiC(0001) surfaces.

Experiments were carried out in an ultra-high vacuum apparatus equipped with a Si dozer, a LEED/AES, a TPD (Temperature Programmed Desorption), a hydrogen gas inlet, and a hot W-filament. We prepared the 3x3, $\sqrt{3}x\sqrt{3}$, and $6\sqrt{3}x6\sqrt{3}$ surfaces by heating the sample at 850°C under the Si flux, heating at 1150°C for 3min, and heating at 1250°C for 3min, respectively. We exposed these surfaces to atomic hydrogen, and measured their TPD spectra. Our TPD indicated that the saturation coverage of H was ≈0.1 monolayer (ML) at these surfaces independent of the surface structure. However, the TPD spectrum changed drastically at the stage from 3x3 to $\sqrt{3}x\sqrt{3}$. The 3x3 surface showed a shoulder at ≈500K, and a dominant peak at 700K, while the $\sqrt{3}x\sqrt{3}$ and the $6\sqrt{3}x6\sqrt{3}$ surface had a single peak at 400K. Comparing to the previous TPD studies at graphite [3], we attributed to the single peak at 400K to the hydrogen desorption from the graphene layer. Meanwhile, the peak at 700K of the 3x3 surface is very close to the hydrogen desorption peak from the Si(111) surface. Both TPD and AES suggests that the π-bonded C-induced benzene ring structure started to grow at the appearance of the $\sqrt{3}x\sqrt{3}$ surface structure. This interpretation is supported by our electron energy loss spectroscopy (EELS) measurements in which the π-plasmon loss peak of the benzene ring started to evolve at the $\sqrt{3}x\sqrt{3}$ surface.

[1] Science 323,610(2009), [2]JPC,B208,19912(2004), [3]JCP117,8486(2002)

9:40am **GR+EM+MS-TuM6 Graphitic Carbon Growth on Si(111) from Solid Source Molecular Beam Epitaxy**, ***J.C. Hackley****, D. Ali, J. Di Pasquale, C.J.K. Richardson*, University of Maryland, College Park

Since the recent discovery of isolated graphene through mechanical exfoliation of bulk graphite, a number of methods have been developed to produce graphene. However, there have been no reports of graphene growth by direct carbon deposition such as solid source molecular beam epitaxy (MBE). Carbonization of a silicon surface is a commonly used first step in the epitaxial growth of SiC films, and is often accomplished by solid source MBE of carbon onto a Si substrate to form a thin SiC buffer layer. Annealing SiC wafers in ultra-high vacuum is a reliable method of producing graphene layers, and is frequently referred to as an epitaxial technique. Consequently, graphene may be synthesized via MBE through a two-step process consisting of first growing SiC, and then annealing this film at high temperatures to desorb Si. A shorter processing route which bypasses the SiC formation would be quite beneficial. In this project, we investigate the growth of graphene directly on Si using solid source MBE at growth temperatures which are much lower than a SiC process.

An EPI-Model 930 MBE system which has been modified to accommodate a Si electron beam source is used for carbon sublimation onto 3" Si wafers. Our carbon source is a Thermionics rod-fed electron beam gun with a highly oriented pyrolytic graphite (HOPG) target. Reflective high-energy electron diffraction (RHEED) measurements are used to monitor the carbon film growth in situ. The film bonding structure is investigated ex-situ with x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman scattering spectroscopy. Film topology is examined ex-situ with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hall measurements in a Van der Pauw configuration are implemented for electrical characterization of the films. Through preparing the Si surface with seeding layers and choosing an appropriate C flux we have been able to suppress SiC formation and grow graphitic carbon at temperatures < 700°C. Raman scattering measurements show the G mode at ~1600 cm^{-1} and the D mode at ~1320 cm^{-1} (Fig. 1), as well as weak overtones of these phonon modes. XPS analysis of the C 1s region shows no significant sp3 carbon bonds, and no SiC formation, which is also verified by FTIR measurements (Fig. 2). SEM and AFM analysis show that the films are smooth and continuous.

We are currently refining our growth process in order to increase graphite grain size and subsequently downscale to 2-dimensional growth. These initial results appear promising for the future development of graphene growth via direct deposition of carbon.

10:40am **GR+EM+MS-TuM9 Epitaxial Graphene: Designing a New Electronic Material**, ***W.A. de Heer***, Georgia Institute of Technology **INVITED**

Since 2001 the Georgia Tech epitaxial graphene research team and its collaborators have developed the new field of epitaxial graphene electronics.The current status of epitaxial graphene research will be presented, including the production methods and recent results from various characterization investigations. Methods have been developed to grow continuous multilayerd epitaxial graphene (MEG) on the C-face of hexagonal silicon carbide with of up to 100 graphene sheets and its extraordinary transport properties have been demonstrated.

Surprisingly, the properties of MEG are closely related to monolayer graphene rather than graphite, as a result of an unusual rotational stacking of the graphene layers that causes the graphene sheets to electronically decouple. Consequently the electronic band structure of MEG is composed of Dirac cones. The charge carries are chiral and exhibit a non-trivial Berry 's phase. Weak anti-localization and quantum confinement has been demonstrated. Landau level spectroscopy further exhibits record-breaking room temperature mobilities and well resolved Landau levels below 1 T, indicating extremely low carrier densities and good homogeneity of the material. Efforts towards large scale electronic device patterning will be reviewed.

11:20am **GR+EM+MS-TuM11 MORTON S. TRAUM AWARD FINALIST: Room Temperature Molecular-Resolution Characterization of Self-Assembled Organic Monolayers on Epitaxial Graphene**, ***Q.H. Wang******, M.C. Hersam*, Northwestern University

Graphene has attracted significant attention due to its unique electronic structure, high carrier mobilities, and quantum relativistic phenomena. Epitaxial graphene grown on SiC(0001) is a promising material for next-generation technology because it allows for wafer-scale processing. In order to realize its full potential for a diverse range of devices, the bare graphene sheet must be incorporated with other materials via chemical functionalization schemes. Recent progress reported in the literature include the demonstration of atomic layer deposition of Al_2O_3 on mechanically exfoliated graphene sheets functionalized by carboxylate-terminated perylene derivatives,[1] and the formation of monolayers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) at cryogenic temperatures on epitaxial graphene.[2] In this study, we report the room-temperature formation of self-assembled monolayers of PTCDA on epitaxial graphene.[3] We characterize the molecular ordering and electronic properties of these monolayers using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM). The molecules self-assemble into stable, well-ordered monolayers that are arranged in a herringbone phase with extended domains spanning hundreds of nanometers. At submonolayer coverage, PTCDA forms stable, isolated molecular islands. The molecular ordering is unperturbed by either defects in the epitaxial graphene or atomic steps in the underlying SiC surface. Scanning tunneling spectroscopy (STS) performed on the PTCDA monolayers reveals strong features in the electronic density of states that are distinct from the pristine graphene regions. The demonstration of robust, uniform organic functionalization of epitaxial graphene presents opportunities for exploring self-assembly chemistry on graphene, tailoring the chemical functionality of graphene, and templated growth and deposition of other materials as potential routes toward realizing graphene-based molecular electronic and sensing devices.

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* Morton S. Traum Award Finalist

[1] X.R. Wang, S.M. Tabakman, and H.J. Dai, *J. Am. Chem. Soc.* **130**, 8152-8153 (2008).

[2] P. Lauffer, K.V. Emtsev, R. Graupner, T. Seyller, and L. Ley, *Phys. Status Solidi B*, **245**, 2064-2067 (2008).

[3] Q.H. Wang and M.C. Hersam, *Nature Chemistry*, in press (2009).

11:40am **GR+EM+MS-TuM12 Effects of Reducing Conditions on Conductivity Change of Graphene Oxide**, ***H. Asano***, *Y. Shimogaki*, The University of Tokyo, Japan

Graphene is an attractive material for electronic devices since it has remarkable electronic properties, such as super high electron mobility. There are some methods to form graphene on SiO_2, however, it is difficult to cover SiO_2 substrate fully by flat graphene flakes on a wide area. For example, micromechanical cleavage of graphite can make graphene sheet on SiO_2, but the largest size of it will be within several micrometers. There is a demand, however, to graphene to use as conductive materials such as wiring material for ULSI interconnects and transparent and conductive electrode for solar cells and flat panel displays. These applications require large area coating and low process temperature. Then, graphene oxide (GO) coating and its reduction to form conductive graphene gets much attention. In the present work, we tried to reduce GO by gas-phase reduction and examined the resistivity change.

To obtain GO dispersion, graphite (Nippon Graphite Industry Co., LTD, SCB-100) was oxidised through the modified Hummer's methods. The dispersion was determined to be 0.965 wt% from the weight change of the dispersion. The dispersion was exfoliated by sonication, diluted by ethanol to 0.20 wt% and spin-coated on SiO_2/n-Si substrate, which was pre-treated by aminopropyltriethoxysilane (APTES). Spin-coated GO film was dried at room temperature. Reduction of GO film to form graphene was carried out in a vacuum, H_2, or formic acid ambient. The temperature of the substrate was ranged from 200°C to 1000°C, base pressure was 2.6×10^{-7} Torr, pressure of reducing agent (hydrogen or formic acid) was 5 Torr.

Thickness of spin-coated GO film was 30±5 nm and the film contents were 90 at% of C and 10 at% of O. Sheet resistance of the film was decreased by annealing in vacuum. The reciprocal of sheet resistance showed the Arrhenius type behaviour and minimum sheet resistance obtained in our work was 0.7 kΩ/sq. This result suggests some thermal activation phenomena that controls resistivity of GO. Thermal Desorption Spectroscopy (TDS) analysis showed that almost all O atoms were removed at 200°C, but very small amount of H_2O, CO, CO_2 was also detected above 200°C. The elimination of remaining oxygen as H_2O, CO, CO_2 at high temperature may be responsible for the Arrhenius type behaviour of the sheet resistance. Sheet resistance became one-third by the reduction using formic acid at 290°C compared with the reduction in vacuum or H_2. The sheet resistance treated over 700°C did not show any ambient dependency. We will also discuss the chemical bond state change observed by XPS and carrier concentration / mobility change measured by Hall measurement.

Electronic Materials and Processing
Room: B1 - Session EM-TuA

High-K Dielectrics on High Mobility Substrates
Moderator: R.M. Wallace, University of Texas at Dallas

2:00pm **EM-TuA1 Process Evaluation for InGaAs n-Channel MOS Device**, *N. Goel,* Intel Assignee at SEMATECH, ***J. Huang***, SEMATECH, *H. Zhao,* University of Texas-Austin*, I. Ok,* SEMATECH*, J. Lee,* University of Texas-Austin*, P. Majhi,* Intel Assignee at SEMATECH*, P.D. Kirsch*, SEMATECH **INVITED**

With the fundamental limits to the aggressive device scaling in Si CMOS technology, there is significant ongoing research exploring alternate channel materials such as III-V and Ge. These materials hold promise to produce more power efficient transistors compared to current silicon technology. Due to their high carrier mobility, compound III-V semiconductors such as InGaAs and InSb, are being investigated in surface as well as buried channel devices where the inversion or majority carriers determine the device characteristics, respectively. The success of III-V in potential CMOS technology depend on heterogeneous integration on silicon with thinner buffer layers; compatible, low leakage and thermally stable gate dielectric with low interface state density; as well as defect free junctions with low external or access resistance. In addition it is key to develop, standardize and orient various physical and electrical characterization techniques to probe and evaluate the interface and bulk characteristics effectively and correctly at the atomic level. Significant amount of promising research is being done in these modules and there still remain several opportunities to reduce parasitic contributions.

2:40pm **EM-TuA3 Band Alignment at High-κ/III-V Interfaces Grown by Atomic Layer Deposition**, ***A. Wan***, *D. Mastrogiovanni, L. Yu, H.D. Lee, T. Feng, E. Garfunkel, T. Gustafsson,* Rutgers University*, M. Xu, P. Ye*, Purdue University

Band offsets and Fermi level pinning are extremely important issues for metal-oxide-semiconductor (MOS) device structures. In particular, there is increased interest in III-V semiconductor/ high-κ dielectric materials as a future replacement to conventional Si-based complementary MOS technology. In this work, we present band alignment measurements of Al2O3 grown by atomic layer deposition (ALD) on n-GaAs and p-GaAs by combined x-ray (XPS) and ultraviolet (UPS) photoemission spectroscopy. Influence of processing conditions (pre-growth, during growth, and post-growth) and substrate orientation on the Fermi level pinning is discussed. Pinning effects are more problematic on n-GaAs than p-GaAs, due in part to the fact that n-GaAs more readily forms As oxides that have been attributed to high interface gap state densities that cause pinning. Interestingly, at the first few layers of ALD grown at "self cleaning" conditions,[1, 2] native oxides on the GaAs for both n-type and p-type are significantly reduced, but the interfaces on n-GaAs are still strongly pinned. Best results for un-pinning of the Fermi levels between n-GaAs and p-GaAs is observed for Al2O3 / GaAs(111) samples having clean interfaces, grown at condition, and post-deposition annealing at 600° C in forming gas.

1. M. M. Frank, G.D.W., D. Starodub, T. Gustafsson, E. Garfunkel, Y. J. Chabal, J. Grazul, and D. A. Muller, Appl. Phys. Lett. 86, 152904 (2005).
2. H.D. Lee, T.F., L. Yu, D. Mastrogiovanni, A. Wan, T. Gustafsson, and E. Garfunkel, Appl. Phys. Letters (submitted), 2009.

3:00pm **EM-TuA4 Reduction of Native Oxides on GaAs during Atomic Layer Deposition of Al_2O_3**, ***H.D. Lee***, *T. Feng, L. Yu, D. Mastrogiovanni, A. Wan, T. Gustafsson, E. Garfunkel*, Rutgers University

The integration of high-*k* dielectrics with high mobility III-V semiconductors is important due to the need for higher speed and lower power electronic devices than are offered by Si-based technologies. While high-*k* dielectric deposition on GaAs and InGaAs semiconductors appears particularly promising, the removal of native oxides and the growth an ideal dielectric layer remains a serious challenge. This obstacle arises in part from the high density of defects present at most GaAs-dielectric interfaces, and is related to Fermi-level pinning at the interface. Several groups have shown that chemical cleaning and subsequent passivation of the interface prior to dielectric deposition can greatly reduce the interface state density (D_{it}). However, few passivation solutions are practical for future large scale CMOS device manufacturing. Although several studies (including our own) have shown the reduction of native oxides on GaAs and InGaAs during atomic layer deposition (ALD) of dielectrics, detailed structural and chemical information about the interface and reduction process have not been reported. We have examined depth profiles of the elements in native oxides and ALD-deposited Al_2O_3 layers on GaAs substrates with an integrated tool that enables ALD growth with *in situ* characterization by medium energy ion scattering spectroscopy (MEIS). Films were also analyzed by x-ray photoelectron spectroscopy (XPS).

We will present data on the reduction of surface "native" oxides from GaAs substrates following reactions with trimethylaluminum (TMA) precursor. MEIS and XPS measurements after one single TMA pulse without oxygen exposure show that ~65% of the native oxide including ~75% of the As oxides are reduced, and a 5Å oxygen rich aluminum oxide layer is formed. XPS also shows that 3 additional TMA pulses reduce all As oxides to a level below our detection limit, and the Ga oxides were also reduced substantially. Further MEIS study of Al_2O_3 grown with the normal atomic layer deposition cycles of TMA and water shows that the growth rate of Al oxide during the reduction of native oxides is faster than the rate after the reduction. The preferential interface reduction of native oxides (especially AsO) helps create a higher capacitance, lower interface defect density CMOS gate stack.

4:00pm **EM-TuA7 Arsenic-dominated Chemistry in the Acid Cleaning of InGaAs and InAlAs Surfaces**, ***Y. Sun***, Stanford Synchrotron Radiation Lightsource*, P. Chen, M. Kobayashi, Y. Nishi,* Stanford University*, N. Goel, M. Garner, W. Tsai,* Intel Corp.*, P. Pianetta*, Stanford Synchrotron Radiation Lightsource

The surface cleaning of InGaAs and InAlAs is studied using Synchrotron Radiation Photoelectron Spectroscopy. Thermal annealing at 400°C can not completely remove the native oxides from those surfaces. Elemental arsenic build-up is observed on both surfaces after acid treatment using HCl, HF or H_2SO_4 solutions, which is similar to acid-cleaned GaAs surface. Cleaned InGaAs surface is oxide free but small amount of aluminum oxide remains on cleaned InAlAs surface. The common chemical reactions between III-As semiconductors and acid solutions are identified and are found to be dominated by arsenic chemistry.

4:20pm **EM-TuA8 Wet Treatment for Se Surface Passivation of GaAs and Ge for Advanced CMOS Applications**, ***F.S. Aguirre-Tostado***, CIMAV-Monterrey, México*, A. Herrera-Gómez,* CINVESTAV-Qro, México*, R.M. Wallace*, University of Texas at Dallas

Surface passivation of III-V and Ge semiconductors is a remaining problem to realize CMOS scaling beyond the 22 nm technology node. Zinc-blende and diamond structure (100) surfaces could be passivated with a single monolayer of divalent atoms like S or Se. In this presentation we show a wet chemical treatment method for the passivation of III-V and Ge (100) substrates with Se and S. The treatment consisted of the dipping of the substrates on a dilution of metallic Se into a 22% ammonium sulfide solution. The treated surface showed 3D structures that are attributed to either clustering during the treatment or during the N2 drying step. AFM, SEM and XPS were used to analyze the surface morphology of the passivation layer and chemical bonding with the substrate atoms. C-V and J-V characteristics of MOS capacitors with and without Se passivation are discussed.

4:40pm **EM-TuA9 The Effect of "Self-Cleaning" ALD Growth on the Electrical Properties of Metal/ High- κ /GaAs and Metal/high-κ/Ge Metal/ MOS Capacitors**, ***L. Yu***, *H.D. Lee, T. Feng, D. Mastrogiovanni, A. Wan, T. Gustafsson, E. Garfunkel*, Rutgers University

The ideas of using high-κ dielectrics as gate oxide and high mobility semiconductor as channel material are promising means of prolonging the scaling of CMOS technology to post Silicon era. However, it has been extremely challenging to produce a high quality oxide/channel interface that yields sufficient device performance for future CMOS. The unwanted chemical species such as residue native oxide, surface carbon, and hydro-carbon can result in defect states at the interface or inside dielectrics. These states can enhance carrier scattering and degrade device threshold voltage. Several recent studies, including ours, showed that, above certain temperature, volatile metal-organic precursors such as TMA can chemically react with the native oxides on the GaAs or InGaAs surface, result in effective removal of native oxide species, and chemically clean interface. This effective is known as the "self-cleaning" ALD growth. Previous studies are largely based on *in situ* XPS and MEIS measurements on ALD grown samples at various stages during the first few cycles. In this work, we will report on the effect of "self-cleaning" ALD growth and post ALD forming gas annealing on the electrical properties of metal/Al_2O_3/GaAs

MOS capacitors. We found the combination of the two treatments can significantly enhance the device C-V characteristics. Our preliminary results showed that frequency dispersion of ~2% per decade in the accumulation capacitance and interface state density (D_{it}) of ~$5x10^{12}$ eV^{-1} can be achieved. We also correlated the electrical result with XPS and MEIS studies of the ALD grown Al_2O_3 films and as well as electronic structure at Al_2O_3/GaAs interface. We will also report on the "self-cleaning" growth study of high-κ (Al_2O_3 and HfO_2) on Ge substrate and corresponding electrical result on MOS-CAPs.

5:00pm **EM-TuA10 Characterization of the "Clean-Up" of the Germanium Surface by ALD using Trimethyl Aluminum and Water**, ***M. Milojevic***, University of Texas at Dallas, *R. Contreras-Guerrero, M. Lopez-Lopez,* CINVESTAV-IPN, Mexico, *J. Kim, R.M. Wallace*, University of Texas at Dallas

The "clean-up" effect on III-V substrates has recently been well documented.[1] For the purpose of this study the "clean-up" of Ge oxides by ALD is explored using XPS. By interrupting the ALD process following individual precursor pulses for in-situ monochromatic XPS analysis the reaction mechanisms can be studied in unprecedented detail. As in the case of III-V substrates native germanium oxides are found to be reduced strongly by TMA. Interestingly if the sample is treated with a plasma nitridation technique a GeON layer is grown that appears impervious to this reaction. This is not unexpected given the reports of the stability of GeON formed by ion rather than radical based plasma processes.[2] Oxide free germanium surfaces behave analogously to a surface with initial native oxides since they are oxidized measurably prior to the first TMA pulse due to residual oxidants in a commercial ALD chamber. The unique aspect of the TMA driven "clean-up" is exposed when comparing it to the reduction of interfacial oxides by a thin metallic aluminum layer.[3,4,5,6] In this case in addition to the reduction of germanium oxides the aluminum layer also results in Ge-Al bond formation. In contrast "clean-up" of the oxide by TMA is characterized by a preferential reduction of higher oxidation states of germanium and the absence of any detectable reduction products on the surface.

This work was supported by the FCRP Focus Center on Materials, Structures and Devices and the Texas Enterprise Fund.

REFERENCES

[1] Milojevic, et al., APL 93 (2008) 202902.

[2] Sugawara et al., J. Vac. Sci. Technol. B 2(5), Sep/Oct 2006.

[3] Larsson et al., J. Vac. Sci. Technol. A 7(3), May/June 1989.

[4] Waite et al., J. Vac. Sci. Technol. A 11(4), July/Aug 1993.

[5] Oshima et al., Vac. Sci. Technol. A 12(2), Mar/Apr 1994.

[6] Margaritondo et al., J. Vac. Sci. Technol. A 1(2), Apr/Jun 1983

5:20pm **EM-TuA11 Processing Controlled Substrate Reactions for Deposition of Monoclinic Textured HfO_2 Thin Films on Pre-Oxidized and Nitrided Ge (001) Substrates**, *K.B. Chung, L. Miotti,* ***K.P. Bastos***, North Carolina State University, *D. Nordlund,* Stanford Synchrotron Research Lightsource (SSRL), *G. Lucovsky*, North Carolina State University

2 nm thick films of HfO_2 have been deposited on Ge(001) substrates by remote plasma chemical vapor deposition for (i) multiple etching cycles in dilute HF followed by distilled water rinsing, and (ii) an in situ remote plasma-assisted nitridation (RPAN) process. In a second set of studies, the step(i) pre-clean was replaced by a basic re-clean using methanol and NH_4OH. Studies by X-ray absorption spectroscopy (XAS) in O and N K edge regimes, were used to monitor HfO_2 nano-grains morphologies. Previous studies indicated epitaxial textured HfO_2 and TiO_2 films were obtained on Ge(001) surfaces. However, these studies were based on a recipe that worked, and did provide insights to significant connections between pre-cleaning and post deposition annealing. We have found two aspects of processing are crucial, and these were evaluated spectroscopically. Electrically active defects in metal-oxide-semiconductor test devices indicated high-defect densities correlated directly with Ge and O reacting with HfO_2 in the interfacial transition region, resulting in mixed-morphology grains.

Interfacial and bulk film degradation are also detected in XAS O K edge measurements. The occurrence of a monoclinic (m-)HfO_2 E_g edge structure is associated with Ge-O free interfacial transition regions. Ge-O interfaces results in tetragonal (t-)HfO_2, or mixtures of t-HfO_2 and m-HfO_2 grains. Acidic and basic pre-cleans each followed by an RPAN process prevented reactions between Ge-O surface bonding and plasma-excited HfO_2 precursors, consistent with textured m-HfO_2 films. Spectroscopic ellipsometry indicated that Ge-O bonding was significantly higher for acidic pre-cleans compared with basic pre-cleans. Post deposition annealing cycles with textured m-HfO_2 films were consistent with this difference. Two step annealing after the acidic clean, the first at 550°C in Ar, and the second at 800°C in Ar, resulted in textured m-HfO_2 directly in contact with a reconstructed Ge(001) surface. N K edge XAS, had previously indicated complete release of N after annealing to 700°C in Ar. In contrast, with less Ge-O interfacial bonding in the basic pre-clean, Ge-O and Ge-N interfacial bonds were eliminated sequentially during an 800°C anneal in Ar. O K edge XAS for HfO_2 with the X-ray polarization in the direction of the dimer rows of Ge(001) wafers, or perpendicular to that direction indicated similar textured growth. This is consistent with the textured m-HfO_2 films having nano-grains aligned at ±45° relative the dimer row direction.

Electronic Materials and Processing
Room: Hall 3 - Session EM-TuP

Electronic Materials and Processing Poster Session

EM-TuP1 Direct Growth of Hexagonal InN Films on 6H-SiC by RF-MOMBE, ***W.-C. Chen***, *C.N. Hsiao*, National Applied Research Laboratories, Taiwan, *D.P. Tsai*, National Applied Research Laboratories and National Taiwan University

Wurtzute InN films were prepared on 6H-SiC substrate by self-designed plasma-assisted metal-organic molecule beam epitaxy system without buffer layer. In our report, we discussed the effects of substrate temperature on structural and optical properties of InN films. The crystalline and microstructure of the thin film was further characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), respectively. Electrical and optical properties were evaluated by Hall and photoluminescence (PL) measurements. XRD results indicated that InN films were polycrystalline and preferential grown along c-axis orientation. Two-dimensional growth mode was clearly shown from SEM images. However, cracks due to the lattice and mainly large thermal expansion coefficient mismatch were observed as well. Cross-sectional TEM images revealed that the InN films were grown continuously from the 6H-SiC substrate, and c-axis lattice constant was about 0.57 nm. Room-temperature PL spectra showed the emission peak is located at ~ 0.83 eV and sheet carrier concentrations is 7.9×10^{15} cm^{-2}. It was found that the optoelectronic properties and crystalline quality can be improved significantly by optimizing growth temperatures.

EM-TuP2 Evolution of the Electrical Conductivity of Amorphous Carbon Nitride Films in Terms of Disorder Parameters and Density of States, *F. Alibart, O. Durand-Drouhin, A. Zeinert, M. Benlahsen*, ***M. Lejeune***, LPMC - UPJV, France

In this study, we discuss the correlations between electrical and optical properties of highly sp^2 amorphous carbon nitride for the development of electronic devices applications. The amorphous carbon thin films have been deposited using reactive plasma ($Ar+N_2$) radio frequency magnetron sputtering. The partial pressure of nitrogen has been used to vary the optoelectronics properties of the films.

The optical gap has been investigated using UV-visible-NIR spectroscopy and linked to the disorder parameter W^{-1}. The electrical conductivity has been studied in the temperature range of -170°C to 300°C and has revealed the presence of two conductivity modes. These results have been interpreted as a function of the density of states (DOS) evolution. The microstructural evolutions of the films with nitrogen incorporation have been investigated by Raman spectroscopy and IR absorption spectroscopy.

The disorder parameter W^{-1} has shown a linear dependence with the optical gap in this range of materials (highly sp^2 carbon films) and has been interpreted as a measure of the overall disorder (structural and topological). At low nitrogen partial pressure, nitrogen incorporation promotes the graphitization and the clustering of the sp^2 phase. The preferential contribution of disorder has been identified as an increase of topological disorder (cluster size dispersion). The increase of electrical conductivity in this stage has been correlated to the increase of disorder and has revealed an increase of the sp^2 connectivity consistent with an increase of the cluster size.

The decrease of conductivity for the higher nitrogen content has been interpreted in a specific model for highly sp^2 materials (adaptation of Robertson's two phase model). The proportion of CN triple bonds has been identified as a major effect on the material connectivity affecting the optoelectronic properties of the films.

EM-TuP3 Characterization of $Zn_{1-x}Mn_xO$ / ZnO Hollow Nanosphere Structures, ***D.R. Liu***, Instrument Technology Research Center, Taiwan, *W.H. Cho, C.Y. Su*, National Applied Research Laboratories, Taiwan, *D.P. Tsai*, National Taiwan University

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnMnO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the surface of polystyrene (PS) nanoshpere by atomic layer deposition (ALD). After removal of PS nanosphere by heating, ZnO hollow nanospheres were formed. Then the $Zn_{1-x}Mn_xO$ (x=0~0.1) coatings were grown on ZnO hollow nanospheres by Nd:YAG pulsed laser deposition(PLD). According to the results of high-resolution x-ray diffraction, the $Zn_{1-x}Mn_xO$ / ZnO hollow nanospheres are polycrystalline with a preferential growth direction of (002). Atomic force microscopy (AFM) and magnetic force microscopy (MFM) images show that the magnetic properties of Mn doped ZnO hollow nanospheres strongly depend on the Mn composition fraction and the size of nanospheres. Photoluminescence spectra demonstrate ultraviolet emission peaks which have shift with the increase of Mn ion concentration. The temperature-dependent magnetization (M-T) curves of the $Zn_{1-x}Mn_xO$ hollow nanospheres were measured by a superconducting quantum interference device (SQUID) magnetometer and also depend on the Mn composition fraction and the size of nanospheres.

EM-TuP5 Lifetime and Defect Characterization of Engineered Germanium-on-Silicon Wafers for III-V Photovoltaics, ***J. Sheng***, *D. Leonhardt*, University of New Mexico, *J.G. Cederberg, M.S. Carroll*, Sandia National Laboratories, *S.M. Han*, University of New Mexico

Demand for low-cost, light-weight, mechanically strong, high-efficiency multijunction solar cells has motivated the development and use of high-quality Ge-on-Si (GoS) heterostructures to integrate III-V films. However, such integration poses many engineering challenges, ranging from lattice mismatch, to thermal expansion coefficient mismatch, to non-planar morphological evolution. To eliminate antiphase domain (APD) boundaries in GaAs grown on GoS, in particular, the Ge surface on GoS substrates must maintain the crystallographic off-cut of the underlying Si. Here, we report a slurry-free chemical-mechanical polish step used to planarize the GoS surface. The root mean square (RMS) roughness of the resulting Ge surface is less than 1 nm. We have also characterized polished GoS substrates for their electrical properties. Due to nanoscale heterojunction engineering involving a SiO_2 template, the experimentally measured recombination velocity (SRV) at the Ge-Si interface approaches 9×10^3 cm/s. Capacitance-voltage (C-V) measurements are also used to determine the density of electrically active defects in the Ge layer of the GoS heterostructure. The *p*-type defect density is approximately 2×10^{16} cm^{-3}. Currently, more steps are taken to reduce the density of active defects.

EM-TuP6 Imaging Characterization Techniques Applied to Cu(In, Ga)Se_2 Solar Cells, ***S. Johnston***, National Renewable Energy Laboratory, *N. Call*, Colorado School of Mines, *R. Sundaramoorthy, I. Repins*, National Renewable Energy Laboratory

Imaging techniques developed over the past few years have the potential for quick and useful solar cell characterization. While initially applied to silicon, imaging techniques such as photoluminescence imaging, electroluminescence imaging, and lock-in thermography can also be successfully incorporated into Cu(In,Ga)Se_2 solar cell development and process feedback. These techniques are capable of collecting images that provide values of minority-carrier lifetime, diffusion length, series resistance, and shunting. While point measurements such as transient decay lifetimes yield quantitative results that are valuable to research and development, imaging data can often be collected in seconds or less with better spatial resolution and be correlated to important solar cell parameters.

EM-TuP7 High Rate Deposition of TiO_2 Films by Reactive Sputtering for Dye Sensitized Solar Cells, *Y. Sato, T. Hashimoto, A. Miyamura*, ***Y. Shigesato***, Aoyama Gakuin University, Japan

Dye-sensitized solar cells have attracted attentions as next generation solar cells which have possibility to perform high efficiency with low cost. In recent years, various applications of the cells, such as colorful or flexible solar cells fabricated on polymer substrates, have been suggested. In conventional processes to form the TiO_2 photoelectrodes in the cell, the substrates should be annealed at higher temperature than 500 ºC, which make it difficult to deposit TiO_2 films on polymer substrates. Sputter depositions should have advantages in fabricating the window-size uniform coatings of anatase TiO_2 at low temperature. In this study, dye-sensitized solar cells with TiO_2 photoelectrodes deposited by reactive magnetron sputtering on flexible substrates were fabricated and characteristics of the cells were investigated. A dual magnetron sputtering (DMS) system was used for the sputter deposition of TiO_2 [1-3]. This system consists of two magnetron cathodes with Ti metal targets, a dc power source with a 50 kHz pulse unit and plasma control unit (PCU) with a feedback system of plasma emission intensity (Fraunhofer Institut fur Elektronenstrahl-und Plasmatechnik, FEP). In the PCU, the plasma emission intensity of the Ti line at 500 nm was transformed into photovoltage (OEI) in order to control O_2 flow ratio. TiO_2 films were deposited on ITO/PET films and FTO glass substrates. Unipolar pulse or pulse packet modes were used for the sputter depositions. In order to control O_2 flow ratio in "transition" and "oxide" regions, oxidation of the target surface was precisely controlled using the feedback system. Sputtering power of each target was kept at 5 kW. Film thickness of TiO_2 was 3-10 μm. A sandwiched photovoltaic device was fabricated with N3-sensitized TiO_2 photoelectrode and Pt-coated glass as a counter electrode. The deposition rates of both the pulse modes were about 7 nm/min in the "oxide region" and about 40 nm/min in the "transition region". The maximum value of conversion efficiency in this study was 3.7 % which was obtained in the cell with TiO_2 deposited with unipolar pulse mode in the oxide mode on FTO glass substrate. On the other hand, the cell with TiO_2 deposited in the pulse packet mode on ITO PET-films performed 1.25 %. Furthermore, we also recognized that TiO_2 with high photocatalytic decomposition activity showed high conversion efficiency where TiO_2 with poor photocatalytic activity showed poor conversion efficiency.

[1] S. Ohno, Y. Shigesato, et al., Thin Solid Films 445 (2003) 207.

[2] S. Ohno, Y. Shigesato, et al., Jpn. J. Appl. Phys. 43 (2004) 8234.

[3] S. Ohno, Y. Shigesato, et al., Thin Solid Films 496 (2006) 126.

EM-TuP8 Life-time Improvement of CdTe/CdS Solar Cells by Application of TiN Diffusion Barrier to Cu_2Te Back Contacts

***C. Lim**, J. Park, S. Ryu,* Chosun University, Korea*, N. Kim,* Chonnam National University, Korea*, W Lee*, Chosun University, Korea

CdTe is one of the most convincing materials for thin-film solar cells shaped as the CdTe/CdS heterojunction structure. The formation of back contact is the most important and immediate problem to be solved with the low-resistance and excellent stability because the formation of an ideal ohmic contact to CdTe is very difficult with the most metals. Copper (Cu) compounds or copper-doped materials were generally employed for the back contact including ZnTe:Cu, Cu_xTe, Cu_xS, and Cu-doped graphite due to its high electrical conductivity, and similar electron affinity to CdTe. However, copper is easily and rapidly diffused to CdTe material; the life-time of CdTe/CdS solar cells is remarkably reduced because the diffused impurity of copper play roles of recombination center and shunt pathway. Therefore, the investigations for an improvement of life-time were widely performed on the formation of the alternative materials without copper or the heat-treatment of copper-containing materials. In this study, a diffusion barrier layer of TiN for an anti-diffusion of copper was employed with the Cu_2Te back contacts. TiN is well known as the diffusion barrier because of its good thermal/chemical stability, and low contact-resistance. The relation between the thickness of TiN layer and the diffusion of copper was analyzed by AES depth profile. The energy conversion efficiency and life-time at the optimized thickness was compared and analyzed to the specimen without the passivation layer. The improved life-time of CdTe/CdS solar cells with the good energy conversion efficiency was successfully obtained by the application of the optimized thickness of TiN diffusion barrier.

EM-TuP9 Intermediate Band Optical Transitions in ZnTe:O for Photovoltaics

*W. Wang, S.C. Lin, **J.D. Phillips**,* The University of Michigan*, W.K. Metzger*, National Renewable Energy Laboratory

The introduction of radiative electronic states within the bandgap of a semiconductor provide a mechanism for enhanced absorption of solar radiation and corresponding increase in short circuit current, while maintaining a large open circuit voltage. Approaches to introduce an intermediate band include the incorporation of quantum dots and doping of isoelectronic impurities. One promising material system is ZnTe (E_G=2.3eV), where the incorporation of oxygen provides a highly radiative state 0.4eV below the conduction band. In this work, the optical properties and photovoltaic response of ZnTe:O grown by molecular beam epitaxy on GaAs substrates will be presented. Photoluminescence measurements confirm a strong radiative transition for oxygen doping. Time-resolved photoluminescence measurements indicate a fast decay process from the conduction band, and a slow radiative decay from the oxygen states. Diodes consisting of ZnTe:O absorbers confirm that the response wavelength is extended to wavelengths beyond 900nm. Measurements consisting of two-photon excitation at wavelengths below the bandedge (650nm and 1550nm) further confirm transitions via intermediate band states. A device model for ZnTe:O intermediate band solar cells will be presented based on measured material parameters, and will be applied to determine both realistic and ideal conversion efficiencies attainable.

EM-TuP11 Characterization of the Electronic Structure of Dye-Sensitized Solar Cells

*S. Gutmann, M. Wolak, M.M. Beerbom, **R. Schlaf**,* University of South Florida

The electronic structure of the interfaces in dye-sensitized solar cell structures was investigated using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS). Electrospray thin film deposition in high vacuum was used to build the interfaces of interest directly in vacuum without exposure to the ambient. Electrospray enables the fabrication of clean, essentially uncontaminated thin films of organic molecules and nanoparticles directly in vacuum. The experiments focused on the investigation of the indium tin oxide (ITO)/nanocrystalline TiO_2 interface, as well as the characterization of the $TiO_2/RuL_2(NCS)_2$ [cis-bis(4,4'-dicarboxy-2,2'-bipyridine)–bis(isothiocyanato)-ruthenium(II)] ("N3", a prototypical dye used in many currently pursued device structures)-dye interface. Both TiO_2 and N3 films were built up in several steps. After each step, characterization by XPS and UPS was performed. The resulting sequence of spectra allowed the determination of charge injection barriers and interface dipoles at the ITO/TiO_2 and TiO_2/N3 interfaces. A particular focus of the experiments was the investigation of the influence of different surface conditions of the ITO on the electron injection barriers between TiO_2 and ITO.

EM-TuP13 Gas Sensing Mechanisms in Sub 6nm Thick Heterostructure Organic Thin Film Transistors

***J.E. Royer**, S. Lee, C.N. Colesniuc, I.K. Schuller, W.C. Trogler, A.C. Kummel*, University of California, San Diego

Understanding vapor interactions with organic thin films is key to application of organic thin films in chemical sensing. Ultra-thin organic thin film transistors (OTFTs) fabricated using only 4 monolayers (4ML) of metal phthalocyanines (MPc) are model devices for studying sensing physics since analyte adsorption is almost entirely restricted to the air/MPc interface since adsorption within the grain boundaries is minimal. Even in ultra-thin MPc OTFT heterostructures the films are sufficiently thin that gas adsorption occurs primarily from interfaces instead of grain boundaries. In an ideal ultra-thin heterostructure, gas adsorption should occur only at the interfaces thereby creating carrier traps which alter the conduction in the OTFT channel. This was directly investigated using MPc heterostructure OTFT s. The response to isophorone doses for metal free phthalocyanine (H_2Pc) OTFTs and cobalt phthalocyanine (CoPc) OTFT s were compared to OTFT s fabricated with bilayer films (CoPc/H_2Pc and H_2Pc/CoPc). The sensitivity to isophorone is more than 5 times greater for H_2Pc OTFTs than CoPc OTFTs, and the desorption kinetics fit a single exponential decay for H_2Pc whereas a bi-exponential decay is required for CoPc. The heterostructure OTFT responses did not strongly correlate with the H_2Pc or CoPc OTFTs which suggests a combination of surface doping and adsorption at the H_2Pc/CoPc interface. This could lead to highly sensitive OTFT sensors based on multilayered MPc film structures.

EM-TuP15 Microstructural Analysis and Luminescent Study of Thin Film Zinc Germanate Doped with Manganese

*K.H. Yoon, **J.H. Kim**,* Chungbuk National University, Korea

Thin films of zinc germanate doped with manganese (Zn_2GeO_4:Mn) were fabricated by radio frequency planar magnetron sputtering, and their microstructural characteristics and luminescent properties were studied. X-ray diffraction measurements showed that the as-deposited Zn_2GeO_4:Mn films were of amorphous structure in nature. Field emission scanning electron microscopy and grazing incidence x-ray reflectivity analyses revealed that the Zn_2GeO_4:Mn films had a smooth surface morphology. The Zn_2GeO_4:Mn films exhibited a high optical transparency in the visible wavelength region with the peak transmittance of 0.926, which is very close to the transmittance of the quartz substrate alone. The Zn_2GeO_4:Mn films became crystalline by the post-deposition annealing above 700 °C in air and the annealed films possessed a rhombohedral polycrystalline structure with a random crystallographic orientation of grains. The broad-band photoluminescence (PL) and cathodoluminescence (CL) emission spectra were obtained from the annealed films. The emission extends from 470 to 650 nm with a maximum at around 535 nm in the green range, which is accounted for by the intrashell transition of $3d^5$ electrons from the $^4T_1$ excited-state level to the $^6A_1$ ground state in the divalent manganese ions.

EM-TuP16 Evaluation of ITO Films Deposited by Pulsed Electron Deposition

*H. V Nampoori, V. Rincon, **M. Chen**, S. Kotru*, University of Alabama

Transparent conducting oxides (TCO) are the materials which combine visual transparency with high electrical conductivity. TCO films such as Indium Tin oxide (ITO) find its applications in photovoltaics, flat panel displays, electrochromic devices etc. ITO films are commonly grown by sputtering technique and presently meet current needs and quality for device applications. However, to achieve such good quality films, the films are grown at elevated substrate temperatures. This work explores a relatively newer vapor deposition technique known as pulsed electron deposition (PED) for the growth of ITO films where the films are deposited at room temperature. A commercially available target of ITO (90/10) was used as the source material. Films were deposited on soda lime glass and on Si (100) substrates. The oxygen pressure in the chamber during growth was varied from 2.8 mTorr to 22 mtorr. All the films were deposited for 5000 pulses. To evaluate the quality of grown films, various characterization techniques were employed. The optical transparency and the electrical conductivity of the films were found to be improving with increasing Oxygen pressure. Effect of Oxygen chamber pressure on resistivity, surface morphology, optical constants and carrier concentration on the films has been carried out. Details about the film preparation and evaluation of film properties will be presented.

EM-TuP17 Investigation of Oxide/InAs Interface via STM, STS, and KPFM, *W. Melitz*, ***J. Shen***, *A.C. Kummel*, University of California, San Diego

III-V MOSFETs have the potential to produce superior devices but formation of low defect density oxide-semiconductor interfaces is critical. While silicon surfaces are highly reactive due to their partially filled dangling bonds, some III-V surfaces have very low reactivity due to absence of partially filled dangling bonds and therefore might be able to form superior interface to high-k dielectrics if processes induce defect formation is avoided. Atomically resolved scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) were employed to determine the atomic and electronic structure of clean InAs surface and oxide/InAs semiconductor interfaces. Kelvin probe force microscopy (KPFM) can be utilized to support the STS and to provide further information on the surface or interface electronic properties. The InAs samples are first annealed at low temperatures to remove a protective arsenic cap, and heated to high temperature to prepare clean InAs(001)-(4×2) surfaces; the (4×2) surface is indium rich and therefore oxidation resistant which is favorable for oxide deposition. An oxide is deposited with a high temperature effusion cell and STS/KPFM measurements are performed to probe the surface Fermi level. SiO has the potential to form an excellent interface to ALD deposited HfO_2 since the $Si/SiO_2/HfO_2$ gate stack is known to have excellent electronic properties. STM images reveal that SiO forms cluster structures on the InAs(001)-(4×2) after annealing and does not desorb from the surface nor diffuse into the substrate after 800 K annealing. STS spectra for submonolayer SiO coverages deposited at 300 K on InAs(001)-(4×2) have shown the Fermi level is close to the conduction band for both n-type and p-type samples consistent with KPFM studies. For submonolayer SiO coverages deposited at 700 K on p-type InAs(001)-(4×2), STS shows the Fermi level near midgap consistent with partial unpinning; better electronic structure is expected for higher coverages of SiO. In_2O could act as a protection layer during high-k ALD and can be removed after ALD by high temperature annealing. STM images of In_2O deposited InAs(001)-(4×2) and annealed at 650 K show that In_2O forms has highly ordered structures. After annealing above 700 K, the In_2O desorbs from the surface and the pristine original clean InAs(001)-(4×2) is observed with no additional defects. Oxides are known to diffuse through HfO_2 and ZrO_2 so ALD deposition on In_2O could be followed by an annealing step which removes the In_2O to form a high-k/InAs without any ALD induced defects. STS and KPFM experiments on In_2O are ongoing.

EM-TuP18 Scaling Behaviors of Silicon Nitride Layer for Charge Trapping Memory, ***D.H. Li***, *I.H. Park, J.-G. Yun, J.H. Lee, D.-H. Kim, G.S. Lee, Y. Kim, S.H. Park, W.B. Shim, W. Kim, S. Cho, B.-G. Park*, Seoul National University, Korea

The scaling behaviors of silicon nitride, as charge trapping layer in embedded nonvolatile (poly) silicon-oxide-nitride-oxide-silicon (SONOS) flash memory application is presented. The conventional SONOS structure shows not only electron back-tunneling and charge retention loss problem, but also similar non-trapping behaviors at 5 nm silicon nitride thickness in our previous work. Therefore, we adopted an ultra thin oxide-nitride-oxide (ONO) barrier to replace the single tunnel oxide in the conventional structure and achieved enhanced memory characteristics. In this paper, we continuously investigate the limitation of scaling behaviors of silicon nitride for bandgap engineered charge trapping memory, according to dimension scaling down tendency in memory cells. The bandgap engineered device consists of multi-layer structure of oxide-nitride-oxide-nitride-oxide, which is fabricated by low pressure chemical vapor deposition (LPCVD). Memory characteristics, such as program/erase speed, and charge retention are characterized by *Quasi-steady static C-V* observation by Agilent 4156C and Agilent 41501B. Detected memory windows (ΔV_{FB}), which is defined as the change of flat band voltage from programmed state to erased state, are 3.32 V, 3.73 V, and 4.05 V, when Fowler-Nordheim (F-N) stresses is applied in 5 nm thickness of silicon nitride at -13 V, -12 V, and -11 V, respectively. These experimental data shows excellent memory operation behaviors, and indicates further scalability of charge trapping layer compared to the conventional structures. Device reliability issue is also evaluated by charge retention measurement. Experimental data demonstrates that device embodies excellent reliable memory operation.

Acknowledgements This work was supported by “Tera-bit Level Nano Device Project”.

EM-TuP19 ESR Spectroscopy of VUV-irradiated HfO_2, *J.L. Lauer*, University of Wisconsin-Madison, *S.L. Cheng, B.B. Triplett*, Stanford University, ***J.L. Shohet***, University of Wisconsin-Madison, *Y. Nishi*, Stanford University

We compare the charging response and defect generation, produced by vacuum ultraviolet (VUV) irradiation, of rapid-thermally annealed (RTA) 4nm thick HfO2 to as-deposited HfO2 on Si substrates. The HfO2 dielectrics were irradiated to 11.6 eV photons. The surface potential of the HfO2 samples was measured before and after VUV irradiation with a Kelvin probe system. The surface potential was determined to be negative before VUV irradiation and positive after irradiation for all samples except the 4nm thick HfO2 layer that was RTAd at 1000C. Paramagnetic defects within the HfO2 samples with and without VUV irradiation were measured with Electron Spin Resonance Spectroscopy (ESR). The VUV-irradiated samples indicate the presences of both E’ and Ex centers. From VUV-spectroscopy, the valence-band structure and location of defects with the band gap of the HfO2 samples were determined and compared to density of states calculations to determine the origin of the electronic states measured. Initial results from VUV-spectroscopy suggest the presence of oxygen-interstitial defects (OID) located within the HfO2 layer and oxygen-deficient Si centers within the SiOx interfacial layer. We show the electronic states of OID in HfO2 line up in energy with oxygen-deficient Si centers within the SiO2 interfacial layer. We believe the oxygen-deficient Si centers are responsible for the accumulation of positive charge in the VUV irradiated HfO2 samples. We conclude that charge exchange between OIDs within HfO2 and the oxygen-deficient Si centers within the SiOx interfacial layer is very important for controlling the radiation-induced trapped charge in HfO2/SiOx/Si dielectric stacks.

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EM-TuP20 Annealing of ZrO_2 Thin Films Studied by Vacuum UV Spectroscopic Ellipsometry, *I. An, S. Lee*, ***H. Cheon***, *J. Kyoung, H. Oh*, Hanyang University, S. Korea

ZrO_2 is one of the high-k dielectrics which can be used for the storage capacitor in dynamic random access memory devices. However, the physical properties of ZrO_2 films are highly dependent on the preparation process and conditions. Particularly, the thickness and temperature effects are most important. In this work, we investigated the annealing effect of ZrO_2 films which were prepared at various thickness ranges using atomic layer deposition. Vacuum ultraviolet spectroscopic ellipsometry (VUV SE) was employed to study the optical and microstructural properties of zirconium oxide (ZrO_2) films. Also XRD and capacitance measurements were performed. ZrO_2 films thinner than ~4 nm remained amorphous even at elevated annealing. Meanwhile thicker films developed into crystalline phases and the degree of crystallinity depended on the thickness.

EM-TuP21 Fabrication of Multilayer Thin Film Micro-Cooling Devices, ***K. Hedgeman***, *M. Harris, Z. Xiao*, Alabama A&M University

Solid state thermoelectric cooling devices have been of current interest for hot-spot thermal management. Cooling hot-spots with high heat flux is becoming one of the most important technical challenges facing today’s IC industry. The rising temperature limits device minimization and decreases its lifetime. In this paper, we report to fabricate in-plane and cross-plane solid-state thermoelectric cooling devices using multilayered Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$ thin films. The Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$ multilayer thin films were deposited using sputtering deposition. The Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$ multilayer thin films have a periodic structure consisting of alternating Bi_2Te_3 and Sb_2Te_3 layers or Bi_2Te_3 and $Bi_2Te_{3-x}Se_x$ layers, where each layer is about 10 nm thick. The films were analyzed by XRD and SEM. The devices were fabricated using the standard integrated circuit (IC) fabrication process; pn junction diodes were fabricated as thermometers for the measurement of temperature in the devices. The fabricated in-plane and cross-plane multilayer thin film cooling devices and the achieved temperature difference from the cooling devices will be reported in the Conference. The developed devices could be a good candidate for the application of high-efficiency solid-state micro-cooling.

EM-TuP22 High-density Chalcogenide Nanostructure Arrays Fabricated by Self-aligned and Maskless Process with Modified Nanosphere Lithography, ***N. Kim***, *H. Yang, H. Lee*, Chonnam National University, Korea

Phase change random access memory (PRAM) was concerned about one of the strongest candidate of non-volatile memory although the fabrication of PRAM has encountered the technical limitations by plasma process induced damage at sub-100 nm sizes. Novel approaches have been attempted to realize the reliability and utilization with a cost-effective production for high-density phase change memories. Nanosphere lithography (NSL) is one of the most useful techniques for the formation of close-packed periodic nanostructures. Polystyrene nanospheres of 500 nm-diameter were arrayed orderly on the photoresist (PR)-covered bottom electrode after dipping the samples into the developer solution for a few seconds to make the PR surface hydrophilic enough. The polystyrene nanospheres-arrayed samples were exposed. Then, polystyrene nanospheres were removed by DI water in an ultrasonic bath before development of PR. The average diameter of holes was about 100 nm. $Ge_2Sb_2Te_5$ (GST) was subsequently deposited into the periodic nanoholes, and then PR was lifted-off. High-density chalcogenide arrays were simply and successfully established by the self-aligned and maskless process of NSL. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2007-412-J02003).

EM-TuP23 Investigation of Crystal Structure and New Ellipsometric Properties of Hexagonal CdS Epilayers

***D.J. Kim**, Y.D. Choi,* Mokwon University, Korea*, J.W. Lee,* Hanbat National University, Korea*, J.C. Sur*, Wonkwang University, Korea

High quality hexagonal CdS epilayer was grown on GaAs (111) substrates by the hot-wall epitaxy method. The crystal structure of the grown CdS epilayers was confirmed to be the hexagonal structure by X-ray diffraction pattern (XRD) and scanning electron microscopy (SEM) image. To explore binding states and their potential applications, the hexagonal structured CdS epilayers have been characterized using x-ray photoelectron spectroscopy (XPS). The optical properties of the hexagonal CdS epilayers were investigated in a wide photon energy range between 2.0-8.5 eV using spectroscopic ellipsometry (SE) at room temperature. The data obtained by SE were analyzed to find the critical points of the pseudodielectric function spectra, $< \varepsilon (E)>=< \varepsilon_1(E)>+i< \varepsilon_2(E)>$, such as E_0, E_{1A}, E_{1B}, E_0', F_1, and two E_2 structures. In addition, the second derivative spectra, $d^2\varepsilon(E)/dE^2$, of the pseudodielectric function of hexagonal CdS epilayers were numerically calculated to determine the critical structures. Four structures, such as E_0', F_1, and two E_2 structures, from 6.0 eV to 8.0 eV were observed, for the first time, at 300 K by ellipsometric measurements for the hexagonal CdS epilayers.

EM-TuP24 A Study on the In-Situ Phosphorus-Doped epi-$Si_{1-x}C_x$ Growth for NMOSFET Application

***J.-H. Yoo**, D.-K. Lee, D.-H. Ko,* Yonsei University, Korea

As the size of complementary metal oxide semiconductor (CMOS) technology devices scales down, studies on strained channel engineering using lattice mismatch have received considerable attention since conventional structures shows serious problems, such as the increase of leakage current and the decrease of channel mobility. Specifically, in order to improve the electron mobility in the channel for NMOSFETs, many researches about source/drain epi-$Si_{1-x}C_x$ are in progress because of the successful employment of source/drain epi-$Si_{1-x}Ge_x$ in PMOSFETs. However, due to the extremely low solid solubility of C in Si in thermodynamic equilibrium, it is difficult to grow epi-$Si_{1-x}C_x$ with $x > 1$ at %. Furthermore, thermal annealing processes for the electrical activation of source/drain implants after the epi-$Si_{1-x}C_x$ growth can easily precipitate C atoms out from the substitutional sites, causing the loss of stress and affecting the junction and transport properties. In-situ doped epi-$Si_{1-x}C_x$ can maintain the strained $Si_{1-x}C_x$ layers with heavy doping because the process need not contain ion implantation and activation annealing. In this paper, we investigated the formation and the thermal stability of in-situ Phosphorus doped epi-$Si_{1-x}C_x$ in order to apply these films to the source/drain region of the ULSI device. The native oxide on Si (100) wafers was completely removed by HF cleaning and 100 nm-thick Phosphorus doped $Si_{1-x}C_x$ films were immediately deposited by UHV-CVD. Disilane (Si_2H_6), monomethlysilane (SiH_3CH_3) and phosphine (PH_3) gases were used for Si, C and P sources, respectively. The strains of the $Si_{1-x}C_x$ layer were investigated by using HR-XRD. The microstructures were observed by using HR-TEM.

EM-TuP26 Photoinhibition of Conductance Switching by Cycloaddition Reactions between Adjacent Molecular Switches

***M. Kim**, J.N. Hohman, S.A. Claridge,* The Pennsylvania State University*, H. Ma, A.K.-Y. Jen,* University of Washington*, P.S. Weiss*, The Pennsylvania State University

Directed assembly and subsequent photomodulation of anthracene-terminated phenylethynylthiolate molecules provide a means to control charge transfer in molecular switches. These fully conjugated molecules were selectively inserted as lone molecules, or in pairs, into defect sites of *n*-alkanethiolate monolayers on Au{111}. Control of the assembly and a fixed molecular conformation on the surface allow a regioselective [4+4] cycloaddition between adjacent anthracene moieties under ultraviolet illumination. This photodimerization breaks the delocalized π network of the anthracene, which results in a dramatic conductivity decrease, observed as a photomodulated "off" state. The reaction between molecules also reduces stochastic conductance switching.

Electronic Materials and Processing
Room: B1 - Session EM-WeM

Organic & Molecular Electronics
Moderator: L.M. Porter, Carnegie Mellon University

8:00am **EM-WeM1 Nanoscale Guided Molecular Engineering of Organic Electro-Optical Materials**, ***D.B. Knorr***, *X. Zhou, Z. Shi, J. Luo, S. Jang, A.K.-Y. Jen, R.M. Overney*, University of Washington

Increasing complexity in bottom-up molecular designs of amorphous structures with multiple relaxation modes demand an integrated and cognitive design approach, where chemical synthesis is guided by both analytical tools and theoretical simulations. This is true of organic second-order nonlinear optical (NLO) materials, which are being actively pursued for applications in photonic devices. For practical applications, NLO materials must have both high macroscopic EO activity and thermal stability. High EO activity can be achieved by acentrically ordering a system containing a high density of high dipole chromophores via electric field poling at elevated temperatures. Thermal stability requires the system to have internal constraints to prevent collapse of the acentric order at operating temperatures. Recent efforts for achieving both requirements have focused on dendrons capable of self-assembly through arene-perfluoroarene (Ar^H-Ar^F) quadrupolar interactions within self-assembled glassy chromophore systems, which provided excellent EO activity above 300pm/V and good thermal stability.

In this study, nanoscale scanning probe based thermo-mechanical analyses, intrinsic friction microscopy (IFM) and shear-modulation force microscopy yield direct insight into the molecular enthalpic and entropic relaxation modes of these materials. Ar^H-Ar^F interactions of dendritic moieties for coarse self assembly are found to impose three phase relaxation regimes with two transition temperatures, T_1 and T_2. Energetic analyses based on IFM identify increasing temporal stability with increasing arene size for the low temperature regime. Electric field poling efficiency is found to be inversely proportional to entropic cooperative contributions. Based on a molecular dynamic simulation, activation energies are tied primarily to interactions between chromophore (dipole), dendritic (quadrupole) moieties and combinations thereof below the incipient glass transition temperature. Above T_1, molecular mobility becomes increasingly cooperative. Sufficient mobility exists in the region of $T_1<T<T_2$ to allow for chromophore acentric electric field alignment, as non-covalent interactions associated with stabilization of the system below T_1 are in competition with melt-like effects. Further, cooperativity increases with increasing arene size, and accounts for approximately 80% of the observed apparent activation energy above T_2. Although beneficial to temporal stability with increased operating temperatures, cooperativity was found to lower the poling efficiency. Future synthesis efforts therefore must balance cooperativity to obtain satisfactory results in both stability and efficiency.

8:20am **EM-WeM2 Perpendicular Interaction between Donor and Accepter Molecules on Au(111) Surface**, ***U.G.E. Perera***, Ohio University, *R. Mishima*, Osaka University, Japan, *S.-W. Hla*, Ohio University

When two types of molecules having opposite tendency to donate and accept electrons are put together, charge transfer between the molecules can take place. Charge transfer alters the frontier molecular orbitals, and thus it can be used to engineer materials having a wide range of properties. Investigation of the charge transfer processes at a molecular level is a new avenue of exciting research. Here, we present a low temperature scanning tunneling microscopy (STM) and spectroscopy study of single molecule level charge transfer process between decamethylmanganocene (Mn(C5Me5) 2) and 7,7,8,8- tetracyanoquinodimethane (TCNQ) on a Au(111) surface at 4.6K. Both molecules are deposited onto an atomically clean Au (111) surface at an ultrahigh vacuum environment. On Au(111), the TCNQ molecules form well ordered two dimensional self-assembled clusters while the Mn(C5Me5)2 molecules adsorb either on TCNQ layer or on the bare surface areas. The STM images show that Mn(C5Me5)2 molecules position on the surface with tilted cyclopentacene rings. A comparative tunneling spectroscopy between the Mn(C5Me5)2 /Au(111) and Mn(C5Me5)2/TCNQ/Au(111) assemblies clearly reveals the shift of frontier molecular orbitals and thus the detailed charge transfer mechanism induced by deposition of Mn(C5Me5)2 has been able to explain. This research is supported by the United States Department of Energy BES grant number DE-FG02-02ER46012.

8:40am **EM-WeM3 An Ultra-Thin Molecular Superconductor**, *K. Clark,* Ohio University, *A. Hassanien,* Nanotechnology Research Institute, Japan, *K.-F. Braun,* Physikalisch Technische Bundesanstalt, Germany, *H. Tanaka,* Nanotechnology Research Institute, Japan, ***S.-W. Hla***, Ohio University

Almost a century after its discovery by H. Kamerlingh Onnes, superconductivity continues to be an inspirational subject for many physicists because of its rich physical phenomena. Among a variety of superconducting materials, the organic superconductors are regarded as “unconventional superconductors” based on the different nature of their superconducting states as compared to the conventional BCS superconductors. A class of Bechgaard type5 charge transfer salts having a D_2A arrangement, where D and A are the donor and acceptor respectively, exhibit superconductivity in the bulk. Here, we form an ultra-thin Bechgaard salt with the smallest possible molecular-unit thickness composed of just a sheet of molecular layer having individual $GaCl_4$ molecules sandwiched between the chains of a double domino stacked BETS on a Ag(111) surface. Remarkably, scanning tunneling spectroscopy of this ultra-thin Bechgaard layer at 5.4K reveals a clear superconducting gap exhibiting d-wave pairing symmetry. Real space spectroscopic images with a molecular resolution provide an experimental paradigm: The stacked BETS chains in the layer act as the superconducting sites. In stark contrast to the high T_c superconductors, the spectroscopic maps clearly display nanoscale electronic order indicating a robust superconductivity down to an extreme spatial limit.

9:00am **EM-WeM4 Correlating Structure and Electronic Properties in Oligothiophene Monolayers, an AFM Study**, ***F. Martin***, *B. Hendriksen, A.J. Katan,* Lawrence Berkeley National Laboratory, *C. Mauldin,* University of California, Berkeley, *J.M.J. Frechet, M. Salmeron*, Lawrence Berkeley National Laboratory

Organic compounds are currently considered as the main building block of electronic devices that could lead to new commercial applications which include flexible electronics as well as organic photovoltaics. Correlating structural and electrical properties is a key requirement to understand charge transport in organic thin films.

We investigated the effect of crystallinity and grain boundaries on the conductivity of Langmuir-Blodgett oligothiophene monolayers using Current-Sensing Atomic Force Microscopy (CS-AFM).

We used the AFM tip as a tool to inject charges and manipulate the crystalline monolayer. We found that passing electrical current locally from the conductive AFM tip led to reversible charging of the native SiO2 layer supporting the film as far as microns away from the charge injection point. This effect, due to charge spreading through the crystalline monolayer, was used to image conduction pathways and study the effect of grain boundaries on the resistivity of the monolayer.

In addition, we found that scanning manipulation at loads in the order of 100nN lead to a 5 fold decrease of the monolayer conductivity in CS-AFM. Subsequent molecular resolution AFM revealed that the degree of crystalline order in manipulated regions of the monolayer had strongly decreased, offering a direct proof of the correlation between order and conductivity in organic monolayers.

9:20am **EM-WeM5 Transport through a Single Octanethiol Molecule Adsorbed on a Pt-modified Ge(001) Surface**, ***D. Kockmann***, *H.J.W. Zandvliet, B. Poelsema*, University of Twente, Netherlands

We have studied (single) octanethiol molecules adsorbed on a Pt-modified Ge(001) surface, using scanning tunneling microscopy/spectroscopy.

On a clean Ge(001) surface we deposited a submonolayer amount of platinum by evaporation. Patches of dimerized atomic chains form via self-organization on the surface during the subsequent annealing-step. We have decorated the Pt-modified Ge(001) surface with octanethiol molecules. STM at 77 K revealed that at low coverage the molecules selectively adsorb on the Pt chains and not on the underlying terrace. The molecules lay down on the Pt chains, in contrast to SAM's, where they stand upwards.

In order to distinguish between the octane-tail and the thiol-head of the molecule, we have performed STS above the different regions of the molecule, again at 77 K. We observed that the I(V) spectra recorded above the thiol-head were conspicuously different from the spectra recorded above the octane-tail. From that we could determine the molecular orientation of the adsorbent.

In addition, we have measured current-time traces on the adsorbed octanethiol molecules. Throughout these experiments we turned off the feedback-loop of the STM. Then each measurable rearrangement or conformational change of the molecule is reflected in the I(t) traces. During these measurements we occasionally found a sudden dramatic increase in current from 1 nA (set point current) to values between 10-15 nA. The residence times at this high current varied between 10-40 seconds. In most cases the current jumps back to its original set point value of 1 nA within the open-loop measurements, which typically last for 50-100 seconds. STM images recorded after the open-loop experiments revealed that the octanethiol molecules remained at their original position.

From these observations we concluded that during the I(t) measurements the molecule wagged its tail upward, thereby making contact with the tip of the STM. Hence, we measured electron transport through the molecule instead of electron tunneling from tip to molecule. The derived single molecule resistance, 100-150 MΩ, is in accordance with literature.

9:40am **EM-WeM6 Modulation of Charge Injection and Transport in Poly(3-hexylthiophene)-Based Field-Effect Transistors by Self-Assembled Monolayers**, ***K.A. Singh***, *T. Nelson, J. Belot, R.D. McCullough, T. Young, T. Kowalewski,* Carnegie Mellon University*, P. Nachimuthu, S. Thevuthasan,* Pacific Northwest National Laboratory*, L.M. Porter*, Carnegie Mellon University

Charge injection and transport in bottom-contact poly(3-hexylthiophene) (P3HT) based field-effect transistors (FETs), wherein the Au source and drain contacts are modified by self-assembled monolayers (SAMs), is reported. Four SAMs of different chemical composition were selected to either enhance or reduce charge injection across the contacts. The rr-P3HT films were drop cast from a solution in chloroform in a saturated environment. Prior to P3HT deposition the FETs were treated with octyltrichlorosilane (OTS) solution in hexadecane for 2 hrs, dried and then immersed in a solution containing one of the SAMs in ethanol for another 2 hrs. The contact resistance (R_C) was measured using the transmission line method and the effective field-effect mobility (μ) was determined from the linear region of the transistor characteristics. Treatment of FETs with the first two SAMs resulted in an increase in μ and a decrease in R_C, whereas treatment with the other two SAMs resulted in a decrease in μ and an increase in R_C. For example, in one case, μ increased from 0.15 to 0.20 $cm^2V^{-1}s^{-1}$ and R_C decreased from 0.61 to 0.34 MΩ; in the opposite case, μ decreased to 0.09 $cm^2V^{-1}s^{-1}$ and R_C increased to 0.90 MΩ. The electrical properties of the transistors correlate with changes in the metal workfunction by up to 0.9 eV, as estimated using ultraviolet photoelectron spectroscopy. Besides using the SAMs for tuning the charge injection, the monolayer formed by OTS on SiO_2 at the insulator/ P3HT interface resulted in improved morphology of the P3HT film, as observed by atomic force microscopy, and an associated increase of μ from 0.03 to 0.15 $cm^2V^{-1}s^{-1}$. In summary, the charge carrier injection and transport in P3HT-based FETs were successfully modulated by treatment with SAMs. The use of OTS at the SiO_2/P3HT interface also resulted in improved morphology and enhanced charge transport. Further details regarding the use of self-assembled monolayers will be presented along with the device and photoemission characteristics.

10:40am **EM-WeM9 Reliable and Selective Formation of Metallic Contacts to Organic Thin Films: Towards Molecular Electronics**, *P. Lu, Z. Shi,* ***A.V. Walker***, Washington University in St. Louis

We have investigated the selective deposition of copper on alkanethiolate self-assembled monolayers (SAMs) using electroless deposition. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. We demonstrate that useful deposition rates can be obtained by "self-seeding" - the immersion of the SAM in a solution containing Cu^{2+} ions prior to addition of the reducing agent, formaldehyde. The selectivity of the deposition is achieved by *increasing* the bath temperature to 45 ºC. At this temperature Cu deposition ceases on $-CH_3$ terminated SAMs but continues on –COOH terminated SAMs. Finally, and perhaps most importantly, copper penetration through SAMs can be prevented by the addition of adenine to the bath. The addition of adenine also leads to smooth film morphologies. Each of these effects is explained by the formation of complexes with the SAM terminal group. Copper-terminal group complexes lead to useful deposition rates and control of the selectivity of the deposition. The formation of adenine-terminal group complexes prevents Cu penetration through the monolayer. Similarly, we observe that strongly adherent nickel films can be selectively deposited on functionalized SAMs through careful control of the bath conditions, especially temperature and pH.

11:00am **EM-WeM10 Quantum Dot Polymer Light Emitting Device With a Zinc Oxide Nanoparticle Film**, ***L. Qian***, *Y. Zheng, J. Xue, P.H. Holloway*, University of Florida

A polymer light emitting device (PLED) with an active layer consisting of CdSe/ZnS or CdS/ZnS core/shell quantum dots (QDs), and an electron transport/passivation layer consisting of 5 nm ZnO nanoparticles has been studied. The complete device consists of a glass substrate with the following layers: glass/ITO/PEDOT-PSS/poly-TPD/QDs/ZnO/Al-top-contact. The PEDOT-PSS, poly-TPD, QD, and ZnO layers were all deposited from solutions using spin casting, while the ITO layer was sputter deposited and the Al contact was deposited by thermal evaporation through a shadow mask. Thus the device is predominantly a solution-processed QD-PLED with simple vacuum processing instead of thermal evaporation of multiple organic small molecule layers. The emitted color was tuned from blue (CdS/ZnS) to green or red (CdSe/ZnS) by adjusting the composition and size of the QDs. Use of the ZnO layer reduced the injection voltage for a brightness of ~200 cd/m^2 from ~11 to ~2.6 V (green light), and improved the stability with time. For example, an unencapsulated QD-PLED with a ZnO nanoparticle layer exhibited a stable ~200 cd/m^2 brightness for 18 hrs in ambient air, while a comparable device without the ZnO layer degraded from 80 to 6 cd/m^2 in 3 hrs under the same conditions. The reasons for these improvements will be discussed.

11:20am **EM-WeM11 Effects of Different Organic Passivation Layers on the Electrical Stabilities of Flexible Organic Thin Film Transistors under Cyclic Bendin**, ***Y.G. Seol***, *J.S. Park, J.H. Ahn, N.-E. Lee*, Sungkyunkwan University, Korea

One of the critical issues for applications of flexible organic thin film transistors (OTFTs) for flexible electronic systems is the electrical stabilities of the OTFT devices, including variation of the current on/off ratio (I_{on}/I_{off}), leakage current, threshold voltage, and hysteresis, under repetitive mechanical deformation. In particular, repetitive mechanical deformation accelerates the degradation of device performance at the ambient environment. In this work, electrical stabilities of the pentacene organic thin film transistors (OTFTs) employing various passivation layers were investigated under mechanical cyclic bending. Flexible bottom-gated pentacene-based OTFTs fabricated on flexible polyimide substrate with poly-4-vinyl phenol (PVP) dielectric as a gate dielectric were passivated by the solution-processed, evaporated, and plasma-deposited organic layers. For cyclic bending experiment of flexible OTFTs, the devices were cyclically bent up to 10^5 times with 5 mm bending radius. In the most of the devices after 10^5 times of bending cycles, the off-current of the OTFT with no passivation layers was quickly increased due to increases in the conductivity of the pentacene caused by doping effects from O_2 and H_2O in the atmosphere, which leads to decrease in the I_{on}/I_{off} and increase in the hysteresis. With passivation layers, however, the electrical stabilities of the OTFTs were improved significantly. In particular, the OTFTs with plasma-deposited organic layers showed the best electrical stabilities up to the bending cycles of 10^5 times compared to the devices with the solution-processed or thermal-evaporated organic layer. Changes in electrical properties of cyclically bent OTFTs with different organic passivation layers will be compared and discussed in detail.

Electronic Materials and Processing
Room: B1 - Session EM-WeA

Contacts, Interfaces, and Defects in Semiconductors
Moderator: K.L. Kavanagh, Simon Fraser University, Canada

2:00pm **EM-WeA1 Contact Resistance and Material Mixing at the Metal/Organic Interface**, ***Y.B. Kim***, *D. Jeon*, Seoul National University, South Korea

The properties of interface formed by depositing metal on an organic substrate is very different from those of an organic film deposited on a metal substrate, which is because metal atoms can easily penetrate into the loose organic substrate. The degree of mixing at the interface of metal-on-organic depends on the growth condition such as temperatrue and deposition rate. We have compared the morphology and the contact resistance of a Au electrode deposited on a pentacene film at room and liquid nitrogen temperature. The samples were prepared by thermally depositing two Au electrodes on a pentacene thin film. The resistance between the two Au electrodes was measured for different channel lengths between them so that the Au/pentacene contact resistance could be estimated by extrapolating the resistance curve to zero channel length. Figure 1 shows resistance vs channel length measured between two Au electrodes deposited at room and liquid nitrogen temperatures. For both samples, the resistance decreases with decreasing channel length. Between the two Au electrodes deposited at room and liquid nitrogen temperature, the latter yields smaller resistance and thus the smaller contact resistance when extrapolated. Atomic force microscopy revealed a much higher degree of interface mixing for Au deposited at room temperature. Interface mixing or alloying is a common method to make an Ohmic contact for the case of metal electrodes on Si. Our experiment implies that the same strategy may not be applicable to the case of metal electrodes on the organic substrates. The structural deformation of pentacene molecules seem to create traps rather than creating conductive channels. We performed Fourier transform infrared spectrascopy to check the amount of deterioration of pentacene molecules due to the Au deposition. For both liquid nitrogen temperature and room temperature deposition, the infrared peak intensity of pentacene decreased due to the Au deposition, but the peak intensity for the latter case decreased more. We will also discuss X-ray photoemission spectroscopy measurements.

2:20pm **EM-WeA2 Schottky Metal-GaN and AlGaN-GaN Interface Issues Critical to HEMTs**, ***P. Shah***, *I. Batyrev, M. Derenge, K. Jones*, US Army Research Laboratory

GaN devices promise advantages over other compound semiconductors including higher power amplification, increased linearity, and less temperature dependent degradation. But today current collapse, slow switching transients, and poor gain profiles are present and may be related to interface trap densities. To shed some light, we analyzed the interfaces found in GaN HEMTs and correlated results with amplifier performance characteristics and first principle atomic and electronic structure simulations.

MOCVD grown GaN Schottky diodes were mesa isolation etched, and KOH etched to remove Ga residue and surface defects. Then Ti/Al/Ti/Au Ohmic and Ni/Au Schottky contacts were deposited and annealed.

These blocked 340V in the off-state. KOH reduced surface roughness and improved the on-state performance (150mA at 3.5V in good devices). The undoped GaN layer had a free carrier concentration of $5x10^{16}$ cm^{-3} from CV measurements. The reverse bias exhibits a soft breakdown due to an initial depletion followed by a slower field spreading. For three devices, the forward (2V) and reverse leakage (-1 V) currents were (A) 45mA, $3.4x10^{-10}$A, (B) 17mA, $2.0x10^{-9}$A, and (C) 4 mA, $3.6x10^{-8}$A. Comparing the ideality factors for the three devices over a voltage range of 0 to 0.5 V, device (A) exhibited no bumps between 0.1 and 0.4 V (n = 1.04 at 0.2 V) and a smooth transition into the series resistance region, device (B) exhibited a bump at 0.4V with a peak n= 4.3. Device (C) exhibited a bump at 0.1V with a peak n=2.08.

These ideality factor bumps were seen with GaAs Schottky diodes and linked to interface trap densities. Our conductance measurements gave corresponding trap densities 0.3 eV from the band edge of (C) $1.02x10^{12}$, and (B) $7.9x10^{11}$ cm^{-2} eV^{-1}, and for (A) much less. Also, the interface trap time constants are (C) 97 ns and (B) 81.9 ns and for (A) much longer.

Our first-principle simulation model of a planar bonded metal-semiconductor interface included an inhomogeneity at the interface and semiconductor interface defect interactions with H atoms and OH radicals during KOH etching. We assume that N antisite defects are common defects in GaN causing point defect pinning. After KOH etching these defects are passivated by two hydrogen atoms forming complexes H-N(Ga)-H and OH-N(Ga)-OH. The complexes do not have dangling bonds and do not participate in hybridization with extended states of a metal. Formation of the complexes could improve the interface state associated electrical properties of the Schottky diode, smooth the GaN (0001) surface and remove oxides residues.

Vendor provided GaN HEMTs were similarly analyzed and will be discussed.

2:40pm **EM-WeA3 The Use of Simulations to Address Current Problems in Schottky Barrier Contacts**, ***S.E. Mohney***, *K. Sarpatwari, O.O. Awadelkarim, N.S. Dellas*, Pennsylvania State University **INVITED**

A combination of simulations and experiments often provides a powerful approach to address scientific and engineering problems. In this presentation, we describe two examples of research on contacts to semiconductors in which we use simulations to develop methods to analyze data collected from Schottky barrier contacts. In the first example, we present an approach to accurately extract the Schottky barrier height from an axial contact to a semiconductor nanowire. Modification of the method usually used to analyze current-voltage (I-V) data from microscale planar Schottky diodes is necessary because of the influence of the semiconductor nanowire surface adjacent to the Schottky barrier contact. Band-bending at this surface influences the shape of the depletion region at the metal/semiconductor interface and must be controlled. We accomplish this control with a wrap-around gate. By analyzing I-V data generated using a commercial device simulator, we identify a method to treat the data to accurately extract the Schottky barrier height. Using the same approach that worked well for the simulated data, we next analyze Schottky barrier contacts to silicon nanowires that we nanofabricated with wrap-around gates. In another investigation, we examine approaches to extract the Richardson constant from planar Schottky barrier contacts that contain nanoscale inhomogeneities. Using Tung's model for inhomogeneous Schottky barrier contacts, we generate simulated I-V data for contacts with inhomogeneities of different sizes, densities, and departures from the homogeneous background barrier height. Then we compare various published approaches for extracting the Richardson constant, identifying their strengths and weaknesses. This section of the presentation concludes with the recommendation of a new approach for treating experimental data, and the approach is demonstrated for Schottky barrier contacts to wide band gap semiconductors.

4:00pm **EM-WeA7 2009 AVS John A. Thornton Memorial Award and Lecture - Nanofabrication Chemistry: The Impact of Solid Interfaces**, ***F.A. Houle****, Fremont, California **INVITED**

The presence of an interface can impose distinct local conditions that can have an important influence on the outcome of a chemical reaction at a nanoscale level. Loosely, two broad types of phenomena can be identified. In one, the interface can serve as an impermeable structure that imposes concentration gradients on materials in contact with it, leading to measurably different chemistry than would occur in its absence. In the other, the interface can serve as a means of accelerating transport, building in significant blur to the contacted regions. Semiconductor fabrication processes are influenced by one or both, directly controlling how well methods developed for the microscale can be adapted to the nanoscale. Examples drawn from etching, deposition, photolithography and nanoimprint lithography will be discussed, illustrating some general principles that may potentially be used to advantage in materials nanoprocess design.

4:40pm **EM-WeA9 A Novel Route Towards Electrical Connection and Probing of Nano-scaled Devices on Semiconductor Surfaces**, ***J. Koeble***, *M. Maier,* Omicron NanoTechnology GmbH, Germany, *D. Jie, N. Chandrasekhar,* Institute of Materials Research and Engineering (IMRE), Singapore, *C. Joachim*, CEMES-CNRS, France

A major challenge in Nanotechnology is the incorporation of single nano-devices into larger integrated circuits. Although work on individual (and non-integrated) nano-structures such as molecules is intense, the question of their electrical connection with more than two probes (such as conventional SPM experiments) remains an open question. Established nano-lithography techniques such as EBL and FIB seem to not satisfy requirements for ultra clean and defined contact structures at the atomic scale. Traditional

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* John A. Thornton Memorial Award Winner

instrumentation for analysis is fundamentally limited: How to cover the dimensional range of an integrated circuit (mm) down to the atomic scale of a single molecule device and at the same time to have an adequate integrated navigation system? To meet these requirements, we have established and being advancing a new approach integrating SPM technology with high resolution electron microscopy: (1) Bridging dimensions by combined SEM (down to below 3nm resolution) and STM operation at the atomic scale; (2) Rapid SEM navigation of four local STM probes; (3) Individual probe fine positioning by high resolution STM imaging; (4) STM based probe approach for "soft-landing" of sharp and fragile probes and controlled electrical contact for transport measurements. To open a route for fundamental evaluation of the potential of single molecule devices, this instrumental technology is employed to establish electrical connection for local transport measurements. As a model system, we have chosen Au nano-islands on MoS$_2$. These islands represent contact pads, each electrically connected by an individual STM probe. As good band gap (approx. 1.3eV transverse gap) semiconductor, MoS$_2$ has the potential to sufficiently decouple those nano-structures electrically at low voltage. Those Au triangular nano-islands have a lateral size of typically 10-30nm and form an "atomically" ultra clean and defined metal-semiconductor interface. We present measurements that prove (1) SEM based navigation and STM based electrical contacting with a tip radius in the 10nm range: (2) reproducible Schottky like IV properties for the individual STM tip/Au nano-island/substrate contact; (3) surface conductance measurements with variable inter-island distance down to 17nm; (4) comparison with surface conductance measurements of the bare MoS2 substrate. We also show that the individual STM probe can be employed under SEM to manipulate those Au nano-islands [1] with high precision in order to generate arbitrary multi probe planar contact configurations.

[1]: J.S. Yang, D. Jie, N. Chandrasekar and C. Joachim J. Vac. Sci. Tech. B, 25, 1694 (2007).

5:00pm **EM-WeA10 Dynamic Imaging and Analysis of the Charge Trapping at the Metal-Organic Interface**, ***C. Kim***, *D. Jeon*, Seoul National University, South Korea

Understanding of metal/organic interfaces is one of the key issues for the design of high performence organic devices. We have studied the interface properties of the Al/pentacene/Au sandwich samples by performing electrostatic force microscopy (EFM) and measuring *I-V* curves at various temperatures. The Al/pentacene/Au sandwich sample showed a typical rectifying *I-V* curve as expected from the energy diagram. Interestingly, the current increased with time when a constant forward bias was applied. In order to understand the reason, we performed EFM of the cross section of Al/pentacene/Au to measure the time variation of the charge density across the interface. The result suggested that there was a charge accumulation at the Al/Pentacene interface and that the reason for the current increase with time was the lowered potential barrier caused by the trapped charges. From the temperature-dependent *I-V* measurement, we could estimate the amount of barrier lowering. When the measurement was performed in UHV environment, the current increase was not observed, which suggested that water molecules diffused into pentacene in the ambient condition played a role of trap sites.

5:20pm **EM-WeA11 Au-Al$_{0.27}$Ga$_{0.73}$N Shottky Barrier Formation and Charge Carrier Mobility Estimation**, ***S. McHale***, Air Force Institute of Technology, *Ya. Losovyj*, Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln and J. Bennett Johnston Sr. Center for Advanced Microstructures and Devi, *D. Wooten, J. McClory, J. Petrosky*, Air Force Institute of Technology

Au-AlGaN Shottky barrier formation is observed using Au evaporation on an Al$_{0.27}$Ga$_{0.73}$N strained Wurtzite structure, thin film that is deposited on GaN. Low Energy Electron Diffraction was performed to verify the integrity of the Au deposition. Energy dependent, synchrotron generated photoemission spectroscopy ranging from 15 to26 eV under UHV conditions clearly determines a Fermi edge shift of up to 0.5 eV. Charge carrier mobility is inferred using valence band mobility edge data.

Magnetic Interfaces and Nanostructures
Room: C1 - Session MI+EM-WeA

Magnetism and Spin Injection in Semiconductors
Moderator: Y.D. Park, Seoul National University, South Korea

2:00pm **MI+EM-WeA1 Anomalous Nernst Effect in Ga$_{1-x}$Mn$_x$As Ferromagnetic Semiconductors**, ***J. Shi***, University of California, Riverside **INVITED**

The origin of the anomalous Hall effect (AHE) in ferromagnets has been a subject of long-standing debate. Dilute magnetic semiconductors (DMS) provide an excellent test ground for clarifying the issues. In our study, we engineered a series of GaMnAs thin films with different doping levels and with perpendicular magnetic anisotropy which allows us to investigate both electrical and thermoelectric transport properties at zero magnetic field. Both Seebeck and Nernst coefficients (S_xx and S_xy) were measured simultaneously with the longitudinal and transverse resistivities (rho_xx and rho_xy). In addition to an usually large spontaneous or anomalous Nernst effect (ANE), we also found that both AHE and ANE arise from the same physical origin. When the temperature is varied, although the sign of AHE (rho_xy) remains unchanged, the sign of ANE (S_xy) switches at an intermediate temperature below Tc. Furthermore, we found that the same Mott relation which links the electrical conductivity and thermoelectric coefficients works very well for the anomalous transport. A simple Mott relation analysis rules out the extrinsic skew-scattering mechanism immediately with the sign change in S_xy. A further quantitative analysis of the overall temperature dependence yields exponent n=2 in rho_xy ~ rho_xx^n, indicating that the intrinsic spin-orbit effect is likely responsible for both AHE and ANE.

2:40pm **MI+EM-WeA3 Local Structure of Cr in the Epitaxial Ferromagnetic Semiconductor Cr-doped Ga$_2$Se$_3$/Si (001)**, ***E. Yitamben****, *T.C. Lovejoy, A. Pakhomov*, University of Washington, *S. Heald*, Argonne National Laboratory, *F.S. Ohuchi, M.A. Olmstead*, University of Washington

The III-VI compound Ga$_2$Se$_3$ is an intrinsic vacancy semiconductor which not only can be grown epitaxially on silicon, but, once doped with a transition metal, presents interesting potential for application in spintronics devices, since we have found it to be ferromagnetic at room temperature. Unlike III-V or II-VI materials, the intrinsic vacancies in Ga$_2$Se$_3$ create both multiple sites for dopant incorporation, raising the possibility of separate control of magnetic and carrier doping, and anisotropic band-edge states, which may increase both the Curie temperature and the magnetic anisotropy. This work presents experimental investigations of Cr-doped Ga$_2$Se$_3$ epitaxially grown on Si(100):As that probe interactions among structure, carriers and magnetism in this new class of dilute magnetic semiconductors.

Inclusion of a few atomic percent Cr into the Ga$_2$Se$_3$ lattice results in laminar semiconducting films that are ferromagnetic at room temperature, with a magnetic moment of 4 μ_B per Cr in 6 nm films, and 40% lower in 20 nm films. X-ray absorption and photoemission measurements reveal Cr in an octahedral environment; X-ray and low energy electron diffraction reveal a cubic structure with lattice constant close to that of the underlying silicon. This is surprising, since both the vacancies and Ga cations occupy tetrahedral sites in pure Ga$_2$Se$_3$.

Above ~6%, scanning tunneling microscopy (STM) reveals the formation of islands within trenches whose shape and size depend on the Cr concentration and whether or not a Ga$_2$Se$_3$ buffer layer is deposited first. The islanded films also exhibit room temperature ferromagnetism, though with about half the magnetic moment per Cr. Unlike low concentration films, they are metallic rather than semiconducting.

Acknowledgments: This work is funded by the NSF Grant DMR-0605601, NSF NER-0508216

3:00pm **MI+EM-WeA4 Ferromagnetism in Gd- and Si-co-implanted GaN**, *R. Davies, B. Gila,* ***C. Abernathy****, S.J. Pearton, C. Stanton*, University of Florida

Ion implantation has been studied as a magnetic ion incorporation method in semiconductor materials for spintronic applications due to excellent control over the amount of the implanted ion and the resultant magnetic properties of the implanted material. GaN thin films grown via metal-organic chemical vapor deposition (MOCVD) were co-implanted with Gd$^+$ ions with an energy of 155 keV and dose of 2.75 × 10^{10} cm^{-2} and Si^{4+} ions

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* Falicov Student Award Finalist

with energies of 5 keV and 40 keV and corresponding doses of 8×10^{11} cm^{-2} and 3.6×10^{12} cm^{-2}. Before annealing, x-ray diffraction measurements revealed that the implanted GaN thin films exhibited no secondary phase formation or clustering effects attributable to Gd. Superconducting quantum interference device (SQUID) magnetometer measurements indicated that a Gd- and Si-co-implanted GaN thin film exhibited about an order of magnitude higher magnetic moment than a Gd-implanted GaN thin film. Both of these thin films displayed ferromagnetic ordering and Curie temperatures above room temperature. The co-implanted GaN thin film also demonstrated a larger magnetic moment than a Gd- and Si-co-doped GaN thin film grown via molecular beam epitaxy (MBE) while possessing a smaller Gd concentration. The orientation of the applied magnetic field with respect to the thin film surface was seen to have an effect on the measured magnetic properties of the thin films. This orientation dependence may help elucidate the relationship between the defects produced by the implantation process and the ferromagnetic ordering exhibited by these materials.

4:00pm **MI+EM-WeA7 Structural and Electronic Properties of EuO and Gd-doped EuO Films Prepared Via Pulsed Laser Deposition**, *X. Wang, K. Fox, W. Wang,* ***J. Tang***, University of Wyoming, *M.J. An, K. Belashchenko, P.A. Dowben*, University of Nebraska-Lincoln

Methods to prepare EuO thin films reported in the literature include reactive thermal evaporation of Eu in the presence of oxygen gas and molecular beam epitaxy (MBE). We have successfully prepared single phase polycrystalline and epitaxially grown EuO and Gd-doped EuO via pulsed laser deposition (PLD) using metal targets. This opens a new route to the preparation of this interesting material with high quality. Samples prepared in vacuum exhibit the typical M(T) curve for a ferromagnet and have a Curie temperature of 70 K. When the samples were grown under ultrahigh purity H_2 flow, they show the “double-dome” feature characteristic of oxygen deficient EuO. Tc as high as 150 K has been observed for EuO. The increased Curie temperature is attributed to the magnetic coupling enhanced by the 4f-5d coupling between the Eu moments and doped electrons. Our results reaffirm that oxygen vacancies alone can substantially increase the Tc. Calculations on the phase diagram (for Gd+EuO), the effects of oxygen vacancies and associated band structures and density of states will be presented.

4:20pm **MI+EM-WeA8 Magnetic Molecules on GaN: A Low Temperature STM Investigation**, ***K. Clark***, *D. Acharya, V. Iancu, E. Lu, A. Smith, S.-W. Hla*, Ohio University

Spin electron interactions involving magnetic molecules and semiconductor surfaces are of great interest for the development of molecular spintronic devices. Due to its wide range of applications, GaN (0001) surface has received a special attention for the development of novel electronic devices. Here, we studied electronic and structural properties of TBrPP-Co molecules deposited on a freshly grown nitrogen polar GaN (0001) surface using a scanning tunneling microscopy and spectroscopy at 4.6 K under an ultra-high-vacuum condition. The TBrPP-Co molecule has a spin-active cobalt atom caged at the center of porphyrin unit and four bromo-phenyl groups are attached to its four corners. On GaN(0001), the molecules bind the surface via two molecular conformations: saddle and planar. In saddle conformation, the central part of the molecule is bent by lifting the two pyrrole units of the porphyrin macrocycle. STM images shows various self-assembled clusters of molecules on GaN(0001) surface. Within the self-assembled molecular clusters, the molecules are aligned either parallel or 90 degree rotated to each other. In the presentation, we will discuss the spin-electron coupling of this molecule-surface system. This work is supported by the Ohio University BNNT, NSF-PIRE: OISE 0730257, NSF-EMT: CCF-0622158, and the United States Department of Energy, DE-FG02-02ER46012 grants.

4:40pm **MI+EM-WeA9 Electrical Injection, Detection and Modulation of Spin Currents in Silicon**, ***O.M.J. van 't Erve***, *C. Awo-Affouda, A.T. Hanbicki, M.A. Holub, C.H. Li, P.E. Thompson, B.T. Jonker*, Naval Research Laboratory **INVITED**

The electron’s spin angular momentum is one of several alternative state variables under consideration on the International Technology Roadmap for Semiconductors for processing information in the fundamentally new ways. Significant progress has recently been made on spin injection into the technologically important semiconductor, Si, using vertical device structures. Here we will present the electrical injection, detection and magnetic field modulation of lateral diffusive spin transport through silicon using Fe/Al2O3 surface contacts. The tunnel contacts are used to create and analyze the flow of pure spin current in a silicon transport channel. A nonlocal detection technique has been used to exclude spurious contributions from AMR and local Hall effects. The nonlocal signal shows that a spin current can be electrically detected after diffusive transport through the silicon transport channel and the signal depends on the relative orientation of the magnetization of the injecting and detecting contacts. Hanle effect measurements up to 125 K demonstrate that the spin current can be modulated by a perpendicular magnetic field, which causes the electron spin to precess and dephase in the channel during transport. By changing the bias on the injector contact we can either inject or extract spin from the Silicon channel. Here we will show using Hanle and lateral spin-valve measurements that we can change the polarization of the spin accumulation by going from the injection regime to the extraction regime and we will compare the efficiency of spin-injection versus spin extraction.

The realization of efficient electrical injection and detection using tunnel barriers and a simple device geometry compatible with "back-end" Si processing should greatly facilitate development of Si-based spintronics.

This work was supported by ONR and core NRL programs.

5:20pm **MI+EM-WeA11 Order From Chaos: α-Fe(001)/GaAs(001)**, ***J.G. Tobin***, *S.W. Yu,* Lawrence Livermore National Laboratory, *S.A. Morton,* Lawrence Berkeley National Laboratory, *G.D. Waddill,* Missouri University of Science and Technology, *J.D.W. Thompson, J.R. Neal, M. Spangenburg, T.H. Shen*, University of Salford, UK

For many years, the technological possibilities of spintronic or magneto-electronic devices [1], particularly when coupled with potentially pure spin sources such as half-metallic ferro-magnets, [2] have engendered great interest. Despite the limitations encountered in such potential sources [3], there is still ample reason to pursue such concepts. This is because, in part, even with sources that operate below 100% polarization, technologically important devices should emerge. [1] However, the challenges of device integration remain significant even for cases with lowered expectations, because often the physical realities of intermixing, disorder and alloying can creep into the attempts to fabricate structures based upon ideal conceptual designs. Within this context, ferromagnetic-semiconductor interfaces are potentially important for the future applications of spintronic devices. One possibility for a room temperature spin injector is Fe/GaAs. The growth of Fe upon GaAs(001) has been studied with Photoelectron Spectroscopy (PES), including Spin-Resolved PES . Despite evidence of atomic level disorder such as intermixing, [4] an over-layer with the spectroscopic signature of α-Fe(001), with a bcc real space ordering, is obtained. The results will be discussed in light of the possibility of using such films as a spin polarized source in device applications. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. Work that was performed by UMR personnel was supported in part by the Office of Basic Energy Science at the U.S Department of Energy. Work that was performed by LLNL personnel was supported in part by the Office of Basic Energy Science at the U.S Department of Energy and Campaign 2 of WCI at LLNL. We would also like to thank J.A.D. Matthew, D. Greig, A.E.R. Malins, E.A. Seddon, and M. Hopkinson for their help with this project.

References

1. G.A. Prinz, Science 282, 1660 (1998).
2. R.A. de Groot, F.M. Mueller, P.G. van Engen and K.H.J. Buschow, Phys. Rev. Lett. 50, 2024 (1983).
3. P. Dowben, J. Phys. Condensed Matter 19, 310301 (2007).
4. J.D.W. Thompson, J.R. Neal, T.H. Shen, S.A. Morton, J.G. Tobin, G.D. Waddill, J.A.D. Matthew, D. Greig, and M. Hopkinson, J. Appl. Phys. 104, 024516 (2008) and references therein.

5:40pm **MI+EM-WeA12 Enhancement of Spin Injection Efficiency by Interface Modification for Fe and $Fe_{31}Co_{69}$ Thin Films on GaAs(001)**, ***S.F. Alvarado***, *G. Salis, A. Fuhrer, L. Gros, R.R. Schlittler*, IBM Zurich Research Laboratory, Switzerland

We report on a detailed study of the influence of ferromagnet/semiconductor interface modifications on the electrical spin injection efficiency of Fe and $Fe_{31}Co_{69}$ thin film electrodes into the GaAs(001) surface. These modifications are induced by: a) Varying the As/Ga surface concentration of GaAs(001); and b) Post-growth annealing of the ferromagnetic thin films. Electrical spin injection experiments are carried out in a non-local device geometry at temperatures between 2.5 and 300 K. Devices were fabricated by means of either optical, e-beam, or nanostencil lithography. Non-local spin signals in the range of 2V/A at a temperature of 5K have been detected between two strip electrodes, one 2 and the other 6 µm in width, 60 µm long, separated 3 µm from each other. The spin-polarization characteristics of the devices are observed to strongly depend on substrate surface preparation and annealing treatment of the metal/semiconductor devices. The latter has a very strong influence on the magnitude of the non-local spin polarization signal, which we observe to increase by about two orders of magnitude after annealing steps from 120 °C up to 290 °C.

Electronic Materials and Processing
Room: B1 - Session EM-ThM

Oxide Semiconductors
Moderator: S.M. Durbin, University of Canterbury, New Zealand

8:20am **EM-ThM2 Defect States in the Wide Gap Semiconducting Oxide Ga_2O_3**, ***T.C. Lovejoy**, S. Zheng,* University of Washington*, E.G. Villora, K. Shimamura,* National Institute for Materials Science, Japan*, F.S. Ohuchi, M.A. Olmstead*, University of Washington

Ga_2O_3 is a transparent wide gap semiconducting oxide with potential applications as a transparent conductive oxide (TCO) or phase change memory (PCM) materials system. The mechanism for conductivity in this material is still under debate. The long established picture involves conduction by oxygen vacancy defect states, but unintentional silicon doping may also contribute. A recent paper [Appl. Phys. Lett. 92 202120 (2008)] shows the conductivity can be intentionally controlled over three orders of magnitude by silicon doping on the order of typical Si impurity levels in Ga_2O_3 source materials. In light of this, the actual role of oxygen vacancies is unclear. We illuminate this issue by studying separately the contribution to the electronic density of states of single crystal β-Ga_2O_3 by intentional silicon doping and oxygen deficiency with X-ray photoemission spectroscopy (XPS). Ar^+ ion sputtering is an effective means of reduction that causes states to appear above the valence band maximum, which disappear on subsequent annealing. We demonstrate qualitative agreement with previously published density functional theory results [Nature Materials 7 391 (2008)] on the effect of oxygen deficiency in Ga_2O_3. Forthcoming hard x-ray photoemission and transport measurements will further elucidate this issue.

8:40am **EM-ThM3 Trends in Surface Electronic Properties of Oxide Semiconductors**, ***T.D. Veal**, P.D.C. King, C.F. McConville*, University of Warwick, UK **INVITED**

Oxide semiconductors have enormous potential for new and innovative uses and may also improve existing device applications. However, the fundamental properties of some of the oxide semiconductors (such as In_2O_3, Ga_2O_3 and CdO) remain either controversial or largely unknown. The semiconducting oxides have traditionally been grown using low cost, low quality techniques, such as sputtering, resulting in poor microstructure material with high levels of impurities and defects. The fact that some of these materials in their low quality form have seen significant industrial use as transparent conductors has perhaps contributed to the belated recognition of their possibilities as semiconductors in their purer form. Relatively recently, with the advent of high-purity oxide semiconductor films by high-quality growth methods, such as molecular-beam epitaxy and metal-organic vapor phase epitaxy, the fundamental properties have begun to emerge and the material characteristics have been vastly improved. Here the surface and bulk electronic properties of several such high-quality oxide semiconductors (In_2O_3, CdO, $SrTiO_3$, ZnO and SnO_2) will be reported. Optical, electrical and structural properties of the semiconducting oxide films will be presented, including data on the revision of the band gap of In_2O_3 from 3.7 eV to less than 3.0 eV [1]. Both the valence band density of states and the surface electronic properties of the oxide semiconductors have been studied using high-resoultion photoemission spectroscopy [1,2]. A common property of the materials with a high size and electronegativity mismatch between the cation and oxygen atoms is found to be the presence of a surface electron accumulation layer [3,4] which is in marked contrast to the electron depletion generally observed at the surface of conventional compound semiconductors. The origin of this phenomenon will be discussed in terms of the band structure of the semiconducting oxides. The five groups where the samples were grown are gratefully acknowledged.

[1] P. D. C. King, T. D. Veal, F. Fuchs, Ch. Y. Wang, D. J. Payne, A. Bourlange, H. Zhang,

G. R. Bell, V. Cimalla, O. Ambacher, R. G. Egdell, F. Bechstedt, and C. F. McConville,

Phys. Rev. B 79 (2009) in press.

[2] P. D. C. King, T. D. Veal, A. Schleife, J. Zúñiga-Pérez, B. Martel, P. H. Jefferson, F. Fuchs,

V. Muñoz-Sanjosé, F. Bechstedt, and C. F. McConville, Phys. Rev. B 79 (2009) 205205.

[3] P. D. C. King, T. D. Veal, D. J. Payne, A. Bourlange, R. G. Egdell, C. F. McConville,

Phys. Rev. Lett, 101 (2008) 116808.

[4] P. D. C. King, T. D. Veal, P. H. Jefferson, J. Zúñiga-Pérez, V. Muñoz-Sanjosé, and

C. F. McConville, Phys. Rev. B 79 (2009) 035203.

9:20am **EM-ThM5 STM and XPS studies of ITO (001) Surfaces**, ***H. Morales**, U. Diebold*, Tulane University

Tin-doped Indium Oxide (ITO) is a transparent conducting oxide and extensively used in flat panel displays, solar cells, and organic-light-emitting-diodes. Despite the industrial significance and versatility of this material, little is known about its surface structure.

Epitaxial In_2O_3 (001) thin films with a Sn content between 0 and 30 at% were grown on Yttria stabilized Zirconia YSZ (001) using oxygen-plasma-assisted molecular beam epitaxy (MBE). The growth was monitored with Reflection-high-energy-electron-diffraction (RHEED). Low-energy-electron-diffraction (LEED) showed well ordered surfaces.

Angle-resolved X-ray photoemission (ARXPS) performed *in situ* shows that Sn^{4+} substitutes In^{3+} in the In_2O_3 bixbyite lattice and Sn enrichment in the near-surface region. A shoulder at the *Sn* $3d_{5/2}$ peak at off-normal-emission angles indicates a Sn^{2+} oxidation state. The *O 1s* peak shows significant asymmetry in In_2O_3 and a more symmetric peak shape with increasing Sn content. This indicates that the charge imbalance, produced by substituting Sn^{4+} for In^{3+} in the In_2O_3 lattice, is compensated by introducing extra oxygen in the bixbyite structure.

Preparing a flat ITO (001) surface is challenging due to its polar character. A Sn concentration of more than 15 at% is necessary to stabilize ITO (001). Empty-states Scanning Tunneling Microscopy (STM) shows terraces 100 to 400nm^2 in size and an overall surface roughness of 0.5nm. In agreement with previous theoretical work we find that the ITO (001) surface is oxygen terminated. Features in atomically-resolved STM images are interpreted with a model involving dimerization of surface oxygen.

9:40am **EM-ThM6 Cyclic In-Situ Deposition and Etching for Growth of High-Quality Zinc Oxide by Metalorganic Chemical Vapor Deposition**, ***E.J. Adles**, D.E. Aspnes*, NC State University

Zinc oxide (ZnO) is a transparent conducting oxide with a room-temperature band gap of 3.37 eV. It is currently under investigation for magneto-optic applications and as a cheap alternative for optic and optoelectronic devices currently depending on gallium and indium. While epitaxial ZnO can be grown by a number of laboratory-scale methods, growth by industrial-scale processes such as metalorganic chemical vapor deposition (MOCVD) is hampered by particulate ZnO formed in the gas phase and by the natural tendency of ZnO to deposit in multiple orientations. Both prevent deposition of high-quality epitaxial material. After careful consideration of gas-phase chemistry and our real-time polarimetric data, we have developed a cyclic MOCVD growth process based entirely on diethylzinc where conditions are alternated between brief periods of deposition and etching. The gas-phase particles are used as the source of ZnO. The etching part of the cycle preferentially removes unwanted orientations, since these typically have higher free energies. The result is dense two-dimensional epitaxial ZnO. Because etching is driven chemically instead of thermally, infilling and smoothing occur at much lower temperatures and shorter time scales than previously discussed in the literature.

10:40am **EM-ThM9 Formation of Zn Nanoparticles on Single Crystal ZnO Surfaces with Ultraviolet Laser Irradiation**, ***E. Kahn**, S. Langford, T. Dickinson*, Washington State University

Many dielectric crystals color in the visible region of the spectrum under intense ultraviolet light such as excimer laser irradiation. We have shown previously that in many cases these are due to electron hole pair production via two photon absorption. Examples are coloration of alkali halides and alkaline earth halides where self=trapped excitons lead to formation of strongly absorbing defects. Recently we were surprised to see dramatic coloration of single crystal ZnO, a wide bandgap (3.37 eV) semiconductor of significant technological interest, under exposure to 193 nm ArF excimer laser radiation. The increase in absorption is very broadband, extending from the bandgap into the infrared, appearing as near black to grey. We present careful measurements of the properties of this coloration and determine its origin. We present convincing evidence that it is due to the formation of zinc metal nanoparticles residing on the surface of the irradiated region. This evidence involves AES, TEM, XRD, UV-VIS reflection and absorption spectroscopy as well as Positron Annihilation Spectroscopy. As expected, laser fluence has considerable impact on the size, number, and spatial distribution of these nanoparticles. We present a model for the production of this Zn metal rich surface and discuss applications including plasmonics. Related optical property measurement will be presented. Furthermore, we show that with suitable choices of laser exposure we are able to convert the originally n-type ZnO to p-type. We are carrying out additional experiments to confirm that this transformation is dependent on the formation of O-vacancies. Supportive UHV mass spectroscopy measurements of the emitted particles during laser exposure show copious release of atomic and molecular oxygen suggesting O depletion is occurring.

This work was supported by the U.S. Department of Energy, DE-FG02-04ER-15618

11:00am **EM-ThM10 Preparation of N-doped p-type ZnO Film by Metal-Organic Chemical Vapor Deposition**, ***W. Chen***, *Y. Chen, J. Liang, C. Lu*, National Dong Hwa University, Taiwan

ZnO is a promising material used in short-wave optoelectronic devices such as light emitting diodes. However, one important issue that should be resolved beforehand is the fabrication of p-type ZnO film, which is difficult due to various intrinsic donor defects inside ZnO crystals such as zinc interstitials or oxygen vacancies. Nitrogen (N) has been considered to be an effective acceptor dopant to realize p-type ZnO. In this work, we prepared N-doped p-type zinc oxide thin films deposited on sapphire by metal organic chemical vapor deposition. We have successfully prepared high quality p-type ZnO film by changing VI/II ratio (O_2 / DMZn flow ratio), and the p-type ZnO film can be fabricated reproducibility using this method. Dimethylzinc (DMZn) and N_2O were used as zinc precursor and N dopant source. The growth temperature was in the range of 300-400°C and the chamber pressure was 100 Torr. The O_2 flow rate is in the range 900-1100 sccm and DMZn carrier gas flow rate is in the range 2-10 sccm. We found ZnO film prepared using N_2O only as O source show n-type. After 800°C under O_2 ambient annealing for 1 hr, a few sample originally n-type became p-type. The p-type concentration is $1.4\text{x}10^{18}$ cm^{-3}. XRD shows higher ZnO (002) peak intensity of the film after annealing than that before annealing. On the other hand, if we use O_2 and N_2O together as O source during ZnO growth, most films show p-type even before annealing. XRD spectrum and PL analysis suggest that appropriate oxygen flows can improve the quality of ZnO film to eliminate those excessive donor defects. Hall measurement shows that the resistance is 0.24 Ωcm and its corresponding hole concentration is $7.16\text{x}10^{18}$ cm^{-3}. The N 1*s* peak in XPS spectra is located at 398.5 eV, which represent N–Zn bonds. The N–Zn bonds imply that N is located at O position in ZnO crystal and forms bond with Zn. N_O is known as an acceptor defect in the ZnO film, so the presence of N-Zn bonds suggest the acceptor formation in the ZnO film. Since N_2O is the only source for N, the formation of N–Zn bond suggests that using N_2O in the process is helpful in p-type formation of ZnO films.

11:20am **EM-ThM11 Growth of Ga-doped ZnO Thin Film Prepared by MOCVD for TCO Application**, *K. Chou*, ***J. Liang***, *Y. Chen, C. Yang*, National Dong Hwa University, Taiwan

The group-III elements, such as Al, Ga and In, are possible dopants for ZnO to improve the electric conductivity of ZnO thin film. Since Ga has lower cost than In and has higher oxidation resistance than Al, it becomes the preferred dopants for ZnO thin film for transparent conducting oxide (TCO) application. In the research, we used MOCVD method with Ga doping to prepare the Ga-doped ZnO thin film (GZO) on the corning-1737 glass substrate. We changed the amount of Ga doping into ZnO thin films to increase the carrier concentration and decrease the electric resistivity of ZnO thin film. We used dimethylzinc (DMZn) and oxygen as Zn and O sources, respectively, and kept both of them constant. The trimethylgallium (TMGa) was used as Ga source, and the Ga/Zn was controlled in the range of 0.8% to 2.8% by adjusting TMGa flow rate. From the top views of GZO thin films, we observed that there are small grains arranged loosely on the surface of the undoped ZnO thin film. After doping Ga into ZnO thin films the grains become bigger, and the arrangement of grains becomes compact. However, when the Ga/Zn flow ratio is over 1.6%, the grains of the GZO thin film become small again. The variation trend of grain size observed by SEM is similar with the results of FWHM in XRD spectra. The FWHM decreases as Ga/Zn flow ratio increases to 1.6%, but then the FWHM increases as Ga/Zn flow ratio increases from 1.6% to 2.8%. It implies the crystallinity of GZO thin films was improved with the Ga/Zn flow ratio and has the best crystallinity at 1.6% of the Ga/Zn flow ratio. Afterwards the crystallinity of GZO thin film worsens when the Ga/Zn ratio increases from 1.6% to 2.8%. The Hall measurement shows the electrical resistivity decreases with increasing Ga/Zn flow ratio, and the carrier concentration increases with Ga/Zn flow ratio. In addition, we found the mobility is still about 29 cm^2/Vs even as the carrier concentration has the highest value around 7.1×10^{19} cm^{-3}. It reveals that the Ga doping can significant improve the conductivity and increase the carrier concentration. Since the site which the Ga occupies in ZnO thin films can influence the electric behavior and the structure, we will use XPS to determine the Ga bond for determining the site of Ga occupied. Because the transparency is an important factor for TCO application, we will also show the transparency of GZO by the transmission spectra.

11:40am **EM-ThM12 Preparation of p-type ZnO by Codoping Method using Gallium and Arsenic**, ***H. Jen***, *Y. Chen, M.S. Wong, H. Kuo*, National Dong Hwa University, Taiwan

In this research, we successfully prepared p-type ZnO films by rapid thermal annealing (RTA) of Ga and As codoped ZnO films deposited by magnetron DC sputtering using target made of ZnO mixed with Ga_2O_3 and Zn_3As_2 powders. These codoped p-type ZnO films were deposited on undoped silicon substrates at 300°C and have hole concentrations of 10^{18}~10^{19} cm^{-3} and resistivities of 10^{-1}~10^{-2} ohm-cm. We changed the oxygen flow rate from 0 to 50 sccm and the RTA time for 30 seconds, 2 minutes, and 5 minutes. From the Hall measurement, the electrical conduction type of codoped ZnO film converted from n-type to p-type after RTA of the films at 1000°C for 30 seconds. But it converted to n-type conduction again for longer annealing time of 2 minutes and 5 minutes. The X-ray diffraction (XRD) data indicates the crystallinity of the codoped films is improved by increased RTA time. From the field emission scanning electronic microscopy (FESEM) observation, we found the grain size of ZnO increases with annealing time, but there is less significant change of grain size after 30 seconds of RTA. The result indicates the grain boundary may not affect the electrical conduction type. According to the room temperature photoluminescence (PL) spectra, we found that the sample prepared with oxygen flow rate of 30 sccm followed by RTA at 1000°C for 30 seconds in O_2 ambient had the highest near band edge (NBE) emission intensity. It indicates this RTA condition is the optimum RTA condition among other conditions. We found that the p-type ZnO films can be obtained with the same RTA parameter even though the ZnO films are prepared with different oxygen flow rate during deposition, i.e., the p-type conduction is independent of the oxygen flow rate in the deposition process and the ZnO films need an RTA process to activate the p-type conduction. From the X-ray photoelectron spectroscopy (XPS), we can not find the Ga-As bonding either in Ga 3d peak or As 3d peak. It indicates the Ga and As do not bond together in the ZnO film. This fact agrees with the codoping theory proposed by Yamamoto and Katayama-Yoshida. According to others researches and calculations, doped p-type ZnO films are produced in the oxygen-rich growth condition. We think the codoping method, which can lower the Madelung energy and activate the deep acceptor state may enhance p-type formation. Thus even in the zinc-rich condition, we can still obtain p-type ZnO thin films at appropriate RTA condition by codoping method.

Electronic Materials and Processing
Room: B1 - Session EM-ThA

Quantum Structures and Nitrides Devices
Moderator: F.Ren, University of Florida

2:00pm **EM-ThA1 Filling of Few Electron Quantum Dots Imaged and Characterized By Scanning Force Microscopy**, ***L.P. Cockins**, Y. Miyahara, S.D. Bennett, A.A. Clerk,* McGill University, Canada*, S. Studenikin, P. Poole, A. Sachrajda,* National Research Council, Canada*, P. Grutter*, McGill University, Canada

The ability of quantum dots to confine single charges at discrete energy levels makes them a promising platform for quantum computation where the intrinsic properties of single electrons, such as spin, act as the conventional 1 and 0 bit in a classical computer. In order to control initialization and to scale up the number of bits, an understanding of both the energy levels of single quantum dots and the variation between dots need to be characterized.

Self assembled quantum dots are of considerable interest in this field because their size, shape, and material can be controlled during the growth process. Controlling these properties is important as these influence the confinement potential, thereby controlling the energy levels of the dot. However, the method of growth makes positioning of the quantum dots difficult and usually they are randomly distributed over the sample surface. This, in addition to the small size of the dot, makes it challenging for lithography techniques to access the quantum dots to perform either charge transport or charge sensing measurements so that the dot properties can be measured.

An atomic force microscope can be used to spatially access the dots, and by applying a voltage between cantilever tip and back-electrode (beneath the dot), the energy levels of individual dots can be probed. At low temperatures the dots are in the Coulomb blockade regime and individual electrons can be controllably added by applying a sufficient bias voltage to overcome this electrostatic repulsive energy. The oscillating cantilever in these experiments is responsible for both loading/emptying the dots through electrical gating and also detecting tunneling events through a change in resonant frequency and/or the amount of energy required to maintain a constant oscillation amplitude. Electrical leads are not required in this experiment which not only leaves the surface electrostatically intact but also gives us the freedom to investigate any dot on the surface.

Using an atomic force microscope we demonstrate the ability to probe the energy levels in few electron self assembled InAs quantum dots. The charging energy, level spacing, and shell structure of single dots are extracted and supported theoretically. Multi-dot complexes are also investigated and pairs of dots which are either capacitively or tunnel coupled are observed. Increasing the oscillation amplitude of the cantilever allows for the additional electron to enter the dot at a higher energy level, in a way probing the excited states of the dot similar to excited state spectroscopy. These findings are also supported by theoretically.

2:20pm **EM-ThA2 InAs Lateral Quantum Dot Molecules with Controllable Configurations**, ***M.K. Yakes**, A.S. Bracker, C.D. Cress, J.G. Tischler, D. Kim, A. Greilich, D. Gammon, A.R. Laracuente*, Naval Research Laboratory

A quantum dot molecule (QDM) is formed when two or more quantum dots are close enough so that the electronic properties of each dot are affected by the presence of the other. Well controlled, vertically-stacked QDMs are now routinely grown for optical investigations.[1] [#_ftn1] For device applications, laterally coupled dots offer compatibility with existing gate technologies and advantages in scalability. However, growth of complex laterally coupled QDMs is more challenging than the vertically stacked dots.

One method for influencing the lateral position of self-assembled QDs is to introduce features on the substrate which will act as preferred nucleation sites for dot growth.[2] [#_ftn2] One promising technique is to use gallium droplet epitaxy to form a template for further dot growth. In droplet epitaxy, gallium is deposited without arsenic overpressure, forming metallic islands without a wetting layer. When these droplets are exposed to arsenic and annealed they crystallize into homoepitaxial mounds. When InAs is grown on these mounds, the islands appear to grow only on the sloping edges of these mounds. Previous structures grown with this technique have demonstrated flexibility in QDM configuration and excellent uniformity.[3] [#_ftn3]

In this presentation, we will describe new growth techniques that can be used to control the configurations of lateral InAs QDMs. By fixing the direction of the incident indium flux, the indium beam is shadowed by the GaAs mounds, so that InAs dots will only form on the sides of the mound which face the indium source. This allows new configurations of QDMs to be grown that cannot be formed using a rotating substrate. In addition, by capping first layer QDMs with GaAs or AlGaAs and growing additional strain-coupled dots, we demonstrate flexible and uniform three dimensional QDM configurations.

With atomic force microscopy it is not possible to determine the structure of the InAs dots once they are buried under a GaAs capping layer. Cross sectional scanning tunneling microscopy (XSTM) is an ideal technique to examine the final structure with atomic resolution. For bi-molecules, the interdot separation is 8 nm and the center to center distance is 30 nm, which makes them excellent candidates for investigations of electron tunneling using photoluminescence spectroscopy.

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[1] [#_ftnref1] E. Stinaff *et al., Science* **311** 636 (2006)

[2] [#_ftnref2] R. Songmuang *et al., Appl Phys Lett* **82** 2892 (2003)

[3] [#_ftnref3] J.H. Lee *et al., Appl Phys Lett* **89** 202101 (2006)

2:40pm **EM-ThA3 MBE Growth and Optical Properties of GaN Quantum Structures**, ***N. Grandjean***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

In this presentation, we will first address the fabrication of III-V nitride based quantum dots (QDs) using molecular beam epitaxy with ammonia as nitrogen source. We will focus on strain-induced Stranski-Krastanov (SK) growth mode in GaN/AlN system and point out the effect of surface free-energy. It is indeed observed that the V/III ratio controls the 3D island formation in a reversible way. In a second part, we will discuss the optical properties of an ensemble of GaN/AlN QDs. Photoluminescence experiments evidence that the transition energies are dominated by a giant quantum confined Stark effect, which results from the presence of a huge built-in electric field of several MV/cm. This electric field is inherent to wurtzite III-nitride based heterostructures when they are grown along a polar axis. It comes from spontaneous and piezoelectric polarization discontinuities arising at interfaces between different materials. Then, mesa are prepared aimed at single dot spectroscopy using micro-photoluminescence. Optical signatures of excitons and bi-excitons are clearly seen on the luminescence spectra. Both positive and negative binding energies are deduced depending on the dot size. A phenomenological model including the built-in electric field present in the dots well accounts for the experimental observations.

3:40pm **EM-ThA6 Growth and Process Technologies for High Efficiency InGaN-Based Light-Emitting Diodes**, ***J.-I. Chyi**, H.-C. Lin*, National Central University, Taiwan **INVITED**

Raising external quantum efficiency has always been the focused area of research in InGaN blue/green light-emitting diodes (LEDs). In the early 90s, breakthroughs in material growth and p-type doping restored the heat of pursuing high brightness InGaN LEDs. It was, however, several other key technology advancements that made solid-state lighting era a reality. Among these technologies, patterning sapphire substrate and semiconductor surface is one of the most essential one. In this report, we present three different patterning techniques, which emphasize different aspects of patterning technology and show how they impact the external quantum efficiency as well as other characteristics of InGaN/GaN quantum well light-emitting diodes. We report the epitaxial growth of GaN on patterned sapphire substrates (PSSs) with micro-lens of three different geometric shapes by metal-organic chemical vapor deposition. Growth mode analysis shows that micro-lens with sharp tips prohibit the nucleation and growth of GaN on their top and lead to a wider lateral growth region with low dislocation density. The external quantum efficiency (at 20 mA) of LEDs is improved by nearly 20% by using this technique. However, the residual strain instead of dislocation density in the GaN buffer layer plays a heavier role in the external quantum efficiency of the light-emitting diodes. Although the PSS approach has been shown effective and gives the freedom of pattern design, it requires extra photolithographic steps that make it more complicated and costly. We propose a maskless wet-etching method to prepare patterned sapphire substrates, namely naturally etched sapphire substrates (NESSs). At 20 mA, nearly 20% improvement in external quantum efficiency is achieved even the LEDs have already an indium-tin oxide transparent contact layer and a roughened surface. It has also been shown that the uniformity of device performance across the wafer is not a concern when using this technique. The surface patterning techniques reported so far involve spatially with the active region of LEDs and make the patterning process very critical in maintaining device performance as well as reliability. To avoid this problem, we propose to pattern the dicing streets around the LED chips where no electrical contacts are present. Forming a triangular lattice consisting of dry-etched circular holes with a diameter/periodicity of 3/3 µm on the dicing street. The external quantum efficiency (at 20 mA) of the LEDs is increased by about 13%. Meanwhile, the forward voltage increases only 0.05 V and improved reliability is observed as expected. In addition, a novel growth technique for improving internal quantum efficiency will also be presented. During the growth of quantum wells, a growth interruption is introduced at each InGaN to GaN interface while having trimethylindium (TMIn) and NH3 continue flowing into the reactor. Photoluminescence, X-ray diffraction, atom force microscopy, and high-resolution transmission electron microscopy indicate that the treatment leads to a smoother InGaN surface and InGaN/GaN interface with substantial decrease in V-shape defects density, compared to the samples without the treatment. The external quantum efficiency of 525 nm green LEDs prepared by this process is increased by as much as 43%.

4:40pm **EM-ThA9 ENABLE-Based Growth of In-Rich InGaN for Photovoltaic and Light-Emitting-Diode Devices**, ***T.L. Williamson***, *M.A. Hoffbauer,* Los Alamos National Laboratory, *K.M. Yu, L.A. Reichertz, N. Miller, J.W. Ager, W. Walukiewicz*, Lawrence Berkeley National Lab

A wide range of photovoltaic (PV) and light-emitting-diode (LED) devices can be made utilizing the wide band gap tunability of InxGa1-xN (0.7 eV to 3.4 eV, 1>x>0). Growing In-rich InxGa1-xN films with strong photoluminescence in the green and red portions of the visible spectrum has faced considerable challenges due to In segregation and other materials issues. These challenges have precluded the growth of both compositionally graded InxGa1-xN materials and higher bandgap Ga-rich materials on top of lower bandgap In-rich materials. Overcoming these difficulties has proved formidable for conventional epitaxial techniques due to the low decomposition temperatures of In-rich materials (e.g. InN~550°C) and the required growth temperatures for Ga-rich materials (e.g. GaN >800°C).

Energetic neutral atom beam lithography & epitaxy (ENABLE) is a recently developed low-temperature thin film growth technology developed at LANL that utilizes a collimated beam of energetic neutral N atoms (kinetic energies 0.5 to 5.0 eV) to react with evaporated Ga and In metals to grow InxGa1-xN. ENABLE is similar to MBE, but provides a much larger N atom flux. The high kinetic energy of the reactive N atoms substantially reduces the need for high substrate temperatures, making isothermal growth over the entire InxGa1-xN alloy composition range possible at rates of >3 mm/hr with no toxic precursors or waste products.

Current progress using ENABLE for growing InN, GaN, InxGa1-xN, and graded InxGa1-xN films over the full composition range will be presented including data on film photoluminescence, crystallinity, electrical properties, doping, and electroluminescence. ENABLE-grown InxGa1-xN films show strong photo- and electro-luminescence spanning the entire visible region of the spectrum, with carrier mobilities ranging from ~10 to >1400 cm2/Vsec and background carrier concentrations typically in the low 1017 range. Evidence for p-type doping of In-rich InxGa1-xN films and characterization of p/n junctions will be discussed along with the prospects for using ENABLE to fabricate efficient devices for PV and LED applications.

5:00pm **EM-ThA10 Self-annealing Effect in Neutron-Irradiated AlGaN/GaN High Electron Mobility Transistors**, ***G. Ko***, Korea University, South Korea, *F. Ren, S.J. Pearton,* University of Florida, *J. Kim, H.-Y. Kim*, Korea University, South Korea

AlGaN/GAN High Electron Mobility Transistors (HEMTs) have been studied due to their chemical and physical stability under harsh environments as well as high power and high frequency applications. Especially, AlGaN/GaN HEMT is considered as the potential candidate for space-based systems such as the space shuttles and the satellites. It is empirically known that displacement threshold energy (E_d) which is the energy required to displace an atom from its lattice position is inversely proportional to lattice constants. Since the lattice constant of GaN (a = 3.2496 Å) is smaller than Si (5.4301 Å) or GaAs (5.6533 Å), its radiation hardness is much better than these. Since neutron-induced effects on AlGaN/GaN heterostructures are not well known. We investigated self-annealing effect occurred in low-dose ($< 10^{12}$ cm^{-2}) neutron-irradiated AlGaN/GaN HEMT at room temperature. The device structure consisted of 25 nm AlGaN with 50 nm GaN cap layer on undoped 2 um GaN. These layers were grown on AlN buffer layer and c-plane sapphire by MOCVD. Ohmic metal was Ti/Al/Ni/Au and gate metal was Ni/Au. Neutron irradiation was performed with MC-50 cyclotron at Korea Institute of Radiological and Medical Sciences. Neutrons were generated when 35MeV protons collided with beryllium target occurring nuclear reaction. The average neutron energy was 9.8 MeV and the total fluence was 5.49×10^{11} cm^{-2}. Electrical properties (V_{ds}-I_{ds}, V_{gs}-I_{gs}, and transconductance) had been measured during 30 days after neutron irradiation. We could observe V_{ds}-I_{ds} drastically decrease for 7 days, which meant surface traps and deep traps were created in AlGaN/GaN HEMT. However its current level was gradually recovered after 7 days. And the recovery of transconductance and leakage current were also confirmed. This self-annealing effect can be attributed to the recombination of the created defects because the distance between the neighboring defects is very short. The defect clusters that are mobile at room temperature were created by neutron irradiation. The details about the irradiation and self-annealing will be presented.

5:20pm **EM-ThA11 Engineering Epitaxial AlN Thin Films on Wide Bandgap Semiconductors**, ***Y.-C. Perng***, *J. Chang*, University of California, Los Angeles

Wide bandgap semiconductors have been interesting for high temperatures operation and serving as materials using in high power and RF devices because of their high breakdown voltages. Aluminum nitride, a wide bandgap material (6.2 eV), is a promising interfacial layer or dielectric material on wide bandgap semiconductors, especially SiC and AlxGa1-xN/GaN. Because of its small lattice mismatch to SiC and AlxGa1-xN/GaN (1.3% and <2%)1 and a similar thermal expansion coefficient, it could potentially lower the interface state densities between the materials. Conventionally, AlN thin films are deposited by molecular beam epitaxy (MBE) on these wide bandgap materials. In this work, ALD is chosen to assess its ability to grow ultra-thin, uniform, and conformal AlN on these substrates, as a potential alternative for synthesizing epitaxial materials over a larger substrate and at lower temperatures.

Atomic layer deposition (ALD) has been utilized to synthesize AlN thin films by using trimethyl aluminum (TMA) and ammonia (NH3) as precursors at 400~500oC under high vacuum as 10-4~10-6 torr. The deposition rate of AlN on SiC and AlGaN were determined to be about 0.08nm/cycle. The composition, microstructure, and surface morphology were determined by x-ray photoelectron spectroscopy, transmission electron microscopy, x-ray diffraction and atomic force microscope. Fourier Transform infrared spectroscopy is implemented to study the change of surface functional groups during TMA and ammonia pulses, in an effort to affirm the mechanism leading to the growth of stoichiometric AlN. The as-deposited AlN was amorphous, as monitored by *in situ* by RHEED analysis but can be transformed into an epitaxial layer on SiC and AlGaN by a high temperature rapid thermal annealing process at 900oC. By synchrotron based XRD, we determined the epitaxial relationship between AlN and SiC to be AlN(11-20)||SiC(11-20) and AlN(0004)||SiC(0008). Similarly, the epitaxial relation to AlGaN is AlN(11-20)||AlGaN(11-20) and AlN(0002)||AlGaN(0002). Capacitance-voltage and conductance -voltage characteristics are used to determine the interface states density between the thin film and wide bandgap substrate. This process is also combined with an ALD Al2O3 process to synthesize aluminum oxinitride as a graded interfacial layer between AlN and Al2O3, to realize the fabrication and testing of viable MIS-HEMT structures.

1 H. Morkoc, S. Strite, G. B. Gao et al., Journal Of Applied Physics 76 (3), 1363 (1994).

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