Electronic Materials and Processing Division
Room 608 - Session EM-MoM

Nitride Epitaxy

Moderator: M.R. Melloch, Purdue University

8:20am **EM-MoM1 GaN Growth Chemistry, System Design and Materials Properties***, **T.F. Kuech**, J. Sun, L. Zhang,* University of Wisconsin, Madison*; J.M. Redwing,* Epitronics **INVITED**

The growth of device-quality GaN by metal-organic vapor phase epitaxy (MOVPE) is often difficult to achieve. The MOVPE growth of GaN is complicated by the extensive and pervasive complex gas phase chemistry within the growth system. This gas phase chemistry leads to the high sensitivity of the materials properties on the detailed fluid dynamics within the system. Through the combination of reactor modeling and gas phase kinetic studies, we have identified a stratified gas phase chemical structure within the reactor that leads to such process complexities. The high gas phase flow rates employed in GaN MOVPE results in a very thin high-temperature gas flow region above the growth front that leads to extremely high thermal gradients. Inside this thin high-temperature flow region, dominant chemical species above the growth surface changes in the gas phase above the growth front as a result of the high thermal gradient present and the high molecular weight species resulting from the oligimerization of the adduct. This chemically stratified region is closely related to the transport and reaction behavior present in GaN MOVPE processes and the modeling of this near-growth-front region serves as an engineering guideline for GaN MOVPE reactor design. We have combined these numerical results with detailed experimental measurements within the modeled system. The implications of these findings for the design of GaN systems and materials performance will be discussed. The extension of these models to the case of selective are growth of GaN will be discussed in terms of the local gas phase activities of the reactants and their influence on the facet formation.

9:00am **EM-MoM3 Mechanisms for Lateral Growth and Coalescence in GaN CVD***, **M.E. Bartram**, M.E. Coltrin, J. Han, C.C. Willan,* Sandia National Laboratories

Recent observations of rapid coalescence occurring upon convergence of lateral growth fronts suggest new strategies for GaN selective area growth (SAG) techniques. A mask with systematically spaced nucleation zones was used to provide a pseudo time-base for observing lateral growth transitions within a single GaN deposition. Scanning electron microscopy (SEM) revealed that the joining of adjacent features initiated a secondary lateral growth mechanism. The profile of the coalescence region suggests this rapid mode of deposition was controlled by layer-by-layer growth in which each new growth surface defined a reactive step against the initial growth front for nucleation of the next layer. This buildup thus driven by the lateral rate, resulted in the vertical growth front in the coalescence region meeting the upper most surface of the initial growth features. The layer-by-layer coalescence mechanism was quite independent of the slower progress of the original growth fronts when the V/III ratio was sufficiently high. However, it was non-existent under low V/III conditions. Correlations with materials quality will be made using TEM and CL measurements.

9:20am **EM-MoM4 Selective Area Growth of GaN on Si by Chemical Beam Epitaxy***, E. Kim, **A. Tempez**, N. Medelci, I.E. Berishev, A. Bensaoula,* University of Houston

One possible advantage of high vacuum deposition techniques over MOCVD is the realization of GaN device structures on Si wafers. In the case of MOCVD and sapphire substrates, selective GaN lateral regrowth over SiO@sub 2@ masks has been shown to reduce considerably the defect density in the epilayers. Thus far, very little data is available for regrowth using MBE techniques. In our previous studies of GaN deposition by chemical beam epitaxy (CBE) with TEGa and ammonia precursors, we have shown that no nucleation occurs on a sapphire surface. Using the same CBE precursors, we investigate here the selective nucleation process on Si wafers patterned with various oxide and nitride masks. The selectivity of the nucleation process was monitored in real time using time of flight ion scattering and recoil spectroscopy and RHEED. Two direct recoil spectroscopy (DRS) detectors mounted at 40 and 70° recoil angles are associated with MSRI (mass spectroscopy of recoiled ions) analyzers (sector and reflectron, respectively). These time refocusing analyzers allow for higher resolution and sensitivity than DRS. Our results show that the MSRI Si to O peak intensity ratio during GaN regrowth of SiO@sub 2@ patterned GaN is constant within the condition range we explored. This shows a 100% selective overgrowth process and is confirmed by SEM analysis. Following these experiments, we then implemented various regrowth schemes such as the use of a thin AlN single crystal layer on Si by a reactive MBE method followed by patterning and etching in an Ar-Cl@sub 2@-BCl@sub 3@ RF plasma. In this presentation, we will summarize our observations on the effect of the growth conditions (growth temperature and Ga/N flux ratio) on the selectivity of the nucleation process and will show our most recent data on the optimized regrown GaN layers- including their optical, electrical and field emission properties.

9:40am **EM-MoM5 The Role of Extended Defects in the Physical Properties of GaN and its Alloys***, **J.S. Speck**,* University of California, Santa Barbara **INVITED**

GaN and its alloys have emerged as the leading wide bandgap materials system for electronics and optoelectronics applications despite the high extended defect densities encountered in state-of-the-art device material. Pure edge character ('a' Burgers vector) or mixed character ('a+c' Burgers vector) threading dislocations with densities in the mid-108 to 1010 level are the predominant extended defects in high quality MOCVD-grown GaN on sapphire or silicon carbide substrates. We review the origin of these along with other extended defects (e.g., stacking disorder and inversion domains) and relate the growth to basic capillary-governed growth phenomena. Recently, a new technique, lateral epitaxial overgrowth (LEO), has emerged as a technique to reduce the density of extended defects by 3 - 4 orders of magnitude. The basic growth processes and extended defect evolution in LEO growth will be presented LEO GaN can also be used to directly compare the physical properties of dislocation-free and dislocated GaN. We show in experiments on LEO and 'normal' (bulk) GaN that threading dislocations behave as charged scattering centers, non-radiative recombination centers, and current leakage paths. Additionally, threading dislocations are the most common origin of deviations from planar growth and lead to a variety of kinetically-limited growth morphologies. Finally, highlights of some of our recent work on MBE growth of GaN will be presented, including record mobilities for 2-dimensional electron gas in AlGaN/GaN heterostructures.

10:20am **EM-MoM7 Growth Kinetics of GaN(0001) as Grown by MBE@footnote1@***, **A. Parkhomovsky**, S.M. Seutter, B.E. Ishaug, A.M. Dabiran, P.I. Cohen,* University of Minnesota*; S. Keller, S.P. DenBaars,* University of California, Santa Barbara

The kinetics of growth of GaN films using molecular beam epitaxy with a Ga K-cell and an NH@sub 3@ leak was studied. GaN(0001) layers grown by metalorganic chemical vapor deposition on c-plane sapphire were used as substrates. In situ growth monitoring was conducted using reflection high energy electron diffraction (RHEED) and desorption mass spectroscopy (DMS). The films were characterized in situ by UHV scanning tunneling microscopy (STM) and ex situ by atomic force microscopy. Prior to the growth the substrates exhibited a 2D RHEED pattern characteristic of a smooth surface with atomic steps. Initial growth of GaN under Ga rich conditions on this surface at 760°C produced a rough surface as indicated by a 3D RHEED pattern. We suggest that the roughening is due to a surface contamination that changes the growth kinetics, causing faceting of the surface. The surface was then gradually smoothened by growing under the same excess Ga conditions. On a smooth surface, RHEED intensity oscillations were observed for both the excess Ga and excess NH@sub 3@ growth regimes. This is very different from the GaN(000-1). Like the GaN(000-1), the RHEED oscillations were observed in the excess NH@sub 3@ regime at Ga beam equivalent pressures ranging from 3x10@super-7@ to 5x10@super-7@ Torr and an ammonia BEP from 0.5x10@super-4@ Torr to 1.0x10@super-4@ Torr at a substrate temperature of 600°C. Unlike GaN(000-1), the RHEED oscillations were seen in the excess Ga regime at a Ga BEP of 1.4x10@super-6@ Torr, NH@sub 3@ BEP of 1.6x10@super-7@ Torr and at a substrate temperature of 760°C. Upon initiation of the Ga flux, DMS measurements indicated a single step increase in the Ga desorption signal which is different from the two-step increase on the GaN(000-1) associated with a physisorbed state. UHV STM studies were conducted on fully gallided and partially nitrided quenched GaN surfaces. Partial nitridation of GaN(0001) surface in ammonia produced nitrided zones at step edges that are 15-20 nm in size and 2-3 ML deep. The size of the zones is much less than that on the GaN(000-1) surface. @FootnoteText@ @footnote1@ Partially supported by the Office of Naval Reasearch and the National Science Foundation

10:40am **EM-MoM8 Dissociation of Al@sub 2@O@sub 3@(0001) Substrates, and the Roles of Silicon, Oxygen, and Nitrogen Vacancies in n-type GaN Grown by MBE**, ***J.E. Van Nostrand,*** Air Force Research Lab; *J.S. Solomon,* University of Dayton Research Institute; *A. Saxler,* Air Force Research Lab

GaN is a semiconductor material that shows great promise for use in optoelectronic and electronic devices due to its large, direct bandgap. However, in spite of astonishing and rapid developmental successes, many problems remain that hinder further progress. Among them is a lack of understanding of the mechanisms underlying impurity incorporation, the nature of native defects, and the dependence of both of these on the thermodynamics and kinetic limitations of the GaN growth technique employed. One nearly universal aspect of unintentionally doped GaN films grown on sapphire by any technique is an n-type background carrier concentration. This phenomenon has been attributed to impurities such as Si or O, or to native defects such as N vacancies. In this work, we identify and quantify an anomalous relationship between the Si doping concentration and free carrier concentration and mobility using temperature dependent Hall measurements on a series of 2.0 µm thick GaN(0001) films grown on sapphire with various Si doping concentrations. Secondary ion mass spectrometry (SIMS) is used to identify the type of the excess free carriers to be oxygen. Further, the source of the oxygen is positively identified to be dissociation of the sapphire substrate at the sapphire-nitride interface. Finally, SIMS is again utilized to show how Si doping can be utilized to control the diffusion kinetics of the oxygen into the GaN layer from the sapphire substrate.

11:00am **EM-MoM9 Growth of GaN Thin Films and Device Structures on Silicon Wafers by Molecular Beam Epitaxy**, ***I.E. Berishev,*** *D. Starikov, N. Medelci, A. Bensaoula, I. Rusakova, E. Kim,* University of Houston

GaN grown on Si wafers has large perspectives in various device applications due to low cost of the substrate and easy integration with well developed Si circuits. More over, molecular beam epitaxy is advantageous in this respect due to low growth temperature and advanced methods of in situ characterization. We report the growth of GaN - based heterostructures and light emitting devices on Si (111) wafers by molecular beam epitaxy with a RF nitrogen plasma source. We found that the buffer layer between the Si and the GaN epilayer is the most critical factor responsible for the properties of the active device layers. To that end, several buffer layers, including AlN, GaN and Si-@sub x@N@sub y@ were studied in situ by RHEED and time of flight mass spectroscopy of recoiled ions and ex situ by transmission electron microscopy. Inter-diffusion between Si and Al(Ga) was studied by SIMS. We found that diffusion of group III elements into the substrate is much stronger than diffusion of Si into the upper layers. Optimized growth conditions for the buffer layer, the thick GaN layer, and p-type GaN layer allowed for injection light emitters to be fabricated. Ternary alloys, including InGaN quantum well active regions, are currently under development. Our most recent data on X-ray diffraction, photo-luminescence and electro-luminescence of fabricated light emitting diodes on Si (111) wafers will be presented at the conference.

11:20am **EM-MoM10 Photoluminescence and Heteroepitaxy of ZnO on Sapphire Substrate (0001) Grown by RF Magnetron Sputtering**, ***K.K. Kim,*** *S.J. Park,* Kwangju Institute of Science and Technology, Korea; *J.-H. Song,* Korea Institute of Science and Technology, Korea; *H.-J. Jung, W.K. Choi,* Korea Institute of Science and Technology, Seoul

ZnO thin films were epitaxially grown on Al@sub 2@O@sub 3@ (0001) single crystalline substrate by RF magnetron sputtering with the variations of RF power P=60-120 W. Crystalline structure of the ZnO films were analyzed by 4-circle X-ray diffraction, backscattering (BS)/channeling, and transmission electron microscopy. At the substrate temperature 550@super o@C, the ZnO film deposited with power of 80W has narrowest full width half maximum(FWHM) of @theta@-rocking curve, 0.16@super o@, indicating an highly c-axis oriented columnar structure. XRD @theta@-rocking curve FWHM of the ZnO film deposited at 120 W and 600@super o@C was 0.13@super o@ and in-plane of ZnO grown on sapphire(0001) substrate was found to be indicated a 30@super o@ rotation of ZnO unit cell about sapphire(0001) substrate. In BS/channeling study, channeling yield minimum (@chi@ @sub m@) was changed with growing temperature and power, and was only 4-5% for the films deposited at 120 W, 600@super o@C. In PL measurement, only the sharp near band edge (NBE) emission were observed at room temperature for the films deposited at 80-120 W and 550@super o@C and 120 W, 600@super o@C. but deep-level emission were also detected in the films deposited at 60 W, 550@super o@C. The FWHM was decreased from 133 meV to 89 meV as RF power increased from 80 W to 120 W at 550@super o@C, and that of film deposited at 120 W and 600@super o@C showed 76 meV which is lower value than any other ever reported, which were somewhat opposite to that of XRD. From TEM analysis, grain size and defect were found to affect the PL properties. In this study, the PL property of undoped ZnO thin films is discussed in terms of the crystalline structure and the quality of grain.

11:40am **EM-MoM11 Characterization of a Very Thin Film: N2 Plasma Nitridation of GaAs (110)**, ***J.E. Hulse,*** National Research Council of Canada, Canada; *D. Landheer, R. Krishnamurthy, S. Moisa,* National Research Council of Canada

GaAs (110) wafers were prepared by cycles of UV-ozone/HF cleaning and inserted into an Ultra-High Vacuum processing system. Nitridation of the wafers by a remote Electron Cyclotron Resonance (ECR) nitrogen plasma produced a porous GaN film of up to about 3 nm in thickness. In situ analysis by X-ray Photoelectron Spectroscopy (XPS) revealed that the plasma both scoured the GaAs substrate surface of carbon and oxygen and produced a GaN film. Ex situ analysis by Spectroscopic Ellipsometry indicated that the GaN layer was porous. Angle-Dependent XPS demonstrated that the GaN layer contained traces of As predominantly in the outer regions of the film, and that the porous GaN can absorb water on exposure to air. A 5 second exposure of a GaAs (110) wafer to the ECR nitrogen plasma simulates the initial stage of ECR plasma deposition of silicon nitride, which exposes the substrate to a nitrogen plasma at turn-on. Such a short nitridation produced a GaN film that was 1.9 nm thick with traces of arsenic throughout and approximately 50 % voids. Longer exposures to the nitrogen plasma produced films whose thicknesses followed an inverse power law time dependence. The wafers were examined by Atomic Force Microscopy both before and after nitridation. Before plasma nitridation, the cleaned wafers showed clearly identifiable roughness features due to chemical-mechanical polishing. Plasma nitridation left the surface smooth and free of identifiable features less than 10 microns in lateral size.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+FP-MoM

Organic Devices

Moderator: A. Kahn, Princeton University

8:20am **OE+EM+FP-MoM1 Invited Paper**, ***C.W. Tang,*** Eastman Kodak Company **INVITED**

NO ABSTRACT SUBMITTED.

9:00am **OE+EM+FP-MoM3 Ultrafast Electron Relaxation in Excited, DCM Doped Alq Films**, ***K. Read,*** University of Michigan; *H.S. Karlsson,* Royal Institute of Technology, Sweden; *M.M. Murnane, H.C. Kapteyn,* University of Michigan; *R. Haight,* IBM T.J. Watson Research Center

Electrons photoexcited into the lowest unoccupied molecular orbital (LUMO) of Alq (tris(8-hydroxyquinoline)aluminum) films doped with DCM (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran) have been studied using excite-probe laser photoemission. DCM doping, achieved by co-evaporation with Alq, is an important means of color tuning and enhancing Alq organic LED emission. In addition, DCM doped Alq films have been shown to lase at low photoexcitation thresholds. A detailed understanding of the involved relaxation mechanisms is beneficial to both applications. Using 3.14 eV excite, and 26.7 eV probe, 100 femtosecond laser pulses, we have observed the LUMO decay rate over the first 175 picoseconds, during which time diffusion is insignificant, and all dynamics occur in the absence of electron transport. We have found that the LUMO population fits to a model wherein the majority of the excitation rapidly transfers from the Alq to the DCM and decays via stimulated emission in the DCM, concentration quenching in the DCM, and bimolecular singlet-singlet annihilation in both the Alq and the DCM. Increasing either the DCM doping percentage, or the excitation intensity, is seen to significantly enhance the early, fast processes. The occupied to unoccupied molecular orbital energy gap shrinks as a function of excite-to-probe delay, in accordance with the expected energy relaxation within the excited states. Pure DCM yields a correspondingly smaller energy gap, and rapid LUMO decay. Analyzing the LUMO decay mechanisms allows an improved understanding of the functions served by DCM doping of Alq films.

9:20am **OE+EM+FP-MoM4 Unoccupied Molecular Orbitals in Organic Electroluminescent Materials Studied by Femtosecond Harmonic Photoemission*, H.S. Karlsson,*** Royal Institute of Technology, Sweden*; K. Read,* University of Michigan*; R. Haight,* IBM T.J. Watson Research Center

We have studied the lowest unoccupied molecular orbital (LUMO) in three organic electroluminescent materials using pump-probe harmonic photoemission based on a femtosecond laser system. The energy gap between the LUMO and the highest occupied molecular orbital (HOMO) in thin films of the blue-light-emitting molecules bis(2-methyl-8-quinolinolato)(para-phenyl-phenolato)aluminum (BAlq) and 1,4-bis(2,2-diphenylvinyl)biphenyl (DPVBi) was established and compared with the green-light-emitting molecule tris(8-hydroxyquinoline)aluminum (Alq). We have also studied the LUMO decay characteristics for the three materials and relate the differences in decay times to the morphology of the evaporated thin films. The effect on the electronic structure of the organics induced by deposition of metallic overlayers will also be shown and discussed.

9:40am **OE+EM+FP-MoM5 Femtosecond Charge Transfer Processes in Organic Molecular Heterostructures*, A.J. Mäkinen*,** *S. Schoemann, Y. Gao,* University of Rochester*; M.G. Mason, A.A. Muenter,* Eastman Kodak Company*; A.R. Melnyk,* Xerox Wilson Center for Research & Technology

The charge transfer (CT) process in organic semiconductor heterostructures is an important problem for applications such as photoreceptors and light-emitting devices. The operation of a photoreceptor structure is based on a CT process at the interface of a charge generator layer and a charge transport layer. We have investigated such a structure formed by vacuum grown thin films of two organic molecules, N,N'-diphenethyl-3,4,9,10-perylenetetracarboxylic-diimide (DPEP) and N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), with femtosecond time-resolved photoemission spectroscopy (TR-PES). By measuring the lifetimes of the excited electron states in the mixtures and in the bilayer structures of these molecules, and by recording the UPS spectra of the films we are able to determine the time-scale and the energy regime for the CT process. Our results show that the CT takes place in less than 10 fs between the DPEP and the TPD molecules. We also demonstrate the significance of the film interface in separating the charges upon CT.

10:00am **OE+EM+FP-MoM6 A Comparison of Organic Light-Emitting Devices Using Transient Current-Transient Voltage, Transient Brightness-Transient Voltage, and Transient Brightness-Transient Current Analysis*, B.J. Norris*,** *J.F. Wager,* Oregon State University*; J. Liu, Y. Yang,* University of California, Los Angeles

Four types of organic light-emitting devices (OLEDs) are compared using transient current-transient voltage [i(t)-v(t)], transient brightness-transient voltage [b(t)-v(t)], and transient brightness-transient current [b(t)-i(t)] analysis.@footnote 1@@footnote 2@ These analysis methods consist of obtaining the instantaneous brightness [b(t)], current [i(t)], and voltage [v(t)] of the device under test when it is subjected to a bipolar, piecewise-linear applied voltage waveform and then plotting these quantities parametrically. The four types of OLEDs considered are: two types of green OLEDs and a blue OLED, provided by the Eastman-Kodak Co., and a polymer light-emitting device (PLED) fabricated at the UCLA. The OLEDs are dual-layer heterostructures, involving an electron transport layer (ETL) and a hole transport layer (HTL). In contrast, the PLED is a single-layer device. The ETL and HTL capacitances of heterostructure OLEDs can be estimated from b(t)-i(t) curves. The b(t)-v(t) curves allow the conduction current to be estimated. Perhaps the most interesting aspect of this study is the existence of a small bump in the retrace portion of i(t)-v(t) curves of heterostructure OLEDs, which is not observed in single-layer PLEDs. This bump is ascribed to the removal of accumulated holes at the ETL/HTL interface. Hole accumulation at the ETL/HTL interface of OLED heterostructures is manifest as hysteresis in b(t)-v(t) curves. @FootnoteText@ @footnote 1@B. J. Norris, J. P. Bender, and J. F. Wager, "Steady-State Transient Voltage-Transient Current Characterization of OLEDs," SID Digest, in press. @footnote 2@ B. J. Norris, "Characterization of Organic Light-Emitting Devices," MS Thesis, Oregon State University, 1999.

10:20am **OE+EM+FP-MoM7 Organic and Polymer Transistors: Device Physics, Functional Blocks, and Circuits*, A. Dodabalapur*,** *B.K. Crone, Y.Y. Lin, J.A. Rogers, S. Martin, R. Sarpeshkar, Z. Bao, W. Li, H.E. Katz, V.R. Raju,* Bell Laboratories, Lucent Technologies **INVITED**

This presentation will begin with a description of the basic physics of typical organic and polymer transistors and the factors which determine and influence the apparent mobility. The transient characteristics organic transistors with sub-microsecond switching speeds will be described. The integration of organic light emitting diodes and transistors is promising for emissive displays. We have developed designs for 'smart' pixels in which an analog circuit consisting of 6-7 transistors drives each LED. The simulated and experimental characteristics of such pixels will be presented. The development of air-stable n-channel organic transistors led to our demonstrating the first organic complementary circuits. The design considerations and characteristics of organic complementary circuits with > 100 transistors will be described. The noise properties of organic transistors and their use in gas sensors will be described.

11:00am **OE+EM+FP-MoM9 Sub-microsecond Switching of n and p-Channel Organic Field Effect Transistors*, B.K. Crone*,** *A. Dodabalapur, Z. Bao, W. Li,* Lucent Technologies, Bell Laboratories

Steady state and transient electrical characteristics are presented for p-channel (@alpha@,@omega@-dihexyl quinquethiophene) and n-channel (copper hexadecaflourophthalocyanine) organic field effect transistors. The structure of the transistor is as follows. The gate electrode is a doped silicon wafer with a thermal oxide gate oxide. Gold source and drain contacts are evaporated and photolithographically defined on the oxide, and finally the active organic film is evaporated. The transistors measured had channel length of 4 µm and width 250 µm. Field effect carrier mobilities are determined for both the steady state and transient response using a simple model for the saturated drain current. The steady state mobility and threshold voltage were determined by a linear fit to the square root of the saturated drain current versus gate voltage. Steady state mobilities of 1.5x10@super -2@cm@super 2@/Vs for the p-channel and 3x10@super -2@cm@super 2@/Vs for the n-channel were measured. Transient mobilities were determined using the same model for the saturated drain current and the threshold voltage obtained in the steady state case. Transient mobilities were higher, 3x10@super -2@cm@super 2@/Vs for the p-channel and 1.5x10@super -1@cm@super 2@/Vs for the n-channel devices. The transient responses showed switching times less than 1 µsec for both p and n-channel devices.

Surface Science Division
Room 606 - Session SS1+EM-MoM
Chemistry on Oxides

Moderator: S.A. Joyce, Pacific Northwest Laboratory

8:20am **SS1+EM-MoM1 The Reactions of Maleic Anhydride Over TiO@sub 2@ (001) Single Crystal Surfaces*, J.N. Wilson*,** *D.J. Titheridge, H. Idriss,* The University of Auckland, New Zealand

The reactions of maleic anhydride have been investigated on the stoichiometric and substoichiometric surfaces of TiO@sub 2@ by Temperature Programmed Desorption (TPD) and Scanning Kinetic Spectroscopy (SKS). SKS technique, showing complementary information to TPD, has been successfully applied to investigate the chemical pathways on this oxide material for the first time. Results from the maleic anhydride TPD and SKS show the desorption of a wide variety of products in several temperature domains. In addition to the decomposition pathway to CO, CO@sub 2@, acetylene, and ethylene, the desorption of coupling reaction products of two molecules of acetylene to vinylacetylene (m/e 52) and of three molecules of acetylene to benzene (m/e 78) is observed. Moreover, the potential desorption of carbon suboxide, O=C=C=C=O, formed by two successive dehydration of both ends of the molecule, is discussed. The coupling pathways of the reactions of maleic anhydride on the substoichiometric surface were more accentuated.

8:40am **SS1+EM-MoM2 S Adsorption on TiO@sub 2@(110) Studied with STM, XPS and LEED*, E.L.D. Hebenstreit*,** *W. Hebenstreit, U. Diebold,* Tulane University

TiO@sub 2@ surfaces are well-known for their catalytic properties. Since sulfur is known as a catalyst inhibitor, its adsorption behavior on TiO@sub 2@ single crystal surfaces are of great interest. Measurements with a scanning tunneling microscope reveal the existence of two different adsorption sites, depending on the sample temperature during adsorption. Adsorption at room temperature leads to very mobile sulfur atoms sitting on titanium sites of TiO@sub 2@(110). Adsorption at 300°C causes the formation of more stable sulfur chains running along the [1-10] direction with an ordered (3x1) structure at saturation. In the latter case the sulfur atoms are located at the positions of oxygen surface atoms. X-ray-photoelectron-spectroscopy confirms the existence of two chemically different S species.

9:00am **SS1+EM-MoM3 Spectroscopic Studies of Sorption Processes at Metal Oxide-Aqueous Solutions Interfaces***, **G.E. Brown, Jr.**, T. Kendelewicz,* Stanford U.*; P. Liu,* LBNL*; J.R. Bargar,* Stanford Synchrotron Radiation Lab.*; J.P. Fitts, A.L. Foster, J.D. Ostergren, G.A. Parks, A.H. Templeton,* Stanford U.*; H.A. Thompson,* LANL*; S.N. Towle,* Intel Corp.*; T.P. Trainor,* Stanford U.*; P. Eng, S. Sutton,* Adv. Photon Source **INVITED**

Chemical interactions at metal oxide-aqueous solution interfaces are of great significance in atmospheric and environmental chemistry. They help control many important processes including dissolution and crystal growth of natural solids and the sorption a nd desorption of aqueous metal ions, which can sequester or release heavy metal contaminants in atmospheric and aquatic environments. Metal oxide-water interfaces in natural systems are extremely complex when viewed at the molecular level because of the many variable that must be accounted for and the difficulty in observing the products of interfacial reactions under in-situ conditions (i.e., with bulk water present). To make this problem more tractable, we have employed a reductionist approach in which interfacial reaction products are examined in simplified model systems under carefully controlled conditions using a combination of classical surface chemistry methods, synchrotron radiation-based surface science methods, and other spectroscopic and scanning force microscopy methods. The resulting information at macroscopic and atomic/molecular scales allows sorption behavior to be correlated with chemical species information, including the structure, composition, and mode of sorption of adsorbates, and, in selected cases, the types of reactive sites on adsorbent surfaces and the effect of aging time. In parallel model system studies, we have also examined the effects of common inorganic ligands, organic ligands, and biofilms on the sorption of metal ions at mineral-water interfaces, and we have used the results as a basis for studies of As and Pb speciation in contaminated soils and mine tailings. These studies have revealed the structure and composition of adsorbates, and for single-crystal adsorbents, have allowed us to place constraints on the stoichiometry of sorption reactions, including the types of reactive sites to which the adsorbate binds. Selected examples of these studies will be presented.

9:40am **SS1+EM-MoM5 Reactions of SeF@sub6@ with Iron and Iron Oxides***, **S.R. Qiu**[1], H.-F. Lai, H.T. Than, C. Amrhein, J.A. Yarmoff,* University of California, Riverside

Concentrated levels of selenium in the groundwater of the western US have been found to cause the death and birth-deformation of wildlife. Zero valent iron has been used to immobilize many soluble toxic groundwater contaminants, including selenate (Se@super6+@), by a surface redox reaction in which aqueous contaminants are reduced to less mobile forms. Only limited success has been achieved in the field, however, as the understanding of the reaction mechanism at the liquid/solid interface is incomplete. In this work, the remediation process is modeled by the reaction of SeF@sub6@ with iron and iron oxide surfaces in ultra-high vacuum. Se in SeF@sub6@ is in the same oxidation state as in selenate, and a similar reduction is observed upon reaction with Fe. X-ray photoelectron spectroscopy (XPS) spectra collected following the exposure of a sputter-cleaned Fe foil to SeF@sub6@ show both Se and F on the surface. The Se is found to be directly bonded to Fe, with no bonds to F remaining, indicative of the complete dissociation of SeF@sub6@. The F-to-Se ratio is close to 6 to 1, showing that all of the products remain on the surface. The Fe 2p spectra show the formation of FeF@sub2@ as the major surface species formed. These results suggest that there is a high activation barrier to adsorption, but that once it occurs, the excess energy liberated by the exothermic reaction promotes complete dissociation. To ascertain the role of oxygen, SeF@sub6@ was exposed to both partially and fully oxidized Fe surfaces. Oxygen was found, in all cases, to inhibit the reaction. We are currently investigating this reaction employing clean and oxygen pre-covered single crystal Fe surfaces. Both XPS and scanning tunneling microscopy are being used to understand the chemical reaction mechanism and to ascertain the adsorption sites. The implications of our results on practical remediation methods will be discussed.

10:00am **SS1+EM-MoM6 Interactions of HCOOH with Stoichiometric and Defective SrTiO@sub 3@(100) Surfaces***, **L. Wang**, F. Ferris, H. Engelhardt,* Pacific Northwest National Laboratories

Interactions of HCOOH with stoichiometric (nearly defect-free) and defective SrTiO@sub 3@(100) surfaces have been studied using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and electronic structure calculations. Two reaction pathways were observed for formaldehyde formation from formic acid on SrTiO@sub 3@(100) surfaces. On stoichiometric surfaces, formaldehyde was produced through bimolecular coupling of two formates. However, on Ar+ sputtered surfaces, formaldehyde formation involves the reduction of surface formate by the oxidation of reduced Ti cations. XPS results show that surface defects on sputtered SrTiO@sub 3@(100) surfaces were reoxidized significantly upon exposure to 30 L HCOOH at 300 K, in contrast to defects on sputtered TiO@sub 2@(110) surfaces where no reduction in defect intensity was observed under the same condition. The fact that surface formate was reduced at 300 K on SrTiO@sub 3@(100) is clearly evident in TPD data where the desorption peak of formaldehyde is shifted to a lower temperature and broadened significantly down to 300 K for Ar+ sputtered SrTiO@sub 3@(100) surfaces as compared with stoichiometric surfaces. Electronic structure calculations have been used to investigate the adsorptive interactions for formate and formaldehyde on the cation sites of both stoichiometric and defective SrTiO@sub 3@(100) surfaces. The results for formate indicate a strong adsorptive interaction consistent with the experimental observations, with significant charge redistribution. Further results will be discussed in terms of potential reaction mechanisms.

10:20am **SS1+EM-MoM7 The Structure of the CeO@sub 2@(001) Surface and its Reactions with D@sub 2@O***, G.S. Herman,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology, Korea*; S.A. Chambers, **C.H.F. Peden**,* Pacific Northwest National Laboratory

Angle-resolved mass-spectroscopy of recoiled ions (AR-MSRI) has been used to determine the surface structure of CeO@sub 2@(001). The results indicate that the surface is terminated with 0.5 monolayers of oxygen which gives rise to a zero dipole moment and, thus, a stable surface. The interaction of D@sub 2@O with the CeO@sub 2@(001) surface was studied with temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). It was found with TPD that D@sub 2@O desorption occurs in three states with temperatures of 152, 200, and 275 K which are defined as multilayer D@sub 2@O, weakly bound surface D@sub 2@O, and hydroxyl recombination, respectively. O 1s XPS measurements for high D@sub 2@O exposures, where multilayer water desorption was observed in the TPD, resulted in emission from only the substrate and surface hydroxyls. This is likely due to a non-wetting behavior of D@sub 2@O on this surface with the formation of nanosized clusters. An analysis of the O1s XPS data indicates that the surface has a hydroxyl coverage of 0.9 monolayers for large water exposures at 85 K. This is consistent with a model in which the polar CeO@sub 2@(001) surface can be stabilized by a reduction of the dipole in the top layer by the formation of full monolayer of hydroxyls. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

10:40am **SS1+EM-MoM8 The Correlation Between MgO (100) Surface Morphology and Chemical Reactivity***, **S.S. Perry**,* University of Houston, US*; S. Imaduddin, O. El-bjeirami, P.B. Merrill, S.M. Lee, H.I. Kim,* University of Houston

A critical ingredient of any surface science study is the preparation of the surface so as to present a uniform and homogeneous distribution of surface sites. For metals, the nature of adsorption site is determined by the crystal face exposed and the local coordination of the different metal atoms at the surface. For compound semiconductors and oxide based materials, the situation can be much more complex as the crystal face and coordination now applies to more than one type of element. The preparation of such materials can be further complicated by the possibility of preferential sputtering of one component of the surface. In this study we have used a combination of microscopy, ex-situ processing, ultrahigh vacuum (UHV) processing and UHV surface analysis to correlate the chemical reactivity of a model metal oxide (MgO) with the nature of surface structure and morphology. Atomic force microscopy, low energy electron diffraction, and reflection high energy electron diffraction studies together have allowed the distinction between amorphous and crystalline surfaces as well as the length scale of surface order. Single crystal MgO(100) surfaces have been prepared by a number of procedures including acid etching, high temperature annealing in ambient pressures of oxygen, UHV annealing, and ion bombardment. The compositional changes of the surface region with respect to these procedures have been followed with X-ray photoelectron spectroscopy. Finally, the chemical reactivity of the MgO(100) surface has been studied using temperature programmed desorption, investigating the desorption properties of water, methanol and carbon monoxide. Together, these studies have generated a complete picture of the relationship between microscopic surface morphology and chemical reactivity for this model metal oxide surface and have highlighted

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

several critical aspects involved in the preparation of single crystal metal oxide surfaces for UHV surface science studies.

11:00am **SS1+EM-MoM9 Photoconversion of Adsorbed Oxygen States On TiO@sub 2@(110)**, ***C.L. Perkins,*** *M.A. Henderson,* Pacific Northwest National Laboratory

By means of postirradiation temperature programmed desorption we have investigated further the states of oxygen adsorbed on rutile TiO@sub 2@. Previous work has shown that annealing the (110) surface in vacuum produces isolated bridging oxygen vacancies, and that these vacancies are intimately connected with molecular and dissociative oxygen adsorption channels. We find that at 120 K illumination of the oxygen exposed surface with photons having energies above the band gap (>3.6 eV) results in depletion of the molecular oxygen state observed at 410 K in TPD, in contrast to the remaining oxygen destined for the dissociative channel. An unusual effect of water overlayers on the O/TiO@sub 2@(110) system is explored. For thick overlayers (> 2 ML), it is possible to generate via UV irradiation a previously unobserved oxygen TPD state. Cross sections for the photoconversion of oxygen into this state are measured, and specific mechanisms for the process are proposed.

11:20am **SS1+EM-MoM10 Reactions of Acetic Acid, Acetaldehyde and Ethanol on the (111) Surface of Uranium Dioxide Single Crystal**, *S.V. Chong,* ***H. Idriss,*** The University of Auckland, New Zealand

The reactions of three C2 molecules having different functional group and polarity, have been investigated on the (111) surface of uranium dioxide single crystal, which has been characterised by LEED and AES. The adsorption of acetic acid, the most polar among the three molecules, indicates a higher sticking probability on the oxygen terminated UO@sub 2@(111) surface, followed by ethanol then acetaldehyde. Temperature Programmed Desorption (TPD) for these molecules displays a rich chemistry. Acetic acid-TPD on a stoichiometric surface yields ketene (dehydration) as the main product, plus acetaldehyde (reduction) as the minor product. While on an electron beam sputtered surface, two additional products were observed - butene and crotonaldehyde. In the case of acetaldehyde, both sputtered and non-sputtered surfaces yield benzene, with ketene as the additional product on the sputtered surface. The reactions of ethanol on a stoichiometric surface give acetaldehyde and ethylene as the only two products with "equal" amount. The comparison of this latter result with those of other metal oxide single crystals indicates a plausible relationship between the dehydrogenation/dehydration selectivity of primary alcohols and the Madelung potential of the cations. In summary, this investigation has shown the ability of UO@sub 2@(111) single crystal to oxidise, reduce, reductively couple, and trimerise organic molecules.

11:40am **SS1+EM-MoM11 Surface Reactions on Cr-doped V@sub 2@O@sub 3@**, ***D.S. Toledano***, *V.E. Henrich,* Yale University

Transition-metal oxides are important as gas sensors due to chemisorption-induced changes in surface conductivity. Conversely, changes in substrate electronic structure may alter surface chemisorption properties. While investigating the effect of metal-insulator transitions in Cr-doped V@sub 2@O@sub 3@ on adsorption, we have observed interesting effects involving surface reduction by CO, as well as differences in adsorption on metallic and insulating substrate phases. (Cr@sub 0.015@V@sub 0.985@)@sub 2@O@sub 3@ exhibits two metal-insulator transitions as a function of temperature; these experiments focus on the insulating phase of single-crystal Cr-V@sub 2@O@sub 3@ using UPS, XPS, LEED and AES. When insulating-phase Cr-V@sub 2@O@sub 3@ (0001) is exposed to CO at 273K, CO appears to adsorb dissociatively up to 10@super 3@ Langmuir. Higher exposures result in a C-containing species, and electron transfer to V cations at energies near E@sub F@; decreased occupation of non-bonding O orbitals is also observed. Heating to 470K desorbs this species, but the surface is further reduced after desorption, with increased charge transfer to V cations. Exposure of a CO-reduced surface to O@sub 2@ does not reoxidize the surface or restore the original electronic structure, but appears to result in adsorbed O@super -@ or (O@sub2@)@super -@ which does not re-enter the lattice unless annealed above 700K. CO adsorption on metallic-phase Cr-V@sub 2@O@sub 3@ differs from that on the insulating phase for intermediate exposures, exhibiting higher initial sticking coefficient and desorption temperature; however, the two phases behave similarly for high CO exposures. Adsorption of H@sub 2@O, SO@sub 2@ and O@sub 2@ on both substrate phases has also been studied. This work was partially funded by NSF grant CTS-96-10140

Electronic Materials and Processing Division
Room 608 - Session EM-MoA

Nitride Processing and Characterization

Moderator: J.S. Speck, University of California, Santa Barbara

2:00pm **EM-MoA1 GaN-Based Diode Structures for Optoelectronic Applications in the Near Ultraviolet Range of the Spectrum***, **D. Starikov**, I.E. Berishev, N. Badi, N. Medelci, J.-W. Um, A. Bensaoula,* University of Houston

We have previously reported that spectrally matched n-SiC and n-GaN-based Shottky barrier diode structures with semi-transparent Au electrodes can be employed for optoelectronic applications in the UV range of the spectrum. Both n-SiC-based and n-GaN-based structures indicated photosensitivity in the range down to 220 nm. The SiC- based structures exhibited optical emission in the avalanche mode at reverse bias down to 300 nm. The avalanche emission from the n-GaN-based samples was unstable and lasted only few seconds. In addition, high dark current and low thermal stability have been observed due to the absence of good ohmic contacts and satisfactory insulation, and poor mechanical and thermal stability of the gold layers. In this work Schottky barrier diode structures were fabricated on p-type GaN layers grown on sapphire using solid metal electrodes. The structures exhibit blue and wide-spectrum optical emissions at forward and reverse bias, respectively, and photo sensitive properties at no bias. Spectra of wide-spectrum optical emission and photo sensitivity measured through the sapphire substrate and 1.5 mm GaN film are matched in the range of 365-400 nm. The Lambertian radiant UV power of the blue emission is 466 mW at 22 V. Employment of wide-band gap oxide semiconductors In@sub 2@O@sub 3@ and SnO@sub 2@ for rectifying contact fabrication in our diode structures should extend the spectral range of our devices beyond 365 nm (the wavelength corresponding to the band gap of GaN) and improve their mechanical and thermal stability. We have incorporated these UV-transparent and electrically-conductive oxide semiconductor materials in our device structures. Our results from the various processing steps (patterning, etching, isolation and contact deposition), as well as from the diode structures characterization will be presented. Perspectives for applications of these structures in chemical sensors are discussed.

2:20pm **EM-MoA2 High Breakdown Voltage Au/Pt/GaN Schottky Diode***, J.I. Chyi, J.M. Lee, C.C. Chuo, G.C. Chi,* National Central University, Taiwan*; **G. Dang**, A.P. Zhang, X.A. Cao, M.M. Mshewa, F. Ren, S.J. Pearton,* University of Florida*; S.N.G. Chu,* Bell Labs, Lucent Technologies*; W.G. Wilson,* Charles Evans and Associates

Au/Pt/GaN Schottky diode rectifiers with a reverse breakdown voltage of -325V were demonstrated. The GaN sample studied in this work was grown on c-plane sapphire by low-pressure metalorganic chemical vapor deposition in a horizontal reactor. Ammonia (NH@sub 3@), trimethylgallium (TMG), and silane (SiH@sub 4@) were used as precursors and dopants, respectively. Two-step growth method was used to obtain GaN films with smooth surface. A low temperature GaN nucleation layer of about 220 nm was first grown at 460 °C after the substrate was heated at 1050 °C in hydrogen ambient for 10 minutes. Then the substrate temperature was raised to 1050 °C for the growth of the 1 µm-thick Si-doped (3E18 cm@super -3@) and 5 µm-thick undoped GaN layers. From the diode C-V measurement, the background doping of the undoped GaN is 1E16 cm@super -3@. The growth rate of high temperature GaN was 1.5 µm/hr, while that for the nucleation layer was about 0.3 µm/hr. TEM cross-sectional view of the sample shows that the growth interruption during the nitride growth reduces the dislocation density significantly. From the SIMS analysis, the concentrations of carbon, oxygen and hydrogen in the undoped layer are 2E17, 3E17, and 3E18, respectively. AFM roughness was around 1nm over 10x10 µm@super 2@.

2:40pm **EM-MoA3 Negative Electron Affinity and Electron Emission at Cesiated GaN and AlN Surfaces***, **C.I. Wu**, A. Kahn,* Princeton University

We present a systematic study of electron affinity and secondary electron emission at clean and cesiated surfaces of p-type GaN and (nominally n-type) AlN using ultraviolet and x-ray photoemission spectroscopy, and total yield spectroscopy. Clean and ordered 1x1 surfaces are prepared by nitrogen ion sputtering and annealing.@footnote 1@ The electron affinity, @chi@, is found equal to 3.3±0.2 eV and 1.9±0.2 eV for GaN and AlN surfaces, respectively, in agreement with previous results.@footnote 2,3@ The deposition of Cs reduces @chi@(AlN) by 2.6±0.3 eV, leading to true negative electron affinity (NEA), i.e. the vacuum level (E@sub vac@) is below the conduction band minimum (E@sub c@) at the surface. With the assist of a 1.2 eV initial downward band bending, effective NEA, i.e E@sub vac@ below the bulk E@sub c@, is achieved on p-GaN following the sequential adsorption of oxygen and deposition of cesium, which lowers @chi@(GaN) by 2.7±0.3 eV. The total yield, defined as the ratio of the total emitted current to the incident current, is strongly affected by the direction of band bending near the surface. For Cs/AlN, the upward band bending limits the total yield which reaches a maximum of 8 for incident electron energies of 600~900 eV and then decreases rapidly because secondary electrons excited deep in the solid are pushed back to the bulk by the field of the depletion region. On the other hand, Cs/GaN gives a maximum yield of 20 at higher incident electron energy (1200~1400 eV). This maximum is preserved up to much higher incident energy because the field of depletion region helps secondary electrons escape from the NEA solid.@FootnoteText@@footnote 1@ C.I. Wu, A. Kahn, E.S. Hellman and D.N.E. Buchanan, Appl. Phys. Lett., 73, 1346 (1998). @footnote 2@C.I. Wu and A. Kahn, Appl. Phys. Lett, 74, 546 (1999) @footnote 3@C.I. Wu and A. Kahn, J. Vac. Sci. Technol. B16, 2218 (1998) .

3:00pm **EM-MoA4 Inductively Coupled Plasma-Induced Etch Damage of GaN p-n Junctions***, **R.J. Shul**,* Sandia National Laboratories*; L. Zhang,* Sandia National Laboratories, US*; A.G. Baca, C.G. Willison, J. Han,* Sandia National Laboratories*; S.J. Pearton, F. Ren,* University of Florida

The fabrication of a wide variety of GaN-based photonic and electronic devices depends on dry etching through a p-n junction. Examples of these devices include laser diodes, light-emitting diodes, heterojunction bipolar transistors, p-i-n photodiodes and junction field effect transistors. The majority of dry etching methods used to pattern such devices rely on ion-assisted removal of the substrate material. Due to the relatively high bond energy (8.92 eV/atom) of GaN, the threshold ion energy for the onset of dry etching is typically on the order of 25 eV. Under conditions of both high ion flux and ion energies above this threshold, etch rates > 5,000Å/min are readily achieved for GaN in Inductively Coupled Plasma (ICP) or Electron Cyclotron Resonance (ECR) etch systems. However, under such conditions, the potential for plasma-induced damage is significant. Attempts to minimize such damage by reducing the ion energy or increasing the chemical activity in the plasma often results in a loss of etch rate or anisotropy which significantly limits critical dimensions and reduces the utility of the process for device applications requiring vertical etch profiles. It is therefore necessary to develop plasma etch processes which couple anisotropy for critical dimension and sidewall profile control and high etch rates with low-damage for optimum device performance. In this study, GaN p-i-n mesa diodes were formed by Cl@sub 2@/BCl@sub 3@/Ar etching at different ion energies and plasma fluxes. Reverse bias leakage currents were measured to evaluate damage created during plasma etch. Despite the increase in GaN etch rates observed with increasing ion energy and flux, damage was able to accumulate ahead of the etch front. Techniques to recover device performance will also be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

3:20pm **EM-MoA5 Schottky Diode Measurements of Dry Etch Damage in n- and p-type GaN***, **X.A. Cao**, A.P. Zhang, G. Dang, F. Ren, S.J. Pearton,* University of Florida*; R.J. Shul,* Sandia National Laboratories*; L. Zhang,* Sandia National Laboratories, US

N- and p- type GaN was exposed to Inductively Coupled Plasma (ICP)of N@sub 2@, Ar or H@sub 2@, as a function of high density source power(0-1400 W) and rf chuck power(20-250 W). For n-GaN there was a strong reduction in diode reverse breakdown voltage and an increase in forward and reverse currents, while for p-GaN the reverse breakdown increased. These results are consistent with creation of point defects with shallow donor nature that increase the conductivity of initial n-GaN or decrease the conductivity of initially p-GaN. Annealing at ~750 @super o@C under N@sub 2@ or removal of 500-600 Å of the surface essentially recovered the electrical properties of the plasma exposed GaN. For completed n-type mesa diode structures exposed to ICP Ar or Cl@sub 2@/Ar discharges, the low-bias forward currents increased by several orders of magnitude. The exposed surfaces became N@sub 2@-deficient in all cases, and both UV-ozone oxidation followed by dissolution of the oxide and annealing in N@sub 2@ were examined for restoration of the diode properties.

3:40pm **EM-MoA6 Process Development for Dry-etched Laser Facets on GaN**, ***L. Zhang***, Sandia National Laboratories, US; *R.J. Shul, G.A. Vawter, C.G. Willison, C.Y. Gao, J. Han,* Sandia National Laboratories; *S.J. Pearton,* University of Florida

With the rapid advance of III-N growth and processing technologies, GaN-based laser diodes (LDs) have been realized with continuously improved lasing thresholds and lifetimes. However, compared to their more mature arsenide and phosphide counterparts, the III-V nitride based LDs suffer from higher threshold current density and lower quantum efficiency. The reason for this is partly due to the lack of vertical profiles and sidewall roughness of the dry-etched laser facets in the III-V nitride structures, resulting in low mode reflectivity and high optical scattering loss. Therefore, it is essential to develop dry etch processes which yield anisotropic, smooth sidewalls. In this work, GaN etched sidewall profiles and morphologies are studied using an Inductively Coupled Plasma (ICP) reactor and will be compared to Reactive Ion Beam Etch (RIBE) results. Highly anisotropic profiles are expected in RIBE due to the acceleration of the ions through a series of grids located between the source and the sample as well as low pressure operation that reduces ion scattering. For BCl@sub 3@/Cl@sub 2@/Ar ICP chemistries, it was found that sidewall angles ranged from less than 70° to greater than 85° as a function of plasma chemistry, plasma density, ion energy, chamber pressure, and etch mask. The best ICP results were obtained using a photoresist mask, at 500 W ICP power, -150 V DC bias, 2 mTorr pressure, 32 sccm Cl@sub 2@, 8 sccm BCl@sub 3@, and 5 sccm Ar flow rate. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

4:00pm **EM-MoA7 Photo-Assisted RIE of III-V Nitrides in BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@**, ***N. Medelci***, *I.E. Berishev, D. Starikov, A. Bensaoula,* University of Houston; *M. Gonin, K. Fuhrer, A. Schultz,* Ionwerks

III-V nitrides are known as superior semiconductor materials for UV optoelectronic and high power, high temperature applications. However, these materials are extremely difficult to etch due to their high molecular bond strength. In order to address the device processing issue, reactive ion etching (RIE) and photo-assisted RIE processes were developed for boron nitride (BN) and gallium nitride (GaN) thin films. Our experiments show that optimum photo-assisted etching using a filtered Xe lamp occurs in Cl@sub 2@/Ar and BCl@sub 3@/Cl@sub 2@/N@sub 2@ chemistries for BN and GaN, respectively.@footnote 1-2@ Etch rates up to 324 (GaN) and 220 (BN) nm/min with smoother and cleaner etched surfaces were obtained with this process. In this work, we extend our studies to the AlGaN and InGaN ternaries. We also address some peculiarities observed in the previous work such as higher GaN etch rates for the UV-filtered Xe lamp, and lower GaN etch rates when a KrF excimer laser was used instead of the Xe lamp. To that end and to better understand these processes and characterize the photo-assisted effects, mass spectrometry determination of volatile species and optical emission spectroscopy (OES) identification of species in the plasma will be performed. The mass spectrometer used is a unique miniature time of flight prototype which employs orthogonal extraction, has a resolving power m/@Delta@m in excess of 500 and a detection limit of 10 ppm for all masses at a one second sampling rate. @FootnoteText@ @footnote 1@ A. Tempez, N. Medelci, N. Badi, D. Starikov, I. Berishev, and A. Bensaoula, "Photoenhanced reactive ion etching of III-V nitrides in BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ plasmas", accepted for publication in J. Vac. Sci. and Technol. A (1999). @footnote 2@ N. Medelci, A. Tempez, I. Berichev, D. Starikov and A. Bensaoula, "Photo-assisted RIE of GaN in BCl@sub 3@/Cl@sub 2@/N@sub 2@", Mat. Res. Soc. Symp. Proc. (1999) (submitted).

4:20pm **EM-MoA8 Effect of N@sub 2@ Discharge Treatment on AlGaN/GaN HEMT Ohmic Contact Using Inductively Coupled Plasma**, ***A.P. Zhang***, *G. Dang, X.A. Cao, F. Ren, S.J. Pearton,* University of Florida; *J.M. Van Hove, P.P. Chow, R. Hickman, J.J. Klaasen,* SVT Associates

Due to the excellent thermal stability and large energy band-gap of GaN based material system, AlGaN/GaN based high electron mobility transistors (HEMTs) have an excellent potential for high temperature and high power applications. The conventional low resistance n@super +@-cap layer structure used to reduce parasitic resistances in GaAs technology is generally not applied in nitride devices as it is difficult to perform the gate recess step. This is due to the high chemical stability of GaN which makes wet etching very difficult except at high temperatures or under optical stimulation. Mochi has demonstrated that an exposure of Ar or N@sub 2@ discharge to ohmic contact region before the metal deposition showed an improvement of contact resistance. However a systematic study of plasma energy and time has not been performed yet. In this work, we investigate the contact resistance by varying the chuck power from 10-60W and ICP discharge power from 100 to 700W and plasma exposure time from 40 to 80 sec. The effect of anneal temperature was also studied. The ion bombardment sample showed two order of magnitude lower contact resistance than that of un-treated sample. Auger and AFM were also used to analyze the effect of ion bombardment. The photoresist was also optimized for the plasma treatment.

4:40pm **EM-MoA9 In-Situ Plasmas Diagnostics for the Etchings of AlGaN/GaN Heterostructures**, *H.S. Kim,* SungKyunKwan University, South Korea; ***G.Y. Yeom***, SungKyunKwan University, South Korea, Korea; *J.W. Lee, T.I. Kim,* Samsung Advanced Institute of Technology, South Korea

AlGaN/GaN heterostructures have been widely used to form the various devices such as field effect transistor(FET), photodiode, bipolar transistor(BT), light emitting diode(LED), and laser diodes(LD). High etch rate of the full structure and reliable etch end point detection are required to form a device by dry etching. In the previous work, plasma characteristics during the GaN etching have been reported using a quadrupole mass spectrometry (QMS) and an optical emission spectroscopy (OES) and an etch mechanism of GaN by Cl@sub2@-based plasmas has been proposed from the detection of etch products. In this study, GaN, AlGaN, and AlN grown on sapphire, and AlGaN/GaN heterostructures were etched using inductively coupled Cl@sub2@/BCl@sub3@ plasmas. Etch rates of GaN were higher than those of AlGaN for the Cl@sub2@ rich plasmas. The increase of Al composition in the AlGaN decreased the etch rate of heterostructures regardless of plasma conditions. These differences in the etch rate could be reduced by the increase of BCl@sub3@ to Cl@sub2@ gas and the decrease of the pressure. The plasma characteristics and their relations to etch rates were investigated using in-situ plasma diagnostics such as QMS and OES. Finally, the etch end point of an AlGaN/GaN heterostructure and a LD structure could be estimated by the monitoring an Al-containing optical emission line. Detailed data will be shown in the presentation.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+FP-MoA

Transport and Nanostructures in Organic Films

Moderator: E. Umbach, Universität Würzburg, Germany

2:00pm **OE+EM+FP-MoA1 Generation and Transport of Charge Carriers in Conjugated Polymers**, *V.I. Arkhipov,* ***H. Baessler***, *S. Barth, C. Im, D. Hertel, B. Schweitzer,* Philipps Universität, Germany **INVITED**

Upon photoexcitation of conjugated polymers, such as ladder-type poly-phenylene (LPPP) and substituted PPVs, both geminately bound electron-hole pairs and free charge cariers are generated. Evidence for geminate pair production in LPPP comes from electric field assisted delayed fluorescence. Intrinsic free charge carrier generation occurs via on-chain dissociation of vibrationally hot singlet excitations. Motion of positive charge carriers has been studied involving time of flight experiments. From the hole mobility in a sieres of substituted PPV as a function of temperature and electric field it will be concluded that transport is disorder controlled as it is in molecularly doped polymers. An exception of this rule is hole transport in LPPP. The question of intra versus inter chain transport will briefly be addressed. This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 383) and the Stiftung Volkswagenwerk.

2:40pm **OE+EM+FP-MoA3 Resistance of Individual Molecular Semiconductor Grains Measured by Conducting Probe Atomic Force Microscopy**, ***T.W. Kelley***, *C.D. Frisbie,* University of Minnesota

Continued interest in organic electronics has underscored the need for better understanding of transport mechanisms in polycrystalline films of organic semiconductors. We are employing conducting probe atomic force microscopy (CP-AFM) to measure the electrical resistances associated with individual grains and grain boundaries in thin films of @alpha@-sexithiophene (6T). These measurements focus on single 6T grains that are several microns in length and width and 1 - 6 molecular layers (2-14 nm) in thickness. The 6T grains are vacuum deposited onto insulating substrates with lithographically patterned gold electrodes. A Au-coated AFM probe is used to image each grain, including any crystal defects, and to subsequently make point-contact electrical measurements at particular positions on the grain. Current-voltage (I-V) curves are recorded at each position as a function of probe-electrode separation. From these data, we estimate tip-grain contact resistance and conductivity of each grain. In general, we show that CP-AFM is a powerful approach to exploring the effects of microstructure on conductivity in organic semiconductor films.

3:00pm **OE+EM+FP-MoA4 Self-Assembled, Template-Based Nanolithography***, **S.R. Cohen**, R. Maoz, E. Frydman, J. Sagiv,* Weizmann Institute of Science, Israel

The versatility of our recently developed technique@footnote 1@ for scanning probe microscope (SPM)-based, non-destructive nanolithography on an organized organic monolayer template is demonstrated here. By building on, rather than destroying the organic "resist", consisting of an ordered self assembled monolayer (SAM), it is possible to construct complex 3 dimensional structures which can ultimately lead to device formation. In the first step, applying a bias voltage between a conductive SPM tip and a silver thiolate-based monolayer surface site leads to "activation" of that site by the tip. The second step, deposition of metal (silver) from solution by interaction with an enhancing solution which specifically deposits silver on these sites, leads to in-situ formation of metallic features with sub-micron resolution. These features are chemically bound to the surface-altered monolayer, and comprise a three-dimensional structure of surface-bound silver. The fabrication of conducting nanowires is demonstrated, which could be extended to device or nanocircuit formation. The formation of complex, three-dimensional structures with order determined by the underlying monolayer has been demonstrated. Considering that the surface template exhibits molecular order, this technique has the potential of creating molecular-scale devices, using standard ambient application of SPM, and solution chemistry. @FootnoteText@ @footnote 1@ R. Maoz, S.R. Cohen, and J. Sagiv, Adv. Mater. 11, 55 - 61 (1999).

3:20pm **OE+EM+FP-MoA5 Fabrication of Organic Microstructures Using Soft Lithography***, **G. Whitesides**,* Harvard University **INVITED**

Chemistry, with stimulus from biology, is beginning to develop a range of new concepts for fabrication of microsystems: these include self-assembly, non-covalent synthesis, microprinting, micromolding, microfluidic patterning, microelectrochemistry, and related techniques designed to make it possible to design complicated structures having electrical, optical, biological or magnetic functionality and to replicate these systems efficiently. These concepts suggest approaches to fabrication that are substantially different from photolithography in their areas of application. The phrase "soft lithography" encompasses one core set of techniques for replication. The techniques included in soft lithography include the formation of self-assembled monolayers, the patterning of these monolayers using microcontact printing, the fabrication of structures inside small channels using microfluidic methods, and the fabrication of small (< 50 nm) polymer structures using transfer molding and replica molding. The adjective "soft" in the phrase "soft lithography" refers to the elastomeric stamps or molds that are important in many of these techniques, and to the properties of organic materials in general. These techniques may use photolithography, but normally primarily during the step that fabricates the master. This talk will outline progress in this area: from homogeneous self-assembled monolayers (SAMs) to transistors, and from molecular self-assembly to the self-assembly of macro-scale objects. Areas of application in which soft lithography is promising include 3-D fabrication and pattern transfer to non-planar surfaces, large-area patterning, low-cost additive fabrication, rapid prototyping (especially of microanalytical and microfluidic systems), fabrication of systems where control of surface chemistry is crucial (e.g., cell biology) and fabrication of MEMS. Key problems are defect densities, distortions in the elastomeric masks/stamps/molds, and fabrication requiring multiple registered levels of fabrication. Reviews: "Soft Lithography" Xia, Y. and Whitesides, G. M., Angew. Chem. Intern. Ed. Engl. 1998, 37, 550-575. "Soft Lithography" Xia, Y. and Whitesides, G. M., Annu. Rev. Mater. Sci. 1998, 28, 153-184.

4:00pm **OE+EM+FP-MoA7 Electron Beam Patterning of Amine-Functionalized Self-Assembled Monolayers***, **C.K. Harnett**, K.M. Satyalakshmi, M.G. Metzler,* Cornell University*; D.R. Medeiros,* IBM T.J. Watson Research Center*; H.G. Craighead,* Cornell University

Amine-functionalized self-assembled monolayers form a hydrophilic surface that can strongly attach other materials. Examples of materials that have been selectively deposited on patterned amine monolayers include nanoparticles,@footnote 1@ metals, fluorescent molecules, and biological cells.@footnote 2@ Nanopatterning of reactive monolayers is therefore of great practical interest. We have studied electron-beam patterning of 3-aminopropyltriethoxysilane (APTS) and other self-assembled monolayers. Submicron features that are difficult to achieve with UV lithography or microcontact printing are accessible with electron beams. Exposed patterns are examined with lateral-force microscopy (LFM) to determine pattern quality vs. electron dose. At 20 kV, a dose of 300 µC/cm@super 2@ is required to produce continuous 1-micron lines. Results from several electron energies will be presented, with the goal of using these monolayers in a low-energy (1-2 kV) electron-beam lithography system. Exposed areas are analyzed with grazing angle IR spectroscopy to determine possible exposure mechanisms. Subsequent deposition of metals, and use of protection-group chemistry to produce a tone-reversed pattern, will also be discussed. @FootnoteText@ @footnote 1@ T. Vossmeyer, S. Jia, E. Delonno, M. R. Diehl, S.-H. Kim, X. Peng, A. P. Alivisatos, J. R. Heath, Journal of Applied Physics 84, 3664-3670 (1998) @footnote 2@ C. S. Dulcey, J. H. Georger, V. Krauthammer, D. A. Stenger, T. L. Fare, J. M. Calvert, Science 252, 551-554 (1991).

4:20pm **OE+EM+FP-MoA8 Liquid Crystal Imprinting: A New Method for Preparing Uniformly Oriented Thin Films***, **D.L. Patrick**,* Western Washington University

A new synthetic strategy is presented for preparing nanostructured thin films possessing macroscopically-uniform organization. The method is based on the use of a thermotropic nematic liquid crystal (LC) solvent, which serves a growth medium for deposition of material onto a suitable substrate. Application of a magnetic field results in the formation of an oriented film whose directionality can be controlled externally. The method has been used to prepare several organic monolayer systems in which the orientation of the films' molecular constituents is highly controlled. We show that orientational order at the solid-fluid interface originates during film nucleation, and that the alignment mechanism is based on anisotropic anchoring interactions between surface adsorbates and the LC solvent. Details of the relationship between molecular-scale surface structure and bulk LC ordering were studied by combining scanning tunneling microscopy and polarized optical measurements of uniformly oriented cells. LC fluids exhibit anisotropic anchoring interactions with most crystalline surfaces, indicating that the method may be applicable to the synthesis of films and layered materials using a wide range of molecular and supramolecular building blocks.

4:40pm **OE+EM+FP-MoA9 Electro-Patterning of Conjugated Polymer Films on Conducting Surfaces Using the Precursor Polymer Approach***, R.C. Advincula,* University of Alabama at Birmingham, US*; S. Inaoka,* University of Alabama at Birmingham*; **D. Roitman**,* Hewlett-Packard Laboratories

Recently, a novel method of depositing ultrathin films of conjugated polymers on conducting surfaces has been investigated by the UAB and HP groups. We report the formation and patterning of conjugated polymer films by novel electro-deposition of materials on specific sites of substrates and sequences. We have investigated a range of feature sizes using this method with features below micron size. We have also investigated the formation of unique blend film structures, with emphasis on light emitting materials. Previous attempts in using electrodeposition resulted in 'brittle' and defective (pinholes) film surfaces. Our results indicate that the overall optical, mechanical quality and physical integrity of the films are superior compared to previously reported systems.

Surface Science Division
Room 606 - Session SS1+EM-MoA
Metals on Oxides

Moderator: U. Diebold, Tulane University

2:00pm **SS1+EM-MoA1 Nucleation and Growth of Copper Islands on TiO@sub2@(110): Evidence for Self-limited Island Sizes***, **D.A. Chen**,* University of South Carolina*; M.C. Bartelt, R.Q. Hwang, K.F. McCarty,* Sandia National Laboratories

Metal-oxide interfaces play an important role in a variety of technological applications, including those involving the design of electronic devices, sensors and heterogeneous catalysts. In order to develop a fundamental understanding of these metal-oxide interfaces, we have studied the formation of Cu islands on TiO@sub2@(110)-(1x1) in ultrahigh vacuum using scanning tunneling microscopy for Cu coverages up to 1.25 ML. The formation of 3D islands at all the coverages reflects the relatively high mobility of Cu atoms on TiO@sub2@ at room temperature and the weak interactions between Cu and TiO@sub2@. Surprisingly, the island diameter remains almost constant for all coverages. Furthermore, the Cu islands exhibit self-limiting growth at low coverages (0.5 ML), the average island size scales with coverage, but this increase in island size is primarily due to an increase in height not diameter. Although larger islands can be formed by annealing, the average size of the islands is independent of coverage for any given annealing temperature. We propose two general schemes that could lead to the observed self-limiting growth. The first is that the attachment rate of adatoms drops as the island size increases. The second is that the rate at which adatoms reach existing islands drops as the islands grow. We will discuss physical scenarios under which each of these effects may be dominant. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported in part by the USDOE-OBES-Division of Materials Sciences.

2:20pm **SS1+EM-MoA2 Influence of Surface Reactions on Morphology: Ag Nanoclusters on TiO@sub 2@(110)**, ***X. Lai***, *T.P. St. Clair, D.W. Goodman,* Texas A&M University

The effects of in situ O@sub 2@ exposure on TiO@sub 2@(110)-supported Ag nanoclusters were investigated using x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). An oxygen-induced cluster ripening was observed by STM after exposing Ag/TiO@sub 2@(110) to 10.00 Torr O@sub 2@ in an elevated-pressure reactor. A bimodal size distribution of Ag clusters was evident after a 10 minute O@sub 2@ exposure at room temperature. Time-dependent studies of the ripening process indicated that the majority of the ripening occurred within the first hour of exposure. The cluster density also increased 5-15%, indicating that redispersion simultaneously occurred with ripening. For comparison, a reduced, roughened TiO@sub 2@(110) and a fully oxidized TiO@sub 2@(110) were prepared and used as Ag supports. Propylene exposure was also studied to further investigate adsorbate-induced morphological changes. Issues relevant to the stability of Ag catalysts for general oxidation reactions were addressed.

2:40pm **SS1+EM-MoA3 Kinetics and Dynamics of Substrate and Metal Atoms on TiO@sub2@**, ***G. Thornton***, *I. Brookes, H. Raza, C.L. Pang, S. Haycock,* Manchester University, UK **INVITED**

TiO@sub2@ substrates have been used as platforms to test ideas about oxide surface reconstruction and metal growth on oxides. This work is motivated by the importance of such interfaces in a number of applications which include catalysis and gas-sensing. As part of this work we have recently studied two aspects of TiO@sub2@ surface science associated with temperature and time dependent structural changes using STM and non-contact AFM. The first involves the study of the 1x1 to 1x3 phase transition of TiO@sub2@(100). In addition to the 1x1 and the high temperature equilibrium 1x3 microfacet termination previously observed, intermediate 1x3 structures are imaged. The relationship between the 1x1 termination and the 1x3 microfacet phase suggests that the latter reconstruction is formed by removing material rather than growing from a lower lying terrace. Intermediate structures point to a mechanism of the phase transition which involves discrete bond breaking steps. Turning to Cu growth on TiO@sub2@(110), at room temperature and at <0.1 ML most of the metal atoms are initially mobile, with some 2D island formation. The cluster size of about 6 Å diameter suggests that they consist of 7 atoms arranged in a centred hexagon. Such an arrangement fits between the bridging O rows. 3D clusters are formed at higher coverage consistent with Volmer-Weber growth. At lower temperatures 1D metastable strings of Cu atoms are formed in the [001] direction, which collapse to 2D islands and subsequently 3D clusters at higher coverage.

3:20pm **SS1+EM-MoA5 Nucleation and Growth of Pt Nanoclusters on TiO@sub 2@ Rutile and Anstase Surfaces**, ***Y. Liang,*** Pacific Northwest National Laboratory*; A.W. Grant,* University of Washington*; D.R. Baer, S. Gan,* Pacific Northwest National Laboratory

Understanding the interaction of ultra-thin metal overlayers with oxide surfaces impacts a wide range of technological applications. One of those is the oxide-supported metal catalysts where unusual surface chemisorption and activity have been observed. In this presentation, we report an investigation of nucleation and growth of Pt on rutile and anatase surfaces using scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low energy electron diffraction. Results show that vapor deposition of 0.1 ML of Pt on a rutile TiO@sub 2@(110) surface at ambient temperature leads to the formation of randomly distributed three-dimensional Pt nanoclusters on the 1x1 surface. However, this random distribution is strongly perturbed by the presence of surface line defects produced by extended sputtering and annealing cycles. As the density of the line defect increases, majority of Pt nanoclusters are preferentially attached at the ends of line defects instead of randomly distributed on the rutile surfaces. This result suggests that the line defects on TiO@sub 2@(110) surfaces have stronger interaction with Pt and thus serve as nucleation sites for Pt growth. Based on the change of distribution of Pt clusters as a function of line defect density, the diffusion length of Pt on rutile surfaces is obtained. In addition to rutile, we also investigate the nucleation and growth of Pt on anatase surface. We have successfully grown anatase single crystal thin films on SrTiO@sub 3@ substrates using oxygen plasma assisted molecular beam epitaxy. Investigation of nucleation and growth of Pt on anatase surface is currently in progress. The results will be presented at the meeting and compared with those obtained on the rutile TiO@sub 2@ surfaces.

3:40pm **SS1+EM-MoA6 Role of Surface Vacancies and Water Products in Metal Nucleation: Pt/MgO(100)**, *A. Bogicevic,* ***D.R. Jennison,*** Sandia National Laboratories

Metal atom adsorption on oxide surfaces, resulting in clusters or thin films, involves a variety of structure-determining chemical interactions. While surface steps have long been known to promote nucleation, it has been speculated in several experimental studies that the most common defect in well prepared surfaces, isolated surface oxygen vacancies, may act as nucleation sites. However, this has not been substantiated via experiment or theory. Here we examine this question and, for completeness, how water dissociation products affect nucleation, since there have been several reports that these are common low-density contaminants on prepared oxide surfaces. Our density-functional calculations reveal that isolated F@sub s@ and V@sub s@ surface vacancies on MgO(100) ionize single Pt atoms, roughly tripling their adsorption energy. This trapping inhibits Pt atoms from binding to other Pt atoms, resulting in a negative addimer binding energy. Hence, isolated surface vacancies demote nucleation, contrary to popular belief. A defect that does promote nucleation is the F@sub s@V@sub s@ divacancy, which increases the addimer binding energy by 20%. Amongst water and its dissociation products, adsorbed hydroxyl ions are found to have a similar but even stronger effect. We discuss the implications of these results for the temperature dependence of nucleation and the generality of these results for other metals and oxides.@footnote 1@ @FootnoteText@ @footnote 1@ Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under Contract DE-AC04-94AL85000.

4:00pm **SS1+EM-MoA7 Metal Particles on Single Crystal Oxides as Model Catalysts**, ***J.H. Larsen***, *J.T. Ranney, A.W. Grant, D.E. Starr, J.E. Musgrove, C.T. Campbell,* University of Washington

The growth morphology and reactivity of model oxide-supported metal catalysts are intimately connected. On some well-defined oxides, vapor-deposited metals form two-dimensional islands, typically up to a critical coverage below 1 monolayer (ML). The local electronic environment of the supported metal particles is modified as compared to the surface of the bulk metal, and so changes in reactivity are expected. Above the critical coverage, three-dimensional growth sets in and it becomes possible to measure reactivities as a function of island thickness. Several metal on metal oxide systems were studied. The surface growth mode was investigated using low energy ion scattering (LEIS) and x-ray photoelectron spectroscopy (XPS). In order to probe the nature of the reaction sites on the surface, the decomposition of hydrocarbons was also studied with temperature programmed desorption (TPD). From these experiments, the dependence of the metal reactivity on the lateral dimensions of the two-dimensional metal islands and the thickness of three-dimensional metal clusters was determined. It was found that Pt particles on ZnO(0001)-Zn exhibit reactivity towards methanol decomposition which is characteristic of low-index Pt facets, even below the critical coverage of ~ 0.6 ML where only two-dimensional islands are present. The adsorption energy of some metal on metal oxide systems was furthermore measured as a function of coverage using single crystal adsorption calorimetry. The adsorption energy is a fundamental quantity that gives important insight into the energetic origins of the growth and reactivity of metal particles supported on metal oxides.

4:20pm **SS1+EM-MoA8 High-Pressure STM Studies of Pt Nano-clusters on Al@sub 2@O@sub 3@/NiAl(110)**, ***L. Österlund***, *M.O. Pedersen, P. Thostrup, K.H. Hansen, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

A novel system in which an STM is incorporated into a high pressure cell has been constructed. The system permits in-situ studies of surfaces with atomic resolution at pressures ranging from UHV to one atmosphere. In the present paper, we have investigated the morphology and structure of well-ordered Pt nano-clusters deposited on thin layers of aluminum oxide created by oxidation of NiAl(110). >From the shape, i.e. the height and width, and from atomic resolved images of the top facets of the clusters, we can quantitatively determine the adhesion energy of the metal cluster to the oxide, using calculated surface free energies for the cluster facets. We have investigated the change in the morphology of the Pt nano-clusters exposed to up to 1 bar of hydrogen and oxygen.

4:40pm **SS1+EM-MoA9 Cu Interaction with Al@sub 2@O@sub 3@ Substrates: Effects of Defects and Coverage***, C. Niu, K. Shepherd,* ***J.A. Kelber****,* University of North Texas

We report UHV surface science studies of the wetting and nucleation behavior of Cu on sapphire(0001). Such fundamental wetting and nucleation interactions are of increasing importance in microelectronics, joining and brazing, as well as in catalysis. This study focuses on the effects of defects and kinetic factors for well-defined systems that are critical to an understanding of behavior for "real world" systems. On clean sapphire, Cu is initially present as Cu(I) to a coverage of 0.35 ML [ML = monolayer], after which a second, metallic Cu layer begins to grow. This behavior is in agreement with recent theoretical calculations by A. Bogicevic and D. R. Jennison[Phys. Rev. B (in press)]. The behavior of Cu on sapphire at elevated temperatures is coverage dependent. For @theta@@sub Cu@ < 0.35 ML, Cu(I) remains stable on the surface for temperatures up to ~ 1000K. However, in the presence of Cu(0), e.g. @theta@@sub Cu@ = 0.75 ML, Cu(I) reacts to form additional Cu(0) at about 500K. Pre-sputtering of the sapphire surface prior to Cu deposition inhibits Cu(I) formation and enhances Cu(0) formation at low coverage, correlating with the sputter-induced dehydroxylation of the sapphire surface and creation of oxygen vacancies. These data indicate that variations of a small number of surface defect densities can explain the large number of contradictory results obtained for the Cu/alumina systems. The significance of these findings to "real world" applications (e.g. Cu on oxidized Ta and other microelectronics diffusion barriers) will be discussed.

5:00pm **SS1+EM-MoA10 Nucleation and Growth of Tungsten on SiO@sub 2@ During Atomic Layer Deposition Using Sequential Surface Reactions***,* ***J.W. Elam****, C.E. Nelson, R.K. Grubbs, S.M. George,* University of Colorado, Boulder

The atomic layer deposition of tungsten (W) can be achieved by separating the binary reaction WF@sub 6@ + Si@sub 2@H@sub 6@ --> W + 2SiHF@sub 3@+ 2H@sub 2@ into two half-reactions. Successive application of the WF@sub 6@ and Si@sub 2@H@sub 6@ half-reactions in an ABAB... sequence produces W atomic layer controlled growth. The nucleation and growth of W on SiO@sub 2@ was examined during alternating exposures to Si@sub 2@H@sub 6@ and WF@sub 6@. Auger electron spectroscopy studies at 573 K revealed an initial nucleation phase that was followed by a layer-by-layer W growth regime. Nucleation occurred during the first 10 sequential Si@sub 2@H@sub 6@ and WF@sub 6@ surface reactions. Layer-by-layer W deposition then proceeded at a growth rate of 2.5 Å per AB reaction cycle. This W growth rate is consistent with one W monolayer per AB reaction cycle. The Auger data was fit well assuming Frank-van der Merwe layer-by-layer growth. These studies reveal that the sequential surface reactions can facilitate metal wetting of oxide surfaces and conformal layer-by-layer metal growth. Additional Auger experiments yielded the adsorption kinetics for both Si@sub 2@H@sub 6@ and WF@sub 6@ during W atomic layer deposition. The WF@sub 6@ half-reaction had an activation energy E=7 kcal/mol and required WF@sub 6@ exposures of 30 L for the WF@sub 6@ half-reaction to reach completion. The Si@sub 2@H@sub 6@ had virtually no temperature dependence and the Si@sub 2@H@sub 6@ half-reaction saturated following 200 L Si@sub 2@H@sub 6@ exposures at 573 K.

Electronic Materials and Processing Division
Room 608 - Session EM-TuM

Si Surface Chemistry and Etching, Passivation, and Oxidation

Moderator: J.E. Crowell, University of California, San Diego

8:20am **EM-TuM1 Structural Transition Layers at the Interface of SiO@sub 2@/Si(100) Fabricated by Ozone***, **K. Nakamura**, H. Itoh, A. Kurokawa, S. Ichimura,* Electrotechnical Laboratory, Japan*; K. Koike, G. Inoue, T. Fukuda,* Iwatani International Corporation, Japan

A novel processing technique for oxidation with rapid growth kinetics at lower substrate temperature is strongly required to fabricate a much thinner silicon dioxide film 1nm thickness. This was confirmed by a change of the etching rate of SiO@sub 2@ film with dilute hydrofluoric acid solution. Such thinner region of transition layers in the ozone-oxide was implemented either on clean Si(100)2x1 or on Si(100) with an already existing native oxide film at 300°C or more. However, exposure of ozone to Si(100) with an already existing thermally grown oxide film, for example at 350°C, caused no change in the distribution of transition layers in the oxide. This contrast indicates that the oxide growth by ozone or the further oxidation of lower oxidized silicon atoms in the native oxide by ozone formed transition layers with much less thickness, while highly oxidized silicon atoms in the thermally grown oxide film remained unreacted even by reactive ozone. Structural transition layers on the opposite side of the interface, i.e. in the substrate, will also be discussed.

8:40am **EM-TuM2 Infrared Spectroscopy as a Probe of Semiconductor/Dielectric Interfaces: Growth and Structure of SiO@sub 2@ on Si***, **K.T. Queeney**, M.K. Weldon, Y.J. Chabal, K. Raghavachari,* Bell Laboratories, Lucent Technologies **INVITED**

The structure and quality of the Si/SiO@sub 2@ interface are crucial to the performance of transistors with gate oxide thicknesses < 20 Å. We have exploited the intrinsic sensitivity of infrared absorption spectroscopy to microscopic chemical environment in order to elucidate structural details of this interface between crystalline Si and amorphous SiO@sub 2@. Infrared spectra of thermally grown SiO@sub 2@ are acquired as a function of film thickness by etchback of device-quality films. Modeling the mechanical and optical properties of these films reveals that substoichiometry at the Si/SiO@sub 2@ interface dominates the spectra of ultrathin (< 10 Å) SiO@sub 2@; different thermal histories are shown to affect the quality of this "transition region." To understand the microscopic structure of this interfacial substoichiometry, we have grown and characterized a model Si/SiO@sub x@ interface via controlled H@sub 2@O reaction of Si(100)-(2x1) in ultrahigh vacuum. Coalescence of dimer-based silicon epoxide species (capped by triangular Si-O-Si linkages) into an extended silicon-oxygen network results in the birth of SiO@sub x@ phonon modes (975 and 1130 cm@super -1@) whose microscopic structural origins are for the first time well understood. This epoxided interface is trnasformed at room temperature into high-quality SiO@sub 2@, and the mechanism for room-temperature H@sub 2@O-induced oxidation is compared to that observed for technologically relevant surface terminations.

9:20am **EM-TuM4 Real Time Observation on Si(001) Surface Oxidation by Scanning Tunneling Microscopy***, **K. Miki**,* Electrotechnical Laboratory, Japan*; Y. Kudo, M. Murata, K. Yamabe,* Tsukuba University, Japan

We have succeeded in real time observation on oxidation of Si(001) surface by scanning tunneling microscopy at elevated temperatures up to 1100 K. First we made clear the boundary between etching and oxidation regions. At the 900 K, etching both from step edges and in the terrace was dominant at low oxygen partial pressure under $1 \times 10^(-5) Pa$ while we observed oxidation island nucleation over this critical pressure. Under low rate oxidation, we found that etching is allowed together and it stops in the vicinity of the oxidation island. Our map whether etching or oxidation occurs is consistent of the previous reports. At the high temperature region the boundary is good agreement with the previous report by Gelain and et al. [Oxidation of metals 3 (1971) 139]. In the low temperature region under 870 K the oxidation speed of the first 1 ML is independent of temperature and this results is consistent with reflection electron microscopy experiment by Watanabe and et al. [Phys. Rev. Lett. 80 (1998) 345] We found three types of absorbant. Although the one type is still a misery, we could identify that one is atomic oxygen adsorbant in the center of a Si dimer and the other is back bond oxidation. First one was well seen in the initial stage, as oxidation proceeded the latter became more dominant. This observation suggests that oxidation of Si(001) surface has dual species at least, which is previously reported by Engstrom and et al. [Surf. Sci. 256 (1991) 317]. Backbond oxidation extended normal to dimer rows as ordered spots. The ordering eventually came to have disordering around 1ML oxidation. This suggests that stress during is very important even in the initial stage.

9:40am **EM-TuM5 Scanning Tunneling Microscopy Study of Surface Morphology of Si(111) after Synchrotron Radiation Stimulated Desorption of SiO@sub 2@***, **Y. Gao**, T. Miyamae, H. Mekaru, T. Urisu,* Institute for Molecular Science, Japan

We have used scanning tunneling microscopy to investigate the surface morphology of Si(111) after the native SiO@sub 2@ layer was removed by synchrotron radiation stimulated desorption at 650 °C. The surface shows large regions of atomically flat Si(111)-7x7 structure. An interesting feature of the surface is the formation of atomic steps nicely registered to the crystal structure, and the pinning of the steps by nanometer scale dust is evident. This is in sharp contrast to Si(111) surfaces after thermal desorption of SiO@sub 2@ at temperatures 880°C and above, where the surface steps are much more irregular. The registration of the surface steps to the underlying crystal structure indicates that the surface atomic layer reaches thermodynamic equilibrium under synchrotron radiation at temperatures much lower than that necessary for thermal desorption of SiO@sub 2@.

10:00am **EM-TuM6 How Important are Second Nearest Neighbor Effects in Silicon 2p Photoemission Spectroscopy of Si/SiO@sub 2@ Interfaces?***, **J. Eng, Jr.**, K. Raghavachari,* Bell Labs, Lucent Technologies

The proper interpretation of Si 2p photoemission spectra of Si/SiO@sub 2@ interfaces has been a controversial topic since 1993, when Banaszak-Holl and McFeely proposed that second nearest neighbor effects can cause significant chemical shifts in Si 2p photoemission features.@footnote 1@ Their claims were based upon model Si/SiO@sub 2@ surfaces produced by the adsorption of H@sub 8@Si@sub 8@O@sub 12@ clusters on Si(100) at room temperature. Arguing that the clusters are bonded to Si(100) dimers through a single vertex (due to Si-H bond cleavage), they proceeded to correlate the relative peak positions and peak intensities with different Si species at the interface. This correlation led them to conclude that the entire formal oxidation state framework is inadequate for interpreting Si 2p photoemission spectra of Si/SiO@sub 2@ interfaces, and that second nearest neighbor effects are important. The key issue in this controversy is understanding how the H@sub 8@Si@sub 8@O@sub 12@ clusters bond to the Si(100) surface. Using transition state calculations, we present detailed mechanistic arguments which show that the clusters do not react with the Si(100) surface through Si-H bond cleavage, but rather through Si-O bond cleavage. The resulting "cracked" cluster allows us to predict the Si 2p photoemission features of the clusters on Si(100) using the conventional formal oxidation state model, without invoking second nearest neighbor effects. Finally, the normal mode frequencies of the "cracked" cluster are in excellent agreement with infrared studies of the clusters on Si(100). @FootnoteText@ @footnote 1@ M. M. Banaszak-Holl and F. R. McFeely, Phys. Rev. Lett., 71(15) (1993) p.2441.

10:20am **EM-TuM7 FTIR Studies of the Nitridation of Si(100)-(2x1) and Oxidized Silicon***, K.T. Queeney, **Y.J. Chabal**, J. Eng, Jr., K. Raghavachari,* Bell Laboratories, Lucent Technologies*; X. Zhang, E. Garfunkel,* Rutgers University*; S.B. Christman, E.E. Chaban,* Bell Laboratories, Lucent Technologies

We have investigated the incorporation of N into Si and SiO@sub 2@ with IR absorption spectroscopy, in order to elucidate the mechanisms by which nitridation and oxynitridation influence the structure and thus the electrical characteristics of Si/SiO@sub 2@ interfaces. Studies of the adsorption and decomposition of NH@sub 3@ on Si(100)-(2x1) demonstrate that the chemistry of this nitriding agent is governed by a combination of dissociative and molecular adsorption, with metastable NH@sub 3(a)@ characterized by a dramatically redshifted NH@sub 3@ deformation mode. Higher coverages and temperatures favor NH@sub 3@ dissociation into H and NH@sub 2@, followed by competing desorption and decomposition. The mechanism for N insertion into the Si substrate is studied via repeated cycles of NH@sub 3@ dosing and annealing with post-dosing of atomic H to identify discrete N-containing structures by the perturbation in @nu@(Si-H) frequencies. Oxynitride growth by reaction of NO on Si(100)-(2x1) reveals the interplay between oxygen and nitrogen, as both Si-O (~900 cm@super -1@) and Si-N (~775 cm@super -1@) modes exhibit frequencies distinct from those observed for pure oxide and nitride films. These fundamental growth studies are used to interpret structural details contained in the complex spectra of device-quality nitride and oxynitride films grown on Si.

10:40am **EM-TuM8 Silicon Passivation Chemistry for MEMS Technology*,* *R. Maboudian,*** University of California, Berkeley **INVITED**

Adhesion, friction , and wear are prevalent problems in a majority of micro-electro-mechanical systems (MEMS) devices. Since gravity is negligible at the dimension of most microstructures, understanding of surface interactions in MEMS is of paramount importance for controlling stiction phenomena. After a brief introduction to Si micromachining, I will discuss the use of various micromachined testing devices, such as cantilever beam arrays, in conjunction with other surface characterization techniques, such as X-ray photoelectron spectroscopy and atomic force microscopy, to measure the surface forces present between polycrystalline silicon surfaces and to manipulate them by utilizing various surface passivation treatments.

11:20am **EM-TuM10 STM Studies of the Site-specific Reactivity of Isopropanol in Aqueous Silicon Etching: Controlling Morphology with Surface Chemistry*,* *M.A. Hines*,** *T.A. Newton, Y.-C. Huang, L.A. Lepak,* Cornell University

Aqueous silicon etchants play an important role in the fabrication of microelectromechanical systems (MEMS). To improve performance, a reputedly inactive chemical agent -- isopropanol [(CH@sub 3@)@sub 2@CHOH] -- is often added to the etchant. Not only does this simple additive reduce undercutting by up to 75%, it also produces much smoother etched surfaces, in part by suppressing the formation of pyramidal etch hillocks. Using a combination of STM measurements and kinetic Monte Carlo simulations, we will show that these morphological changes have a simple, chemical origin. The site-specific rates of isopropanol reaction on vicinal Si(111) surfaces were studied by kinetic competition with an etchant of known anisotropy and quantified using concentration-dependent changes in the etched surface morphology. The unique properties of isopropanol-enhanced etchants are explained by the relatively high reactivity of the isopropoxide ion. Once formed, the silicon isopropoxy species transiently suppresses etching at specific surface sites and modifies the anisotropy of the etchant.

11:40am **EM-TuM11 Removal of Native Oxide Employing Heated NH@sub 3@/NF@sub 3@ Mixture*,* *H. Ogawa,*** The University of Tokyo, Japan*; T. Arai, T. Ichiki,* Toyo University, Japan*; Y. Takamura, Y. Horiike,* The University of Tokyo, Japan

The removal of the native oxide employing a heated NH@sub 3@/NF@sub 3@ mixture was studied using in-situ XPS and FTIR-ATR/RAS. The mixture was heated in an 13 mm diameter Al@sub 2@O@sub 3@ tube whose surface was wound by a resistive heater, then being exposed to a sample set on a stage cooled by a N@sub 2@ gas with room temperature. The chemical oxide was grown in a H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@ solution. The NH@sub 3@/NF@sub 3@ mixture with partial pressure ratio of unity at a pressure of 1 Torr started to remove the oxide from a Al@sub 2@O@sub 3@ tube temperature of 500 °C. For the Si surface after removal of the oxide, new XPS peaks appeared at 103.8 eV in Si2p and 402.2 eV in N1s, respectively. Absorption spectra of Si-H(2100 cm@super -1@), N-H(stretching; 3330 cm@super -1@, bending;1454cmcm@super -1@) and Si-F (783 cm@super -1@) were also observed in the IR measurement. These results exhibit the presence of a (NH@sub 4@)@sub 2@SiF@sub 6@ film deposited on the Si surface after removal of the oxide.@footnote 1@The film desorbed readily at 100 °C in a vacuum and then was terminated by hydrogen. The higher the partial pressure, the faster the oxide removal rate, whereas NH@sub 3@ or NF@sub 3@ alone did not demonstrate any etching reaction. The result that the Al@sub 2@O@sub 3@ tube heated at higher temperature led to the higher etch rate implies generation of the oxide etchant within the tube. Thus, NH@sub 3@ and NF@sub 3@ were introduced separately to two tubes, and when NF@sub 3@ alone was heated, the present reaction was confirmed. The result implies thermally decomposed NF@sub 3@ reacts with NH@sub 3@, generating the oxide etchant. The removal rate ratio of thermal grown SiO@sub 2@ to BPSG (boron phosphorus silicate glass) films was almost unity. It is well known that the usual HF solution produces about ten times higher etch rate for BPSG than for the thermal SiO@sub 2@. Accordingly, this technology allows us to offer a new dry cleaning method of the contact hole surface in ULSI multi-level interconnection process. @FootnoteText@ @footnote 1@M. Hirose, S. Yokoyama and Y. Yamakage: J. Vac. Sci. Technol., B3 (1985)1445.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+AS-TuM

Interfaces and Characterization of Organic Thin Films

Moderator: Y. Gao, University of Rochester

8:20am **OE+EM+AS-TuM1 Electronic Properties of Organic Semiconductor Interfaces*,* *I.G. Hill,*** Princeton University*; C. Shen,* Princeton University, US*; D. Markiewicz, J. Schwartz, A. Kahn,* Princeton University **INVITED**

The alignment of molecular energy levels at the interfaces of organic semiconductor films plays a critical role in determining organic light emitting device (OLED) efficiencies. At a metal/semiconductor interface, the positions of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) relative to the metal Fermi level determine the barriers for charge injection into the organic. At organic/organic heterointerfaces, the relative alignment of the HOMO and LUMO levels of the two organics determines whether charges will flow freely across the interface or result in charge accumulation. It is now widely accepted that vacuum levels do not, in general, align at metal/organic interfaces,@footnote 1,2@ implying that techniques such as ultraviolet photoelectron spectroscopy (UPS) and internal photoemission must be used to determine barrier heights. Vacuum levels do align at the majority of organic/organic heterointerfaces, with a few notable exceptions.@footnote 3@ Using UPS, we have studied a variety of both metal/organic and organic/organic interfaces with the goal of understanding the origin of, and therefore ways to control, the interface dipoles which result in vacuum level discontinuities. The results of these studies will be discussed with an emphasis on our attempts to understand the roles of surface modifying procedures, such as oxygen plasma treatment of indium tin oxide (ITO), on improving device performance. @FootnoteText@ @footnote 1@H. Ishii and K. Seki, IEEE Trans. Electr. Devices 44, 1295, (1997) @footnote 2@I.G. Hill, A. Rajagopal and A. Kahn, Appl. Phys. Lett., 73, 662, (1998). @footnote 3@I.G. Hill and A. Kahn, Proceedings of SPIE, Organic Light-Emitting Materials and Devices II, 3476, 168, (1998).

9:00am **OE+EM+AS-TuM3 Photoemission Characterization of Al/Alq@sub 3@ and Al/LiF/Alq@sub 3@ Interfaces*,* *L. Yan,*** *Q.T. Le, Y. Gao,* University of Rochester*; M.G. Mason, C.W. Tang,* Eastman Kodak Company

We have investigated the interface formation of Al on tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@) and Al on LiF/Alq@sub 3@ using X-ray and ultraviolet photoemission spectrascopy (XPS and UPS). We observed significant modifications of O1s, N1s and Al2 p core level spectra as Al was directly deposited on the Alq@sub 3@ surface. The Alq@sub 3@ features in the UPS spectra were also quickly destroyed. In contrast, a dramatically different behavior was observed for Al on the LiF/Alq@sub 3@ interface. With o nly 5Å of LiF deposited on the Alq@sub 3@ surface as a buffer layer, the reaction between Al and Alq@sub 3@ is significantly suppressed. A well-defined gap state is formed. The Alq@sub 3@ features in UPS shift to higher binding energies but remain easily recognizable. Both the core level spectra and the gap state suggest that the Alq@sub 3@ anion is formed in the presence of Al and LiF.

9:20am **OE+EM+AS-TuM4 Charge Injection vs. Chemical State of Electrode Surfaces in Metal/Alq@sub 3@/Metal Structures*,* *C. Shen,*** Princeton University, US*; I.G. Hill, A. Kahn,* Princeton University

The effect of the deposition sequence on the electrical behavior of metal-organic interfaces is an important issue in the context of multiple layer organic light emitting devices (OLED). Metals deposited on organics generally lead to more extensive interface chemistry, and have been reported to produce different electrical behavior, than organics deposited on metals. To address this issue, we investigate the interface chemistry, electronic structure and electrical transport in nominally symmetric Mg:Ag/8-hydroxyquinoline aluminum(Alq@sub 3@)/Mg:Ag structures fabricated and tested in ultra-high vacuum and under controlled atmosphere. We perform detailed X-ray photoemission spectroscopy measurements which confirm that the metal-organic chemical reaction and interdiffusion are different at the Mg-on-Alq@sub 3@ interface than at the of Alq@sub 3@-on-Mg interface. We also show, however, that the chemical state of the bottom electrode surface plays a major role in the device electrical behavior. The Mg:Ag/Alq@sub 3@/Mg:Ag structure built in ultra-high vacuum leads to symmetric top and bottom electron injection, whereas controlled oxidation of the bottom metal surface leads to a two-order-of-magnitude lower bottom contact injection. These results fully explain earlier results obtained for devices made under "standard" conditions, i.e. in moderate 10@super -5@ Torr vacuum. A similar study of the Al/Alq@sub 3@/Al structure is under way and will be reported as well at the conference.

9:40am **OE+EM+AS-TuM5 Investigation of the Electronic Structure of Organic Schottky Contacts with Photoemission Spectroscopy: Discrimination Between Interface Dipole, HOMO Offset, Band Bending and Charging Related Spectral Shifts***, **R. Schlaf**, G.P. Kushto, L.A. Crisafully, C.D. Merritt, Z.H. Kafafi,* US Naval Research Laboratory

We have determined the electronic structure of several organic Schottky contacts formed between the organic luminescent semiconductor tris (8-hydroxyquinolinato) gallium (Gaq@sub 3@) and the metals Al, Mg, Ag, Au, and Pt. The investigated interfaces were prepared by vapor deposition of Gaq@sub 3@ on in-situ deposited metal films or thin sputtered high purity metal foils in a multi step growth procedure. Before growth and after each Gaq @sub 3@ deposition step the samples were characterized in situ using a combination of x-ray and ultraviolet photoemission spectroscopies (XPS, UPS). UPS was used to measure the highest occupied molecular orbital (HOMO) positions and interface dipoles, while XPS was used to determine the band bending (bulk charge redistribution) at the interface. In addition, simultaneous measurements of the high binding energy cutoff of the XP- and UP-spectra allowed the determination of the onset of charging phenomena observed at around 100Å Gaq@sub 3@ film thickness. Our results demonstrate that both, charging and band bending effects, may result in strong shifts of the PES spectra which need to be carefully evaluated in order to accurately determine the orbital line-up and the dipole at the interface. Our experiments suggest that the investigated organic Schottky contacts have large interface dipoles due to the chemisorption of the first organic layer in contact with the metal surface. All investigated interfaces also exhibit strong band bending in the organic layer, which strongly depends on the work function difference between Gaq@sub 3@ and the particular metal in contact.

10:00am **OE+EM+AS-TuM6 Examination of Band Bending at Organic Semiconductor / Metal Interfaces Studied by Kelvin Probe Method***, **H. Ishii**, N. Hayashi, E. Ito, K. Seki,* Nagoya University, Japan

How the energy levels of an organic semiconductor and a metal electrode align at the interface between them is a critical and basic issue for understanding organic electronic devices. So far, Mott-Schottky (MS) model has been applied for the estimation of the electronic structure at organic/metal interfaces. In the model, vacuum level alignment is assumed right at the interface, while the Fermi level alignment is achieved through band bending in space charge layer. In order to examine the validity of this model, the film-thickness dependence of the location of the vacuum level of TPD (N,N'-bis(3-methylpheyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine) on various metals(Au, Cu, Ag, Mg and Ca) were measured by Kelvin probe method in ultrahigh vacuum (UHV). At all the interfaces, an abrupt shift of the vacuum level was observed within 1 nm thickness, while further deposition of TPD up to 100 nm led to no change of the location of the vacuum level. These results indicate that the possible space charge layer is much thicker than 100 nm in UHV. The observed relation between the vacuum level shift and the work function of the metals suggests that (1) the Fermi level of TPD is located around the midgap in UHV condition and that (2) the Fermi level alignment is achieved only at TPD/Cu,Ag,Mg interfaces, not by band bending but by dipole layer formation right at the interface. These findings clearly demonstrate the invalidity of MS model for organic / metal interfaces in UHV. The results for the interface between Alq@sub 3@ (tris(8-hydroxyquinolino)aluminum) and metal will be also presented.

10:20am **OE+EM+AS-TuM7 Schottky Energy Barriers and Charge Injection at Metal/Organic Interfaces***, **I.H. Campbell**,* Los Alamos National Laboratory*; B.K. Crone,* Lucent Technologies*; R.L. Martin, D.L. Smith,* Los Alamos National Laboratory*; C.J. Neef, J.P. Ferraris,* University of Texas, Dallas **INVITED**

We present independent measurements of metal/organic Schottky energy barriers and their charge injection characteristics in metal/organic/metal structures. The Schottky energy barriers were measured using internal photoemission and built-in potential techniques. The Schottky energy barriers to a poly (p-phenylene vinylene) based polymer (MEH-PPV) and to Alq were measured for a variety of metals with work functions ranging from 2.7 eV (Sm) to 5.6 eV (Pt). For MEH-PPV we find good agreement with the ideal Schottky model. In contrast, for Alq we find that the ideal Schottky picture is not applicable and that electron injecting contacts are pinned about 0.6 eV below the electron conducting states. The charge injection characteristics of these contacts were investigated by measuring the current-voltage characteristics of single carrier structures. The dependence of the current-voltage characteristics on the Schottky energy barrier is quantitatively described by a device model which includes charge injection, transport and space charge effects in the structure. For Schottky barriers less than about 0.3 eV the current in the structure is space charge limited and the contact is ohmic. Finally, we present results using organic self-assembled monolayers to manipulate the metal/organic Schottky energy barrier and to control charge injection into the organic material. The monolayers are used to insert a thin (1 nm) dipole layer between the metal contact and the organic material. Depending upon the orientation of the dipole layer the Schottky energy barrier may be increased or decreased and the corresponding charge injection properties degraded or enhanced.

11:00am **OE+EM+AS-TuM9 Interfacial Electronic Structures between p-Sexiphenyl and Metals Studied by Electron Spectroscopies***, **E. Ito**, H. Oji, H. Ishii, Y. Ouchi, K. Seki,* Nagoya University, Japan

Recently, organic electroluminecent (EL) devices have attracted much attention in relation to application to flat panel display. In order to understand the charge injection mechanism in such devices, the energy level alignment at the interfaces between organic films and metal electrodes is of crucial importance. In this study, we investigated electronic structures at the interfaces between p-sexiphenyl (6P) and a metal (Au or Mg) by ultraviolet photoelectron spectroscopy (UPS), metastable atom electron spectroscopy (MAES), and X-ray photoelectron spectroscopy (XPS). MAES is an extremely surface sensitive method because the excitation source is metastable atoms which can not penetrate into a sample. The abrupt shift of the vacuum level by 6P deposition on the evaporated metal film (Au or Mg) was observed in the UPS spectra. MAES spectrum of 6P on Au with the thickness of 0.3nm is almost similar with that of 20nm thick 6P film. This suggests that the flat-lying 6P molecules uniformly covered Au substrate. We also measured the spectra of Au on 6P/Au. Even when Au was evaporated with the thickness of 50nm, the spectral feature of 6P dominates in the MAES spectra, suggesting that Au does not cover completely with the 6P film, while the core level peak of Au gradually increased in XPS spectra with deposition of Au. Similar trend was also observed for Mg deposited on 6P/Mg. These results indicate the diffusion of Au into 6P film, leading to formation of the intermixing region. In the system of Au on 6P film, we observed downward shift of the energy levels with irradiation of UV-light (the excitati on source of UPS), probably due to the photovoltaic effect. These results show the the formation of the different interface between the 6P/metal and the metal/6P.

11:20am **OE+EM+AS-TuM10 A Photoemission Investigation of Interfaces of poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) with an oligomer (p-sexiphenyl) and a Metal - Calcium***, **A. Rajagopal**,* Univ. Notre-Dame, Belgium*; N Koch,* Tech. Univ. Graz, Austria*; J Ghijsen,* Univ. Notre-Dame, Belgium*; K. Kaeriyama,* Kyoto Inst. of Tech., Japan*; R.L Johnson,* Univ. Hamburg, Germany*; G. Leising,* Tech. Univ. Graz, Austria*; J.J. Pireaux,* Univ. Notre-Dame, Belgium

Poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) (PDHPT) is a blue light emitting conjugated polymer with a band gap of ca. 3 eV, and is a promising candidate as an active material in organic light emitting diodes. The interface of this polymer with a) a blue light emitting oligomer (sexiphenyl- 6P), and with b) a low work function cathode material, calcium (Ca) have been investigated using both ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS). Both 6P and PDHPT have a band gap of ca. 3 eV, as well as similar ionization potentials, and this makes the interface an interesting one. A systematic study of the in-situ growth of 6P on PDHPT allows the estimation of the relative positions of the HOMOs and the vacuum levels. We find that the HOMO of PDHPT is below that of 6P, and there is a vacuum level offset of 0.3 eV suggesting charge transfer from 6P to PDHPT. In the case of metal-PDHPT interface, Ca was deposited in extremely small steps in-situ, and both XPS and UPS data were recorded after each subsequent deposition. Contrary to what can be predicted based on calculations and experiments on similar systems, namely phenylenes and thiopehenes, we propose that Ca forms covalent bonds with the polymer. The consequences of these experimental findings will be discussed within the context of LEDs.

11:40am **OE+EM+AS-TuM11 A Photoelectron Study of Chemically Treated Indium Tin Oxide Surface and Its Reactivity with Phenyl-Diamine***, **Q.T. Le**, F. Nuesch, E.W. Forsythe, L.J. Rothberg, Y. Gao,* University of Rochester

We report on the effect of various treatments by base and acid solutions on the work function of indium tin oxide (ITO). Ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) were used to measured the work function and chemical composition, respe ctively, of the processed ITO surface. The results indicate that the magnitude of the work function shift is highly dependent on the nature of the solution. In contrast, for the same solution, the concentration of the solution appears to have little effect on the work function shift. In addition, the interface formation between processed ITO and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) using XPS and UPS is presented. The reactivity of the treated ITO surfaces versus NPB is compared with the case of plasma-treated sample. The low current onset obtained from the single-layer devices based on acid-treated ITO can be attributed to the low energy barrier for hole injection at the ITO/hole-transporting material interface. This work was supported in part by DARPA DAAL 0196K0086, NSF Grant DMR-9612370, and the Swiss National Science Foundation.

Surface Science Division
Room 606 - Session SS1+EM-TuM
Nitrides and Compound Semiconductors

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

8:20am **SS1+EM-TuM1 Reconstructions and Growth Kinetics of GaN Surfaces with and without Adlayers*, R.M. Feenstra,*** Carnegie Mellon University **INVITED**

Reconstructions of the gallium nitride (0001) Ga-face and N-face surfaces have been studied using scanning tunneling microscopy, with growth performed by molecular beam epitaxy. Distinct families of reconstruction are observed on each face, with most of the structures involving the presence of one of more adlayers of gallium bonded to underlying nitrogen atoms. For the N-face, this Ga-adlayer is in a 1x1 arrangement and further reconstructions are formed by additional Ga adatoms weakly bonded on the Ga-adlayer. For the Ga-face, the Ga-adlayer is incommensurate with the GaN lattice. For both the Ga- and N-face, growth under Ga-rich conditions yields smooth surfaces whereas growth under N-rich conditions produces rough surfaces. The latter case is indicative of limited surface diffusion rates. However, in the presence of surfactant layers such as Mg or As, smooth growth is also obtained in the N-rich regime. For sufficiently high surface coverage of Mg, a remarkable transition is observed in which Ga-polar material converts to N-polarity, with the inversion domain boundary extending along the c-plane. For growth of InGaN alloys, the role of surface metal layers (mainly indium) is also found to play an important role in the growth kinetics and incorporation efficiency. @FootnoteText@ Work supported by Office of Naval Research and National Science Foundation, and performed in collaboration with V. Ramachandran, H. Chen, A. Smith, D. Greve, J. Northrup, J. Neugebauer, W. Sarney, and L. Salamanca-Riba.

9:00am **SS1+EM-TuM3 Increase of Electrical Conductivity in p-GaN by Immersion in H@sub2@O@sub2@ Solution*, *B. Liu,*** *M.H. Ahonen, P.H. Holloway,* University of Florida

Immersion in a peroxide solution was found to increase electrical conductivity in p-GaN films. Auger electron spectroscopy (AES), current-voltage and Hall measurements were used for characterization. All samples in this study were grown on the c-plane of sapphire substrates by metallorganic vapor phase epitaxy (MOVPE) with a carrier concentration of 1.1x10@super 17@ cm@super -3@. The samples were first cleaned in boiling aqua regia (3HCl+3HNO@sub 3@) for 10min, rinsed in DI water, and blown dry with N@sub 2@. Metal contacts (10nmNi/100nmTi/100nmAu) were deposited with an electron beam evaporator (~10@super -6@ Torr). After metal deposition, samples were immersed in a H@sub 2@O@sub 2@ solution (1H@sub 2@O@sub 2@ : 5H@sub 2@O or 1H@sub 2@O@sub 2@ : 1H@sub 2@O, in volume) for different time (30sec to 300sec). This was followed by DI water rinse and N@sub 2@ blowing dry. Surface composition analysis using AES showed differences in N concentration versus treatments with the highest increase of N (5.67at%) found after immersion in 1H@sub 2@O@sub 2@ : 1H@sub 2@O for 300sec. Corresponding to this increase in N, improved electrical conductivity was confirmed by current-voltage data. The highest (a factor of two) increase of conductivity was measured for the sample with the highest increase of N concentration. No increase of carrier concentration was found in these samples with Hall measurement. The increase of N atoms at the sample surface and improvement of electrical conductivity will be discussed based on the chemical reaction of H@sub 2@O@sub 2@ with GaN and the effects of N vacancies in p-GaN. * This work is supported by EPRI and DARPA under agreement W08069-07.

9:20am **SS1+EM-TuM4 Structure of GaN(0001)-1*1: Holography Study of Mg Adsorption on GaN(0001) Surface*, G.J. Lapeyre,*** *S.H. Xu, H. Cruguel, Y. Yang,* Montana State University*; J.F. Schetzina,* North Carolina State University

The adsorption site and surface atomic structure of Mg on GaN(0001)-1*1 surface has been studied by photoelectron holographic imaging technique. The results clearly show that Mg adsorbs on T4 site and there is one monolayer Ga adatoms on the surface. They are on H3 sites.

9:40am **SS1+EM-TuM5 Angle Resolved Photoemission Studies of the Surface Electronic Structure of GaN(0001)*, K.E. Smith,*** *Y.C. Chao, P. Ryan, J. Downes, C.B. Stagarescu, R. Singh, T.D. Moustakas,* Boston University*; D. Hanser, R.F. Davis,* North Carolina State University

The physical properties of GaN are under intense study due to its use in optoelectronic and high temperature semiconductor devices. However, the surface electronic structure of GaN remains poorly understood. Numerous reconstructions of GaN are observed, but very little is known about the detailed electronic structure of clean, ordered GaN surfaces. We report the results of an extensive synchrotron radiation excited angle-resolved photoemission study of n-type and p-type wurtzite GaN(0001)1x1 surfaces. GaN thin films were grown both by MOCVD on SiC, and by MBE on Al@sub 2@O@sub 2@. Surfaces were cleaned by repeated cycles of N@super 2+@ ion bombardment followed by annealing in UHV. We have observed a number of different surface states on these materials. For n-type MBE samples we find a non-dispersive surface state just below the valence band maximum that is highly sensitive to surface contamination and disorder. This state shows no dispersion perpendicular to the surface and exists across the surface Brillouin zone in a region devoid of bulk states. Polarization measurements reveal that this feature originates from a state with sp@sub z@ character. Destruction of this state only partially removes the observed band bending. For n-type MOCVD samples, cleaned in an identical fashion, we find at least two surface states. One is similar to that seen on the MBE material, while the second is a highly dispersive back bonding state, extending to the bottom of the valence band at points in the surface Brillouin zone. Removal of these states does not alter the observed band bending. For p-type MBE samples, we also find a surface state in the fundamental band gap, above the valence band maximum. Such states are not observed for the n-type material. We will discuss the surface electronic structure of GaN in the context of these measurements. @FootnoteText@ Work supported in part by NSF grant DMR 95-04948. Experiments were performed at the NSLS, which is supported by US DOE.

10:00am **SS1+EM-TuM6 The Reaction of Oxygen with GaN(0001)*, B.D. Thoms,*** Georgia State University, US*; V.J. Bellitto, Y. Yang,* Georgia State University*; D.D. Koleske, A.E. Wickenden, R.L. Henry,* Naval Research Laboratory

In addition to optoelectronic applications, Group III Nitrides also exhibit properties appropriate for their use in high power and high temperature transistors. Oxidation of the surface influences several aspects of device fabrication including surface passivation and the production of metal contacts. We have characterized the reaction of oxygen with MOCVD-grown GaN(0001) using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), high resolution electron energy loss spectroscopy (HREELS), and temperature programmed desorption (TPD). AES of GaN(0001) following exposure to O2 at room temperature results in an increased O(KLL) Auger intensity which saturates after approximately 200 L. AES following heating shows that oxygen is present to temperatures of 900 C. No surface reconstruction is observed by LEED, but rather a reduction in contrast between diffraction spots and background with increasing oxygen exposure. The reaction with oxygen produces a reduction in the ELS intensity at loss energies of 3.5 and 6 eV. A similar reduction is observed after exposure to atomic hydrogen, consistent with the reaction of both oxygen and hydrogen with surface dangling bonds. Oxygen exposure also produces an increase in ELS intensity at 10 eV. In HREEL spectra acquired following oxygen exposures up to 200 L, no adsorbate vibrational features are resolved from Fuchs-Kliewer phonon losses at integer multiples of 700 cm-1. These data are consistent with the chemisorption of oxygen on Ga sites.

10:20am **SS1+EM-TuM7 Deep Level Electronic States of Clean GaN (0001)(1x1) Surfaces Prepared by In Decapping*, A.P. Young,*** *L. Brillson,* Ohio State University*; C. Tu,* University of California, San Diego

The tremendous interest in the properties of GaN surfaces and interfaces has created a need for new techniques for preparing clean, ordered surfaces under ultrahigh vacuum (UHV) conditions. Furthermore, the electronic properties associated with different interface preparations are not well understood at present. In contrast to surfaces prepared by N+ bombardment or Ga overcoat annealing cycles at 900C, clean and ordered GaN (0001) (1x1) surfaces can be produced directly from MBE-grown surfaces after removal of an In cap layer at 650C. These surfaces are comparable to those clean, ordered surfaces reported elsewhere. We have used electron-excited nanometer luminescence spectroscopy (EENLS) to measure these states in the band gap of MBE-GaN deposited on a GaN/sapphire composite substrate. The GaN was cleaned in UHV via thermal desorption of a thin (~50 ML) metallic In layer deposited prior to removal of the specimen from the growth chamber. This relatively low temperature desorption presents a benign method of transporting and processing GaN for device applications. Auger Electron Spectroscopy (AES) results show that if the In can uniformly cover the surface, it can prevent contamination during atmospheric exposure without reacting or diffusing into the GaN layer. The as-prepared surface morphology, measured via ex situ atomic force microscopy (AFM), indicated significant islanding of the In on the surface with approximate lateral size of 250 nm and height of 30 nm. Furthermore, a Ga signal, probably in the form of an oxide, was observed via AES indicating that some of the surface was not covered by In. The In was selectively desorbed from the GaN without reacting to produce InGaN. 8 ML of Ga were then deposited and the surface flashed once to 690C to reduce residual O and C contamination yielding a sharp (1x1) low energy electron diffraction (LEED) pattern. EENLS at a probe energy of 350 V (probe depth » 3 nm) indicated substantial "yellow" (YL) emission within the bandgap centered at 2.22 eV (FWHM = 0.4 eV) with only minimal near band edge (NBE) emission. YL emission remains constant while NBE increases with depth of excitation, indicating only states intrinsic to the GaN bulk. Subsequent AFM reveals Ga droplets residual to the flash annealing. Thus, In decapping introduces no new states at the clean, ordered GaN surface.

10:40am **SS1+EM-TuM8 Characterization of MOCVD ZnO Buffer Layers for CIS Solar Cells*, L.C. Olsen,*** Washington State University*; G.J. Exarhos,* Pacific Northwest National Laboratory*; F.W. Addis, L. Huang,* Washington State University

This paper concerns studies carried out to characterize MOCVD ZnO films grown for buffer layers in CIGS solar cells which have exhibited efficiencies between 12 and 14%. Further understanding of properties of these devices are required in order to increase efficiencies above 18% as demonstrated by CIGS cells with CdS buffer layers. Work is focusing on buffer layers grown with a two step process involving nucleation of ZnO at 250 C and subsequent growth at 100 C to achieve a total film thickness on the order of 800 A. The purpose of this work is to characterize the physical and electro-optical properties of MOCVD ZnO layers, and relate the results to device processing. All ZnO films examined were grown onto copper-indium-diselenide (CIS) substrates. XPS examination of films for which the growth was terminated at various stages of the two-step process show that good coverage of CIS is achieved after 100 A of growth, although some outdiffusion of indium does occur. XPS analyses of 800 A films indicate the MOCVD ZnO films have no major impurities and that films are slightly oxygen deficient. Ellipsometry studies indicate that results for the index of refraction and extinction coefficient vs photon wavelength are well understood if one assumes that there are no secondary phases between the ZnO buffer layer and CIS, and that the ZnO band structure is characterized by three transitions, one at 3.2 to 3.4 eV, one at 3.8 to 4.0 eV, and one at 4.8 to 5.2 eV. The transitions are fairly consistent with theoretical results for the ZnO band structure. Raman spectroscopic studies of the ZnO buffer layers are also being carried out. Finally, results for ZnO buffer layers grown with the two-step process will be compared to characteristics of films grown with different procedures and which yield poor performing cells.

11:00am **SS1+EM-TuM9 Photoelectron Diffraction of GaSe Bilayer Grown on Si(111)*, S. Meng,*** *B.R. Schroeder, A. Bostwick,* University of Washington*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; F.S. Ohuchi, M.A. Olmstead,* University of Washington

Initial nucleation of GaSe on Si(111)7x7 results in formation of a pseudomorphic bilayer, which passivates the substrate dangling bonds and serves as the interface for further film growth. Component-resolved photoelectron diffraction (PED) and low-energy electron diffraction show this bilayer is oriented in a single domain, with the Ga-Se bond aligned with the substrate Si-Si bond. Combining scanned-angle and scanned-energy PED with theoretical calculations reveals the Ga and Se atomic positions. Ga sits directly atop surface Si, and the resultant interface bonding leaves Se lone-pair states on the surface. This makes the Si(111):GaSe surface highly resistant to contamination, and even additional GaSe does not stick for T@sub substrate@@>=@550°C. The measured PED patterns of Ga and Se 3d states show strong forward focusing along Ga-Se bond as well as diffraction rings from in-plane Se-Se scattering. The Ga-Se bond angle is between that for layered GaSe and cubic Ga@sub 2@Se@sub 3@. PED also shows strong (>20%) angular variation of the Ga3d spin-orbit branching ratio, while the Se 3d branching ratio is constant within 5%. This is likely associated with differences in photoionization matrix element and propogation of 3/2 and 5/2 states for the different local environments. * Supported by NSF DMR9801302.

11:20am **SS1+EM-TuM10 An Example of a Compound Semiconductor Surface that Mimics Silicon: The InP (001) (2x1) Reconstruction*, L. Li,*** *Q. Fu, B. Han, M. Begarney, D. Law, C. Li, R.F. Hicks,* University of California, Los Angeles

An InP (001) (2x1) reconstruction was prepared by metalorganic vapor-phase epitaxy. Scanning tunneling micrographs and infrared spectra of adsorbed hydrogen revealed that the (2x1) is terminated with a complete layer of buckled phosphorous dimers, giving rise to p(2x2) and c(4x2) domains. A surface band gap of 1.2 ± 0.2 eV was measured by scanning tunneling spectroscopy. The buckling can be explained by electron correlation among the dangling bonds of pairs of phosphorous dimers. This allows the surface to achieve a lower energy, semiconducting state. This reconstruction mimics the Si (100) (2x1), which is terminated with buckled silicon dimers.

11:40am **SS1+EM-TuM11 STM Studies of Sulfur Passivated InP(100)*, G.P. Lopinski,*** *R.A. Wolkow,* National Research Council, Canada*; C.D. MacPherson,* Nortel Networks, Canada

While sulfur passivation of InP(100) has been extensively studied by a number of techniques the details of the surface structure are still not definitively established. In this work we report STM studies of sulfur passivated InP(001) surfaces, prepared by wet chemical treatment in ammonium sulfide followed by annealing in UHV. Although the as prepared surface is disordered due to the presence of excess sulfur, highly pitted terraces evolve for annealing temperatures above 300C. Further annealing to 450C results in emergence of atomically flat terraces. LEED observations indicate the existence of a (3x1) phase in addition to the previously reported (2x1) structure. Atomically resolved STM images reveal the coexistence of local (3x1) and (2x1) periodicity. These surfaces are found to be stable with respect to brief air exposures.

Electronic Materials and Processing Division
Room 608 - Session EM-TuA

High Dielectric Constant Materials and Thin Oxides

Moderators: Y.J. Chabal, Bell Laboratories, Lucent Technologies, K.T. Queeney, Bell Laboratories, Lucent Technologies

2:00pm **EM-TuA1 Challenges in Gate Dielectric Scaling***, D.P. Monroe*, *B.E. Weir, M.A. Alam, J. Bude, P.J Silverman, T. Sorsch, M.L. Green, A. Ghetti, Y. Ma, Y. Chen, F. Li,* Bell Labs, Lucent Technologies **INVITED**

Extrapolation of current trends in CMOS suggest that the gate dielectric of 2010 will have a capacitance equivalent to <15Å of SiO@sub 2@, including the nonzero thickness of the charge sheets in gate and substrate. It must withstand penetration of elements such as Boron during processing, and of electrons and holes during operation. It must tolerate damage from highly energetic carriers excited by the voltages on gate and drain over a multi-year operating life. Proposed replacements for SiO@sub 2@ must also demonstrate materials compatibility with the Si substrate and the gate material (currently also Si). The successful candidate will have a fewer than one interface defect for 10,000 atoms, and a uniformity across wafers, lots, and runs of better than 10% (3@sigma@). We will discuss these daunting materials and processing challenges from a transistor and circuit perspective, concentrating on the capacitance, mobility, boron penetration, and time-dependent dielectric breakdown of SiO@sub 2@ and nitrided oxides thinner than 30Å, as measured by ellipsometry. The electrical thickness of such oxides is thicker by at least 5Å, depending strongly but reproducibly on the oxide field. Simple measurements of this dependence are critical to understanding the transistor drive capability and the leakage current. The breakdown properties are more strongly governed by the applied potentials than the field. However they are strongly sensitive to the polarity of the gate voltage, even after care has been taken to include the large effects of band bending. This indicates the important role of the carrier dynamics in the anode. The "soft" breakdown of these thin oxides indicates a reduced role of positive feedback that results in higly conductive filaments in thicker oxides; indeed, some transistors continue to function even after "breakdown." We will outline some ideas for the physical mechanisms underlying the special properties of breakdown in these films.

2:40pm **EM-TuA3 Investigation of Titanium Nitride Gates for Tantalum Pentoxide and Titanium Dioxide Dielectrics***, D.C. Gilmer*, *C.C. Hobbs, L. La, B. Adetutu, J. Conner, M. Tiner, L. Prabhu, S. Bagchi, P. Tobin,* Motorola

The continuing push to decrease the feature size of microelectronic devices is hampered by some of the physical properties of the current materials. According to the National Technology Roadmap for Semiconductors (NTRS) projections, deep sub-micron device scaling indicates that silicon dioxide gate dielectrics must be scaled to less than 25 angstroms. It is generally accepted however, that such scaling will not be practical due to the rapid increase in tunneling current and resultant decrease in lifetime for these very thin silicon dioxide gate dielectrics. One alternative is to replace silicon dioxide with a material having a higher dielectric constant that will allow the use of thicker, less leaky, films. Towards this end, compounds such as tantalum pentoxide and titanium dioxide have been evaluated to replace silicon dioxide as a gate dielectric. Poly-silicon, currently used as the gate metal in MOSFETs, has been shown to react with transition metal oxides such as tantalum pentoxide and titanium dioxide to form an undesirable interfacial layer between the poly-silicon and metal oxide. Due to this incompatibility of poly-silicon metal gates with tantalum pentoxide or titanium dioxide gate dielectrics, an alternate metal gate material will need to be adopted for these alternative gate dielectrics. Titanium nitride (TiN), a mid-gap metal, has been extensively studied (and used) as a barrier material in many microelectronic devices. This paper reports on the investigation of physical vapor deposited and chemical vapor deposited titanium nitride for the application of a gate metal in capacitors (with sidewall spacers) using tantalum pentoxide or titanium dioxide as the gate dielectric. Electrical characteristics from C-V and I-V data, along with high resolution transmission electron microscopy of the TiN/gate oxide interface, for as-deposited and thermally annealed samples will be reported.

3:00pm **EM-TuA4 Separate and Independent Reductions in Direct Tunneling in Oxide/Nitride Stacks with Monolayer Interface Nitridation Associated with the i) Interface Nitridation and ii) Increased Physical Thickness***, Y. Wu*, *H. Niimi, H. Yang, G. Lucovsky,* North Carolina State University

Reduction of direct tunneling in aggressively-scaled CMOS devices with deposited oxide/nitride stacks and/or oxynitride alloys is crucial for replacement of thermally-grown oxides. We have identified two separate and independent mechanisms for tunnel current reduction that have been combined in oxide/nitride stacks with monolayer interface nitridation to yield current densities <10@super -2@ A/cm@super 2@ for stacks with oxide-equivalent thickness <1.6 nm. Fabrication of these stacks combines remote plasma-assisted nitridation and deposition processes to independently control nitrogen concentration profiles at the atomic layer level at interfaces and in bulk films. The order of interface nitridation is crucial and monolayer concentrations to reduce direct tunneling by ~ten require two 300°C steps: i) first, remote plasma-assisted oxidation of H-terminated Si(100) to form a ~0.6 nm passivating oxide, followed by ii) remote plasma-assisted nitridation to insert a monolayer of N-atoms at the Si-interface. XPS results indicate that the reduction in tunneling derives from differences in interfacial suboxide bonding associated with nitridation. Since tunneling increases exponentially with decreasing film thickness, incorporation of nitride layers in O/N stacks allows use of physically thicker films while maintaining capacitance equivalent to thinner oxides. We find that increases in thickness are in part mitigated by decreases in the product of the tunneling mass and thickness-averaged-barrier-height in the nitrides, limiting tunneling decreases to ~10-20 with respect to single layer oxides. However, using remote plasma-assisted processing to separately control interfacial and bulk dielectric nitrogen profiles, it has been possible to combine these two order of magnitude decreases and achieve reductions in tunneling of more than 200 in N/O/N stacks. These have been included in NMOS- and PMOSFETs which display excellent current drive and high reliability.

3:20pm **EM-TuA5 High K Gate Dielectrics for Sub-100nm CMOS***, D.L. Kwong*, University of Texas, Austin **INVITED**

With the scaling down of device dimensions, conventional SiO2 and oxynitride films will reach their physical limits in terms of thinning. As a result, there has been a great interest in the development of high permittivity materials as MOS gate dielectrics for sub-100nm CMOS. In this talk, the requirements and significant challenges in developing high K gate dielectrics with performance and reliability specs consistent with NTRS roadmap are reviewed. Results will be presented to demonstrate the importance of the interface layer at highK/Si interface. The choice of high K materials and issues associated with process integration for sub-100nm CMOS will also be discussed.

4:00pm **EM-TuA7 Evidence of Aluminum Silicate Formation at the Al@sub2@O@sub3@/Si Interface for Thermal and Plasma Enhanced Chemical Vapor Deposited Al@sub2@O@sub3@ Thin Films***, D. Niu*, *T.M. Klein, G.N. Parsons,* North Carolina State University

An important issue in the determination of a suitable high k gate dielectric for advanced CMOS device is the stability of the material with the Si substrate. An insulator with a covalent nature, a limited number of oxidation states and a resistance to ionic transport would be an attractive candidate for this application. This paper investigates the properties of thin Al@sub2@O@sub3@ films as a possible higher-k (12~15) alternative to SiO@sub2@. The films were formed in a 6" compatible triode plasma reactor which was also used for thermal CVD. A variety of aluminum precursors were studied, including Al acetylacetonate, Al sec-butoxide, and Al isopropoxide. A new liquid precursor, triethyl-dialuminum tri-sec-butoxide was also tested. The new precursor is safe, easy to handle and does not decompose with prolonged heating at 150°C. O@sub2@, N@sub2@O and H@sub2@O were used as oxygen sources in both plasma and low temperature (300-400°C) thermal deposition. In the thermal process, H@sub2@O resulted in deposition rates >10 Å/sec, with Ea=0.16 eV, compared to 0.1 Å/sec and Ea=1.1 eV for O@sub2@ precursor. IV, CV, TEM, ellipsometry and nuclear reaction profiling were used to characterize thin (20-300 Å) Al@sub2@O@sub3@ films on silicon. The films show acceptably low leakage current, 3X10@super-5@ A/cm@super2@ at 1 V for a 5 nm thick film. In some process conditions, clear evidence for mixing of aluminum oxide and silicon is observed in the capacitance measurement, consistent with the optical and structural evaluations. A fit of the capacitance data to a simple model is used to predict the dielectric constant of aluminum silicate layer.

4:20pm **EM-TuA8 Thermally Grown Gate Insulators for Heterostructure p-MOSFETs*, D.W. Greve*,** *A.C. Mocuta,* Carnegie Mellon University

With decreasing channel length and increasing channel electric field, it is increasingly difficult to maintain adequate transistor ON currents in scaled MOS technologies. Germanium-silicon heterostructure p-MOSFETs potentially offer improvements in channel mobility of 30-50%; however, devices with thick channels and high germanium fraction may relax during thermal oxidation or other subsequent high-temperature processing. We have fabricated heterostructure MOSFETs and MOS capacitors using germanium-silicon-carbon epitaxial layers grown by UHV/CVD. We will show that low-carbon Si@sub 1-x-y@Ge@sub x@C@sub y@ channels do not relax for thermal anneals as high as 900 C. Consequently it is possible to use a thermally grown gate SiO@sub 2@ gate insulator while still maintaining a high channel charge capacity in the Si@sub 1-x-y@Ge@sub x@C@sub y@ layer. This has been demonstrated using heterostructure MOS capacitors with 30 nm Si@sub 1-x-0.002@Ge@sub x@C@sub 0.002@channels in which the germanium fraction x has been linearly graded from x=10% to x=40%. For cap layers approximately 6 nm in thickness after gate insulator growth, germanium surface segregation during epitaxial layer growth leads to a poor quality insulator-semiconductor interface. However, for thicker cap layers nearly ideal MOS C(V) characteristics are observed. We will also report on heterostructure p-MOSFETs which have been fabricated with Si@sub 1-x-y@Ge@sub x@C@sub y@ channels and thermally grown gate insulators. It will be shown that these devices exhibit channel mobilities of 200 cm@sup 2@/Vsec at room temperature, which is comparable to that reported with Si@sub 1-x@Ge@sub x@ channels and plasma silicon dioxide gate insulators. This demonstration opens the way toward the application of heterostructure p-MOSFETs in practical CMOS technologies.

4:40pm **EM-TuA9 Deposition of ZrO@sub 2@/SiO@sub 2@ Alloys by 300° Remote Plasma Processing for Alternative High-K Gate Dielectrics in Aggressively Scaled CMOS Devices*, R. Therrien*,** *B. Raynor, D. Wolfe, G. Lucovsky,* North Carolina State University

Stimulated by targeted performance goals for aggressively-scaled CMOS devices, there has been much interest in alternative gate dielectric materials to replace SiO@sub 2@. The choice of materials is based on identifying insulating oxides with dielectric constants greater than SiO@sub 2@, so that physically-thicker films, anticipated to have reduced direct tunneling, will be equivalent to thinner oxides. This paper describes the deposition of ZrO@sub 2@/ SiO@sub 2@ alloy films by 300°C remote plasma-assisted CVD. This approach has two potential advantages with respect to conventional thermal CVD. First, by injecting the Zr precursor, Zr(IV) t-butoxide, and the Si precursor, silane, downstream from the plasma region, and driving the CVD reaction with active O-species extracted from an upstream O@sub 2@/He plasma, complete oxidation of Zr and Si has been confirmed by on-line AES and off-line FTIR. Films prepared in this way are amorphous as-deposited, as determined from FTIR and electron diffraction, and more importantly remain amorphous up to at least 900°C after annealing in an inert ambient. This paper describes the deposition process, and identifies the way in which the relative concentration of ZrO@sub 2@ to SiO@sub 2@ has been controlled to achieve deposition of films approaching the compound ZrSiO@sub 4@ composition. Other properties of these films relative to their role as a replacement dielectrics are discussed; e.g., optical studies of the band-gap, and electrical capacitance-voltage and current-voltage characteristics are presented. These allow us to obtain i) the static dielectric constant, ii) the conduction band offset energy with respect to Si and iii) the tunneling electron mass. Based on these measurements, ZrO@sub 2@/SiO@sub 2@ alloys in conjunction with hyper-thin (~0.5 nm), nitrided SiO@sub 2@ interfacial layers can be used to scale the oxide-equivalent dielectric thickness down to about 1 nm.

Flat Panel Displays Topical Conference
Room 604 - Session FP+OE+EM-TuA
Thin Film Transistor Materials and Devices

Moderator: G.N. Parsons, North Carolina State University

2:00pm **FP+OE+EM-TuA1 Nanoprobing Electrical Transport in Organic Semiconductors*, C.D. Frisbie,*** University of Minnesota **INVITED**

Commercial interest in mechanically flexible plastic electronics is the key motivator behind efforts to fabricate transistors, light-emitting diodes, and lasers from organic thin films. Continued development depends on increasing comprehension of factors affecting charge carrier mobility. In particular, the importance of film microstructure on transport in organic films has been recognized, but is currently not well understood. In this talk, I will describe experiments designed to address microstructural effects on conductivity in polycrystalline organic films. Our approach is to probe transport in individual grains, or even small collections of grains, which we characterize by atomic force microscopy (AFM). Experiments have focussed on crystalline grains of the molecular semiconductor sexithiophene (6T). Isolated grains of 6T are grown by vacuum sublimation onto SiO2/Si substrates. The crystals range from 1-6 molecular layers (2-14 nm) in thickness with diameters on the order of a micron. In one approach, these thin crystals are contacted with source and drain electrodes fabricated by electron-beam lithography; heavily doped Si underneath the SiO2 serves as a gate electrode. The resulting transistor structures are used to probe field effect conductance and carrier mobility as a function of temperature (5-300K) and the number of discrete molecular layers in the crystals. The second experiment uses a conducting AFM probe as a positionable electrical contact to grains contacted by a fixed electrode at the other end. This configuration allows variation of the tip-electrode separation, yielding the single grain resistivity and an estimation of the organic-metal contact resistance. Resistances associated with defects, e.g., a single grain boundary between adjacent crystals, may also be measured. In both types of experiments, the conjunction of AFM imaging with transport measurements is critical to correlating transport properties with specific microstructures.

2:40pm **FP+OE+EM-TuA3 Photolithographically Defined Pentacene Thin Film Transistors on Flexible Plastic Substrates*, D.J. Gundlach,*** *C.D. Sheraw, H. Klauk, J.A. Nichols, J-R. Huang, T.N. Jackson,* The Pennsylvania State University

We report photolithographically-defined pentacene thin film transistors (TFTs) on flexible plastic substrates with performance similar to hydrogenated amorphous silicon (a-Si:H) devices. Organic TFTs fabricated on flexible plastic substrates are of interest for mechanically rugged, low-cost broad-area electronic applications. Pentacene TFTs with performance similar to a-Si:H TFTs have been reported,@footnote 1@ however, such devices are typically fabricated on oxidized silicon or glass substrates. Since photolithographic processing of organic semiconducting materials is problematic, such devices, including more recent devices on polymeric substrates,@footnote 2@ typically use source and drain contacts deposited through a shadow-mask after the organic active layer deposition. We have fabricated photolithographically-defined pentacene TFTs on polyethylene naphthalate (PEN) and polyimide (PI) films. For ease of processing, the films were mounted to silicon wafers using a pressure sensitive silicone adhesive and pre-shrunk by heating to 150°C for 1 hour in vacuum. A 30 nm thick Ni gate electrode, 160 nm thick SiO@sub 2@ gate dielectric, and 80 nm thick Pd source/drain contacts were deposited by ion-beam sputter deposition. The TFTs were completed by thermally evaporating pentacene onto substrates heated to 60°C. All deposited layers were photolithographically-defined using a two-layer resist lift-off process. Field-effect mobility larger than 0.3 cm@super 2@/V-s was extracted for TFTs on both PI and PEN film, current on/off ratio was greater than 10@super 5@, and subthreshold slope was less than 1.5 V/decade, all obtained using drain-to-source and gate-to-source biases of -30 volts or less. @FootnoteText@ @footnote 1@ Y-Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, IEEE Electron Device Lett., vol. 18, pp. 606-608, 1997. @footnote 2@ C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J. M. Shaw, Science, vol. 283, pp. 822-824, 1999.

3:00pm **FP+OE+EM-TuA4 Reduced Process Complexity Organic Thin Film Transistors*, H. Klauk,*** *D.J. Gundlach, M. Bonse, T.N. Jackson,* The Pennsylvania State University

The performance of organic thin film transistors (TFTs) has improved dramatically over the past few years and recently, pentacene TFTs with carrier mobility of 0.6 cm@super 2@/V-s were demonstrated on glass substrates.@footnote 1@ The TFT device structure used in this earlier work required 4 material depositions and 4 lithography steps: one each for the gate, the gate dielectric, the source/drain contacts, and the pentacene active layer. Patterning of the pentacene layer is important to avoid leakage since pentacene TFTs often have large positive threshold voltage. We report here a simplified device structure for depletion-mode pentacene TFTs. Only 3 material depositions and 3 lithography steps are required and the same metal deposition is used for the gate electrode and the source/drain contacts. Gate-to-source and gate-to-drain overlap are not required, since the pentacene layer is normally conducting, thus allowing a drain current to flow at zero gate bias; devices are turned off by applying a positive gate bias. Palladium was used for the gate and source/drain metal, and low-temperature (80°C) ion-beam sputtered SiO@sub 2@ was used as the gate dielectric; both layers were patterned by lift-off. To pattern the pentacene active layer, a double-layer photoresist technique was used to create a reentrant profile over which the pentacene was deposited by evaporation. Upon deposition, the pentacene layer breaks over the resist profile, leaving isolated TFT areas. At a relatively low drain-source voltage of -20 V, devices have carrier mobility as large as 0.3 cm@super 2@/V-s, on/off current ratio near 10@super 5@, subthreshold slope as low as 0.9 V/decade, and threshold voltage between +10 V and +17 V. @FootnoteText@ @footnote 1@ Hagen Klauk, David J. Gundlach, Jonathan A. Nichols, and Thomas N. Jackson, "Pentacene Organic Thin-Film Transistors for Circuit and Display Applications," IEEE Transactions on Electron Devices, vol. 46, no. 6, June 1999.

3:20pm **FP+OE+EM-TuA5 Soft Lithographic Patterning and Low Temperature Film Deposition: Methods to Fabricate Amorphous Silicon Thin Film Transistors at Low Temperature***, **H.-C. Jin**, J.R. Abelson, M.K. Erhardt, R.G. Nuzzo,* University of Illinois, Urbana

We fabricate amorphous silicon thin film transistors on glass substrates at low temperature (125@super o@C) using "soft" lithographic patterning in place of traditional photolithography. In soft lithography, polymer templates are formed on the film by holding an elastomer block containing the desired pattern in contact with the substrate, flowing an uncured precursor into the micro-channels of the pattern, then curing the polymer. Such templates replace photoresist for all etch and deposition steps, and have been successfully used for the fabrication of multilayer device architectures with micron-scale feature resolution. It appears possible to pattern sub-micron features, as well as large area and curved substrates. In this talk, we show the patterning methodology, preliminary results for TFT devices on planar and curved substrates, and discuss future prospects.

3:40pm **FP+OE+EM-TuA6 Low Damage Etching Utilizing Activated Hydrogen Beam for ITO Transparent Electrode in Flat Panel Display***, **T. Miyata**, T. Minami, M. Ishii,* Kanazawa Institute of Technology, Japan

Recently, low damage dry etching has become necessary for transparent electrode patterning in flat panel display fabrication. This paper introduces a newly developed low damage and high rate etching technique utilizing an activated hydrogen beam to etch Sn-doped indium oxide (ITO) transparent conducting films. The etching was carried out using an apparatus consisting of an etching chamber and an activating chamber interconnected with a 0.9 mm-diameter orifice; the pressure in the activating chamber was higher than that in the etching chamber. The hydrogen gas introduced into the activating chamber was first activated by applying microwave power and then introduced through the orifice into the etching chamber. The etching was accomplished by the activated hydrogen beam acting on patterned photoresist coated ITO films placed on a sample holder. The etching rate was strongly dependent on conditions such as sample temperature, orifice-sample separation and pressure in the etching chamber. It should be noted that the ITO film was only etched at sample temperatures above 160@super o@C and the etching rate increased as the sample temperature was increased. A maximum etching rate above 50 nm/min was obtained at a sample temperature of 220@super o@C. These results suggest that ITO films are mainly etched by chemical reactions.

4:20pm **FP+OE+EM-TuA8 Excimer Laser Processing for a-Si and poly-Si Thin Film Transistors for Imager Applications***, **J.P. Lu**, P. Mei, R.T. Fulks, J. Rahn, J. Ho, Y. Wang, J.B. Boyce, R.A. Street,* Xerox Palo Alto Research Center **INVITED**

Pulsed Excimer-Laser Annealing (ELA) has become an important technology to produce high performance Thin Film Transistors (TFTs) for large area electronics. The application of these advanced TFTs in flat pannel displays@footnote 1@ and flat panel imagers for two-dimensional X-ray imaging have attracted much interest. TFTs made from laser crystallized poly-Si thin films with mobility higher than 100 cm@super 2@/Vs can be consistently achieved and are well suited for the integrated driver circuits. Recently, leakage currents as low as 2fA/µm at 5V for these poly-Si TFTs have been achieved and enable one to consider making flat panel imagers using a full poly-Si process. Laser doping@footnote 2@ or dopant activation is another important application of the ELA process. Using a laser doping process, we have fabricated a-Si TFTs with self-aligned poly-Si source/drain contacts. These new devices have reduced source/drain parasitic capacitance and their channel length can be easily scaled down without stringent lithography requirements. Excellent DC performance, such as low leakage current (0.02fA/µm), sharp turn on (0.44V/decade) and high mobility of a-Si TFTs are preserved. In addition, good AC performance of these self-aligned a-Si TFTs has been demonstrated in four phase dynamic shift registers operating at 250kHz. In this talk, these two areas will be reviewed along with a report on the current status in developing poly-Si TFTs and self-aligned a-Si TFTs using ELA process for flat panel imager applications. @FootnoteText@ @footnote 1@ J. G. Blake, M. C. King, J. D. Stevens III, and R. Young, Solid State Technology, p151, May 1997. @footnote 2@ P. Mei, G. B. Anderson, J. B. Boyce, D. K. Fork, and R. Lujan, Thin Film Transistor Technologies III, Electrochemical Soc. Proc., PV 96-23, p51 (1997).

5:00pm **FP+OE+EM-TuA10 Solid-phase Crystallization of Hydrogenated Amorphous Silicon-Germanium Alloy Films***, **O.H. Roh**, I.H. Yun, J.-K. Lee,* Chonbuk National University, Korea

We have investigated the solid-phase crystallization of hydrogenated amorphous silicon-germanium alloy (a-Si@sub 1-x@Ge@sub x@:H) films by using electron spin resonance (ESR) and x-ray diffraction measurements. The films were deposited on Corning 1737 glass in a plasma-enhanced chemical vapor deposition system using SiH@sub 4@ and GeH@sub 4@ gases. The substrate temperature was 200°C and the r.f. power was 3W. The films were then annealed to be crystallized at 600°C in a N@sub 2@ atmosphere. The total spin density first increased with annealing time due to hydrogen evolution, and then rapidly decreased as the film was crystallized. The Ge dangling bond spin density increased faster with annealing time than the Si dangling bond spin density. However, it was observed that the H evolution from Si-H bond and Ge-H bond was strongly affected by the Ge composition of the films.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+AS-TuA

Organic Thin Film Growth

Moderator: H. Baessler, Philipps Universität, Germany

2:00pm **OE+EM+AS-TuA1 Tailoring of Properties of Organic Thin Films by Interface Control***, **E. Umbach**, M. Sokolowski, R. Fink,* Universität Würzburg, Germany **INVITED**

The properties of ultrathin organic films in organic/inorganic hybrid systems are largely determined by their interfaces. This is particularly true for the electronic and structural properties which depend on chemical bonding and ordering processes. In favourable cases weak chemisorption on smooth single-crystal surfaces leads to long-range lateral order, and even true epitaxial growth of organic overlayers can be achieved. For such structurally well-defined films significantly improved transport and optical properties can be expected. It will be shown how high-quality organic thin films can be prepared by vapour-deposition on suited substrates and how the observed superstructures depend on the molecular shape and the functional groups, on the substrate material and orientation, and on the preparation parameters. Moreover, based on a few examples it is demonstrated that epitaxial growth with huge domains and even with new, substrate-induced structural parameters can be achieved. In view of their optical properties, for instance, such films show very few defects, considerably improved quantum efficiency, and reduced substrate-induced quenching. The knowledge about the various properties and their interdependences has been achieved by combining a number of surface-sensitive methods for studying the geometric (STM, (SPA)LEED), chemical (XPS, TDS, HREELS), orientational (NEXAFS), and electronic (UPS, NEXAFS) properties with in-situ measurements of the optical and electric properties. As substrates different metal (e.g., Ag, Ni, Cu) and semiconductor surfaces (Si, Ge, ZnSe, HOPG) have been investigated, and the properties of more than 20 different large organic molecules have been compared. On the basis of the present results one can now start to tailor the properties of ultrathin organic films by selecting a proper combination of molecules, substrates and preparation conditions.

2:40pm **OE+EM+AS-TuA3 Ordering in Two Dimensions - Phthalocyanines, Perylenes, and Related Molecular Thin Films***, **N.R. Armstrong**,* University of Arizona **INVITED**

Well-ordered two-dimensional thin films can now be routinely produced by either vacuum deposition and/or self-assembly deposition technologies, and rules for epitaxial growth of such materials on a variety of single crystal substrates are becoming well understood. This talk will review recent work on the growth of both phthalocyanine and perylene dye thin films, on both single crystal metal and nonmetal surfaces. Many of the crystalline organic dyes tend to form flat-lying ordered monolayers, with coincident epitaxial relationships with the substrate. Several interesting cases have recently emerged, however, where such flat-lying monolayers are not formed, and/or where neither coincident nor commensurate epitaxial structures are formed, but ordered films result nevertheless. In all events organic heterojunction formation is of interest for these materials, and characterization of such heterojunctions by combinations of XPS/UPS will be discussed. In addtion, we will discuss recent self-assembly approaches to ordered phthalocyanine thin films, by non-vacuum deposition approaches, which produce coherence in thin film structures rivaling the best vacuum deposited materials.

3:20pm **OE+EM+AS-TuA5 Influence of Steps on the Orientation of Monolayer Films of Copper Phthalocyanine (CuPc) on Au(111)***, **I. Chizhov**, A. Kahn, G. Scoles,* Princeton University

The structure of monolayer films of copper phthalocyanine (CuPc) deposited on Au(111) surface in ultrahigh vacuum is studied via scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). CuPc molecules adsorb with the molecular planes parallel to the surface and form a highly ordered overlayer with a square unit cell. The structure of the CuPc molecular layer is analyzed via correlation of STM and LEED data. The azimuthal orientation of the monolayer is found to be distinctly different on wide and narrow terraces of the Au(111) substrate. On wide terraces the azimuthal orientation of the monolayer is determined by the underlying substrate with the sides of CuPc square unit cells aligned within a few degrees off the [11(bar)0] and [112(bar)] directions of the Au(111) surface. On the other hand, on narrow terraces and in the vicinity of the Au substrate steps the sides of CuPc unit cells are aligned along the step edges. Thus, CuPc/Au(111) represents a good model system for which a balance between the energy of interaction of a molecule with the metal surface and that of interaction with the step edges can be studied in detail. For CuPc films with coverages below and above 1 monolayer no molecular structure can be reproducibly resolved by the STM.

3:40pm **OE+EM+AS-TuA6 Growth Modes of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-Diamine on Standard and Ultra-flat Indium Tin Oxide***, **E.W. Forsythe**, Q.T. Le, Y. Gao, L.J. Rothberg, M. Abkowitz,* University of Rochester

The ITO substrate morphology influences the growth conditions of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-diamine (NPB) for organic light emitting diodes. We have studied the growth modes of NPB on as-received indium tin oxide (ITO) and ultra-flat ITO using atomic force microscopy (AFM). The ITO surface morphology has been reduced from an average area roughness of 1.8nm to less than 0.2nm with clearly distinguishable atomic terraces corresponding to the ITO lattice spacing. The room temperature NPB growth mode is initially islands with complete ITO coverage at 15nm for both ITO surfaces. With a substrate temperature less than 15C above room temperature, the growth modes are laminar with full ITO coverage at 7.5nm. The final NPB film on the ultra-flat ITO has an average roughness equivalent to the size of the NPB molecule, more than an order of magnitude less than NPB on standard ITO. Because NPB is trap free, a direct and self-consistent measure of the injection efficiency as a function ITO surface morphology and growth temperature can be determined at a given applied field from the ratio of the measured dark current to the calculated trap free space charge limited current. The trap free space charge limited current is calculated from the time of flight drift mobility measured in the same specimen at the same applied field.@footnote 1@ The OLED device performance shows an approximately 15% increase in the cd/A efficiency on the ultra-flat ITO as compared to standard ITO. Understanding the role of the ITO surface morphology on OLED device characteristics may contribute to improved large area device performance. This work was supported by DARPA DAAL01-96-K-0086, NSF DMR-9612370, AFOSR 96NL245, and the NSF Center for Photoinduced Charge Transfer. 0. @FootnoteText@ @footnote 1@ M.Abkowitz,J.S.Facci and J.Rehm. J. Appl. Phys. 83, 2670 (1998).

4:00pm **OE+EM+AS-TuA7 Self-Assembled Monolayers on Indium Tin Oxide***, C. Yan, M. Zharnikov, **A. Gölzhäuser**, M. Grunze,* Universität Heidelberg, Germany

Self-Assembled Monolayers (SAMs) of functionalized alkanethiols X(CH@sub 2@)@sub n@SH (X=CH@sub 3@, COOH) and carboxylic acid CH@sub 3@(CH@sub 2@)@sub n@COOH were prepared on indium tin oxide (ITO) surfaces and have been characterized by X-ray photoelectron (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopies as well as by Atomic Force Microscopy (AFM). Thiols as well as carboxylic acids form homogeneous, ordered films on ITO. NEXAFS data suggest that the films are molecularly oriented with average alkyl chain tilt angles between ~34° for thiolate and ~31° for bifunctional SH(CH@sub 2@)@sub 15@COOH. From coadsorption experiments we find that on ITO the COOH group adsorbs preferentially over the SH group. AFM and LFM images indicate a smoothing of the relatively rough ITO surface by the adsorbed films. These results suggest that ITO surfaces can be passivated with Self-assembled monolayers and that SAMs can be utilized to covalently attach specific chemical functionalities to ITO electrodes.

4:20pm **OE+EM+AS-TuA8 Mechanism of Formation of Self-Assembled n-Octadecylsilane Monolayers on Indium-Tin-Oxide***, **K.-W. Lee**, A.M. Raphel, S.L. Buchwalter,* IBM T.J. Watson Research Center*; M.M. Poliks,* IBM Microelectronics

Mechanism of formation of self-assembled n-octadecylsilane monolayers on indium-tin-oxide (ITO) has been studied. n-Octadecyltrimethoxysilane (OTMS) was hydrolyzed to n-octadecylmethoxysilanediol or n-octadecylsilanetriol in isopropanol/water (95/5). The 0.5 % hydrolyzed solution was spin-coated onto ITO substrate and then baked at 85 deg.C for 30 min. The subsequently formed organic layers were analyzed with dynamic contact angles, X-ray photoelectron spectroscopy (XPS) and reflection-absorption infrared spectroscopy (RAIR) and determined to have densely packed SAMs. Its RAIR and XPS spectra indicate that lots of silanol groups are left unreacted at the foot of SAMs and a small amount of unhydrolyzed Si-OCH3 groups may also be present. Silanol groups are expected to interact with each other and ITO surface through hydrogen bonding. The distance between Si atoms can be long enough to have a normal tilt angle (app. 30 deg.) of typical SAMs. Si-OH and Si-OCH3 groups were fully condensed to polysiloxane by further thermal treatment at 230 deg.C for 30 min, as evidenced by the disappearance of the O-H band in RAIR as well as by the decrease of the O1s band corresponding to silanol. The possible structural changes in the SAM driven by this condensation are discussed. In contrast to the fully hydrolyzed OTMS solution, a partially hydrolyzed OTMS solution provided loosely packed monolayers, apparently in islands of densely packed alkyl chains rather than as monotonically diminishing coverage.

4:40pm **OE+EM+AS-TuA9 Growth and Characterization of Poly(arylamine) Thin Films Prepared by Vapor Deposition***, **G.J. Szulczewski**, T. Selby, S. Blackstock,* The University of Alabama

We have synthesized a novel series of redox-gradient poly(arylamines) dendrimers for potential applications in organic-based electronic devices. The thermal properties of these materials have been measured by gravimetric analysis and differential scanning calorimetry. In general, these materials exhibit a glass transition temperature near 100 C and show negligible weight loss below 400 C. Thin films (1-100 nm) of these materials were grown under high vacuum conditions by vapor deposition onto a variety of substrates, including: gold, Si(100), and indium-tin oxide coated glass. Ex situ surface characterization was performed with reflection-absorption infrared spectroscopy, x-ray photoelectron spectroscopy, spectroscopic ellipsometry, and atomic force microscopy. These analyses show the formation of high quality films from the organic precursors with molecular weights exceeding 1300 amu without molecular decomposition. Thus, a new class of functional organic films for potential use in charge storage and transport have been prepared. The efficacy of these films as hole transport materials in electroluminescent devices and charge storage media is under current investigation.

5:00pm **OE+EM+AS-TuA10 HREELS Study of Ultra-thin Polyaniline Films Grown on Cu(110) by Vapor Deposition of Aniline Tetramers***, **K.K. Lee**, J.M. Vohs,* University of Pennsylvania*; N.J. DiNardo,* Drexel University

Substrate-dependent reactivity, thin film polymerization, and metallic conductivity upon doping have been demonstrated in previous HREELS studies of vapor-deposited emeraldine thin films on metal surfaces.@footnote 1@ In those studies, the chemical vapor was composed of a distribution of oligomeric sizes. In this HREELS study, the effect of the size of vapor-deposited oligomers on the growth of polyaniline at a metal surface is addressed through deposition of aniline tetramers on Cu(110). Analysis of vibrational and electronic spectra for growth up to ~70 Angstroms shows polymerization reactions with shorter chain lengths of the resulting polyaniline ultra-thin films than for deposition from emeraldine vapor. Upon doping, the far-infrared region exhibits intense tailing and a plasmon loss indicating that local conductivity is similar to ultra-thin films composed of longer chains. @FootnoteText@ @footnote 1@K. K. Lee - Surf Sci. 420 (1999) L115 and references therein.

Surface Science Division
Room 606 - Session SS1+EM-TuA
Oxides: Growth and Structure

Moderator: E.G. Seebauer, University of Illinois, Urbana

2:00pm **SS1+EM-TuA1 Noncommutative Band Offset at @alpha@-Cr@sub 2@O@sub 3@/@alpha@-Fe@sub 2@O@sub 3@(0001) Heterojunctions***,* ***S.A. Chambers****, Y. Liang,* Pacific Northwest National Laboratory

We have measured the valence band discontinuity at artificially structured, epitaxial heterojunctions of @alpha@-Cr@sub 2@O@sub 3@(0001) and @alpha@-Fe@sub 2@O@sub 3@(0001) grown on @alpha@-Al@sub 2@O@sub 3@(0001) substrates. Oxygen-plasma-assisted molecular beam epitaxy was the growth technique, and band offsets were measured by core-level and valence-band photoemission. Layered film structures of these two materials maintain the in-plane lattice parameter of @alpha@-Fe@sub 2@O@sub 3@(0001). Thus, the @alpha@-Cr@sub 2@O@sub 3@(0001) layers are under a 2.3% tensile stress. The valence band offsets are 0.3±0.1 eV and 0.7±0.1 eV when the top layer is Fe@sub 2@O@sub 3@ and Cr@sub 2@O@sub 3@, respectively. The noncommutativity in band offset appears to be due to a growth-sequence-dependent interface dipole caused by different extents of intermixing for the two kinds of interfaces.

2:20pm **SS1+EM-TuA2 Ultrathin Iron Oxide Films***,* ***R.L. Stockbauer****, J. Karunamuni, A. Koveshnikov, R. Madjoe, R.L. Kurtz,* Louisiana State University

Thin films of spin polarized conductors are receiving increased attention as potential contacts for devices such as spin-valves and high-sensitivity disk sensors. We have succeeded in producing ultra thin films of FeO and Fe@sub 3@O@sub 4@ and characterized their morphology using STM and LEED. The oxides are grown by depositing thin films of Fe on a Cu(100) surface at room temperature. The Cu substrate has terraces ca. 100Å wide with steps perpendicular to the [010] direction. The Fe grows layer-by-layer in islands uniformly distributed on the Cu terraces. The oxides are formed by heating to 840K in 10@super -6@ Torr O@sub 2@. The change in the morphology of the surface after oxidation is truly striking. At low Fe coverage (<2ML), FeO completely rearranges the Cu substrate. Large terraces up to 1µm wide are now observed. The FeO itself forms long stripes typically 0.2µm wide and up to 10µm long parallel to the [011] direction. Shorter stripes are observed in the perpendicular direction. The FeO stripes display two superstructures. A coarse structure consists of a series of dark bands parallel to the stripe direction and spaced at 360Å intervals. The fine structure is a 20.5Å hexagonal pattern. A comparison of LEED data and simulations indicates that the overlayer is FeO(111) with stripes aligned along the [110] directions. Oxidizing Fe films thicker than 2ML results in the oxide phase of device interest, Fe@sub 3@O@sub 4@. These patches show a 170Å banded structure and the same size hexagonal superstructure but rotated 30° from that observed for the FeO . LEED data, simulations, and thermochemistry are consistent with the overlayer being Fe@sub 3@O@sub 4@(111) rotated 15° from the [001] azimuth. Surprisingly, these highly oriented oxide films do not show strong angular dependence in photoemission. MOKE, circular dichroism, and spin polarized measurements are underway to determine the magnetic properties of the oxide films.

2:40pm **SS1+EM-TuA3 Islanding, Facetting, and the Lattice Relaxation in the Growth of @alpha@-Fe@sub 2@O@sub 3@ on @alpha@-Al@sub 2@O@sub 3@***,* ***S.I. Yi****, Y. Liang, S. Thevuthasan, S.A. Chambers,* Pacific Northwest National Laboratory

The growth of @alpha@-Fe@sub 2@O@sub 3@ on c- and r-oriented @alpha@-Al@sub 2@O@sub 3@ by oxygen-plasma-enhanced molecular beam epitaxy has been investigated with reflection high-energy electron diffraction, non-contact atomic force microscopy, X-ray photoelectron spectroscopy, X-ray photoelectron diffraction, low-energy electron diffraction, and high-energy ion scattering. The epilayer is facetted due to compressional stress on the c-plane during growth of the first two monolayers. The epilayer structure is significantly distorted, with considerable in-plane strain. However, the film exhibits a constant Fe 2p binding energy with respect to the O 1s binding energy for all thicknesses, revealing the growth of phase-pure @alpha@-Fe@sub 2@O@sub 3@ throughout. A growth-mode transition begins at approximately two monolayers from strained wetting layer to the formation of clusters of rhombohedral islands when a relatively slow growth rate of 1 Å/min is used. However, this transition occurs over several monolayers at a growth temperature of 400 @super o@C. A film with high structural order and orientational stability grows as the islands coalesce to form new and larger terraces. This transition to island-mediated growth can be kinetically impeded for higher growth rates of 0.1-0.3 Å/sec.@footnote 1@ In contrast, the growth-mode transition will occur more rapidly if temperatures of 450 to 500 @super o@C are used along with the slower growth rate. However, sustained growth at temperatures in excess of 500 @super o@C results in the simultaneous formation of Fe@sub 3@O@sub 4@ (111) and/or @gamma@-Fe@sub 2@O@sub 3@ (111) along with @alpha@-Fe@sub 2@O@sub 3@(0001). In contrast to growth in the c-plane, the epilayer shows only facetted growth on the r-plane, regardless of the deposition rate and substrate temperature. This result may be due to the lower surface symmetry of the r-plane compared to the c-plane. @FootnoteText@ @footnote 1@ S. I. Yi, Y. Liang, S. A. Chambers, to be published in JVST A, Jul/Aug, 1999

3:00pm **SS1+EM-TuA4 Surface Reconstructions of Fe@sub 3@O@sub 4@(001)***, B. Stanka, W. Hebenstreit,* ***U. Diebold****,* Tulane University*; S.A. Chambers,* Pacific Northwest National Laboratory

We have investigated the structural changes to the Fe@sub 3@O@sub 4@(001) surface which are induced by different sample treatments. The samples consisted of ~5000 Å thick films of Fe@sub 3@O@sub 4@(001) , grown with oxygen-plasma-assisted molecular beam epitaxy (OPA-MBE) on MgO(001) substrates. To study the surface termination, structure, morphology, and composition, scanning tunneling microscopy (STM), low energy electron diffraction (LEED), low energy He@sup +@ ion scattering (ISS), and x-ray photoelectron spectroscopy (XPS) were used. A (@sr@(2) x @sr@(2))R45° reconstruction relative to bulk-terminated Fe@sub 3@O@sub 4@ is induced by heating in oxygen (10@sup -6@ - 10@sup -7@ mbar) at temperatures between 250°C and 500°C after a through-air transfer from the MBE chamber. Our STM results show an appearance consistent with a B-layer termination, which consists of a layer of octrahedrally coordinated Fe and tetrahedrally coordinated O, along with one O vacancy per unit cell. This surface is autocompensated, or charge neutral, and is therefore expected to be stable. Further annealing in UHV causes a transformation to either a (1 x n) or a (2@sr@(2) x @sr@(2))R45 structure. In both cases, a (@sr@(2) x @sr@(2))R45 reconstructed surface can be regained reproducibly by annealing in oxygen. Interestingly, at no time do we observe the other autocompensated termination, which consists of one-half monolayer of tetrahedrally coordinated Fe(III), despite its observation in other laboratories. Thus, it appears that the surface termination is critically dependent on the method of surface preparation.

3:20pm **SS1+EM-TuA5 The Surface Structure of @alpha@-Al@sub 2@O@sub 3@(0001) Studied by LEED***,* ***C.F. Walters****,* Sandia National Laboratories*; E.A. Soares, M.A. Van Hove,* Lawrence Berkeley National Laboratory*; K.F. McCarty,* Sandia National Laboratories

The surface structure of @alpha@-Al@sub 2@O@sub 3@(0001) has been investigated using normal-incidence low-energy electron diffraction. High quality sapphire samples were produced by ex-situ annealing in air, followed by in-situ cleaning using atomic deuterium at an elevated sample temperature. To investigate the possible occurrence of different surface structures and/or stoichiometries, the samples were processed, subsequent to the atomic deuterium cleaning, using several different procedures. These included annealing the sample in oxygen, and exposing the cooled sample to atomic deuterium. The experimental data were compared to results of calculations performed using an automated tensor LEED program. Several different models were used as the starting point for the analysis. These included termination by: an oxygen layer, a single aluminum layer, a double aluminum layer, and a "hydroxyl" covered single aluminum layer. Additionally, we have analyzed mixtures of these terminations, with the mixtures including different species, as well as the same species but containing different crystallographic planes (i.e., terraced surfaces with fractional unit cell step heights). For each sample preparation, the best structural model was determined via an analysis of the Pendry R-factor that took into account the effect of the additional fitting parameters for the models containing mixed terminations. The best-fit models derived from the tensor LEED analysis will be discussed with respect to the preparation method used, as well as compared to the results of recent first-principles calculations. This work supported by USDOE-OBES-Division of Materials Sciences.

3:40pm **SS1+EM-TuA6 Formation of Epitaxial Al@sub 2@O@sub 3@ on Ni@sub 3@Al(111) Studied by STM, HREELS, UPS, @DELTA@@PHI@, and LEED**, ***A. Rosenhahn****, J. Schneider, J. Kandler, T. Pelster,* Universität Bonn, Germany*; R. Linke,* Eindhoven University of Technology, The Netherlands*; C. Becker, K. Wandelt,* Universität Bonn, Germany

The formation of oxides on the Ni@sub 3@Al(111) single crystal surface has been studied in the temperature range from 300K to 1000K by STM, HREELS, UPS, @DELTA@@PHI@, and LEED. The experiments reveal a strong temperature dependence of the structure and the chemical composition of the resulting oxides, which is caused mainly by a rising aluminum mobility with increasing temperature. Adsorption of oxygen at room temperature creates a disordered surface which appears rough in STM images and shows a diffuse LEED pattern. At 600K STM images show patches of different appearance on the alloy surface. At low coverages the small oxidic nuclei possess a triangular shape, and HREELS measurements show a Al@sub 2@O@sub 3@-like composition. At higher coverages two areas with different appearance can be distinguished in STM, accompanied by the observation of mixed Ni/Al-oxide vibrations in HREELS. At 800K STM measurements show highly ordered triangular shaped oxidic islands. A moiré structure can be observed which corresponds to a superstructure due to an unrotated single O/Al overlayer, that has also been found by LEED and HREELS measurements. The electronic structure of the film being very similar to that of O/Al(111). Adsorption at 1000K finally leads to the growth of an oxidic film, that proceeds from steps exclusively. The oxide exists in two rotational domains that can be detected in LEED and STM. Both HREELS and UPS measurements show the formation of a Al@sub 2@O@sub 3@-doublelayer. Only at this temperature the chemical order of the underlying Ni@sub 3@Al(111) substrate is completely restored.

4:00pm **SS1+EM-TuA7 Surface Structure Determination of Yttrium-Stabilized ZrO@sub 2@(001) Surface Using X-Ray Photoelectron Diffraction**, ***S. Thevuthasan****, S.I. Yi,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology, Korea*; T.T. Tran, S.A. Chambers, C.H.F. Peden,* Pacific Northwest National Laboratory

The physical and chemical properties of oxide surfaces are strongly influenced by several structural properties. As such, there is a growing interest in determining surface termination and relaxation in single crystal oxides. The yttrium-stabilized ZrO@sub 2@(001) surface can in principle be either O terminated or Zr terminated. However, neither of these surfaces is autocompensated as a (1x1) structure. The Zr terminated @sr@2x@sr@2)R45@super o@ reconstruction is autocompensated. It was recently reported that the CeO@sub 2@(001)surface, which is similar to ZrO@sub 2@(001), is terminated with 0.5 monolayers of oxygen.@footnote 1@ We have carried out low-takeoff-angle x-ray photoelectron diffraction (XPD) measurements using Zr 3d, Y 3d and O1s core levels on a oxygen-plasma-cleaned ZrO@sub 2@(001) surface to determine the surface structure. Low-energy electron diffraction data show broad (1x1) spots that are characteristic of many oxide surfaces, and no half-order spots are visible. Currently single and multiple scattering simulations and R-factor analysis are being performed using model clusters generated using both O and Zr terminated surfaces. Preliminary analysis indicates that the surface is Zr terminated with the first layer spacing contracted by 23% relative to the bulk interlayer spacing. Detailed analysis is in progress and results will be presented at the meeting. @FootnoteText@ @footnote 1@G.S. Herman, Phys. Rev. B Rapid Comm. (in press). Work supported by the U.S. Department of Energy (DOE), Offices of Basic Energy Sciences, Division of Chemical Sciences and the DOE's Environmental Management Science Program.

4:20pm **SS1+EM-TuA8 Epitaxial Growth and Characterization of Zirconium-Doped CeO@sub 2@(111) Thin Films on Yttria-Stabilized Zirconia(111)**, ***T.T. Tran,*** Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology, Korea*; S. Thevuthasan, G.S. Herman,* Pacific Northwest National Laboratory

Doping of the ceria lattice with Zr has been shown to enhance the oxygen storage capacity and the rate of oxygen release, and thus the catalytic properties of noble metals supported on these oxides.@footnote 1@ The ability to obtain a detailed knowledge of the effect of the surface structure and zirconium doping levels on oxygen exchange rates requires high-quality single crystalline materials. In a previous study, pure and Zr-doped CeO@sub 2@(001) thin films were grown on SrTiO@sub 3@(001).@footnote 2@ Due to the good lattice match and identical crystal structure, yttria-stabilized zirconia (YSZ) was chosen as the substrate for the growth of CeO@sub 2@(111) in this study. Both pure and Zr-doped CeO@sub 2@(111) thin films were grown on YSZ(111) by oxygen-plasma-assisted molecular beam epitaxy. After deposition, the films were compositionally and structurally characterized by in-situ reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), x-ray photoelectron diffraction (XPD), and x-ray photoelectron spectroscopy (XPS), as well as by ex-situ Rutherford backscattering spectrometry. RHEED, LEED, and XPD results indicated that the materials are well-ordered at the surface for zirconium doping levels up to 40%. Furthermore, a +4 oxidation state was confirmed for both Zr and Ce using XPS. RBS results showed that Zr was found to incorporate substitutionally at cation sites in the ceria lattice. @FootnoteText@ @footnote 1@ P. Fornasiero, G. Balducci, J. Kaspar, S. Meriani, R. Di Monte, and M. Graziani, Catal. Today, 29, 47 (1996); Hamada, H., Catal. Today, 22, 21 (1994); Ozawa, M., M. Kimura, and A. Isogali, J. Alloys Comp., 193, 73 (1993). @footnote 2@ Y. Gao, G.S. Herman, S. Thevuthasan, C.H.F. Peden, and S.A. Chambers, J. Vac. Sci. Technol. (in press).

4:40pm **SS1+EM-TuA9 Structure and Dynamics of KTaO@sub 3@(001) via Elastic and Inelastic Helium Atom Scattering@footnote 1@***, J.A. Li, T.W. Trelenberg, E.A. Akhadov, S.A. Safron,* ***J.G. Skofronick****,* Florida State University*; L.A. Boatner,* Oak Ridge National Laboratory

Although bulk KTaO@sub 3@ is considered an incipient ferroelectric which remains cubic at all temperatures, He diffraction on the (001) surface, cleaved in situ, shows reconstruction of the (1x1) surface to (2x1). The surface behavior, however, seems to depend on its thermal history as, for example, in the following observations: 1)After the sample is cleaved at about 300K and cooled to about 190K, He diffraction reveals a (1x1) surface which appears to be stable indefinitely. 2)If the target is then warmed from 190K to about 220K, reconstruction to the (2x1) phase takes place gradually over a period of about 2 days, whereas if it is warmed to about 260K, the (2x1) phase becomes evident after about 3 hours. 3)When the target is instead taken from 190K to approximately 60K and then to about 260K, the (2x1) surface is apparent immediately. 4)Restoration to (1x1) can be achieved (a) in a few hours or (b) immediately by warming the surface to about 330K or to about 360K, respectively. In addition, there is considerable hysteresis in the intensities of the He diffraction spots for the (2x1) surface over the thermal cycle from 260 K to 50 K to 260 K. Helium time-of-flight (TOF) spectra were obtained to determine the surface phonon dispersions of the (1x1) and (2x1) surfaces for several surface temperatures between 80K and 300K. These appear very similar over the entire surface Brillouin zone. The dominant peaks in the TOF spectra correspond to a dispersionless mode at about 13.5meV, which stiffens slightly as the temperature is raised. However, the lowest energy branch which is quite flat at low temperatures seems to soften near the zone center as the temperature increases. @FootnoteText@ @footnote 1@Supported by U. S. Department of Energy grant number DE-FG02-97ER45635.

5:00pm **SS1+EM-TuA10 Deposition of Highly Oriented Mg@sub 3@(VO@sub 4@)@sub 2@ Thin Films for Use in Catalysis Studies***,* ***J.A. Ruffner****, A.G. Sault,* Sandia National Laboratories

Magnesium vanadates are potentially important catalytic materials for the conversion of alkanes to alkenes via oxidative dehydrogenation. However, little is known about the active sites at which the catalytic reactions take place. It may be possible to obtain a significant increase in the catalytic efficiency if the effects of certain material properties on the surface reactions could be quantified and optimized through the use of appropriate preparation techniques. Given that surface reactivity is often dependent upon surface structure and that the atomic level structure of the active sites in these catalysts is virtually unknown, we desire thin film samples consisting of a single magnesium vanadate phase and a well defined crystallographic orientation in order to reduce complexity and simplify the study of active sites. We report on the use of reactive RF sputter deposition to fabricate very highly oriented, stoichiometric Mg@sub 3@(VO@sub 4@)@sub 2@ thin films for use in these surface analysis studies. Preliminary depositions of Mg@sub 3@(VO@sub 4@)@sub 2@ onto amorphous substrates resulted in amorphous thin films. However, deposition of Mg@sub 3@(VO@sub 4@)@sub 2@ onto well-oriented, lattice-matched thin film "seed" layers such as Ti (0002), Au (111) or Pt (111) resulted in very strong preferential (042) crystallographic orientation (pseudo-hexagonal planes parallel to the substrate). This strong preferential growth of the Mg@sub 3@(VO@sub 4@)@sub 2@ suggests epitaxial (single-crystal) growth of this mixed metal oxide on the underlying metal seed layer. The effects of the substrate material, seed layer material, deposition temperature, and post-deposition anneal temperatures on thin film properties such as stoichiometry, crystallographic orientation, and chemical interactions will be reported.

Surface Science Division
Room 6C - Session SS2+EM-TuA
Semiconductor Surface Chemistry

Moderator: R.M. Feenstra, Carnegie Mellon University

2:00pm **SS2+EM-TuA1 Medard W. Welch Award Address: Halogen Etching of Si with Emphasis on Atomic-Scale Processes***, J.H. Weaver*[1]*,* University of Minnesota **INVITED**

Etching is the process of producing a pattern on a surface, and it is central to a great many technologies. Indeed, etching (material removal) plays a complementary role to growth (material addition), and product fabrication includes both etching and growth. This talk will review recent progress made in understanding surface etching of semiconductors. Emphasis will be on atomic-scale changes in surface morphologies for Si(100) etched with halogens, where the parameters that are controlled are the flux and the fluence of the beam and the reaction temperature of the substrate. The kinds of information that can be gained from atomic-resolution scanning tunneling microscopy will be highlighted. Etch morphologies will be linked to site-specific desorption energies, with consideration of terrace pitting and the formation of nanometer-scale patterns. The sequence of events leading to dihalide desorption and the role of vacancies will be described. Comparison of results for F-Si(100) and Cl-Si(100) shows the formation of defects in the second layer for F, a process that results in roughening rather than layer-by-layer etching observed for Cl.

2:40pm **SS2+EM-TuA3 Micrometer-scale "Grooves" and Step Bunching during Extended Oxidation-induced Etching of Si(001) Surfaces***, **J.F. Nielsen**,* The Ohio State University*; M.S. Pettersen,* Otterbein College*; J.P. Pelz,* The Ohio State University

We have used in-situ STM and ex-situ AFM to observe large-scale step rearrangement on Si(001) surfaces that were heated by DC current at ~1000@super o@C for 3-43 hrs in ~10@super -5@ Torr of oxygen. Depending on sample miscut and current direction, these conditions produced either (1) no significant step rearrangement, (2) large scale (5-10µm) step-bunched regions (with separation increasing roughly as t@super 1/2@), or (3) large "grooves", consisting of a highly-ordered sinusoidal step array with in-phase alignment. The grooved and step-bunched phases can coexist on the same wafer, forming neighboring semi-coherent patches extending over hundreds of microns. The interface between the two phases is remarkably sharp. The step-bunching was also observed on surfaces heated in vacuum (no oxygen), and may be similar to electromigration-related behavior reported by Doi et al.@footnote 1@ Regular arrays of "crossing steps" are also seen on the step bunched regions. It is not yet clear whether oxygen is required for the formation of the grooves. The grooves appear to be qualitatively different from the "wavy" steps reported by Tromp and Reuter@footnote 2@ in that they extend coherently over large areas and are not confined to sample regions of extremely low-miscut. We are currently mapping out the precise conditions necessary to produce each surface phase, and are using the wide terraces resulting from step-bunching in on-going studies of spontaneous step creation on ultra-flat Si(001) surfaces. @FootnoteText@ @footnote 1@ T. Doi, M. Ichikawa, and S. Hosoki, Phys. Rev. B. 55, 1864 (1997) @footnote 2@ R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. 68, 820 (1992).

3:00pm **SS2+EM-TuA4 The Structure of Steps on Hydrogen-Passivated Si Surfaces***, **A. Laracuente**, L.J. Whitman,* Naval Research Laboratory

Steps play a critical role during epitaxy, so knowing their structure is crucially important to understanding how films grow. There has been a considerable effort to determine the step structure on Si surfaces oriented near (001).@footnote 1@ On surfaces tilted toward (111), there are four distinct step configurations, single- and double-layer A-type and B-type steps, commonly denoted as S@sub A@, S@sub B@, D@sub A@, and D@sub B@. B-type steps are almost always "rebonded," with two extra atoms per unit cell at the step edge. The extra atoms halve the dangling bond density along each step and thereby make this structure energetically preferred over a non-rebonded configuration. On surfaces tilted more than 3°, only rebonded D@sub B@ steps occur. Because most industrial Si film growth happens in the presence of hydrogen, an accurate picture of such growth requires an understanding of how H affects the Si step structure and dynamics. It was recently predicted theoretically that non-rebonded steps should be energetically more favorable on H-terminated Si.@footnote 2@ We have now verified this prediction experimentally on a range of surfaces oriented from (001) to (114). We find that S@sub B@ steps "unrebond" after H-passivation, as predicted, completely altering the step energetics. Similarly, H passivation splits a large fraction of D@sub B@ steps into S@sub A@+S@sub B@ step combinations. These changes in step structure have a dramatic effect on the step dynamics and the resulting surface morphology, generally leading to much rougher surfaces. We will discuss how these changes can explain a variety of previous observations about the effects of H on Si film growth. @FootnoteText@ @footnote 1@ A. A. Baski, S. C. Erwin, and L. J. Whitman, Surf. Sci. 392, 69 (1997). @footnote 2@ S. Jeong and A. Oshiyama, Phys. Rev. Lett. 81, 5366 (1998).

3:20pm **SS2+EM-TuA5 Microscopy of Si(001) Surface Defects Produced by keV He Ion Irradiation at Low Temperatures***, K. Kyuno, **D.G. Cahill**, R.S. Averback,* University of Illinois, Urbana-Champaign*; J. Tarus, K. Nordlund,* University of Helsinki, Finland

The interactions of bulk point defects (interstitials and vacancies) with silicon surfaces influences microstructures and dopant profiles created by low-energy ion implantation. To gain insight on the migration of ion-induced defects and their interactions with surfaces, we use variable temperature scanning tunneling microscopy (STM) to measure the areal density of surface defects created by 5 keV He ion irradiation of Si(001) at low temperatures. Samples are irradiated to a dose of 1.7 and 3.4x10@super 13@ ions cm@super -2@ at 80, 130, 180, and 294 K, and imaged at the same temperature. Because of the background density of surface vacancies, we focus our analysis of the STM images on the densities of adatoms, dimers, and clusters formed by the ion bombardment. The density of these protrusions at 80 and 130 K is approximately linear in dose, independent of temperature, and in reasonable agreement with our molecular dynamics calculations of surface defect concentrations. At 180 K, the measured density of protrusions is enhanced by a factor of ~3; we interpret this result in terms of the onset of bulk defect migration. Surprisingly, the Si(001) surface appears to be a relatively inefficient trap for bulk defects under our experimental conditions; our results can be explained by the migration and trapping of defects formed within less than 1 nm of the surface.

3:40pm **SS2+EM-TuA6 A Variable Temperature Scanning Tunnelling Microscopy Study of Si(100) Etching Dynamics***, **C.F. Herrmann**, J.J. Boland,* University of North Carolina

The etching behavior of bromine on the Si(100) surface was investigated using variable temperature scanning tunneling microscopy (VT-STM). The clean Si(100) was initially dosed with bromine to passivate the surface. The passivated surface was then heated slowly and imaged simultaneously with no additional bromine exposure. STM images were taken at several temperatures from 600K to 750K to study the etching dynamics of Si(100) with bromine. The initial distribution of vacancies peaked at a single dimer unit and decayed monotonically to higher lengths. After further heating, repartitioning was observed and dimer vacancies of odd lengths were preferentially formed. The motion of single dimer vacancies was also observed in addition to a novel etching structure. The implications for chemical etching are discussed.

4:00pm **SS2+EM-TuA7 Dissociative Adsorption and Recombinative Desorption of H2 on Si(100)-2x1***, **F.M. Zimmermann**, X. Pan,* Rutgers University

The interaction of hydrogen with Si(100) is of considerable technological importance since hydrogen desorption is the rate-limiting step in low-temperature chemical vapor deposition of Si. Furthermore, this system is intriguing from a fundamental point of view, due to a multitude of unusual and remarkable experimental observations, such as desorption kinetics intermediate between first order and second order, and the so-called 'barrier puzzle': A large barrier to adsorption is seen in adsorption experiments, whereas in desorption dynamics experiments the desorbing molecules paradoxically show no signs of having traversed such a barrier. Using surface second harmonic generation, we have measured the adsorption and desorption kinetics as a function of surface temperature, H coverage, and exposure pressure. These measurements reveal more highly unusual kinetic behavior. Contrary to what is expected from Langmuirian site-blocking considerations, the sticking probability increases markedly with coverage, indicating a self-catalyzed adsorption mechanism. In addition, the sticking probability exhibits a pronounced dependence on exposure pressure, ruling out most 'simple' adsorption mechanisms. The observations are interpreted in terms of a self-catalyzed, barrier-less, inter-dimer adsorption mechanism (observed with the STM by Biedermann, Knoesel, Hu, and Heinz, submitted to Phys. Rev.). Our model quantitatively

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[1] **Medard W. Welch Award Winner**

explains the measured adsorption and desorption kinetics (temperature, coverage, and pressure dependence), and provides a natural explanation of the vexing barrier puzzle. Fitted model parameters are in very good agreement with independently obtained experimental and theoretical values.

4:20pm **SS2+EM-TuA8 Novel Mechanisms for Plasma Etch Front and CVD (Chemical Vapor Deposition) Growth Front Roughening**, ***Y.-P. Zhao***[1], *J.T. Drotar, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

Plasma etching and chemical vapor deposition (CVD) are major tools for thin film processing in microelectronic industry. Although kinetic roughening of thin films has attracted considerable attention in recent years, very little work has been focused on the study of surface roughening mechanisms during plasma etching and chemical vapor deposition. Here, we report a novel etch front roughening phenomenon during the plasma etching of Si(100) substrates. The surface power spectrum shows an obvious wavelength selection which does not occur in conventional noise-induced roughening. The average local surface slope is almost invariant while the vertical roughness grows as a power law in time, w ~ t^@beta@, with a growth exponent @beta@ = 0.91 ± 0.03. We develop a general non-local model to describe the roughening process in plasma etching based on the gas transport kinetics for a large Knudsen number. The flux of the reactive particles redistributes according to the re-emission mechanisms that are influenced by the surrounding morphology. Our extensive numerical calculations and Monte Carlo simulations for various re-emission modes show that @alpha@ (roughness exponent) ~ @beta@ ~ z ~ 1 for plasma etching, which is consistent with our experimental results. Our calculations demonstrate that the proposed model is universal in describing the roughening of plasma etching. In addition, the reverse of this model can be used to describe CVD growth. Our Monte Carlo simulations show that @alpha@ ~ @beta@ ~ 0, z ~ 2 for CVD growth. Detailed comparisons between local and non-local dynamic growth models, as well as the growth and etching processes will also be presented. @FootnoteText@ Work supported by NSF.

4:40pm **SS2+EM-TuA9 Resonance-Enhanced Multiphoton Ionization Studies of the Etching of Silicon by Molecular Chlorine**, ***T.A. Barckholtz***, *L. McDonough, S.R. Leone,* University of Colorado, Boulder

Laser ionization time-of-flight mass spectrometry is a powerful technique for characterizing the neutral products of the etching of semiconductor materials. We previously showed that single photon ionization (SPI), which uses the 9th harmonic of a Nd:YAG laser, provides excellent characterization of the neutral products of the etching of silicon by molecular chlorine, both thermally@footnote 1@ and during ion-enhanced etching.@footnote 2@ Two drawbacks of using the SPI technique are the low laser power available (ca. 10 µJ/pulse) and the lack of resolution of the state distributions (electronic, vibrational, rotational) of the products. To address these deficiencies, we recently implemented a Nd:YAG-pumped dye laser on an etching apparatus that enables resonant electronic multiphoton ionization (REMPI) schemes for the detection of the neutral species. Because of the greater laser power available (several mJ/pulse), the detection sensitivity has been dramatically increased. For example, the REMPI signal intensity of neutral atomic Si during thermal etching is approximately 200 times greater than the SPI intensity. Furthermore, complete state resolution of the Si spin-orbit (@super 3@P@sub 2@, @super 3@P@sub 1@, and @super 3@P@sub 0@) and metastable (@super 1@D@sub 2@) states is obtained. For SiCl, due to its broad rotational and vibrational distributions, the detection sensitivity is increased by a smaller factor, and only partially resolved state distributions are possible. We plan to use the enhanced sensitivity and partial state resolution to investigate the mechanism for the ion-enhanced etching of silicon by chlorine in greater detail than was possible with the SPI technique. The results of these studies will be compared with the predictions of published molecular dynamics simulations. @FootnoteText@ @footnote 1@Materer, N.; Goodman, R. S.; Leone, S. R. JVST A 1997, 15, 2134-2142. @footnote 2@Goodman, R. S.; Materer, N.; Leone, S. R. JVST A, submitted for publication.

5:00pm **SS2+EM-TuA10 Femtosecond Photo-induced Dynamics on a Cleaned and a Chlorinated Si(111) Surfaces**, ***S. Haraichi***, *F. Sasaki,* Electrotechnical Laboratory, Japan

A photo-induced chemical etching of Si is considered as a powerful candidate of the next-generation device fabrication thechnology from the view point of extremely low damage. However the atomic and/or dynamic mechanisms of the photo-induced reaction of Si/halogen systems have not been well understood. We have investigated photo-induced dynamics on a cleaned and a chlorinated Si(111) surfaces using femtosecond second-harmonic generation (SHG). For the pump-probe measurements, Ti-sapphire laser at 1300nm and 800nm with a 100fs pulse width were used as the probe and the pump beams, respectively. With the wavelength at 1300nm, a contribution of absorption is negligible and the surface specific information can be obtained. SHG intensities from a cleaned 7x7 surface decay rapidly just after the pump beam coincides with the probe beam and increase with a rapid and a slow time constants of around 1ps and more than several tens ps. These results were probably due to an immediate photo-excitation and two kinds of relaxation of 7x7 surface states. On the other hand, SHG intensities from a chlorinated Si surface increase rapidly just after the pump beam irradiation and decay with a time constant of around several ps, based on Si-Cl bonding states. On both a cleaned and a chlorinated Si surfaces, the time constants show no significant dependence on the pump beam fluency under the critical fluency of the etching reaction.

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

Electronic Materials and Processing Division
Room 6C - Session EM+NS-WeM

Nano-characterization of Molecules, Materials, and Devices

Moderator: R.S. Goldman, University of Michigan

8:20am **EM+NS-WeM1 Homoepitaxy on AlSb(001): Novel Reconstructions and Their Implications for Nucleation and Growth***, **W. Barvosa-Carter,*** HRL Laboratories*; A.S. Bracker, J.C. Culbertson, B.V. Shanabrook, B.R. Bennett, L.J. Whitman,* Naval Research Laboratory*; N. Modine,* Sandia National Laboratories*; H. Kim, E. Kaxiras,* Harvard University

Strained-layer heterostructures involving the 6.1 Å family of III-V semiconductors (InAs, GaSb, and AlSb) are being investigated for use in a growing number of high-frequency and infrared devices. The structure of the interfaces in these heterostructures can be critical to device performance, and device optimization will ultimately require precise and reproducible control over surface morphology during growth. To accomplish this level of morphological control, models are being developed which relate process parameters to surface roughness. These models require a detailed understanding of the relevant surface reconstructions and the mechanisms by which epitaxy proceeds. Using MBE, RHEED, and STM (performed at NRL), combined with first-principles theoretical calculations, we have discovered a novel (4x3) reconstruction on the nominally "(1x3)" AlSb(001) growth surface. This new reconstruction is different than those previously proposed for this surface and, surprisingly, includes mixed III-V dimers in the top layer of the reconstruction. The presence of surface Al atoms close to their natural lattice sites leads to nucleation and growth mechanisms that are fundamentally different than for III-As systems. We have also studied AlSb homoepitaxy as a function of coverage. The relationship between the observed reconstructions, island structure, island distributions, and possible growth modes will be discussed.

8:40am **EM+NS-WeM2 A New Point Projection Microscope for the Holographic Imaging of Single Macromolecules***, **A. Eisele**, B. Völkel, A. Glenz, B. Jäger, A. Gölzhäuser, M. Grunze,* Universität Heidelberg, Germany

In Low Energy Electron Point Source microscopy the spatial coherence of electrons from point sources can be utilized to image single molecules. A molecular object is positioned ~100 nm in front of the source and interference patterns between the part of the electron's wave function that scatters at the object and the part that passes by unscattered are recorded.@footnote 1@ Structural information on the molecule can then be obtained by numerical reconstruction of the hologram.@footnote 2,3@ We have built a new microscope for the recording of holograms at high magnification (@>=@10@super 6@) and under the minimization of critical disturbances like vibrations and alternating magnetic fields. In the presented instrument projection microscopy can be interleaved with in-situ preparation of the source via field emission / field ion microscopy. The microscope has been tested by the imaging of single DNA molecules that were deposited on thin structured siliconmembranes. Numerical reconstructions of the obtained holograms show corrugated strands with a diameter of ~2 nm. @FootnoteText@ @footnote 1@ H.-W. Fink, W. Stocker, and H. Schmid, Phys. Rev. Lett. 65, 1204 (1990) @footnote 2@ H. J. Kreuzer, K. Nakumura, A. Wiezbicki, H.-W. Fink, and H. Schmid, Ultramicroscopy 45, 381 (1992) @footnote 3@ A. Gölzhäuser, B. Völkel, B. Jäger, M. Zharnikov, H.J. Kreuzer, M. Grunze, J. Vac. Sci. Technol. A16(5), 3025 (1998)

9:00am **EM+NS-WeM3 Single Molecule Vibrational Spectroscopy with a Variable Temperature STM***, **L.J. Lauhon**, W. Ho,* Cornell University **INVITED**

The ultimate sensitivity for vibrational spectroscopy is the detection of a single bond. The vibrational spectrum of a single molecular adsorbate carries information about the effects of the local environment on chemical bonding. Such effects are the basis of important processes such as catalysis. Single bond sensitivity was recently demonstrated by using a scanning tunneling microscope to perform inelastic electron tunneling spectroscopy (STM-IETS) on a single acetylene molecule.@footnote 1@ We have extended this technique to other molecules at temperatures from 8 K to 60 K in an effort to both better understand and widen the applicability of STM-IETS. Two 'tunneling-active' vibrational modes have been identified for CO adsorbed on Cu(001) and Cu(110). The effects of monatomic steps and coadsorbed potassium on the vibrational spectra, including peak shifting and quenching, were found to be local in nature. The increase in the vibrational peak width with temperature was measured up to 40 K, beyond which thermal diffusion prevented STM-IETS spectra from being recorded. STM-IETS was also performed on pyridine and benzene adsorbed on Cu(001). Though these molecules differ only in the substitution of a nitrogen atom for one C-H group, their bonding geometries and vibrational spectra are very different. Achieving the spatial limit of nanotechnology depends on the ability to perform chemistry on the atomic scale. To this end, tunneling electrons were used to dissociate individual pyridine and benzene molecules. The adsorbtion geometries of the reaction products differ from the parent molecules and lead to changes in the vibrational spectra which provide insights into the identities of the reaction products and the tunneling mechanism. The extension of STM-IETS to new functional groups, including larger molecules, will also be discussed. @FootnoteText@ @footnote 1@ B. S. Stipe, M. A. Rezaei, and W. Ho, Science Vol. 280, p. 1732 (1998).

9:40am **EM+NS-WeM5 Characterization of Electronic Materials and Devices by Scanning Probe Microscopies***, **C.C. Williams**, V. Zavyalov, L. Klein,* University of Utah*; J. Kim,* Korea Advanced Institute of Science and Technology **INVITED**

Several studies of the electrostatic properties of oxides and silicon devices have been performed by the Scanning Capacitance Microscope (SCM) and the Electrostatic Force Microscope (EFM). The SCM provides a method for measuring topographical and electrical roughness of thin oxides, surface charge and local carrier and dopant density in semiconductors. On thin oxides, the SCM reveals a nanometer scale variation in the "electrical thickness" of the oxide. The thickness variations seen by SCM have been compared with topographical (AFM) and surface potential measurements by EFM in UHV. Surface potential variations of order 5 mV are observed on the same spatial scale as the thickness variations seen by the SCM. Calculations show that the measured surface potential variations correspond to less than one electron per tip area (30 nm radius). Single MOSFET devices have been imaged in cross-section under active electrical bias by SCM. The images provide a measure of the distribution of the carriers in a device under bias. Finally, a new technique will be described for detecting the transfer of a single electron between a SPM tip and surface.

10:20am **EM+NS-WeM7 Mapping Composition and Electrostatic Potential in Devices***, **A. Ourmazd**, A. Orchowski, W.-D. Rau, P. Schwander,* IHP, Germany **INVITED**

An electronic device is, in essence, a microscopically varying electrostatic potential surface, which steers the charge carriers between the device's terminals. Until recently, there were no means for directly measuring the electrostatic potential distribution in the bulk of devices. It is now possible to map the electrostatic potential in two dimensions by electron holography. Maps of deep submicron transistors have been obtained with nanometer spatial resolution and 0.1V sensitivity. The electrostatic potential surface can be tailored by changes in composition and/or doping. It is often important to separate the two effects. Electron holography alone, however, cannot distinguish between them; they both change the electrostatic potential. QUANTITEM, on the other hand, is sensitive to compositional changes only. Efforts are under way to combine the results from electron holography and QUANTITEM, in order to separate the effects of composition and doping, with first encouraging results.

11:00am **EM+NS-WeM9 Failure Analysis of Sub 1/4-Micron Contacts by Means of TEM-EELS***, **F. Yano**, Y. Nakamura, T. Aoyama, Y. Mitsui,* Hitachi Ltd., Japan

Although TEM-EELS (Transmission Electron Microscope-Electron Energy Loss Spectroscopy) has practically been used for elemental analysis for nanometer area, its full potential, we believe, is achieved when it is used for chemical analysis just like ESCA. This paper uncovers our experience of thermally stable contact development, in which our advanced TEM-EELS@footnote 1@ has revealed reactions in the contact during thermal process, which have detrimentally increased its resistivity.@footnote 2,3@ The contact holes are filled with sputtered Ti, which is annealed to form TiSi@sub 2@, CVD-TiN and CVD-W. Alathough the contact resistivity was low enough just after contact processes, it became higher after thermal process. The resistivity was varied 10@super 2@ to 10@super 6@ @ohm@ depending on the process conditions. Chemical analysis of loss energies showed that Si substrate in the contact is fully covered with SiO@sub 2@ in the fatal worst case. Even somewhat better cases, TiSi@sub 2@ formation was partial and still SiO@sub 2@ was formed. In other cases, TiO@sub x@ was also observed. These oxidized layers clearly increased resistivity. However, the mechanism of oxidation was unclear, especially the origin of the oxygen was, because neither oxygen nor water was applied. To clarify the mechanism, we made a model, in which residual TiCl@sub x@ on CVD-TiN forms titanium acid gel (TiO@sub x@(H@sub 2@O)@sub n@) which works as a water reservoir. During thermal process, the water in the gel is released, which goes through TiN grain and finally oxidizes silicon at the interface of TiN and Si substrate. To prove this model, the relation between the amount of residual Cl and the contact resistivity was measured. The results supported the model above, i.e., the more Cl observed, the higher the resistivity is. Based on this mechanism, all cases of high resistivity failures in the thermally stable contact were explained. Chemical analysis by TEM-EELS will be a key technique for failure analysis of 1/4-micron devices and after. @FootnoteText@ @footnote 1@ T. Sekiguchi, et al., Jpn. J. Appl. Phys., vol. 37 (1998) L694. @footnote 2@ Y. Mitsui, et al., Ext. Abst. IEDM (1998) 329.@footnote 3@ Y. Nakamura, et al., Proceedings of Advanced Metallization Conference, Colorado (1998) 661.

11:20am **EM+NS-WeM10 Applications of AFM/SCM in Imaging Implant Structures of Semiconductor Devices*, K.-J. Chao,*** *J.R. Kingsley, R.J. Plano, X. Lu, I.D. Ward,* Charles Evans & Associates

The scanning capacitance microscopy (SCM) has been widely used to investigate the two-dimensional carrier profile of semiconductor devices. In this work, SCM is used to investigate several different semiconductor devices. First, one commercially purchased integrated circuits (IC) device was cross-sectioned and polished for the SCM investigation. Implant structures near the gate were clearly resolved. Second, two semiconductor devices, one was good and the other was failed, were prepared by cross-sectioning and then followed by polishing. Implant profiles of similar structures on both devices were revealed by SCM. As compared with the good device, the thickness of the N-well structure was found to be thinner by about 0.4um for the failed device. Third, a GaAs device with Zn thermally diffused through the Si3N4 mask was studied to determine the lateral diffusion length of Zn. Applications in other cases will be presented at the conference.

11:40am **EM+NS-WeM11 Capacitance Measurements on Gold Nanowires*, A. Wlasenko,*** McGill University, Canada

There are several assumptions made about classical capacitors (C=Q/V): the density of states(DOS) of the plates is infinite, the potential drop occurs entirely across the plates, electrons don't interact, and there is no tunnelling. In mesoscopic capacitors, the voltage drop doesn't occur entirely across the plates, and the finite DOS plays an important role. In the experimental setup presented, the voltage-dependence of C is measured for gold nanowires allowing the DOS to be deduced according to theory [H. Guo et al., APL 74, 2887-2889 (1999)]. A piezotube is used to retract a gold sample in contact with a gold tip to form a nanowire. Along with measurements of C, simultaneous measurements of conductance(G) are made with a current preamplifier to monitor the transmission properties of the contact. Changes in the C of this nanowire are measured by a modified RCA Video Disc sensor: a resonant circuit is connected to a 915 MHz oscillator, and the amplitude of the signal is measured. A change in C leads to a shift in the resonance peak which is detected by the sensor. The sensor is calibrated using a ball bearing and metal plane geometry in comparison with classical calculations. The sensor is sensitive to C changes as low as 10@super -17@ F. When the tip and sample are in contact, the sensor measures a convolution of C and G. Where a variation in C leads to a shift in the resonance peak, a variation in G leads to a change of the FWHM. Measurements on either side of the resonance peak can be made in order to seperate C and G.

Magnetic Interfaces and Nanostructures Technical Group Room 618/619 - Session MI+EM-WeM

Spin-Dependent Tunneling and Transport

Moderator: K. Bussmann, Naval Research Laboratory

8:20am **MI+EM-WeM1 Models of Spin-dependent Tunneling*, S. Zhang,*** University of Missouri, Rolla **INVITED**

There are a number of theoretical models of spin-dependent tunneling. Some are based on toy models and others are built on electronic structures of ideal tunnel junctions obtained from ab-initio methods. The question is whether these models are relevant to the experimental realization of the magnetotransport of magnetic tunnel junctions. We analyze these model predictions by taking into account non-ideal nature of the magnetic tunnel junctions studied to date. It is shown that most of the theoretical conclusions are not reliable in interpreting experimental data. There are at least three intrinsic mechanisms on the voltage dependence of magnetoresistance: the effect of electronic structure, inelastic tunnel channels, and spin-dependence of electric field penetrations. The last effect comes from spin-polarized electron screening. When a voltage is applied across a magnetic tunnel junction, charges and spins are accumulated at the interfaces. The conduction electrons tend to screen these charges and spins via Coulomb and exchange interactions; this leads to a spin-dependent voltage absorption by the electrodes. We calculate the voltage dependence of magnetoresistance by including this field penetration effect. When one considers magnetic tunnel junctions beyond simple trilayer structures, e.g., double barrier junctions, a number of additional complications arise. Among them, the energy and spin relaxation of tunnel electrons becomes important. We examine these processes in detail, and present the I-V characteristics and junction magnetoresistance for both two-terminal and three-terminal geometries.

9:00am **MI+EM-WeM3 High Performance Demonstration of Magnetic Tunnel Junction Random Access Memory*, *W.J. Gallagher,*** *S.L. Brown, Y. Lu, E.J. O'Sullivan, P.L. Trouilloud, D.A. Abraham, J. Bucchignano, R.H. Koch, Y.H. Lee, R. Robbertazzi, M. Rooks, J. Yoon, R.A. Wanner, S.S.P. Parkin, D. Pearson, K.P. Roche, M.G. Samant, P.M. Rice, A. Lee, R.E. Scheuerlein,* IBM **INVITED**

We describe a magnetic tunnel junction (MTJ) RAM demonstration involving the integration of 0.25 µm CMOS technology with a special research-scale magnetic tunnel junction "back end." The magnetic back end is based upon state of the art mutilayer magnetic growth technology available on a research scale. For the demonstration, the wafers were cut into one-inch squares for depositions of bottom-pinned exchange biased magnetic tunnel junctions. The samples were then processed through four additional lithographic levels to complete the circuits. Special care was required to achieve fine lithography on the one-inch pieces aligned to the underlying circuits. Both deep uv stepper lithography and e-beam lithography were utilized. Patterning of the magnetic layers involved physical removal of the magnetic material by means of ion beam milling, an etching process not commonly used in semiconductor technology. Redeposition, which accompanies ion milling and is exacerbated in dense arrays, had to be carefully controlled with combinations of angled mills in order to minimize the occurrence of junction shorts and maximize the yield of working bits. Key performance aspects demonstrated in 1 K bit arrays included reads and writes in less than 10 ns and nonvolatility. These results suggest that MTJ MRAM might simultaneously provide much of the functionality now provided separately by SRAM, DRAM, and NVRAM. . @FootnoteText@ @footnote *@ Work supported in part by DARPA contract MDA972-96-C-0014.

9:40am **MI+EM-WeM5 Pinhole Decoration in Magnetic Tunnel Junctions*, D. Allen*[1]*,*** *R. Schad, G. Zangari, I. Zana, D. Yang,* University of Alabama*; M.C. Tondra, D. Wang,* Nonvolatile Electronics

Magnetic tunnel junctions are of interest for their possible applications in magnetic sensors and nonvolatile memory devices. The possibility of local shortcuts in the insulating layers of magnetic tunnel junctions, known as pinholes, can cause malfunctions in these devices. The reduction of insulator thicknesses will make this problem more severe. The ability to image pinholes could lead to further development of magnetic tunnel junctions. The imaging of structures that are not directly observable with imaging is traditionally done by decoration. This can be achieved by exploiting the conductivity of the pinholes. We decorated pinholes in a 1.8nm thick Al@sub2@O@sub3@ layer by electrodeposition of copper. These copper cauliflower-like structures can be imaged by conventional microscopies. Dielectric breakdown could be a source of pinhole creation. Applying 0.5 V for electrodeposition (as used here) would exceed the breakdown threshold for weak points in the insulator. This would create pinholes at points with insulator thickness less than 0.5 nm. This is an opportunity of the method. Upon application of increasing voltage pulses prior to deposition it will allow discrimination of potential breakdown spots as a function of their thickness. The chemical conditions were tailored to avoid damaging the insulator layer or creating new pinholes. This was verified by studying surface roughness (Atomic Force Microscopy), chemical composition (X-ray Photoelectron Spectroscopy) and layering quality (X-ray Diffraction).

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[1] **Falicov Student Award Finalist**

10:00am **MI+EM-WeM6 Novel Hybrid Magnetoelectronic Device for Magnetic Field Sensing**, ***D.M. Schaadt**, E.T. Yu, S. Sankar, A.E. Berkowitz,* University of California, San Diego

Structures in which magnetic and electronic materials are combined offer a variety of possibilities for realization of devices with dramatically improved functionality or performance as compared to conventional devices. We have designed, characterized, and analyzed a novel hybrid magnetoelectronic device: a monolithic field-effect-transistor-amplified magnetic field sensor in which a granular Co-SiO@sub2@ tunnel magnetoresistive (TMR) thin film is incorporated into the gate of a p-channel Si metal-oxide-semiconductor field-effect transistor (MOSFET). In this structure, current flow through the TMR film leads to a buildup of electronic charge within the gate, and consequently to a transistor threshold voltage shift. For a fixed voltage applied across the TMR layer, an external magnetic field changes the TMR film resistance, and consequently the current and charge within the gate. The resulting threshold voltage shift leads to a pronounced response to the external magnetic field in the transistor current-voltage characteristics. The relative current change induced by application of a 6 kOe external magnetic field at room temperature was amplified from 5% for the current through the TMR film to 21% for the transistor subthreshold current. The absolute current response in the saturation regime increased by a factor of about 500 compared to that of the TMR film alone. These results were achieved in a non-optimized device structure; substantially better performance should be achievable with relatively straightforward improvements in device design and processing. A detailed analysis of the operation of this device and of methods for optimization of performance will be presented.

10:20am **MI+EM-WeM7 Andreev and Conduction Electron Spectroscopy of Interfacial Spin Transport**, ***R.A. Buhrman,*** Cornell University **INVITED**

The enhanced interfacial conductance of an N-S contact, due to the Andreev reflection of electrons with energy below the superconducting energy gap, provides a powerful means of measuring interfacial transmission rates, as well as any net spin polarization in the non-superconducting electrode. Thus very small F-S nanocontacts can be used to quantitatively measure the interfacial transmission probability for each spin orientation. This technique can also be extended to the determination of the spin-dependent transmission rates through thin magnetic layers. We have produced F-S and N-F-S nanocontacts lithographically, and have determined the net spin-polarization of the direct current emerging from several bulk ferromagnetic films, and the spin filtering behavior of ultra-thin ferromagnetic layers. Measurements with different N electrodes illustrate the importance of the band structure mismatch in determining the degree of the spin-filtering. The bias dependence of the nanocontact interface resistance in the normal state can also be used to examine the degree to which the interface results in inelastic, spin-flip scattering processes. For certain N electrodes, very strong inelastic scattering is observed at relatively low energies. I will compare these single interface measurements with the current-perpendicular-to-the-plane magnetoresistance results that we have obtained with spin-valve and GMR nanopillar devices less than 100 nm in diameter. The low energy spin filtering measurements will also be compared with higher energy, ~ 1eV, spin filtering measurements that our group has been conducting with an STM-based magnetic microscope.

11:00am **MI+EM-WeM9 Spin-Polarization of La@sub 2/3@Sr@sub 1/3@MnO@sub 3@**, ***D.C. Worledge**, T.H. Geballe,* Stanford University

Spin-polarized tunneling measurements using La@sub 2/3@Sr@sub 1/3@MnO@sub 3@/SrTiO@sub 3@/Al tunnel junctions are reported. The deposition technique and efforts to control the interface quality will be discussed. At sufficiently low temperatures the application of an applied magnetic field splits the peaks in the dI/dV curve, allowing a measurement of the spin polarization to be made.

11:20am **MI+EM-WeM10 Electrical Spin Injection into LED Heterostructures**, ***B.T. Jonker**, B.R. Bennett,* Naval Research Laboratory*; G. Kioseoglou, A. Petrou,* State University of New York, Buffalo

Optical excitation has routinely been used to create spin polarized carrier populations in semiconductor heterostructures. Surprisingly long spin lifetimes and diffusion lengths have been reported in optically pumped GaAs in studies which have addressed both semi-classical@footnote 1@ and quantum coherent regimes.@footnote 2,3@ It is very desirable to electrically inject spin polarized carriers via a ferromagnetic contact to increase the potential for practical applications. This has been an elusive goal, however, and only modest effects (@<=@ 1%) have been obtained.@footnote 4@ In an effort to investigate the efficiency of electrical spin injection into semiconductors, we have fabricated light emitting diode structures with ferromagnetic contacts. The radiative recombination of spin polarized carriers in quantum wells results in the emission of circularly polarized light, with the degree of optical polarization directly proportional to the carrier spin polarization. The samples consist of FM / InAs / AlSb / GaSb / AlSb heterostructures grown by MBE on p-GaAs(001) substrates in which the GaSb quantum well serves as the active region for radiative recombination. Standard optical lithography and chemical etch procedures were used to define mesa structures with transparent surface contacts. Measurements are performed as a function of injection current, magnetic field, and temperature. We compare results from ex situ contacts with those obtained from samples for which the ferromagnetic films are deposited in situ via MBE. @FootnoteText@ @footnote *@ This work was supported by the Office of Naval Research. @footnote 1@ D. Hagele, M. Oestreich, W.W. Ruhle, N. Nestle and K. Eberl, APL 73, 1580 (1998). @footnote 2@ A.P. Heberle, W.W. Ruhle and K. Ploog, PRL 72, 3887 (1994). @footnote 3@ J.M. Kikkawa and D.D. Awschalom, PRL 80, 4313 (1998); Nature 397, 139 (1999). @footnote 4@ Y.Q. Jia, R.C. Shi and S.Y. Chou, IEEE Trans. Magnetics 32, 4707 (1996).

11:40am **MI+EM-WeM11 Electron Spin Interferometry**, ***C.H. Back**, S. Egger,* ETH Zürich, Switzerland*; J. Krewer,* Blaupunkt-Werke GmbH, Germany*; D. Pescia,* ETH Zürich, Switzerland

Quantum interference of electron waves in Fabry-Perot type solid-state resonators has been observed in a number of experiments. The applications of this phenomenon include quantum-well based semiconductor devices,@footnote 1@ accurate mapping of the band structure of solids and surfaces@footnote 2,3,4,5@ and visualizing the spatial dependence of quantum mechanical wave functions by means of Scanning Tunnelling Spectroscopy (STS).@footnote 5@ Here we use quantum interference to switch the spin state of the electrons. The spin quantum resonator consists of a Cu-film of variable thickness sandwiched between vacuum and a magnetic Co-film. Electrons are injected into the resonator from the vacuum side. The Co-film provides a spin dependent reflector. Varying the resonator thickness results in periodic switching of the spin state of the specularly reflected electrons. We apply spin interferometry to study oscillatory interlayer exchange coupling and find a divergence of the coupling period predicted by theory.@footnote 6@ We discuss the implications of spin interferometry as spin polarimeter or spin polarized source and propose that interferometric spin selection should be observable in Spin Polarized STS. @FootnoteText@@footnote 1@Corcoran, E., Diminishing Dimensions, Sci.Am. 263, p.74-83, November Issue, (1990). @footnote 2@Paggel, J.J., Miller, T., Chiang, T.-C., Quasiparticle Lifetime in Macroscopically Uniform Ag/Fe(100) quantum Wells, Phys.Rev.Lett.81, 5632-5635, (1998). @footnote 3@Ortega, J.E., Himpsel, F.J., Mankey G.J., Willis, R.F., Quantum-well states and magnetic coupling between ferromagnets through a noble-metal layer, Phys.Rev.B 47, 1540-1552 (1993). @footnote 4@Kawakami, R.K. et al., Quantum-well states in copper thin films, Nature 398, 132-134 (1999). @footnote 5@Crommie, M.F., Lutz, C.P., Eigler, D.M., Imaging standing waves in a two-dimensional electron gas, Nature 363, 524-527 (1993). @footnote 6@Edwards,D.M., Mathon, J., Oscillations in exchange coupling across a nonmagnetic metallic layer, J.Magn.Magn.Mat. 93, 85-88 (1991).

Surface Science Division
Room 604 - Session SS3+EM-WeM

Surface Electronic Structure

Moderator: G.O. Sitz, The University of Texas, Austin

8:20am **SS3+EM-WeM1 Spectroscopic Nonlinear Optical Responses of Clean, H-terminated and Ge-covered (2x1)Si(001)**, ***L. Mantese**, D. Lim, M.C. Downer,* University of Texas, Austin

Nonlinear optical spectroscopies are becoming important in elucidating the electronic structures of surfaces and interfaces. Yet, the accurate theoretical calculation of these spectra remains a difficult challenge. Recently, theoretical models have been developed to predict the nonlinear optical responses of clean and absorbate-covered (2x1)Si(001) surfaces.@footnote 1,2@ Here, we report the second harmonic (SH) responses of clean, H-terminated and Ge-covered (2x1)Si(001) to provide a direct test of predictive models. We have extended the range of previously reported results@footnote 3,4@ further into the IR where tunable IR femtosecond pulses in the range of ~1.15 to 2.5 microns were generated by a commercially available optical parametric amplifier (OPA) system. In this excitation region the SH response is resonantly enhanced by surface states including those from the dangling bonds and reconstruction-induced bonds. In addition, by directly using our oscillator output (700 to 800nm), we measure nonlinear optical responses in the E@sub 1@ region of Si. In this spectral range the SH response is highly sensitive and is altered in contrasting ways to ML coverages of H and Ge on (2x1)Si, originating from a surface electric field related to dimer charge transfer. The two measurement regions are discussed in comparison with theoretical predictions. @FootnoteText@ @footnote 1@B. Mendoza et al., PRL 81 (1998) 3781. @footnote 2@V.I. Gavrilenko et al., PRL submitted (1999). @footnote 3@U. Hofer, Appl. Phys. A 63 (1996) 533;J.I. Dadap et al., PRB 56 (1997) 13367. @footnote 4@P. Parkinson et al., Appl. Phys. B 68 (1999) 1.

8:40am **SS3+EM-WeM2 Si Surface Passivation: Si(111):GaSe versus Si(111):As***, **A. Bostwick**, S. Meng, B.R. Schroeder,* University of Washington*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; F.S. Ohuchi, M.A. Olmstead,* University of Washington

Heteroepitaxy on Si(111)7x7 requires removal of the deep reconstruction and accompanying dangling bonds. One way to passivate the Si(111) surface and remove the reconstruction is exposure to As, forming Si(111):As 1x1.@footnote 1@ The initial chemisorption of GeSe on Si(111)7x7 surfaces also results in a nearly ideally terminated 1x1 surface, quite similar to Si(111):As. Ga and Se occupy bulk Si sites, with Ga directly above Si (T1 site) and Se forming three back-bonds to Ga (H3 site). This (1x1) structure is the same as half a bulk GaSe layer, and initiates GaSe heteroepitaxy on Si(111). The very small (less than 0.1 eV) Si 2p core level shift shows the interface silicon to be in a bulk-like environment with minimal charge transfer, in contrast to As terminated silicon (0.75 eV shift). Electron counting arguments predict a lone-pair state on the Si(111):GaSe 1x1 surface, very similar to the As case. We observe such a state with angle-resolved ultraviolet photoemission spectroscopy. It has a similar E(k) dispersion to Si(111):As, though a somewhat larger bandwidth. We find a second surface state between this lone-pair state and the first bulk state, which we attribute to Ga-Se bonds. In addition, the zone-center bulk state, degenerate in bulk Si, is split by about 0.5 eV. This surprising result is not found for Si(111):As. We tentatively attribute the splitting to the Si-Ga interaction. @FootnoteText@ M. A. Olmstead, R. D. Bringans, R. I. G. Urhberg and R. Z. Bachrach, Phys. Rev. B 34, 6401 (1986).

9:00am **SS3+EM-WeM3 Electron Excitations and Optical Properties of Semiconductor Surfaces***, **S.G. Louie**,* University of California, Berkeley and Lawrence Berkeley National Laboratory **INVITED**

The presence of electronic surface states and resonances often strongly modifies the structural, chemical, electronic, and optical properties of a surface. Over the past two decades, many sophisticated experimental methods (e.g., photoemission, scanning probes, and optical techniques) have been developed to investigate the spectroscopic properties of surfaces. In this talk, we discuss some of the theoretical developments in studying surface spectroscopic properties. Ab initio quasiparticle calculations can now be used to understand and predict surface-state excitation spectra such as those measured in photoemission and scanning tunneling spectroscopy experiments. A recent advance in treating excitonic effects further allows the first-principles study of surface optical processes. Results on several semiconductor surfaces will be presented. The possibility of using NMR chemical shifts as a probe of surface states will also be discussed.

9:40am **SS3+EM-WeM5 Low Temperature Scanning Tunneling Microscopy and Spectroscopy of the @sr@3x@sr@3 R30° Phase of Sn/Si(111)***, **L. Ottaviano**,* INFM, Italy*; A. Continenza, M. Crivellari, L. Lozzi,* University of L'Aquila and INFM, Italy*; S. Modesti,* University of Trieste and Laboratorio TASC-INFM, Italy*; S. Picozzi, G. Profeta, S. Santucci,* University of L'Aquila and INFM, Italy

In these years there has been a great deal of efforts in the understanding of the low temperature transition from a @sr@3x@sr@3 R30° to a 3x3 phase of Sn(Pb)/Ge(111).@footnote 1@,@footnote 2@ On the other hand, little attention has been devoted to the investigation of iso-electronic interfaces like Sn(Pb)/Si(111) at similarly low temperatures. Among other experimental techniques, STM can provide a deep understanding of the electronic structure of these surfaces by performing measurements at various tunnelling voltages. Theorist who proposed different model interpretations have recently called for STM experiments at low temperatures on such systems.@footnote 3@ We show the first STM atomically resolved images of the low temperature (100 K) 1/3 ML-Sn/Si(111) @sr@3x@sr@3 R30° phase. Correspondingly we have measured tunnelling I-V spectra. Data are compared with all electron ab-initio calculations performed on a slab of Si(111) covered with 1/3 ML-Sn in the @sr@x@sr@3 R30° reconstruction. In particular we compare the ab-initio results with surface and electronic properties as obtained by STM/STS and photo-emission results. @FootnoteText@ @footnote 1@ L.Petaccia, L.Grill, M. Zangrando, and S. Modesti, Phys. Rev. Lett. 82 (1999) 386. @footnote 2@ A. Mascaraque et al., Phys. Rev.Lett. 82 (1999) 2524. @footnote 3@ S. Scandolo, F. Ancilotto, G.L.Chiarotti, G. Santoro, S. Serra, and E.Tosatti, Surf. Sci. 402-404 (1998) 808.

10:00am **SS3+EM-WeM6 Electronic Structure of the 3C-SiC(001)-c(4x2) Surface***, **L. Duda**, L.S.O. Johansson, B. Reihl,* Universität Dortmund, Germany*; H.W. Yeom,* University of Tokyo, Japan*; S. Hara, S. Yoshida,* Electrotechnical Laboratory Tsukuba, Japan

We provide the first investigations of the electronic structure of the Si-rich 3C-SiC(100)-c(4x2) surface using angle-resolved photoemission and synchrotron radiation. The surface is found to be semiconducting. The Fermi level position was determined to be at 1.9 eV above the valence-band maximum. Three surface states are identified within the bulk band gap. We measured the dispersion of these states along the high-symmetry directions of the surface Brillouin zone (SBZ). The upper band at 1 eV binding energy and the third band at 2.6 eV are non-dispersive. The second band is located at 1.5 eV at the center of the SBZ and shows a weak dispersion of 0.3 eV in the @Gamma@-X direction, whereas, it is dispersionless in the other directions. We compare these results to calculated band structures.@footnote 1@ In addition, the comparison with experimental observed band structures of the 2x1 surface@footnote 2@ gives important new insight into the reconstruction behaviour of the SiC surface, supporting the close similarity of both reconstructions. @FootnoteText@ @footnote 1@ W. Lu, P. Krüger, J. Pollmann, Phys. Rev. Lett. 81 (1998) 2292 @footnote 2@ L. Duda, L. S. O. Johansson, B. Reihl, H. W. Yeom, S. Hara, S. Yoshida, submitted to Surface Science (1999).

10:20am **SS3+EM-WeM7 Photoemission Spectroscopy of Platinum Overlayers on Silicon Dioxide Films***, **J.W. Keister**, J.E. Rowe,* Army Research Office*; J.J. Kolodziej, T.E. Madey,* Rutgers University

Soft x-ray photoelectron spectroscopy has been used to study ultrathin Pt films on silicon dioxide as model supported-catalyst materials. Using monochromatic synchrotron radiation (NSLS U4A - Brookhaven), platinum and silicon core-level photoelectron peaks were measured as a function of platinum coverage in the range, 0 - 10 monolayers (ML). The bulk Si and SiO@sub 2@ film Si(2p) peaks both show a binding energy drop within the first ~ 0.5 ML of dosing. However, the effect is stronger for the SiO@sub 2@ film Si(2p) peak, indicating an increased screening of the 2p electrons by the metal overlayer. We also observe a monotonic increase of the Pt film workfunction with coverage from 4.52 eV initially to 5.59 eV at ~ 10 ML. The Pt(4f) and valence band spectra display changes with Pt dose which are also consistent with increased screening, from non-metallic below ~ 0.5 ML to metallic as coverage increases. The Pt core level decreases its binding energy from ~ 72.2 eV to ~ 70.9 eV between 0 and 10 ML coverage. The coverage dependence of the Pt lineshape and intensity, and the large saturation coverage for the workfunction change indicate cluster growth (Volmer-Weber growth). The increasingly metallic nature of the Pt overlayer with dose is quantified by numerical lineshape fitting with Gaussian-broadened Doniach-Sunjic functions, as appropriate for varying amounts of metallic screening. Further quantitative results and interpretation in terms of nucleation and growth of Pt clusters will be discussed.

10:40am **SS3+EM-WeM8 The Behavior of Metallic Quantum Well State Dispersions in the Cu/fccCo/Cu(100) System as a Function of Film Thickness***, **W.K. Siu**, R.A. Bartysnki,* Rutgers University

The magnetic coupling of ferromagnetic (FM) layers separated by a nonmagnetic (NM) layer has been associated with the formation and behavior of metallic quantum well (MQW) states in the spacer layer. Inverse photoemission has been used to investigate the MQW states in the prototypical Cu/fccCo/Cu(100) system for very thin Cu layers. These studies have shown that their dispersion with parallel momentum can be strongly affected by the electronic structure of the underlying FM material. Specifically, rapidly dispersing MQW states in the NM layer will acquire an uncharacteristically large effective mass when they encounter a projected band gap in the FM material. The experimental result shows the the behavior over severval Cu monolayers. In the Cu/fccCo/Cu(100) case, this occurs near the neck of the Cu Fermi surface and affect the states responsible for the short period coupling in this system. We have investigated how the dispersion of these levels develops as a function of Cu layer thickness and, in particular, how it evolves towards the behavior found for the single crystal Cu(100) surface. These results are explained in terms of a phase accumulation model for the electronic structure of the MQW system. Funded by the National Science Foundation under grant No. NSF-DMR98-01681. and the Petroleum Research Fund under grant No. ACS-PRF-33750-AC6,5.

11:00am **SS3+EM-WeM9 Atomic and Electronic Structure of Ag/Ni(110) and Ni/Ag(100)**, *P.T. Sprunger,* ***D.A. Hite,*** Louisiana State University

The atomic and electronic structure of Ag on Ni(110) and Ni on Ag(100) has been studied by synchrotron-based angle-resolved photoemission spectroscopy (ARUPS), low energy electron diffraction and scanning tunneling microscopy. These systems are of interest due their high bulk lattice mismatch and immiscibility. STM results of the Ag/Ni(110) system have revealed a novel pseudomorphic, surface-confined alloy phase at a coverage of ~0.5 ML. ARUPS results of this phase show a bulk-like, 3-D Ag electronic structure due to strong hybridization with the Ni bands. However, at a coverage of 1 ML, the Ag "de-alloys" and structurally forms a strained ~ Ag(111) overlayer. The electronic structure of this phase is radically different, namely, the laterally localized Ag d-bands show only k-parallel dispersion, that is, 2-D structure. In contrast, ARUPS results of Ni monolayer deposition on Ag(100) reveals no alloy formation below 150 K. However, at deposition temperatures above 400 K, Ni segregates subsurface, resulting in a Ag surface termination. The underlying Ni adopts Ag lattice parameters. ARUPS data from this latter phase reveals 3-D, bulk-like electronic structure due to strong mixing of states. The results will be compared and contrasted with theoretical band-structure calculations. This research is funded by DOE through contract DE-FG-02-98ER45712.

11:20am **SS3+EM-WeM10 Spin-Orbit-Split Surface States in Clean and Alkali-Metal-Covered W(110)@footnote 1@**, ***E. Rotenberg,*** Lawrence Berkeley National Laboratory*; J.W. Chung,* Pohang Institute of Science and Technology, Korea*; S.D. Kevan,* University of Oregon

The broken symmetry at surfaces can give rise to a non-zero spin-orbit splitting of valence bands, as has recently been observed for the s-p derived surface state on Au(111).@footnote 2@ We now observe such a splitting of the d-derived surface state on W(110) and to a lesser extent, on Mo(110), and follow the evolution of the splitting as monovalent atoms are adsorbed. We find a dramatic increase in the splitting as a function of deposition for H and all alkali metals for coverages up to 1 ML. For Li, which shows the strongest change in splitting, we find a decrease in the splitting at the highest coverages near 1 ML. Our findings show that the spin-orbit splitting is a sensitive probe of the local surface conditions, to the extent that they are sampled by the surface state's wavefunction. The observed evolution is also directly relevant to recent observations of altered orbital magnetic structure vs. adsorbate coverage in magnetic materials. We propose a spin ordering for the associated Fermi contours which has important implications for spin excitations at surfaces. @FootnoteText@ @footnote 1@E. Rotenberg, J. W. Chung, and S. D. Kevan, Phys. Rev. Lett. 82 4066 (1999). @footnote 2@S. LaShell, B. A. McDougall, and E. Jensen, Phys. Rev. Lett., 3419 (1996).

11:40am **SS3+EM-WeM11 Resonant Auger Studies of Metallic Systems**, ***I. Coulthard,*** *J.W. Freeland, S.P. Frigo, J.F. Moore, W.S. Calaway, M.J. Pellin, M. Mendelsohn,* Argonne National Laboratory*; T.K. Sham, S.J. Naftel,* University of Western Ontario, Canada*; A. Stampfl,* Australian Nuclear Science and Technology Organization

Auger electron emission at photon energies near the asoociated absorption edge which generates the initial core hole is a complex process. Excitation and decay become linked such that the process must be described as a single-step process rather than the classical two step process for Auger emission. This results in the production of discrete lines which are resonantly enhanced at the absorption edge, and whose intensity vanishes far below or above the edge. Another result of utilizing resonant photon energies is that the Auger line width may no longer be limited by the intrinsic lifetime resulting in a narrowing of the Auger spectrum.@footnote 1@ Results will be presented for a variety of systems including, Cu, Co, Al, CuNi alloys, and CuAl alloys. Specific attention will be paid to:probing unoccupied densities of states, very high resolution x-ray absorption spectroscopy utilizing auger yields to produce sub-lifetime narrowed x-ray absorption spectra, and the use of the technique for non-homogeneous sample systems. Work at Argonne is supported by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. @FootnoteText@@footnote 1@T.M. Grehk, W. Drube, R. Treush, and G. Materlik. Phys. Rev. B 57, 6422 (1998).

Electronic Materials and Processing Division
Room 608 - Session EM-WeA

Novel Materials and Devices for Computation and Communication

Moderator: H.A. Atwater, California Institute of Technology

2:00pm **EM-WeA1 Materials and Devices for Optical Communication*, K.J. Vahala,*** California Institute of Technology **INVITED**

The performance requirements of commercial lightwave communication systems have systematically exceeded expectations for over a decade. Driven by explosive Internet growth, current commercial trunk-line systems are approaching 1 Terabit/sec of aggregate bandwidth on a single optical fiber and use as many as 80 channels (wavelengths). Optical switching, channel add/drop, wavelength conversion, and other functions are needed in these systems and there is a premium on functions that can be all-optical and preferably fiber based. This talk will over view some of the materials and devices that are now finding use in telecom systems. It will also suggest some performance issues in these systems that are material-related.

2:40pm **EM-WeA3 Nano-Crystal and Quantum-Dot Memories: Implications Small Dimensions, Quantum Confinement and Interface States*, S. Tiwari,*** Cornell University*; A. Kumar, J.J. Welser,* IBM T.J. Watson Research Center **INVITED**

For field-effect devices, one of the most significant effects of scaling of critical dimensions to the 1--10~nm range is a reduction in collective effects whose reproducibility has been so profitably applied over the last many decades. Examples of such collective phenomena are the number of electrons flowing through the channel, the number of electrons transferred during a CMOS switching event, and the number of dopants used to control the threshold voltage. A larger number of electrons flowing in the channel leads to smaller fluctuations in the current, a larger number of electrons transferred during switching leads to smaller fluctuations in the switching voltage levels, and a larger number of dopants leads to smaller fluctuations in the threshold voltage. The scaling of device dimensions has been driven by higher function and lower cost gained from an increase of device density and performance, a lowering of power density, and mixing of logic and memory technologies. Logic and memory have to co-exist at such small dimensions, and the various forms of memory have to be capable of providing a range of performance from high speed to low power and non-volatility. Nano-crystal and Quantum-Dot memories, examples of flash memories, are small dimension structures that utilize quantum-dot(s) between the gate and the channel of a field-effect transistor to store electron(s), which screen the mobile charge in the channel and thus induce a change in the threshold-voltage or conductivity. These quantum-dots are transmissively coupled to the channel and isolated from the gate. Their reduced dimension and confinement brings forth two important features that are absent in the conventional silicon field-effect transistors: a reduced density of states, restricting the states available for electrons and holes to tunnel, and the Coulomb blockade effect, arising from a larger electrostatic energy associated with placing a charged particle onto a smaller capacitance.

3:20pm **EM-WeA5 Fabrication and Manipulation of Silicon Nanocrystals for Non-Volatile Memory Applications@footnote 1@*, L.D. Bell,*** Jet Propulsion Laboratory, California Institute of Technology*; E.A. Boer, D.H. Santamore, H.A. Atwater, K.J. Vahala, M.L. Ostraat, R.C. Flagan,* California Institute of Technology **INVITED**

Silicon-based devices continue to decrease in size, and fast, low-power devices sensitive to small numbers of electrons are now feasible. MOS structures with large arrays of Si nanocrystals can form the basis for a floating gate memory that is extremely fast, reliable and non-volatile, and in which charge stored may be as little as one electron per nanocrystal. To date, these devices have exhibited a distribution of charge transit times during writing of nanocrystal ensembles, which limits speed and array uniformity. This could be related to nanocrystal interface states, a dispersion in oxide thicknesses, or nanocrystal size variations. To address these limitations, we have developed an aerosol vapor synthesis/deposition technique for Si nanocrystals with active size classification, enabling narrow distributions of nanocrystal size. One goal of these experiments was to use atomic force microscopy (AFM) to perform nanocrystal manipulation and charging on a single-particle basis. Si nanocrystal structures (such as lines and arrows) have been formed by contact mode AFM and subsequently imaged in non-contact mode without additional particle motion. Single nanocrystal charging by a conducting AFM tip has been observed, detected as an apparent height change due to electrostatic force followed by a slow relaxation as the charge dissipates. To investigate the charge trapping characteristics of nanocrystals in device structures, we have made samples of Si nanocrystals embedded in thermally grown SiO@sub 2@ films by ion implantation of Si, followed by annealing at 1100°C. A conducting AFM tip has been used to inject charge into these samples and to observe the charge dissipation as a function of time. The relative contributions of surface defects, bulk irradiation damage and nanocrystals to the resultant trapped charge have been studied and have been shown to be dependent on processing parameters. @FootnoteText@ @footnote 1@Research supported by JPL DRDF and NASA.

4:00pm **EM-WeA7 Architectonics of Defect-Tolerant Molecular Circuitry*, R.S. Williams,*** Hewlett-Packard Labs **INVITED**

Economic and physics considerations indicate that the exponential scaling of CMOS will saturate in a decade. However, the power efficiency of present electronics technology is at least a billion times smaller than the non-reversible thermodynamic limit.@footnote 1@ Thus, there is a huge incentive to invent new devices with nanometer dimensions. In addition, vast quantities of these devices must be manufactured and interconnected inexpensively. Two lines of complementary research are necessary for future nanoelectronics: the development of quantum-state switches and the design of circuit elements that can be assembled into complex systems via chemical processes. A recent proposal for the construction of molecular-electronic computers involves the explicit incorporation of defect tolerance, which is the capability to operate perfectly even in the presence of manufacturing mistakes, into the architecture of the circuit.@footnote 2@ An example of such a defect-tolerant computer was built and tested at Hewlett-Packard Laboratories with standard Si technology. The Teramac experimental supercomputer replaced logic with memory whenever possible and relied on sophisticated computer algorithms to identify and route around defects. This architecture is currently being explored as the basis for molecular-electronic memory, logic, signal routing and multiplexing/demultiplexing in a joint research project involving HP Labs (the Quantum Structures Research Initiative), UCLA (the research groups of Profs. J. R. Heath, F. Stoddart and V. Roychowdhury) and UC Berkeley (Prof. Paul McEuen). Experimental results on prototype devices and circuits will be presented and discussed. @FootnoteText@ @footnote 1@ R. P. Feynman, Feynman Lectures on Computation, edited by A. J. G. Hey and R. W. Allen (Addison-Wesley, 1996). @footnote 2@ J. R. Heath, P. J. Kuekes, G. S. Snider and R. S. Williams, "A Defect-Tolerant Computer Architecture: Opportunities for Nanotechnology," Science 280 (1998) 1716.

4:40pm **EM-WeA9 Carbon Nanotubes - a New Class of 1D Conductors*, P.L. McEuen,*** University of California, Berkeley and LBNL **INVITED**

Carbon nanotubes are single graphene sheets rolled into nanometer diameter cylinders. They are a new class of one-dimensional conductors that can be either metallic or semiconducting, depending upon their structural details. In this talk, I will discuss experiments by our group to probe the electrical properties of these fascinating systems. Wires are attached to individual tubes and a nearby gate is used to control the charge per unit length of the tube. If the tube is semiconducting, the resulting device operates as the world's smallest transistor. For a metallic tube, behavior characteristic of a correlated electron state known as a Luttinger liquid is found. Short tubes act like one-dimensional boxes for electrons whose quantized energy levels and spin states can be probed. Crossed metal and semiconducting tubes act as ultra-small Schottky diodes. As these experiments show, nanotubes offer an unprecedented opportunity to explore the physics and technology of the one-dimensional electron gas.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-WeA

Nanotubes: Growth, Characterization and Properties I

Moderator: S.B. Sinnott, University of Kentucky

2:00pm **NT+NS+EM+MS-WeA1 Making and Modifying Carbon Nanotubes*, R.E. Smalley,*** Rice University **INVITED**

The last year has produced exciting developments in our ability to produce and modify single wall carbon nanotubes (SWNT). New experiments have shown the feasibility of producing nanotubes in an efficient gas-phase process, sometimes having diameters down to approximately 0.6 nm. These methods involve chemical vapor deposition in high-pressure carbon monoxide. We are now pursuing this growth technique as a potentially viable means for cost-effective production of large amounts of SWNT. Development of new methods for purification and characterization of nanotubes has given new insight into their growth mechanisms. I will present new data on the morphology and length distributions of SWNT grown by traditional laser-oven methods, and outline new results on the behavior and characteristics of tube samples. Perhaps the most remarkable developments have been in the chemistry of SWNT as a new molecular species. Several groups have discovered means of covalent attachment of other chemical species to the tube ends and sidewalls. This derivatization significantly modifies the properties of SWNTs, permits the first true solutions of tube segments, and opens the door to a remarkable new realm of chemistry, materials science, and electronics.

2:40pm **NT+NS+EM+MS-WeA3 Roles of Fe, Co, and Ni in the Formation of Single-Walled Carbon Nanotubes and Encapsulated Nanoparticles***, **J. Jiao,*** Portland State University

The preparation and structural properties of carbon nanoclusters synthesized by having the transition metals Fe, Co, and Ni react with carbon in three different methods were investigated comparatively with the focus on single-walled nanotubes and encapsulated nanoparticles. The carbon nanoclusters were synthesized first by the high temperature (~3000°C) and high carbon-content process of the conventional arc discharge, secondly by the high temperature but low carbon-content process of the modified arc-discharge, and finally by the relatively low temperature (~500°C) process of catalytic decomposition of carbon monoxide (CO). The samples were characterized with respect to morphology, internal structure, and related properties. The carbon nanoclusters prepared by three different methods appear quite different on the surface, but have features in common that this report emphasizes. The same element can apparently serve different functions, serving as catalyst under one set of condition, and being encapsulated into the growing cages in a different environment. The elements of the iron group (Fe, Co, and Ni) were known as catalysts for growing the single-walled nanotubes and strings of spherical particles in conventional arc discharge, but could be encapsulated into the graphitic particles in the modified arc discharge and the CO disproportion that this study demonstrates. It was found that variation of the metal-to-carbon ratio is required to make these elements assume the double roles of either catalyst or encapsulant. In this report, an assembly of growth phenomena of carbon nanoclusters indicating the roles of the Fe, Co, and Ni will be presented. The growth mechanisms of these structural phenomena in relation to the preparation conditions in particular to the ratio of carbon content in the reaction chamber during the preparation are discussed.

3:00pm **NT+NS+EM+MS-WeA4 Plume Diagnostics During Carbon Nanotube Production by Laser Ablation***, **S. Arepalli,*** G. B. Tech./Lockheed Martin*; C.D. Scott,* NASA/Johnson Space Center

We report recent results of our plume diagnostics during carbon nanotube production by double pulse laser oven method. The evolution characteristics of different species in the plume from different regions of the laser ablated plume will be presented. Transient emission data is compared with plume images to formulate dynamics of plume expansion. Vibrational and rotational temperatures of C@sub 2@ and C@sub 3@ are estimated by comparison with computations. Excitation spectra of LIF are used to deduce ground state temperatures and populations.

3:20pm **NT+NS+EM+MS-WeA5 Synthesis and Integration of Carbon Nanotubes***, **H. Dai,*** Stanford University **INVITED**

This talk focuses on controlled growth and properties of multi-walled and single-walled carbon nanotubes on catalytically patterned substrates. It will be shown that new possibilities are opened up in nanotube science and applications by synthesizing nanotubes at desired locations and orientations in ordered fashions. A recently developed chemical vapor deposition method for high quality single-walled nanotubes is combined with microfabrication methods to reliably integrate single-walled nanotubes into various electrical architectures. The transport properties of individual single-walled nanotubes will be presented. Functional nanotube electrical devices with advanced performances will be shown. Issues in further control of nanotube growth will be addressed.

4:00pm **NT+NS+EM+MS-WeA7 Growth of Vertically Aligned Carbon Nanotubes on Transition-metal Catalyzed Plain Silicon Substrates using Thermal Chemical Vapor Deposition***, **Y.H. Lee**, Y.C. Choi,* Jeonbuk National University, Korea*; C.J. Lee,* Kunsan National University, Korea*; Y.B. Han,* Jeonbuk National University, Korea

Vertically aligned carbon nanotubes have been grown on a large area of transition-metal coated plain silicon substrates by thermal chemical vapor deposition method. We find that vertically aligned growth is critically dependent on the domain density in the transition metal cluster. Steric hindrance between nanotubes at an initial stage of the growth forces nanotubes to align vertically. Nanotubes are then further grown by the catalyst-cap growth mechanism. We also show emission patterns from aligned nanotubes. Our current approach of simple integration of stable field-emission displays on a large area puts a step forward to future display applications.

4:20pm **NT+NS+EM+MS-WeA8 Carbon Nanotube Tips: Structures and Properties***, **J. Han**, L. Yang, R.L. Jaffe,* NASA

A variety of structures and properties of carbon nanotube tips present challenges in understanding of electron tunneling and field emission of carbon nanotube materials. Topologically, a nanotube tip can be formed by joining a tube bulk and a cone or a half the fullerene. Different configurations can be resulted from arrangement of topological defects. Energetically favorable configurations are identified and classified using functional theory and molecular mechanics calculations. They are further used for electronic structure calculations based on tight-binding approaches. The location and intensity of localizes states at tips are studied as functions of the size and configurations of tips. The differences in localized stated between one and four-orbital calculations are also compared. Experimental results of carbon nanotube field emission properties are related to the calculations of the localized stated of nanotube tips.

4:40pm **NT+NS+EM+MS-WeA9 Electrochemical Deposition of Carbon Nanofilaments***, E. Anoshkina, **D. Zhou**, L. Chow, V. Desai,* University of Central Florida

Carbon nanofilaments are conventionally made from thermal catalytic chemical vapor deposition with carbonaceous gases as growth precursors. Based on their unique mechanical, thermal, and electrical properties, many applications of carbon nanofilaments have been realized in advanced technologies. We report here on a new method to prepare carbon nanofilaments, in which the nanofilaments have been made from organic solvents such as methanol through an electrochemical deposition process. Silicon wafers coated with Fe or Ni nanoparticles were employed as the electrodes, and the depositions were carried out at room temperature. It has been found that electrical field between the electrodes, conductivity of the solvent, and size of the catalysts play important roles in control of morphologies of the carbonaceous deposits. Furthermore, based on characterization of the nanofilaments using scanning electron microscopy, transmission electron microscopy, and energy dispersive x-ray spectroscopy, the formation and growth mechanism of carbon nanofilaments from the electrochemical deposition has been discussed.

5:00pm **NT+NS+EM+MS-WeA10 A Study on the Growth of Carbon Nanotubes with Respect to Process Conditions***, J.N. Srivastava, K.K. Awasthi, **C.D. Dwivedi**, G.N. Mathur,* Defence Materials & Stores Research & Development Establishment, India

Carbon nanotubes have been produced by graphite evaporation method in macroscopic quantities with reproducible results at different conditions. A study on the growth of CNT against the variation in Helium / Argon / Nitrogen pressure has been done and some interesting results are found with respect to geometry, density and alignment of the tubes. Total yield of the material is also found to be having correlation with the pressure and current. Material produced in different conditions has been characterized by XRD, SEM, TEM, TGA and FTIR techniques.

Surface Science Division
Room 606 - Session SS1+EM-WeA

Semiconductor Surface Science

Moderator: C.T. Campbell, University of Washington

2:00pm **SS1+EM-WeA1 Electronic Transport Properties of Silicon Surfaces@footnote 1@*, K. Yoo,*** University of Tennessee*; A.P. Baddorf,* Oak Ridge National Laboratory*; H.H. Weitering,* University of Tennessee

Most of our information about surface electronic properties has come from spectroscopic measurements and first principles electronic structure calculations. Direct measurements of transport properties of ultrathin films have revealed interesting physical properties, including quantum size effects. However, to correctly measure the surface or thin film conductivity, the conduction path through the bulk or substrate must be eliminated. We attempt to accomplish this by using crystalline silicon of "silicon on insulator''(SOI) material. Using STM, we have recently shown that 40 nm-thick Si(100) layers on SOI can be prepared with a comparable degree of structural perfection as the surfaces of bulk Si.@footnote 2@ For these SOI films, we also observed that at room temperature, LEED spots drift and gradually disappear during prolonged exposure to the electron beam, indicating that the ultrathin Si top layer is fully depleted of mobile carriers, i.e. non-conducting. This leaves surface states as the only conduction channel. We have measured the surface conductivity of the Si(100)2x1 reconstruction on SOI as a function of temperature and Si film thickness during exposure to molecular oxygen using a four-point probe technique in ultrahigh vacuum. The oxygen induced conductivity changes strongly depend on the Si film thickness (@DELTA@@sigma@=-1.75x10@super -5@(@ohm@@super -1@) for 40 nm and (@DELTA@@sigma@=-9.219x10@super -6@(@ohm@@super -1@) for 90 nm thick films at room temperature. Differences are also observed in the temperature dependence, with possibly significant surface contributions to total sheet resistance at low temperature. These results indicate a correlation between transport properties and surface states, which will be discussed. @FootnoteText@ @footnote 1@ Work supported by National Science Foundation(DMR-9705246). @footnote 2@ K. C. Lin et al, Appl. Phys. Lett. 72, 2313(1998).@footnote *@ Managed by Lockheed Martin Energy Research Corp.

2:20pm **SS1+EM-WeA2 Reinterpretation of the Scanning Tunneling Microscopy Images of Si(100) (2x1) Dimers-Observation on a Defect Free Surface*, K. Hata*,** *S. Yasuda, H. Shigekawa,* University of Tsukuba, Japan

In this presentation, we demonstrate that STM images of dimers of Si (100) taken with usual tunneling conditions are seriously characterized by tunneling from surface resonances and bulk states. In some cases, tunneling from these states overwhelm tunneling from the surface states which STM is generally believed to observe. The key point was the success to fabricate an almost defect-free Si(100) clean surface (defect density ~0.1%), making observations at a very low bias possible (0.5V). STM images of the dimers at 80K and room temperature taken at such low biases showed several new features. (1) In the empty states, when the surface bias is above ~1.4V, regions between the dimers are observed. (2) At 80K, a bright row similar to that observed at room temperature is obtained, though a bright and dark (2x1) unit align alternatively along the dimer row direction. The brighter units observed at the high bias corresponds to the location of the upper atom. (3) In the filled states, each atoms of the dimers at room temperature when the surface bias is lower than ~-1V. Every time when the bias is increased, the STM images of the dimers would gradually revert to the usual bean-type image of dimers at ~-1V. High resolution CITS measurements and first principle calculations also showed consistent results. We revisit and refine the interpretation of the STM images of the dimers, insisting that tunneling from surface resonances and bulk states are very important. The new interpretation brings results of many experimental and theoretical researches into an unanimous agreement.

2:40pm **SS1+EM-WeA3 STM-Study of the Absorption of Molecular Oxygen on GaAs(100)*, P. Kruse*,** *J.G. McLean, A.C. Kummel,* University of California, San Diego

There is currently a strong interest in making GaAs-oxide interfaces with very low defect densities to enable the use of GaAs-based FET technology. The interaction of oxygen with the GaAs surface plays an important role in this process. In this study, high-resolution scanning tunneling microscopy (STM) was used to image the chemisorption sites of molecular oxygen on the three most common reconstructions of the GaAs(100) surface, c(2x8), 6x6 and c(8x2) . All studies were performed at room temperature. The sticking probability was greatest on the surfaces with As-As dimer bonds. Even though the molecular oxygen prefers to initially react with the empty dangling bonds of the Ga atoms, after dissociation the oxygen atoms seek to form bridge bonds between an electron rich As atom from an As-As dimer and a second atom, either As or Ga. These dimerized As atoms do not exist in the c(8x2) reconstruction, hence the greater inertness of that surface. This is in contrast to the reaction of these surfaces with halogens which only need to form one bond per halogen atom and equally attack all reconstructions.

3:00pm **SS1+EM-WeA4 Chaotic-like Wavefunction Beating in Thin Silver Films with a Quasiperiodic Superstructure*, C.-S. Jiang*,** *H. Yu,* University of Texas, Austin*; Ph. Ebert,* Forschungszentrum J@um u@lich, Germany*; X.-D. Wang, R. Diener, Q. Niu, C.K. Shih,* University of Texas, Austin

It has been shown that atomically-flat Ag films can be grown on GaAs(110) substrates. These surfaces with (111) orientation exhibit, in addition, a one-dimensional quasi-periodic superstructure. Taking such surfaces as a model system, we investigated the effect of quasi-periodic scattering potential on the electronic structure by using spatially resolved scanning tunneling spectroscopy. Quantum well states due to the z-confinement of the 2-D thin film are clearly observed as a function of thickness. In addition, we have observed very intriguing chaotic interference patterns The observation of chaotic interference pattern is found to arise from the quasiperiodic superstructure acting as scattering potential for the 2-D electronic system. Theoretical calculations of the electronic states of quasi-periodic structure are currently underway.

3:20pm **SS1+EM-WeA5 3C-SiC(100) c(4x2) Surface and Sub-Surface Probed by Core Level Photoemission Spectroscopy Using Synchrotron Radiation and by Scanning Tunneling Microscopy*, V. Derycke*,** *H. Enriquez, P. Fonteneau, V.Yu. Aristov, P.G. Soukiassian,* Commissariat à l'Energie Atomique and Université de Paris-Sud/Orsay, France*; G. Le Lay,* CRMC2 - CNRS and Université de Provence, France*; C. Grupp, A. Taleb-Ibrahimi,* LURE, Université de Paris-Sud/Orsay, France

We investigate the 3C-SiC(100) c(4x2) reconstruction surface and sub-surface regions by Si 2p core level photoemission spectroscopy using synchrotron radiation at various photon energies and by atom resolved scanning tunneling microscopy (STM). The latter experiments are performed by tunneling into the empty and filled electronic states which allows to clearly identify both up- and down dimers (AUDD) [1] of the c(4x2) surface reconstruction. Contrary to earlier core level studies, we identify two surface shifted components at the Si 2p core level having the same intensity. These two Si 2p spectral surface features are clearly related to the up- and down-dimers (AUDD) of the c(4x2) surface reconstruction.@footnote 1@ In addition, two sub-surface shifted components are also found which shows that the sub-surface region is also significantly affected by stress far away from the outer surface, indicating the long range influence of the latter. The results also confirm that the c(4x2) reconstruction is terminated by one Si monolayer as already well established by various quantitative experimental investigations.@footnote 2@ These novel core level photoemission using synchrotron radiation and STM results further support the AUDD model of the 3C-SiC(100) c(4x2) surface reconstruction.@footnote 1@ However, they are clearly inconsistent with predictions of a "missing row asymmetric dimers" model (MRAD) recently proposed on the basis of ab initio pseudopotential calculations and STM image simulations.@footnote 3@ @FootnoteText@ @footnote 1@P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli and C. Joachim, Phys. Rev. Lett. 78, 907 (1997). @footnote 2@see e.g. V.M. Bermudez, Phys. Stat. Sol. (b) 202, 447 (1997); and references therein. @footnote 3@3-W. Lu, P. Krüger and J. Pollmann, Phys. Rev. Lett. 81, 2292 (1998).

3:40pm **SS1+EM-WeA6 Mechanistic Studies of SiO@sub 2@ Deposition from TEOS / Ozone***, L.D. Flores, C. Tindall,* ***J.E. Crowell,*** University of California, San Diego

The low temperature deposition of SiO@sub 2@ from the reaction of tetraethoxysilane (TEOS) and ozone has been studied in-situ at atmospheric pressures. The studies were performed in a prototypical atmospheric pressure chemical vapor deposition (APCVD) reactor utilizing a commercial injector / vent assembly. The gas phase reactions were followed during deposition at 400°C using gas-phase transmission FTIR spectroscopy. Evolution of gas phase products during TEOS / O@sub 3@ reactions were compared and quite distinct from those observed during reaction of TEOS / O@sub 2@. The primary products produced upon ozonolysis of TEOS are acetic acid, formic acid, formaldehyde, carbon monoxide, carbon dioxide, and water. Mechanistic details of the deposition process were aided by model reaction studies performed in a gas cell using transmission FTIR spectroscopy. The model studies involved reaction of ozone with observed and potential deposition byproducts, such as acetaldehyde. The spectroscopic observations will be discussed with an emphasis on reaction mechanisms and the reactive pathways leading to the production of deposition precursors, and the influence of additives and byproducts on the morphological nature of SiO@sub 2@ film growth.

4:00pm **SS1+EM-WeA7 Microcalorimetric Heats of Adsorption of Metals on Metal Oxide and Si(100) Surfaces*, D.E. Starr,*** University of Washington*; D.J. Bald,* Intel Corporation*; J.E. Musgrove, J.T. Ranney, J.H. Larsen, C.T. Campbell,* University of Washington

Single crystal adsorption microcalorimetry has been proven to be a powerful method to study the heats of adsorption of gaseous atoms or molecules onto single crystal surfaces. Recently, a microcalorimeter has been built which possesses the capability to measure heats of adsorption of metal atoms onto single crystal surfaces as a function of coverage. A sensitive pyroelectric polymer is used to detect the heat released due to the adsorption of pulses of gaseous metal atoms, each containing ~2% of a monolayer, onto the surface. The microcalorimeter has been employed to study the energetics of film growth from the initial stages of deposition through the multilayer regime for metal on metal and metal on metal oxide systems. For the metal on oxide systems, an initial heat of adsorption which is much lower than the heat of sublimation of the metal is observed. This provides detailed insight into the thermodynamic driving force for the metal overlayer to form three dimensional islands. Auger electron spectroscopy was used to verify the growth morphology. In addition, the extension of this technique to study the heats of adsorption of metals onto silicon substrates allows the study of many systems important to metal-semiconductor contact technology. In order to accurately quantify the heats of adsorption, the metals sticking probability on the surface must be known. These have also been measured and will be discussed. In addition, via a thermodynamic cycle the adhesion energy of the metal to the substrate is obtained from the measured microcalorimetric heats of adsorption.

4:20pm **SS1+EM-WeA8 Nucleation and Growth of Hemispherical Grained Silicon*, D. Llera-Rodriguez,*** *E.G. Seebauer,* University of Illinois, Urbana

Hemispherical grained silicon (HSG) is a material beginning to find widespread use for electrodes in DRAM applications. HSG is formed by the chemical vapor deposition of amorphous Si, followed by a CVD "seeding" step under slightly different growth conditions to form nuclei for surface crystallization. Subsequent rapid thermal annealing to above 600°C induces the nuclei to grow into 100-nm hemispheres via surface diffusion, yielding an electrode with high surface area that increases the capacitance of the resulting device. In addition to the practical applications, however, HSG formation provides useful insights into the fundamental mechanisms of nucleation and growth in a two-dimensional amorphous-to-crystalline phase transition. For example, we can rationalize our experimental results for nucleation density in terms of a rate-equation-based nucleation theory. Furthermore, through a series of growth studies we show that subsequent growth of the initial nuclei can be well-described by a two-dimensional continuum model based on adatom-vacancy pair formation on the amorphous surface, together with diffusion of the atoms toward the growing hemispheres. The activation energy of 2.5 eV describing growth represents the sum of energies for adatom diffusion and surface vacancy formation on the amorphous surface. Somewhat surprisingly, this value for amorphous Si matches that measured by separate experiments for crystalline Si.

4:40pm **SS1+EM-WeA9 Characterization by STM of Interface between Silicon and Silicon Dioxide Layers Fabricated by Highly Concentrated Ozone*, H. Itoh,*** *A. Kurokawa, K. Nakamura, S. Ichimura,* Electrotechnical Laboratory, Japan

We will show that the silicon dioxide film fabricated by ozone exposure@footnote 1,2@ has smooth and flat interface keeping the original step and terrace feature. Hydrogen-terminated Si(100) wafer was used as a substrate. Flat surface was prepared by additional growth of epitaxial Si layers (thickness; 120 nm) on Si substrate, and atomic hydrogen was adsorbed on the surface for passivation. STM images showed that the prepared surface was atomically flat with wide terraces which is larger than 100nm. A high-concentration ozone generator was used to form ultra thin silicon dioxide film on the surface. The output from ozone generator was the mixture gas of ozone(30 vol%) and oxygen. The substrate was exposed to the gas at room temperature for half an hour to form silicon dioxide film. The thickness of the oxide film formed by the exposure was estimated to be 1 nm, which was analyzed from intensity of XPS Si-2p peaks. After the oxidation, the silicon dioxide fil! ! m was carefully removed by rinsing in HF solution to observe the interface structure. Slow etching rate in dilute HF solution(0.1%) was chosen to avoid uneven etching and the thickness was monitored every several minutes by XPS peaks to avoid overetching. The sample was inserted into ultra high vacuum(UHV) chamber and surface and interface was observed by scanning tunneling microscopy. STM images were obtained on the etched surface with monoatomic height resolution. Large terraces and few steps were observed in the STM images and surface roughness is estimated to be below 0.15 nm (rms.). This indicates that the silicon dioxide film was grown keeping the original step and terrace feature. The result suggests that Si was oxidized homogeneously and supports that the film was grown layer-by-layer mode. @FootnoteText@ @footnote 1@ A.Kurokawa et.al., Mater. Res. Symp. Proc.Vol. 513, p38, 1998, @footnote 2@ A.Kurokawa et.al., Mater. Res. Soc. Symp. Proc., 1999, in press

5:00pm **SS1+EM-WeA10 Significant Effects of Arsenic Ion Implantation on Si Selective Epitaxy by Ultra-High Vacuum Chemical Vapor Deposition*, T. Furukawa,*** *T. Nakahata, S. Maruno, Y. Tokuda, S. Satoh,* Mitsubishi Electric Corporation, Japan

Great attention has been paid on Si selective epitaxial growth for an application into ultra large scale integration. For the practical application, however, surface conditions of a Si substrate, which is affected by preceding process steps such as plasma etching and ion implantation, may have a great influence on growth behaviors. In this work, we have investigated the effect of low energy arsenic ion implantation on the Si selective epitaxy by use of ultra-high vacuum chemical vapor deposition. The substrates were prepared through conventional n-channel MOSFET fabrication sequence. In the arsenic ion implantation, dosage was varied from 0 to 4x10@super 15@cm@super -2@, while acceleration energy was fixed to be 10 keV. Before the Si growth, the wafers were cleaned by chemical wet etching, whereas chemical oxide was removed by diluted HF solution. The epitaxy was performed at nominal temperature of 600°C with a pure Si@sub 2@H@sub 6@ source gas. For a non-implanted wafer, island-like growth occurs. With sufficient dosage of arsenic ions, however, an epitaxial Si layer with excellent surface morphology was successfully grown. X-ray photoelectron spectroscopy measurements reveal that a thin SiO@sub x@ layer is formed below the substrate surface by a preceding plasma etching process. The growth mode change is interpreted in terms of reduction of the SiO@sub x@ layer by means of an additional sputtering effect of the ion implantation.

Electronic Materials and Processing Division
Room 4C - Session EM-WeP

Poster Session

EM-WeP1 Comparison of Plasma Chemistries for Dry Etching of Ta@sub 2@O@sub 5@*, K.P. Lee*, *K.B. Jung, R.K. Singh, S.J. Pearton,* University of Florida*; C.C. Hobbs, P. Tobin,* Motorola

Inductively Coupled Plasma etching of Ta@sub 2@O@sub 5@ was performed in a variety of different chemistries, including SF@sub 6@ with additions of O@sub 2@, Ar, CH@sub 4@ or H@sub 2@ ; Cl@sub 2@/Ar ; N@sub 2@/Ar and CH@sub 4@/H@sub 2@/Ar. Etch rates up to ~1200 Å ú min@super -1@ were achieved with either SF@sub 6@ or Cl@sub 2@ based chemistries. Under these conditions the etch rates for Si were approximately 4-7 times faster, although equi-rate etching was achieved at low source powers and low halogen gas percentages in the plasma chemistry. The etched Ta@sub 2@O@sub 5@ surfaces were smooth (RMS roughness @<=@ 0.5 nm) over a broad range of conditions of source power, chuck power and process pressure. The etch rates with N@sub 2@/Ar and CH@sub 4@/H@sub 2@/Ar were an order of magnitude lower than with SF@sub 6@ or Cl@sub 2@. There was no effect of post deposition annealing on the Ta@sub 2@O@sub 5@ etch rates, at least up to 800@super o@C.

EM-WeP2 Study of the Impact of Time-Delay Effect on the Critical Dimension of Tugnsten Silicide/Polysilicon Gate After Reactive Ion Etching*, S.P. Lin, C.H. Ou,* ***S. Lee****, Y.C. Tien, C.F. Hsu,* Winbond Electronics Corporation, Taiwan

In the fabrication of submicron devices with high-density integration, the control of critical dimension (CD) of tungsten silicide/polysilicon gate becomes extremely crucial in device performance. To ensure a reliable gate patterning process, etching recipe with a very high selectivity is used to control the gate profile to be notching-free and vertical as well as keeping the gate oxide loss minimized. Besides the use of oxygen and chlorine-based chemistry in gate stack etching, HBr is also used to improve the selectivity of polysilicon to gate oxide. As a consequence of high selectivity, polymer residues become a major factor in CD control. It is believed that the presence of HBr in the plasma is responsible for polymer formation. HBr and its polymer residues may induce surface reactions to form thin oxide layers. Such a phenomenon has been observed if the wafers are not treated with HF vapor (for the removal of polymer residue) immediately after reactive ion etching (RIE) of the gate. The magnitude of the oxide film growth is proportional to the time delayed between RIE and HF vapor treatment. The sidewall thickness of the gate is also affected by the time-delay effect. The growth of oxide film on sidewalls can eventually affect the gate CD and thus the device performance. A simple reaction model for the growth of oxide film is proposed to explain the correlation between delayed time, CD bias, and product yield.

EM-WeP3 Effects of Deposition Temperature of Co Thin Films on (100)Si*, H.Y. Huang,* National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China*; W.F. Wu, R.P. Yang,* National Nano Device Laboratories, Taiwan, R.O.C.*; L.Y. Chen,* United Microelectronic Corporation, Taiwan, R.O.C.

Low resistivity silicide films have received a great deal of attentions because of their applications in ULSI in recent years. Low resistivty silicides have been widely used in source/drain as contacts. They reduce both the parasitic source/drain resistance and the contact resistance. Among all the silicides, NiSi, TiSi@sub 2@, and CoSi@sub 2@ are of the lowest resistivity. TiSi@sub 2@ is currently the most common silicide used as contact metal in IC industry. However, as devices are scaled down to deep submicron dimensions, it is difficult to transform TiSi@sub 2@ from high resistivity C49 phase to low resistivity C54 phase in small dimension features owing to the lack of nucleation sites. CoSi@sub 2@ is also of low resistivity and has been a promising candidate to substitute TiSi@sub 2@ for various processing advantages. In addition, its good lattice match with Si makes it possible to grow epitaxial silicide layer on Si. High temperature sputtering deposition (HTSD) was previously found to facilitate the phase transition from C49 to C54-TiSi@sub 2@. This method also reported as a new salicide technology for deep submicron devices to reduce the complicated process steps including TiN capping layers and preamorphization of substrate. In the present study, the Co films were deposited at different temperatures from room temperature to 550@super o@ C on (001) Si using UHV sputtering cluster tools. One- and two-step annealings were performed. TEM, XRD and AES were used to examine the samples. HTSD was found to improve both the thermal stability of CoSi@sub 2@ and CoSi@sub 2@/Si interface smoothness.

EM-WeP4 Growth of Ultra Thin Oxides of Silicon by Wet Oxidation Technique: Effect of Water Vapor Pressure*,* ***B. Viswanath Krishna****, K.N. Bhat,* Indian Institute of Technology, India

The rapid scaling down of silicon device dimensions has renewed interest in ultra thin oxides. The desirable properties of ultra thin oxides for gate dielectric applications are: very low defect densities, low charge trapping characteristics and high break down voltages. Although the ultra thin oxides grown by wet oxidation technique have higher breakdown strengths compared to that of dry oxide, the wet oxide has invariably large trapping characteristics and has problems in uniformity and surface roughness. In the present investigation, the effect of water vapor pressure (0.004 - 1.0 atm) on the ultra thin oxides of silicon grown by wet oxidation technique has been attempted. The wet oxidation is carried out in a quartz furnace maintained at 800@super o@C for 5 - 120 minutes. The ultra thin oxides are grown on single crystal CZ silicon wafers : n-type, (100) oriented, single side polished, of resistivity 1.0 - 10 @ohm@cm. The thickness of the grown oxides(3- 10 nm) has been estimated from the measured C-V characteristics and are also confirmed by ellipsometer measurements. The thickness of the oxide (60 minutes) seems to be rather independent at water vapor pressures till 0.05 atm. In order to understand the electrical performance of these thin oxides, Al/thin SiO@sub 2@ / n-Si MOS structures are fabricated and their Capacitance (C) - Voltage (V) (in the frequency range : 10 KHz - 1 MHz), conductance (G) - voltage (V) and Current (I) - Voltage (V) characteristics have been studied. Interface density (D@sub it@) and fixed oxide charge density (Q@sub f@) have been evaluated to asses the quality of the thin oxide layer. The breakdown voltage and the charge trapping characteristics have also been studied. The results indicate that reproducible ultra thin oxides can be grown with sufficient control by wet oxidation technique at reduced water vapor pressure.

EM-WeP5 Nanoscale Silicon Features Produced by Slow Highly Charged Ions*,* ***M.W. Newman****, A.V. Hamza, H. Lee, A.V. Barnes, T. Schenkel, J.W. McDonald, G.A. Machicoane, T. Niedermayr, D.H. Schnieder,* Lawrence Livermore National Laboratory

Phase transformations induced by intense, ultrafast electronic excitation from slow highly charged ions from the Lawrence Livermore National Laboratory (LLNL) Electron Beam Ion Trap(EBIT) have been studied. A 308 keV beam of Xe@super 44+@ (~51 keV of potential energy) was used to irradiate a 3 mm spot of clean float zone (FZ) silicon (100) (2X1) for a total dose of ~5x10@super 11@ ions. Due to the indirect nature of its band gap, bulk silicon is typically a poor photon emitter upon external excitation. However, as the crystal size approaches nanometer scales, the band gap widens due to quantum confinement and becomes direct allowing for more efficient photon emission. Ex-situ room temperature photoluminescence (PL) spectra were measured using a high resolution grating spectrometer with an excitation wavelength of 379 nm from a Titanium-Sapphire laser. PL spectra from areas exposed to SHCI bombardment show a broad emission centered at 504 nm. This is consistent with emission observed from 1-2 nm silicon nanocrystals. No PL is observed from similarly prepared FZ Silicon samples exposed to beams of 308 keV Xe@super 27+@ (~10 keV of potential energy) and 5 keV Xe@super 1+@ with comparable doses. A series of sharp lines at 548 nm, 534 nm, and 530 nm are also present in the PL spectrum from areas exposed to Xe@super 44+@ which is characteristic of an excitonic series in nanometer size direct band gap materials. The deposition of potential energy from Xe@super 44+@ produces a phase transition in silicon surfaces at nanometer size level that is not produced from normal ion bombardment. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No, W-74505-ENG-48.

EM-WeP6 Formation of Ni-silicides on (001)Si with a Thin Interposing Pt Layer*,* ***L.-W. Cheng****, S.-L. Cheng,* National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

As devices dimensions scale down to deep sub-micron regime, a linewidth dependence of sheet resistance was observe for TiSi@sub 2@. Among metal silicides, low resistivity NiSi is currently one of the two most promising silicides to replace TiSi@sub 2@ for the self-aligned technology of ULSI. NiSi possesses low resistivity, low silicon consumption, low processing temperature and relative insensitivity to the linewidth of the silicide. Previous works showed that the process window of NiSi can be extended to higher temperatures by nitrogen ion implantation. In the present work, the formation of Ni-silicides on (001)Si with a thin interposing Pt layer have investigated. TEM, XRD, SIMS and four point probe were used to analyze the characteristics of nickel silicide thin films. Pt addition was found to retard significantly the formation of nickel silicides on (001)Si. The process window of NiSi was extended to a higher temperature and the sheet resistance maintained the same low level in a wide temperature range. NiSi was observed to be the dominant phase for the samples annealed at 400-800 0C with a thin interposing Pt layer. Since nickel atoms are the dominant diffusing species in the Ni/Si binary system, the results implied that the diffusion of nickel atoms through Ni/Si interface is retarded by the presence of a thin interposing Pt layer.

EM-WeP7 The Interfacial Reaction between Ti and (001)Si with an Interposed Mo Layer*, S.-M. Chang,* National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

Low resistivity TiSi@sub 2@ has been widely used in ultralarge scale integrated circuits because it possesses the low resistivity and compatibility with the SALICIDE processing. However, as the devices dimension shrinks to the deep submicron regime, it becomes increasingly more difficult to use thermal annealing to transform a structure from the high resistivity C49 phase to the low resistivity C54 phase due to insufficient nucleation sites of C54 phase at the C49 phase grain boundaries. Recently, a new and simple method for the reduction in the C54 transformation temperature was demonstrated. The formation temperature of the C54 TiSi@sub 2@ phase from the bilayer reaction of Ti on Si is lowered by about 100@super o@C by placing an interfacial layer of Mo between Ti and Si. However, the detailed mechanism is still not well understood. In the present study, high-resolution transmission electron microscopy (HRTEM) was utilized to study the interfacial reaction between Ti and Si with an interposed molybdenum layer. A thin amorphous TiSi@sub x@ layer was found to form and a thin Mo@sub 5@Si@sub 3@ layer was formed at the interface between the Si substrate and amorphous interlayer after 500@super o@C rapid thermal annealing (RTA) for 30 s. In addition, island formation was found to occur for Mo@sub 5@Si@sub 3@ after 535@super o@C RTA for 30 s. C49-TiSi@sub 2@ and Ti@sub 5@Si@sub 4@ phases were found to form simultaneously after 550@super o@C RTA for 30 s. The growth rate of amorphous TiSi@sub x@ layer was delayed with the presence of metallic interfacial layer. The formation temperature of the C49 TiSi@sub 2@ phase was also found to increase. The redistribution of Mo atoms, in the form of a ternary Ti-Mo-Si phase, after 550@super o@C RTA for 30 s, leads to the enhancement of the formation of C54-TiSi@sub 2@ by providing more heterogeneous sites needed for the transformation from C49- to C54-TiSi@sub 2@ phase.

EM-WeP8 Characterizing and Modeling the Electronic Conduction in CrB2-SiC-Si Thin Films*, F. Wu,* Medtronic, Inc.

Characterizing and modeling the electronic conduction in CrB2-SiC-Si thin films The CrB2-SiC-Si material system is used in thin film resistors in very large scale integrated circuits application. The films are sputter deposited onto dielectric substrates from composite target using various reactive gas mixtures. The microstructure of the sputter deposited CrB2-SiC-Si films is characterized by TEM as a distribution of darker 'island' regions within an lighter 'boundary' medium. In a wide range from 10-3 to 103 ohm -cm, the film resistivity is found as a function of the CrB2, Si and N composition. A model is proposed in this paper and computer simulation is perform to model the film resistivity behavior.

EM-WeP9 Silicon Nano-dots Fabricated on a Si(100) Surface via Thermal Nitridation and Oxygen Etching Reactions*, J.S. Ha, K.-H. Park, W.S. Yun,* ETRI, Republic of Korea

We have fabricated silicon nano-dots with a very uniform size distribution on a Si(100) surface via a thermal nitridation followed by an oxygen etching reaction. Nitrogen gas was exposed to a clean Si(100) surface at 800 @super o@C and this surface was subsequently reacted with O@sub 2@ gas at 700 @super o@C under an oxygen partial pressure of 1x10@super -7@ Torr. Scanning tunneling microscope (STM) measurement of the surface morphology showed that silicon nano-dots with an average size of 5 nm were formed as a result of selective oxygen etching of silicon surface. It is considered that nanometer-scale silicon nitride islands worked successfully as masks for the oxygen exposure at high temperatures. The number density of silicon nano-dots is estimated to be 1 x 10@super 12@ / cm@super 2@. Reduction of the nitridation temperature to 700 @super o@C resulted in the similar surface features with a little bit smaller sizes, indicating that silicon nitride islands formed even at this temperature can be successfully used as masks for oxygen exposure. Further investigation of the post-annealing effect on the resultant surface morphology showed that the coalescence of small sized silicon nitride islands into larger ones, which was clearly observed in the case of Si(111) surface, was not noticeable on the Si(100) surface. Therefore, uniform and small size distribution of Si nano-dots could be obtained on the Si(100) surface. In this paper, we will also discuss on the underlying reaction mechanisms based upon experimental results. This study suggests a simple but efficient fabrication method of silicon nano-dots using gas-surface reactions on the silicon surface in an ultra-high vacuum system.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 4C - Session NT+NS+EM+MS-WeP

Poster Session

NT+NS+EM+MS-WeP1 Growth of Carbon Nanotubes at Low Temperature by Microwave Plasma-enhanced Chemical Vapor Deposition*, Y.C. Choi, D.J. Bae, Y.H. Lee, B.S. Lee,* Jeonbuk National University, Korea

We have grown carbon nanotubes at temperatures below 520 C by microwave plasma-enhanced chemical vapor deposition using methane and hydrogen gases. Carbon nanotubes were uniformly grown in large area of transition metal-coated Si substrates with high density. Each nanotube is terminated by transition metal cap, suggesting that the transition metals play an important role in the nanotube growth. Carbon nanotubes are curly in all cases, indicating the nanotubes to be defective due to very low growth temperature. Diameters and lengths of the nanotubes could be controlled by changing the ratio of methane to hydrogen and growth time. Raman spectum clearly shows the peak at 1592 cm-1 (G-band), indicating the formation of well graphitized carbon nanotubes.

NT+NS+EM+MS-WeP2 Nanoscale-controlled Handling of Carbon Nanotubes*, O. Jaschinski, P. Bernier, L. Vaccarini, C. Goze,* Universite Montpellier II, France*; G. Duesberg,* Trinity College Dublin, Ireland*; C. Journet, S. Roth,* Max-Planck-Institut fuer Festkoerperforschung Stuttgart, Germany

Carbon nanotubes are the most promising materials for applications in nanoelectronics and nanomechanics. For the determination of the electrical and mechanical properties of nanotubes and for the production of nanotube devices one needs the ability to handle nanoscale materials in a controlled way . We demonstrate how atomic force microscopy (AFM) can be used as a tool for manipulating and investigating carbon nanotubes. For an optimal use of AFM it is necessary to control the substrate-nanotube interaction. We present results of measurements of the mechanical properties of nanotubes obtained with various kinds of substrates. We show how the combination of lithography, manipulation by AFM and control of the adsorption process of nanotubes allow to prepare well defined sample configurations for very sophisticated measurements of the electrical and mechanical properties of carbon nanotubes. Based on these methods, techniques for the production of nanotube devices can be developed. This work was supported by European TMR contract NAMITECH ERBFMRX-CT96-0067 (DG12-MIHT)

NT+NS+EM+MS-WeP3 Aligned Carbon Nanotubes with Controlled Diameters Using Anodic Alumina Template*, S.-H. Tsai, H.C. Shih,* National Tsing Hua University, R.O.C.

The microwave plasma enhanced chemical vapor deposition (MPECVD) system had been successfully fabricated the well-controlled diameters of aligned carbon nanotubes on the anodic alumina template with a mixture of methane and hydrogen. Prier to test, the anodic alumina with pore arrays in various diameters were prepared by anodizing aluminum using oxalic, sulfuric, and phosphoric acid solutions. By adjusting the pore size of the anodic alumina, various carbon nanotube diameters can be obtained in a range of 30 to 100 nm and were examined by scanning electron microscopy and transmission electron microscopy.

NT+NS+EM+MS-WeP4 The Selective Growth of Aligned Carbon Nanotubes by PECVD Using Nickel Catalyst*, H. Jeon, K. Ryu, M. Kang,* Hanyang University, Korea

Carbon nanotubes have been studied extensively because of their own unique physical properties and also of their application potential for field emitters. One of the interesting applications is reported for display application, but neither industrial fabrication technology nor performance has been reported for practical display application. Here we tried to grow aligned carbon nanotubes selectively by plasma enhanced chemical vapor deposition (PECVD) method using nickel catalyst@footnote 1@ at temperatures below 600°C. These conditions for low temperature growths are suitable for field emission display which requires carbon nanotube emitters grown perpendicular to the Si substrate. In our experiment, a thin film of nickel(10-100nm) was deposited through a pattern mask on a Si substrate in UHV e-beam evaporator and was agglomerated by in-situ annealing for thirty minutes at 700°C. The use of a patterned catalyst enhanced the formation of selectively aligned nanotubes at low temperatures. After this process, Ni particles deposited on Si substrate were examined by AFM and SEM. Carbon nanotubes were selectively grown on Ni particle by PECVD with using the mixture of CH@sub 4@ and NH@sub 3@ at 600°C. In this process, CH@sub 4@ was used as the carbon source and NH@sub 3@ was used as a catalyst and dilution gas. During the process, many carboneous impurities can be produced and tried to eliminated by introducing H@sub 2@ plasmas. We examined the physical properties of carbon nanotubes by SEM, XRD and Raman spectroscopy. And we investigated the formation temperature of carbon nanotubes on silicon substrate and controlled the selective growth of aligned nanotubes. @FootnoteText@ @footnote 1@ Masako Yudasaka, et al.,Appl. Phys. Lett. 70(14), 7 April 1997.

Thursday Morning, October 28, 1999

Electronic Materials and Processing Division
Room 608 - Session EM1-ThM

Cu, Low-k Dielectrics and Interfaces

Moderator: H.A. Atwater, California Institute of Technology

8:20am **EM1-ThM1 Strength of Nanoscale Copper Under Shear***, P. Heino,* Tampere University of Technology, Finland, FINALND*; P.H. Holloway,* University of Florida*; **E. Ristolainen,*** Tampere University of Technology, Finland

Since 1995 when IBM proposed that copper can be used in electrical interconnections, its properties have received a lot of interest in the electronics community, mainly because of its low electrical resistance. Previously we have shown by comparison with experimental data that mechanical properties of copper can be well described using the effective-medium theory (EMT), molecular dynamics simulations, and more than 100k atoms.@footnote 1@ Here we use these methods to study thermally induced shear strain and stress in several nanoscale copper systems consisting of about 200k atoms. The shear strain in the system is generated by moving the top and bottommost boundaries, corresponding to a common deformation mechanism in flip chip interconnect.@footnote 2@ Plastic deformation mechanisms, stress concentration and stress relaxation were studied. The role of microstructure of the system was analyzed. We studied three monocrystalline systems and several polycrystalline structures, in which the grain size was varied. The results show that the strength of the system decreases with decreasing grain size. This is contrary to macroscale behavior, but has recently been found in similar systems under tension. The reason behind this behavior is the soft grain boundary and grain boundary sliding. The strength of the small systems can decrease by a factor of ten, when the structure changes from monocrystalline to polycrystalline. In monocrystalline structures we studied dislocation formation. The results showed that dislocations prefer to initiate at the compressive side of the system rather than at the tensile side. This peculiar behavior could be exlained with the stacking fault energy and its dependence on the state of strain in the context of EMT. More details will be discussed. @FootnoteText@ @footnote 1@P. Heino, H. Häkkinen and K. Kaski: Europhysics Letters 41 (3) 278 (1998) @footnote 2@P. Heino and E. Ristolainen: Proc. Second Int. Conf. on Modeling and Simulation of Microsystems, Apr. 19-21 (1999), San Juan, PR, USA.

8:40am **EM1-ThM2 A Discussion of the Interconnection Science and Technologies***, **S.P. Murarka,*** Rennselaer Polytechnic Institute **INVITED**

Shrinking device dimensions have affected the interconnect performance leading to replacement of Al with Cu and investigations of a variety of low-K materials to replace SiO@sub 2@ and of other modes (e.g. optical) of signal transmissions between devices and devices and the outside world. As the surface-to-volume ratio increases, the surfaces and interfaces will control the properties and reliability of the interconnection and dielectric materials. In this paper, we will review and discuss the science and technology of interconnections for semiconductor circuits and the impact of surfaces and interfaces on their performance.

9:20am **EM1-ThM4 Electrochemical Deposition Cu Films for ULSI Applications***, **J.C. Hu,*** National Tsing Hua University, Taiwan, R.O.C.*; T.C. Chang,* National Nano Device Laboratory, Taiwan, R.O.C.*; W.C. Gau, C.L. Cheng,* Chung-Yuan University, Taiwan, R.O.C.*; M.S. Feng,* National Chiao-Tong University, Taiwan, R.O.C.*; Allen Yang, Kevin Lee,* Merck-Kanto Advanced Chemical Ltd., Taiwan, R.O.C.*; L.-J. Chen,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

Cu is being considered to replace aluminium in ULSI circuit metallization for better conductivity, higher electromigration resistance and reliability. CVD and PVD used to deposit Cu layer have been well documented. Relatively little is known about electrochemical deposition method to deposit copper films despite successful applications in ULSI by a number of manufacturers. The additives play a very important role in super-filling behavior. However, most of additives in electoplating solution are not disclosed in the literatures. In the present work, the new additives of electroplating solution without brightening-agents were investigated. The texture of the electroplated Cu films was studied with various applied current densities. A kind of ester was investigated as a leveling-agent. The polyethers were used as surfactants. ECD Cu deposited on low dielectric constant material like hydrogen silsesquioxane (HSQ) was studied. The basic electroplating solution was composed of CuSO@sub 4@.5H@sub 2@O (50-100 g/l), H@sub 2@SO@sub 4@ (150-200 g/l), HCl (50-80 ppm). Patterned wafers were fabricated to examine the ability of gap filling of electroplated Cu. 30-nm-thick TaN films as barriers and 100-nm-thick Cu films as seed layers were deposited by ionized metal plasma (IMP) PVD, respectively. The opening width of trenches/vias was 0.18-0.8 µmm . Applied current densities were less than 1.0 A/dm@super 2@. Transmission electron microscopy and X-ray diffractometry were utilized to investigate the microstructures and crystal orientation. Auger electron spectrocopy was applied to determine the stoichiometry and uniformity along the depth direction. The morphology was studied by a scanning electron microscope. Low resistivity, low porosity, and highly uniform electroplated Cu films were obtained, even without brightening-agent. 0.2 µmm vias and trenches with an aspect ratio of 5 were filled completely without void or seam. The Cu films exhibit a good super-filling behavior. Super-filling behavior can be explained by a diffusion-controlled theory of leveling-agents. The resistivity of a 450-nm-thick Cu film is 1.84 µm@ohm@-cm. From XRD analysis, strong (111) texture was obtained in the electroplated Cu films. The concentration of oxygen in the sample was found to be rather low.

9:40am **EM1-ThM5 Complete Filling of High-Purity Copper in Subquarter-Micron Trench Structure Using Plasma CVD Reactor with H Atom Source***, **H.J. Jin**, M. Shiratani, Y. Nakatake, K. Koga, T. Kinoshita, Y. Watanabe,* Kyushu University, Japan

Complete filling of high-purity copper in subquarter-micron trench structures is a key requirement in formation of metal interconnects carrying signals in ULSI. For this interconnect application, we have developed a plasma CVD reactor equipped with an H atom source in order to control independently the concentration of H atoms and the degree of dissociation of Cu(hfac)@sub 2@, since H atoms are extremely effective in removing impurities within the film and deposition rate and film conformality presumably depends on the degree of dissociation of Cu(hfac)@sub 2@.@footnote 1,2,3@ High-purity Cu films (about 100%) with the low resistivity of 2 @micro n@@ohm@cm can be deposited, even with the low H@sub 2@ gas volume fraction of 50-67%, by using the H atom source, while high-purity films are obtained only for an H@sub 2@ gas volume fraction above 90% for the CVD reactor without the source. In order to evaluate Cu filling property in trench structures using the plasma CVD reactor with the H atom source, coverage shape of the Cu deposited film in a trench 0.4 µm wide and 3.25 µm deep is examined under conditions for which high-purity (about 100%) Cu films are obtained. While the coverage at the bottom of trench is 0% for the main discharge power P@sub m@ = 80 W, it increases with decreasing P@sub m@ to reach 95% for P@sub m@ = 15 W. These results show that a decrease in P@sub m@ leads to a reduction in the sticking probability of Cu-containing radicals, a low value of which is essential for the achievement of complete filling of extremely small width and high aspect ratio trench structures. We also have succeeded in complete and void free filling in trench 0.3 µm wide and 1 @micron@ deep using such control. Cross sectional TEM observation of Cu films shows that size of Cu grain is above 0.5 µm. @FootnoteText@ @footnote 1@M. Shiratani, et al., J. Phys. D, 29 (1996) 2754. @footnote 2@H. J. Jin, et al., J. Vac. Sci. & Tech. A17 (1999). @footnote 3@H. J. Jin, et al., Jpn. J. Appl. Phys. July (1999).

10:00am **EM1-ThM6 The Stability of Thin TiN and TaN Layers as Diffusion Barriers for Copper under Thermal Annealing and Bias Temperature Stress Conditions***, H. Kizil, G. Kim, **C. Steinbrüchel,*** Rensselaer Polytechnic Institute*; B. Zhao, L. Tsau, M. Brongo,* Conexant Systems

The stability of TiN and TaN as diffusion barriers for Cu has been investigated using capacitance-vs-voltage (C-V) and leakage current-vs-voltage (I-V) measurements as a function of thermal annealing and bias temperature stress (BTS) conditions. Samples consisted of MOS capacitors with a film stack of 300 nm Cu/barrier/25 nm thermal silicon dioxide on Si. The barrier thickness was 5, 10, or 20 nm. Samples were pre-annealed in Ar/3% hydrogen for 30 minutes at various temperatures. BTS treatments were performed at 2 MV/cm and 250 C, 2 MV/cm and 200 C, and at 1.5 MV/cm and 250 C, for periods of up to one hour in flowing nitrogen. The main results can be summarized as follows: In order for BTS to yield negligible flat-band voltage shifts, pre-annealing at 350 C is necessary. This produces a substantial number of initial leakage current failures (i.e. before BTS) with TiN but not with TaN. BTS of samples pre-annealed at lower temperatures causes significant shifts in the C-V plots. However, the flat-band voltage shift (or the absence thereof) is not a very good indicator of barrier stability, in the sense that samples with minimal shifts in the C-V plots may still give unacceptably high leakage currents. TaN consistently behaves better than TiN under all stress conditions.

10:20am **EM1-ThM7 Surface Modification and Cleaning Enhancement of TaSiN Films with Dilute Hydrofluoric Acid***, ***P.J.S. Mangat****, W.J. Dauksher, K.D. Cummings,* Motorola, Inc.*; W.L. O'Brien,* Mad City Labs, Inc.

Amorphous TaSiN and TaSi alloys films are of great interest for application in the fabrication of reticles for Next Generation Lithography (NGL) and for incorporation in semiconductor devices. TaSiN films act as absorber and scatterer, respectively, on the masks for X-Ray Lithography and Scattering with Angular Limitation in Projection Electron-beam Lithography. Recently, we have successfully extended its application to an absorber for Extreme Ultra-Violet Lithography reticles. The films have been extensively characterized in terms of resistivity, composition, defectivity, surface roughness, crystalline state, and chemical robustness. One little understood, but critical characteristic of these films, is that they undergo stress change from tensile to compressive upon interaction with dilute Hydrofluoric (HF) acid. We have investigated the cause of this behavior using high-resolution core level (Ta 4f and Si 2p) photoemission spectroscopy with synchrotron radiation. Our results using photoemission and Auger electron spectroscopy confirm that surfaces of as-deposited and annealed films are composed primarily of Si-oxides with trace amounts of Ta-oxide. Upon interaction with HF, the surface oxide undergoes major reorganization and Ta gets heavily oxidized resulting in the formation of Ta2O5. Such a reaction would lead to a build up of strain in the oxidized region, which we interpret as being contributing factor for the observed stress changes in the TaSiN thin films. We further extended the study in terms of desorbtion of the surface oxide. Upon annealing the surface, we observe that the temperature for oxide desorbtion is reduced by 200 oC from 650 oC due to the HF interaction. This can be attributed to a change in the bonding configuration by HF, wherein the Si-O bonds are broken and weak Ta-O bonds are formed. This causes the loosely bonded oxide to desorb at lower temperatures. * Work Performed at Synchrotron Radiation Center,UW-Madison, Stoughton, WI 53589.

10:40am **EM1-ThM8 Fluroinated Amorphous Carbon - A Low Dielectric Constant Material for Multilevel Interconnect Applications**, ***W. Zhu****, C.S. Pai, H.E. Bair, H.W. Krautter, B.S. Dennis,* Lucent Technologies **INVITED**

Low dielectric constant (k) materials are key components for the next generation backend-of-the-line interconnect architectures. We investigated the fundamental relationships among the deposition, structure and properties of low k fluorinated amorphous carbon (a-C:F) films. We found that the useful low k a-C:F films need to possess a carbon structure with an optimal amount of crosslinked, sp3 bonded carbon atoms. This dictates that the F/C atomic ratio is in a narrow range of 35-45%, and the films contain no hydrogen. We have successfully deposited robust a-C:F films with k<2.8 and with physical properties meeting stringent requirements for device integration.

11:20am **EM1-ThM10 Multilayered Si-Based Organic Thin Films with Low-Dielectric-Constant Formed by Plasma-Enhanced Chemical Vapor Deposition from Hexamethyldisiloxane**, ***M. Okumura****, S. Ichiyanagi, T. Fujii, M. Hiramatsu, M. Nawata,* Meijo University, Japan

As the device geometries of ultralarge scale integration (ULSI) circuits continue to shrink, low-dielectric-constant interlayer dielectric films are required in order to realize ULSI devices of high performance. We have previously reported a remote plasma-enhanced chemical vapor deposition (PECVD) from hexamethyldisiloxane (HMDSO) and O@sub 2@ using a radio-frequency (rf, 13.56MHz) inductively coupled plasma (ICP) source for the formation of Si-based organic thin films as a new insulator with a dielectric constant lower than 3.0. In this work, to improve the thermal stability and dielectric property of Si-based organic thin films fabricated by PECVD with HMDSO, multilayered structure of methyl-siloxane layer and thin silicon-oxide layer has been proposed. After the deposition of the first Si-based organic film using PECVD from HMDSO and O@sub 2@ at room temperature, the film was rapidly annealed by the irradiation of CO@sub 2@ laser beam with exposed to O@sub 2@ plasma without HMDSO in order to transform the surface of the organic film into silicon oxide for the improvement of thermal stability. The second Si-based organic layer was deposited on the transformed layer, and the surface of the top layer was transformed into silicon oxide in the same manner. This procedure was repeated at most 20 times. Chemical compositions and structures of the multilayered films were analyzed by x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The dielectric constant of the multilayered Si-based organic thin films varied from 2.6 to 4.5. The effects of deposition conditions on the film properties were investigated.

11:40am **EM1-ThM11 Low-k Si-O-C-H Composite Films Prepared by Plasma Enhanced Chemical Vapor Deposition using BTMSM(bis-trimethylsilylmethane) Precursor**, ***Y.-H. Kim****, H.J. Kim,* Seoul National University, Korea

As the ultra-large scale integrated circuits(ULSI) are shrunk to deep sub-micron dimension, RC signal delay, cross-talk, and power consumption are seriously increased. Therefore, there has been a strong demand for low-k inter-metal dielectric materials instead of the conventional SiO@sub 2@ in order to improve the performance of ULSI devices. Many researchers have proposed various organic and inorganic materials as the substitute for SiO@sub 2@. Among them, silicon oxide-based dielectric materials containing alkyl groups have been attractive alternatives due to their high thermal stability. The steric hindrance of the alkyl groups remains nano-pores in silicon oxide and the dielectric constant is decreased. Therefore, in order to get lower value of dielectric constant, the more alkyl groups have to be included in silicon oxide. However, the over-much alkyl groups could degrade the thermal stability of this material. To achieve good thermal stability as well as the low dielectric constant, we prepared the Si-O-C-H composite films by plasma enhanced chemical vapor deposition using bis-trimethylsilylmethane(BTMSM, H@sub 9@C@sub 3@-Si-CH@sub 2@-Si-C@sub 3@H@sub 9@), which is neither toxic nor flammable. Major feature of this precursor is a very strong Si-CH@sub 2@-Si bond between two silicon atoms, therefore, the Si-O-C-H composite films deposited using BTMSM were expected to have good thermal stability as well as low dielectric constant. To investigate the thermal stability of the Si-O-C-H composite films, FT-IR analysis and capacitance-voltage measurement were carried out before and after heat-treatment. Film morphology and step coverage were examined by the electron microscopy (SEM and TEM).

Electronic Materials and Processing Division
Room 612 - Session EM2-ThM

Dielectric Passivation/Oxides on Compound Semiconductors

Moderator: K.G. Eyink, Air Force Research Laboratory

9:00am **EM2-ThM3 Dielectric Passivation/Oxides on Compound Semiconductors**, ***F. Ren,*** University of Florida*; M. Hong,* Bell Laboratories, Lucent Technologies*; S.J. Pearton, C.R. Abernathy, G. Dang,* University of Florida*; J.R. Lothian,* Multiplex Inc. **INVITED**

Electronic and optical devices based on GaAs, InGaAs and GaN material systems have been widely used in telecommunication and wireless communication applications. In order to improve the device performance and reliability, device passivation is one of the critical steps in the device fabrication. An electron cyclotron resonance chemical vapor deposition (ECRCVD) silicon nitride (SiN@sub x@) was successfully demonstrated to passivate submicron T-gate. Combining ECRCVD SiN@sub x@ and an in-situ dielectric film passivation technique by dividing a thick film deposition into many thin film (<40Å) depositions and using a N@sub 2@ ion bombardment between the depositions. A thermally stable (up to 800 °C) SiN@sub x@ was achieved with this process. The refractive index of N@sub 2@ treated SiN@sub x@ film only changed 0.3% when the SiN@sub x@ film was heated up to 1000 °C and the film with a continuous deposition showed a 2.5% change. The etch rates of passivated SiN@sub x@ film in BOE and diluted HF are 40 Å/min which is much slower than that of un-treated SiN@sub x@(135 Å/min). Recently, an in-situ deposition of Ga@sub 2@O@sub 3@(Gd@sub 2@O@sub 3@) on InGaAs, GaAs and GaN has been demonstrated. The Ga@sub 2@O@sub 3@(Gd@sub 2@O@sub 3@)/GaAs interfaces showed a very low interface state densities. Enhancement and depletion mode GaAs metal oxide semiconductor field effect transistors (MOSFETs) have been demonstrated with excellent performance. Enhancement mode InGaAs and depletion mode GaN were also demonstrated.

10:00am **EM2-ThM6 Study of GaAs Oxidation in H@sub 2@O@sub 2@ and H@sub 2@O using Spectroscopic Ellipsometry**, ***S.-J. Cho****, P.G. Snyder,* University of Nebraska, Lincoln

Oxidation of GaAs in hydrogen peroxide (H@sub 2@O@sub 2@) and deoinized H@sub 2@O (DH@sub 2@O) at room temperature was studied using in-situ real time spectroscopic ellipsometry (RTSE) and ex-situ spectroscopic ellipsometry (SE). GaAs samples were immersed in H@sub 2@O@sub 2@ for periods of up to 2 hours while RTSE data were recorded, then rinsed in flowing DH@sub 2@O and blown dry. SE data (1.5-5.5 eV) were taken before and after immersion. Analysis of the SE data indicated the development of a 2-3 nm interface (modeled as porous GaAs) between the oxide and GaAs, which was not present before immersion. The oxide itself had also become more porous as well as thicker. Accurate modeling of the interface and oxide layers required data in both the E@sub 2@ (~4-5 eV) and E@sub1@ (~2.5-3.5 eV) spectral regions. The RTSE spectral range was limited to below 3.5 eV by UV absorption in the H@sub 2@O@sub 2@ ambient, so the interface could not be included in the real time analysis. Another problem was the formation of bubbles on the surface, which became visible after about 30 minutes. Within these limitations on the RTSE data, their analysis indicated that the oxide growth was approximately logarithmic over at least the first 10-15 minutes. The oxidation rate varied from 0.21 to 0.54 nm/decade (minutes). In DH@sub 2@O no bubbles formed, but an interface again appeared to be present. Oxidation was nearly linear in time, at a higher rate than in the H@sub 2@O@sub 2@, and with a higher void volume (more porous oxide). Growth rates again varied considerably, with a typical rate 0.16 nm/min. Research supported by AFOSR Grant #49620-96-1-0480.

10:20am **EM2-ThM7 The Effective Two-step Passivation of Metal/GaAs Interface with Sulfur and Hydrogen Plasma**, ***M.G. Kang,*** *J.W. Kim, H.H. Park,* Yonsei University, Korea

In application of GaAs to device integration, the reliable and controllable Schottky contact property of metal/GaAs is urgently necessary to yield. However, it is limited to develop furthermore due to the existence of defects at/near the metal/GaAs interface. In this study, a novel method of passivating the defects with sulfur and hydrogen plasma at/near the metal/GaAs interface was investigated. The sulfur-passivation was employed to passivate the defects at GaAs surface, and the defects in GaAs adjacent to the surface were co-passivated using hydrogen plasma. The native oxide of GaAs was completely removed by the surface treatment using HCl solution. The GaAs surface was then passivated with sulfur in a monolayer thickness using (NH@sub 4@)@sub 2@S@sub x@ solution. After the treatment, the surface could be protected from air-oxidation and preserved oxide-free-surface during a followed metallization. In particular, ultra thin Au metal of 5 nm thickness was deposited on the sulfur-passivated GaAs surface prior to hydrogen plasma treatment, in order to protect the GaAs surface from plasma-induced damage. The defect density of the metal/GaAs interface was greatly reduced by this two-step passivation method, compared to GaAs treated with either sulfur or hydrogen. The defects were evaluated by low temperature photoluminescence and deep level transient spectroscopy. The chemical bonding state of GaAs before and after Au-metallization was characterized using an angle-resolved X-ray photoelectron spectroscopic technique.

10:40am **EM2-ThM8 Advanced Selective Dry Etching of GaAs/AlGaAs in High Density Inductively Coupled Plasmas**, ***J.W. Lee,*** *M.W. Devre, B.H. Reelfs, D.J. Johnson, J.N. Sasserath,* Plasma-Therm, Inc.; *F. Clayton,* Motorola, Inc.; *S.J. Pearton,* University of Florida

We report a breakthrough for selective etching of GaAs over Al@sub X@Ga@sub 1-X@As, x = 0.2, etching with a high density plasma source. This results is particularly important for III-V devices such as HBTs or HEMTs. For example, fabrication of HBTs requires a process for selective etching of a GaAs contact layer while stopping on AlGaAs layer. Inductively coupled plasma (ICP) etching with BCl@sub 3@/SF@sub 6@/N@sub 2@/He chemistries showed extremely high selectivity of GaAs over AlGaAs (> 200 : 1) and a photoresist (> 10 : 1). This process also produced excellent sidewall passivation on GaAs with reasonablely high rate (> 1500 Å/min.). Both SEM and AFM data showed AlGaAs etch stop layer was quite smooth after processing. We found that He played a key role in enhancing selectivity and obtaining smooth AlGaAs surfaces. When used with resist masks, addition of N@sub 2@ into BCl@sub 3@/SF@sub 6@ plasma helped formation of passivation on the sidewall and maintained high anisotropy. An optimized condition with BCl@sub 3@/SF@sub 6@/N@sub 2@/He ICP plasmas showed excellent pattern transfer into GaAs with high rate, anisotropy and selectivity.

11:00am **EM2-ThM9 Characterization of Hydrogen Passivation in p-type InP (100)**, ***W.E. Henderson,*** Clark Atlanta University; *M.D. Williams,* Clark Atlanta University, US

Hydrogen in p-type semiconductors acts to passivate (i.e. neutralize) the charge carrier contribution of impurity charge centers by forming acceptor-H+ complexes. We study the passivation of several common p-type dopants in InP (100) including Zn, Be, and Cd. The InP substrates are exposed to atomic hydrogen created by a radio-frequency generated plasma source. Secondary ion mass spectrometry and capacitance-voltage profiling are used to determine the degree of neutralization as a function of depth. This work is supported by the DoE through grant # DE-FG02-97ER45647.

11:20am **EM2-ThM10 Synchrotron Radiation-Induced Wet Processing of GaAs***, ***Q. Ma,*** *D.C. Mancini, R.A. Rosenberg,* Argonne National Laboratory

To explore the potential for photoelectrochemical processing of materials using hard x-rays generated by a third-generation synchrotron radiation (SR) light source, we initiated studies of SR-induced surface wet etching and metal deposition. We report in this paper a room-temperature, x-ray-induced chemical wet etching process that produces smoothly etched surfaces on n-GaAs using a HNO@sub 3@ solution as the reagent. Atomic force microscope measurements indicate a root-mean-square surface roughness of @<=@ 1.5 nm, which compares favorably to the unetched surface roughness. An etch rate of up to 64 nm/min was achieved under current experimental conditions, which still leaves room for significant enhancement. Dependence of the etching rate on photon intensity, photon energy, semiconductor doping types, and solution concentration, as well as the etched surface chemistry have been studied in order to understand the underlying mechanism. We will also report a preliminary result of patterned wet metal deposition on n-GaAs using a commercial Ni-containing electrolyte and describe the processing. *The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-ThM

Nanotubes: Nanoelectronics and Field Emission

Moderator: N.J. Halas, Rice University

8:20am **NT+NS+EM+MS-ThM1 Carbon Nanotube Molecular Electronics**, ***C. Dekker,*** Delft University of Technology, The Netherlands **INVITED**

I will present various recent results from electron transport measurements and scanning-probe microscopy on individual single-wall carbon nanotubes. Our early electrical transport work showed mesoscopic signatures at cryogenic temperatures. Additionally, a room-temperature transistor based on an individual semiconducting nanotube was established. Recent results in transport studies include first measurements on samples with low-ohmic contacts. The nanotubes are found to sustain very high current densities (~10^9 A/cm^2). I will show first measurements on kinked nanotubes, which act as an ontube intramolecular junctions. If time allows I may also present our results on AFM manipulation of nanotubes, and electrical measurements on manipulated nanotubes.

9:00am **NT+NS+EM+MS-ThM3 Electrical Transport in Single-Wall Nanotube Rings: Coherence and Localization**, *H.R. Shea, R. Martel,* ***Ph. Avouris,*** IBM T.J. Watson Research Center

Understanding electrical transport in carbon nanotubes is essential for their possible use in nanoelectronics. Furthermore single-walled carbon nanotubes (SWNTs) provide ideal model systems on which to test theories of transport phenomena in 1D-systems. Linear SWNTs, however, do not have self-folding electron trajectories which can enclose magnetic flux. Thus, the technique of magneto-resistance (MR) cannot be applied directly to obtain information on the mechanism of electrical transport. Recently, we have developed a procedure by which linear SWNTs can be induced to form ring structures. Despite the high flexural rigidity of these materials, coils stabilized only by van der Waals forces can be produced in yields of ~50 %. These rings provide an ideal geometry for MR measurements. The MR is negative over the range of 0-5 T and from it we are able to determine the coherence length of the electrons in the rings. We found that over the entire range of 3 K - 60 K the SWNT-rings are in a state of weak localization induced by the constructive interference of electron waves propagating in opposite directions around the ring. Electric transport is not ballistic, and the coherence length reaches 520 nm at 3 K. From the temperature dependence of the coherence length we determine that the dominant dephasing mechanism at low T involves electron-electron interactions (Nyquist mechanism). Below ~1 K we observe an electronic phase transition to a strongly localized state. This transition is accompanied by the opening of a small energy gap and very strong MR and universal conductance fluctuations. An interesting zero bias anomaly (ZBA) is also observed below ~0.7 K. This ZBA is sensitive to magnetic fields and is ascribed to Kondo-type scattering from localized magnetic moments.

9:20am **NT+NS+EM+MS-ThM4 Analysis of Carbon Nanotube Field-Effect-Transistors (FETs)***,* ***T. Yamada,*** NASA Ames Research Center

Recent experiments on carbon nanotube FETs@footnote 1@ are analyzed theoretically. Comparing to the familiar Metal-oxide-semiconductor (MOS) FET characteristics, two qualitatively different behaviors can be pointed out:@footnote 1@ (1) the channel conductance g@sub d@ as a function of gate voltage V@sub g@ is not linear but somehow saturates, and (2) the drain current I@sub d@ does not saturate with the drain voltage V@sub d@ but rather monotonically increases. As for g@sub d@(V@sub g@), a staircase-like curve is expected with possible rounding. Each time the Fermi energy crosses a degenerate new subband, the nanotube conductance increases by double the quantum conductance, and thus g@sub d@ forms steps. When moving up to a next step, one new additional degenerate subband needs to be filled in the inversion layer, where larger V@sub g@ has to be applied. This will be a mechanism for the g@sub d@ saturation. The absence of I@sub d@(V@sub d@) saturation is due to the infrequent inelastic scattering by phonons or other carriers in the channel, regardless of the frequent elastic scattering by defects or impurities determining the small g@sub d@ (1/g@sub d@ ~ 2.9 M@ohm@).@footnote 1@ Carriers are not thermalized in the channel without efficient inelastic scattering, resulting in no channel pinch-off formation and no I@sub d@ saturation. These reflect the nanotube electronic properties. We need to take them into account in the future device/circuit design, and develop a scheme best suitable for nanotube FETs. @FootnoteText@ @footnote 1@S.J. Tans, R.M. Verschueren & C. Dekker, Nature, 393, 49 (1998); R. Martel, T. Schmidt, H.R. Shea, T. Hertel, Ph. Avouris, Appl. Phys. Lett. 73, 2447 (1998).

9:40am **NT+NS+EM+MS-ThM5 Novel Length Scales in Nanotube Devices***,* ***F. Léonard,*** *J. Tersoff,* IBM T.J. Watson Research Center

We calculate the properties of p-n junctions, n-i junctions, and Schottky barriers made on a single-wall carbon nanotube. In contrast to planar bulk junctions, the depletion width for nanotubes varies exponentially with inverse doping. In addition, there is a very long-range (logarithmic) tail in the charge distribution, extending over the entire tube. These effects can render traditional devices unworkable, while opening new possibilities for device design. Our general conclusions should apply to a broad class of nanotube heterojunctions, and to other quasi-one-dimensional ``molecular wire" devices.

10:00am **NT+NS+EM+MS-ThM6 Field Emission from Carbon Nanotubes and Its Application to Electron Sources in Display Elements***,* ***Y. Saito,*** Mie University, Japan*; S. Uemura,* Ise Electronics Corp., Japan **INVITED**

Carbon nanotubes posses the following properties favorable for field emitters: (1) high aspect ratio, (2) small radius of curvature at their tips , (3) high chemical stability and (4) high mechanical strength. Field emission microscopy was carried out for both multiwall nanotubes (MWNTs) and single-wall nanotubes (SWNTs) produced by arc discharge between carbon. Four kinds of nanotubes were investigated; viz., (1) as-grown MWNTs prepared in the helium arc (called "pristine MWNTs"), (2) as-grown MWNTs in hydrogen ("nanog rafibers"), (3) purified MWNTs with open ends ("purified MWNTs" or "open MWN Ts"), and (4) purified SWNTs. Field emission patterns as well as current versus voltage characteristics and Fowler-Nordheim plots for respective nanotubes will be discussed. As an application of nanotube field emitters, we manufactured cathode-ray tube (CRT) type lighting-elements and vacuum-fluorescence display (VFD) panels. In both display elements, conventional thermionic cathodes were replaced with MWNT field emitters which were fixed onto a stainless steel cathode by using conductive paste. In CRT-type lighting elements, the nanotube cold cathode was covered with a grid electrode, the gap between the cathode and the grid being in a range from 0.2 to 0.7 mm. Current density on the cathode surface was on the order of 10 - 100 mA/cm@super 2@ at an average field strength of 1.5 V/ µm. Luminance of the phosphor was intense enough for practical use; e.g., 6.3x10@super 4@ cd/m@super 2@ for green light at an anode current of 0.2 mA and an anode voltage of 10 kV. A direct-current driving test revealed a lifetime over 10,000 hours.

10:40am **NT+NS+EM+MS-ThM8 Emission Properties of Large-area, Fully-sealed Carbon Nanotube Field Emission Display***,* ***W.B. Choi,*** *H.Y. Kim, D.S. Chung, J.H. Kang, I.T. Han, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Fully sealed field emission display (FED) in size of 4.5 inch has been fabricated by using carbon nanotubes. Carbon nanotubes were fabricated by arc discharge technique. Carbon nanotube aligning techniques with the aid of slurry squeezing and electrophoresis were used for making large-area cathode. The Y@sub 2@O@sub 2@S:Eu, ZnS:Cu,Al, and ZnS:Ag,Cl, phosphors are deposited on the anode glass for red, green, and blue colors, respectively. The assembled structure was sealed in an atmosphere of highly purified Ar gas by means of a glass frit. The display plate was evacuated down to the pressure level of 1x10@super -7@ Torr. Three non-evaporable getters of Ti-Zr-V-Fe were activated during the final heat-exhausting procedure. Finally, the active area of 4.5-inch panel with fully sealed carbon nanotubes was produced. The turn-on field for lighting phosphor was 1.5 V/µm. Brightness of over 1000 cd/m@super 2@ at 4V/µm was achieved on the entire area of 4.5-inch panel from the green phosphor-ITO glass. The fluctuation of the current was satisfied for the field emission display. These reliable results enable us to produce carbon nanotube-based large area full-color FEDs in the near future. In this presentation, fabrication techniques and emission properties of large area carbon nanotube FED will be demonstrated.

11:00am **NT+NS+EM+MS-ThM9 The Structure of Nanotubes Observed with Thermal Field Emission***,* ***K.A. Dean,*** *B.R. Chalamala,* Motorola Flat Panel Display Division*; O. Groening, O.M. Kuettel,* University of Fribourg, Switzerland

We studied the structure of single-walled nanotubes (SWNTs) using field emission microscopy. The field emission images obtained after thermal cleaning depict the spatially-resolved electronic structure of the individual SWNT caps. Using high temperature field emission, we demonstrate how to distinguish between the patterns of individual SWNTs and those of clusters, how to alter the structure of the nanotube cap, and how to extract information about the SWNT structure and chirality from the field emission image. In addition, we demonstrate a technique for measuring the SWNT local density of states through thermal field emission energy distribution measurements. With this technique, we observe that nanotubes have discrete electronic states several eV above the Fermi level, and we suggest that these states are responsible for the large variation in emission current vs. temperature behavior observed among nanotubes.

11:20am **NT+NS+EM+MS-ThM10 Fabrication and Field Emission Properties of Adherent Carbon Nanotube Films***,* ***C. Bower,*** University of North Carolina at Chapel Hill*; W. Zhu, G. Kochanski, S. Jin,* Bell Laboratories, Lucent Technologies*; O. Zhou,* University of North Carolina at Chapel Hill

We report on the fabrication and field emission properties of carbon nanotube films. Films of randomly oriented carbon nanotubes were deposited onto substrates using a variety of techniques. The nanotube films exhibited stable field emission current at low turn-on fields (electric field needed to generate 1 nA of current) and threshold fields (electric field needed to generate 10 mA/cm@super 2@). A single-walled carbon nanotube film with approximately 20% surface coverage showed a turn-on field of 1-1.2 V/µm and a threshold field of 1.3-1.7 V/µm. The emission characteristics deviated from typical Fowler-Nordheim behavior at high current densities. The nanotube films were capable of generating large current densities (> 4 A/cm@super 2@). The emission properties were found to be stable over several days of emitting at 10 mA/cm@super 2@. The emission site density of the films was measured to be 10@super 4@-10@super 5@ sites/cm@super 2@ and the emission patterns were studied.

11:40am **NT+NS+EM+MS-ThM11 Characterization of Oriented Carbon Nanotube Cathodes for Field Emission Flat Panel Display and Light Source Applications***,* ***N.N. Chubun,*** SRPC Istok, Friazino, Russia*; A.G. Chakhovskoi, C.E. Hunt,* University of California, Davis*; A.N. Obraztsov,* Moscow State University, Russia

Oriented carbon nanotubes were recently reported as a viable material for fabrication of field emission cathodes applicable to flat panel displays and vacuum light sources.@footnote 1@ Field emission properties of diode and triode structures with oriented nanotube cathodes were studied in DC-mode in ultra-high vacuum chamber and in sealed glass prototype devices. Cathodes of 9x9mm grown using glow-activated direct current discharge CVD method on molybdenum and single crystal silicon substrates were studied at currents up to 2 milliamps using metal or phosphor coated anodes. The nanotubes exhibited various degrees of initial surface orientation depending on parameters of the deposition process. An additional orientation of the nanotubes in electric filed during first activation of the cathodes was observed. Monochrome low-voltage FPD phosphors were used for cathodoluminescent brightness/light efficiency characterization and for monitoring of distribution of the filed emission sites. Turn-on voltages varied from 1 to 5 V per micron depending on the extraction electrode configuration. Influence of vacuum conditions and initial training on stability and lifetime of the cathodes was studied. I/V characteristics of the nanotube cathodes were directly compared to those of carbon fiber and carbon foam emitters and to diamond-coated field emission arrays showing potentially greater reproducibility and uniformity of filed emission of the oriented nanotube cathodes. @FootnoteText@ @footnote 1@ A.N.Obraztsov, I.Yu.Pavlovsky, A.P.Volkov, V.L.Kuztetsov, A.L.Chuvilin. MRS 1999 Spring Meeting, San Francisco, CA, April 1999, p.B.4.9/C.2.9.

Surface Science Division
Room 607 - Session SS2+EM+NS-ThM
Nucleation and Growth

Moderator: G.M. Nathanson, University of Wisconsin, Madison

8:20am **SS2+EM+NS-ThM1 Evolving Surface Morphology: An In Situ STM Study of 2-20 nm SiGe Quantum Wells Grown on 75 mm Si (100) Wafers***,* ***G.G. Jernigan,*** Naval Research Laboratory, US*; P.E. Thompson,* Naval Research Laboratory

Electrical device improvement will come from the understanding and control of interfaces at the atomic level. We have integrated an STM with a commercial Si MBE system for in situ examination of device structures grown on full 75 mm wafers. Our first system of study is the growth of SiGe quantum wells on Si (100). SiGe is being investigated for its use in optoelectronics and high speed circuits. We will present a description of the atomic surface morphology of the initial 100 nm epitaxial Si buffer layer, followed by a Si@sub 0.8@Ge@sub 0.2@ quantum well of thickness up to 20 nm, and a Si capping layer deposited after the quantum well. The Si buffer layer is grown using a 0.08 nm/s Si flux onto a 650 @super o@C substrate. Step-flow growth occurs, but the different adatom sticking probabilities at the S@sub A@ and S@sub B@ steps produces a "wavy" surface which is the result of alternating terraces growing rapidly in different directions rotated by 90@super o@. The deposition of Si@sub 0.8@Ge@sub 0.2@, by co-depositing Ge with a 0.02 nm/s flux and Si, disrupts the "wavy" growth morphology. Ge segregation during deposition produces a "2xn" surface reconstruction that consists of rows which run perpendicular (G@sub A@) and parallel (G@sub B@) to a step edge in a manner analogous to the S@sub A@ and S@sub B@ steps, respectively. The quantum well morphology consists of a mosaic of small terraces containing short rows of G@sub A@ steps and long rows of G@sub B@ steps. The Si capping layer grown on the quantum well reinstates the "wavy" morphology. However, in addition to the S@sub A@ and S@sub B@ step-flow growth, dimer vacancy lines are now observed within the S@sub A@ terraces and are due to Ge segregation from the quantum well. The effects of S@sub A@/S@sub B@ waves, Ge "2xn" terraces, and dimer vacancy lines as a function of growth rate and temperature will be discussed. This work was supported by the ONR.

8:40am **SS2+EM+NS-ThM2 Hydrogen-Mediated Surface Morphological Evolution in Si@sub 0.7@Ge@sub 0.3@/Si(001) Layers Grown by Hydride Gas-source Molecular Beam Epitaxy***,* ***T. Spila****, P. Desjardins, H. Kim, N. Taylor, D.G. Cahill, J.E. Greene,* University of Illinois, Urbana*; S. Guillon, R.A. Masut,* Ecole Polytechnique de Montréal, Canada

The primary mechanisms for relieving misfit strain @epsilon@ during heteroepitaxy are the formation of misfit dislocations (MD) and strain-induced roughening. These mechanisms are initially competing (due to @epsilon@-dependent activation energies) and eventually interacting once relaxation is initiated. Si@sub 0.7@Ge@sub0.3@ layers were grown on Si(001) (miscuts @<=@ 0.1°) to quantitatively investigate the effects of Ge surface segregation and steady-state hydrogen coverage @theta@@sub H@ on mechanisms of surface morphological evolution during GS-MBE from Si@sub 2@H@sub 6@/Ge@sub 2@H@sub 6@. For growth temperatures T@sub s@ > 600 °C where @theta@@sub H@ = 0, layers exhibit (by AFM and XTEM) surface morphologies similar to that observed in solid-source MBE. The islanding process observed at T@sub s@ = 800 °C relieves 45% of the strain (determined from x-ray reciprocal lattice maps) without the introduction of MDs for thicknesses t up to 31 nm. The dominant facet planes evolve from {105}/{113} to {518}/{111}/{011} with increasing t until coalescence (t = 180 nm). Decreasing T@sub s@ < 600 °C to a regime where @theta@@sub H@ > 0 allows an opportunity to probe new hydrogen-mediated surface morphological pathways. The tendency toward strain-induced roughening and faceting decreases with decreasing T@sub s@ as the initial low-thickness strain-relaxation mechanism and corresponding in-plane feature size changes from strain-induced roughening to MD nucleation when T@sub s@ is decreased below 525 °C. We discuss the details of surface morphological evolution in each of the three temperature regimes (< 525, 525-600, and > 600 °C) in terms of local precursor adsorption and H-desorption kinetics.

9:00am **SS2+EM+NS-ThM3 Interdiffusion During Growth of Ge on Si(100)***,* ***H. Jonsson****, B.P. Uberuaga, M. Leskovar, B.R. Schroeder, S. Meng, M.A. Olmstead,* University of Washington

We present both experimental evidence and a theoretical explanation of sub-monolayer Ge epitaxy on Si(100) interdiffusion to the 4th layer of the Si substrate. XPD measurements at both 500 C and 700 C show the presence of Ge atoms in the 4th layer. DFT/GGA calculations of the energetics of a Ge atom in the Si surface, together with a statistical model of Ge occupation of the lattice sites, predict occupation of sub-surface sites, with enhanced occupation in the sites under tensile strain. The calculations indicate that the formation energy of a Ge interstitial near the surface (about 1 eV higher energy than the adatom) is significantly reduced as compared with an interstitial in bulk Si, thus lowering the energy barrier for the interstitial diffusion mechanism near the surface. This work was supported by the National Science Foundation, the University of Washington Royalty Research Fund and the Japanese New Energy and Technology Development Organization.

9:20am **SS2+EM+NS-ThM4 Confined Intermixing of Ge and Si***,* ***S.-J. Kahng****,* Seoul National University, Korea*; Y.H. Ha, D.W. Moon,* Korea Research Institute of Standards and Science, Korea*; Y. Kuk,* Seoul National University, Korea

In Ge-Si superlattice system, the efficiencies of a possible optoelectric and fast devices can be improved by optimizing the composition at each layer and the abruptness at the interface. It is well- known that intermixing between Ge and Si atoms mainly occurs during the growth process of Si layers on the previously grown Ge layers. Ge atoms tend to segregate toward the surface since the surface free energy of Ge is lower than that of Si. Howerver, with hydrogen adsorbate, the surface free energy of Ge is lower than that of Si, possibly inducing segregation of Si in the Ge overlayer. In this study, Si surface segregation was studied quantitatively for the Ge overlayers grown on Si(100)-(2 x 1) with channeled medium energy ion scattering spectroscopy. The intermixing between Ge and Si presents only at the initial layer in the presence of hydrogen surfactant. Microscopic mechanism for the growth process will be discussed in the view point of kinetics as well as energetics.

9:40am **SS2+EM+NS-ThM5 Surface Segregation and Surface Reactivity in Heteroepitaxial Vapor Phase Thin Film Growth: Si@sub 1-x@Ge@sub x@ on Si(111)***,* ***Y.-J. Zheng****, A.M. Lam, J.R. Engstrom,* Cornell University

Supersonic molecular beam scattering, x-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectrometry (LEISS) have been employed to examine the heteroepitaxial growth of Si@sub 1-x@Ge@sub x@ thin films on Si(111) surfaces. Molecular beam scattering has been employed to measure the reactivity of Si@sub 2@H@sub 6@ and GeH@sub 4@ on the Si@sub 1-x@Ge@sub x@ alloy surfaces for a variety of growth conditions (composition and substrate temperature), and these results are compared with results obtained on the clean Si(111) and Ge(111) surfaces. We find that the alloy surfaces are less reactive than both of the pure elemental Si and Ge surfaces. This is in stark contrast to our results for the (100) orientations, where alloy reactivity was always intermediate to that observed on clean Si and Ge. These results reflect the important role played by surface reconstructions on the (111) orientations. XPS and LEISS have been employed in situ to quantify the near-surface Ge concentration of the Si@sub 1-x@Ge@sub x@ epitaxial thin films. Ge segregation is significant, although somewhat less pronounced compared to what we have observed previously on the (100) orientations. Ge segregation, which occurs also in the subsurface layers, has been successfully modeled using both a statistical thermodynamic analytical model, and Monte Carlo simulations.

10:00am **SS2+EM+NS-ThM6 The Role of Arsenic Surfactant in the Growth of Germanium Thin Films on Si(100) Surfaces***,* ***C.L. Berrie****, J. Bright, S.R. Leone,* University of Colorado, Boulder

The role of arsenic surfactant in the growth of germanium films on Si(100) substrates is investigated using laser single photon ionization time of flight mass spectrometry, reflection high energy electron diffraction, and atomic force microscopy. The energetics of arsenic interaction with Si(100) and Ge(100) are investigated by monitoring the temperature dependence of the desorbing fluxes of As@sub 4@, As@sub 2@ and As atoms from the substrate under a constant incident As@sub 4@ flux. These measurements indicate that the As@sub 2@ interactions with Si(100) and Ge(100) differ dramatically. In particular, the As@sub 2@ flux plateaus in the case of the Si(100) substrate from 800 K to 1000 K. In the case of the Ge(100) substrate, the As@sub 2@ flux monotonically increases over this temperature range and a similar plateau is not observed. Measurements of the desorbing As@sub n@ fluxes are also made during Ge growth on a Si(100) surface. The dramatic difference in the arsenic interaction on these two surfaces is evident in these measurements as well. The morphologies of the resulting films are monitored ex-situ using atomic force microscopy to determine the effect of arsenic coverage on the size and density distributions of islands formed. As the arsenic coverage is increases, the observed island size decreases and the density of islands increases dramatically. The mechanisms for the Ge growth and the interaction in the presence of the arsenic surfactant will be considered.

10:20am **SS2+EM+NS-ThM7 The Dynamics of the Si(111) (7x7) to (1x1) Phase Transition Investigated by Low Energy Electron Microscopy***, J.B. Hannon,* Carnegie Mellon University **INVITED**

We have used low-energy electron microscopy (LEEM) to investigate the dynamics of the (7x7) to (1x1) phase transition on the Si(111) surface. Because the density of the (1x1) surface is 6 percent larger than that of the (7x7) surface, the conversion from (7x7) to (1x1) requires transport of mass to the domain boundary. By measuring the time evolution of complicated configurations of triangular (7x7) domains, and comparing the results to detailed simulations, we are able to quantify the role of mass transport in the dynamics of this phase transition. We find that individual domains decay approximately linearly in time, with a decay rate determined, not by the domain size, but by the local arrangement of neighboring domains. This observation is counter to the simplest picture of phase boundary motion, in which domain walls move with a constant velocity (independent of environment) determined by the free energy difference between the two phases. We have modeled the effect of the mass transport requirement on the observed decay by solving the two-dimensional diffusion equation for the experimentally-observed configuration of 7x7 domains. We find that the (7x7) domain decay is indeed limited by the supply of the additional material to the boundary. Detailed comparison of the diffusion model with experiment suggests the surprising result that the terrace (rather than surface steps) acts as the primary source of the additional atoms required for the (7x7) to (1x1) conversion. This model reproduces the simultaneous decay of all islands in the field of view with only one adjustable parameter.

11:00am **SS2+EM+NS-ThM9 The Motion of Atomic Steps on Ultra-Flat Si(111)***, **P. Finnie**, Y. Homma,* NTT Basic Research Laboratories, Japan

The flattest silicon surfaces are typically made up of terraces of a low index crystal plane connected by atomic steps. We have studied sublimation and growth on ultra-flat Si(111) substrates@footnote 1@ which have (111) terraces of up to 50 microns in width separated by monoatomic steps. The motion of atomic steps is revealed in time lapse movies made by in situ scanning electron microscopy. When samples are heated to high temperatures (about 1000°C) the surface erodes in a step-flow mode: steps retreat in an orderly fashion, one after the other. Since new terraces are nucleated when step spacings exceed a temperature dependent critical length, the spacing between steps is tunable. Measurements of step velocities as a function of terrace width compare well with theory. The interactions between steps are observed directly by forcing steps to collide@footnote 2@ either destructively, in which opposing steps annihilate, or constructively, in which steps moving in tandem coalesce into double (or triple, or larger) steps. We also studied molecular beam epitaxy in this high temperature regime. Using an electron beam to supply a flux of elemental silicon, desorption is countered and growth occurs in the step-flow mode. Remarkably flat grown surfaces can be obtained in this way since step-flow growth maintains an ultra-flat profile. Monoatomic height island nucleation can also be observed, with circular islands growing to diameters of tens of microns, seamlessly merging with neighboring terraces as the steps collide destructively. @FootnoteText@ @footnote 1@ Y. Homma, H. Hibino, T. Ogino, and N. Aizawa, Phys. Rev. B 55 (1997) R10237 @footnote 2@ P. Finnie and Y. Homma, Phys. Rev. Lett. 82 (1999) 2737.

11:20am **SS2+EM+NS-ThM10 Novel Growth Behavior of Ge on Pb Covered Si(111) Surface***, I.S. Huang,* Academia Sinica, ROC*; T.C. Chang,* Academia Sinica, ROC, Republic of China*; **T. Tsong**,* Academia Sinica, ROC

A surfactant can modify the growth behavior of a system to our advantages. We report discovery of a novel growth behavior in a Pb-layer promoted growth of Ge on Si(111). For this system, not only can Ge atoms grow on Si(111) surface layer by layer for many layers, but the growth behavior is contrary to traditional nucleation and growth theory and most experimental results in epitaxy. This growth is not governed by the reaction-limited-aggregation (RLA) process at low temperature as has been found in traditional epitaxy. The most interesting feature we find is that a compact-to-fractal island shape transition occurs when the sample temperature is increased, or the deposition flux is decreased. In traditional epitaxy, fractal growth occurs by diffusion-limited-aggregation (DLA) at low temperatures, thus fractal growth will disappear as the sample temperature is raised to the extent that step edge diffusion can occur. Our observation demonstrates that fractal islands can also be grown by RLA, and the importance of reactions in aggregation of Ge atoms in this system. Earlier theories neglect the reaction processes which may be acceptable for metal-on-metal systems, but are not good enough for other systems. Our result points to a need to develop a more complete nucleation theory where both diffusion and reaction are properly taken into account.

11:40am **SS2+EM+NS-ThM11 The Growth of High Density, Small Ag Islands at the Si(111)7x7 Surfaces with Adatom Defects***, **H. Hirayama**, H. Okamoto, K. Takayanagi,* Tokyo Institute of Technology, Japan

We studied the growth of Ag islands on the Si(111)7x7 surfaces with missing adatoms. The missing adatoms were created by 0.5keV Ar ion bombardment. Ag atoms were deposited on the surfaces at room temperature. The growths were observed by using scanning tunneling microscope (STM). At the Si(111)7x7 surface of no missing adatoms, several half unit triangular cells of the 7x7 reconstruction changed their contrast to be bright in the initial stage of the Ag deposition . Then, at the coverage above 0.03 monolayer (ML), each bright triangular cell changed to a bright spot. With the coverage, the number of bright spots increased, and occasionally two spots in neighboring cells kissed. At 0.8ML, the surface was covered by the two-dimensional (2D) percolating network of kissing spots. On the network, three-dimensional (3D) Ag islands grew. Meanwhile, at the Si(111)7x7 surfaces with missing adatoms, the bight spots appeared at the very early stage of the Ag deposition. The spots appeared as to avoid missing adatom sites. This resulted in an imperfect 2D network; the connection of kissing spots were cut into pieces here and there. On the imperfect 2D network, 3D islands grew above 0.7ML. At the stage of the 3D island growth, the missing adatom sites of the underlying 2D network was never filled up. However, we found strong dependence of the size and density of the 3D islands on the number of missing adatoms at the starting surfaces. With an increase of missing adatoms, the size of the islands decreased, while the density increased dramatically. The effects of the missing adatoms on the 3D Ag islands growth were attributed to the substantial increase of the super saturation and the decrease of the diffusion constant of Ag atoms on the imperfect 2D network.

Electronic Materials and Processing Division
Room 608 - Session EM1-ThA

Chemical Mechanical Planarization

Moderator: Y.J. Chabal, Bell Laboratories, Lucent Technologies

2:00pm **EM1-ThA1 Surface Chemical Changes during Cu Chemical Mechanical Polishing***, **S. Seal**, D. Tamboli, V. Desai,* University of Central Florida*; S. Joshi, G. Shinn,* Texas Instruments

The current USLI manufacturing technology is continued to be driven towards miniaturization of integrated circuits (< 0.1 micron feature size). As the devices and circuits have increased their complexity, densification and miniaturization, CMP has emerged to be the key technology for feature sizes of 0.35 micron and below to meet the stringent requirements for next generation microelectronic devices. Cu CMP@footnote 1@ is the "technology" for producing submicron Cu line in multilevel metallization structures and satisfies the global planarization, the most important issue for lithography. During Cu CMP, oxidation, dissolution and surface modification take place due to slurry/wafer interaction. While electrochemical measurements are performed to determine corrosion rate, degree of surface passivation and dissolution, detailed surface chemistry is carried out using XPS and AES techniques. Special emphasis is focused on monitoring changes in copper oxide/hydroxides stoichiometry. The surface chemical changes are correlated to Cu polishing rate and slurry chemistry @FootnoteText@ @footnote 1@J. M. Steigerwald, S. P. Muraraka and R. J. Gutmann, Chemical Mechanical planarization of Microelectronic Materials, John Wiley and Sons, Inc. 1997.

2:20pm **EM1-ThA2 Effect of Thin Film Properties on Copper Removal in CMP***, **D. Tamboli**, S. Seal, V. Desai,* University of Central Florida*; S. Joshi, G. Shinn,* Texas Instruments

Currently there is a significant efforts directed towards integrating copper interconnect technology into semiconductor device fabrication because of advantages such as lower RC delays and superior electromigration performance with the use of copper. CMP of copper is a relatively new technology. It is also extremely challenging because of low hardness of Cu films (which makes it prone to defects such as scratches, dishing etc.) and its poor electrochemical properties. Performance of Cu-CMP process is greatly dependent on properties of the deposited copper films. In this study, we report the effect of thin film properties on CMP performance of Cu. As deposited Cu films are first characterized using techniques such as XPS, glancing angle XRD (to measure internal stress), AFM (to study grain morphology), nano-indentation and 4-probe sheet resistivity measurement, and electrochemical polarization measurements. These wafers are then polished. CMP performance as measured by removal rates and in-situ dissolution rate measurements is then correlated with the thin film properties of Cu.

2:40pm **EM1-ThA3 Damascene Patterning of Advanced Interconnect Structures***, **R.J. Gutmann**,* Rensselaer Polytechnic Institute **INVITED**

Advanced IC interconnect structures incorporate damascene patterning (in-laid metal) to improve packing density and reduce manufacturing cost. Chemical-Mechanical Planarization (CMP) of copper or aluminum is used to delineate the trenches and/or vias after dielectric etching and metal deposition. The Damascene patterning process is presented, with an emphasis on CMP issues. The role of the metallic liner and the interlevel dielectric (ILD) are highlighted, the effect of alternative CMP consumables (slurries and pads) discussed, and the interaction between the CMP process and post-CMP cleaning in establishing a robust manufacturing capability presented. Examples used to highlight these issues will include dual Damascene patterned copper interconnects with polymer ILDs and tantalum liners and single Damascene patterned copper and aluminum interconnects with oxide ILDs and magnetic liners. The possibility of scaled copper interconnects without conventional conducting liners will be presented.

3:20pm **EM1-ThA5 Tungsten CMP Process Post Tungsten Etch Back Process to Improve the Reliability for Sub-Micron Device Technology***, **A. Sidhwa**, H. Minssieux, C. Spinner,* STMicroelectronics, Inc.

In this paper we will discuss the importance of the CMP process used on wafers after the Tungsten Etch Back step. The purpose of the CMP step was to polish of the remaining Tungsten residue from the etch back process along with the Ti/TiN (barrier) layer and stop on the PMD layer. In the back end of the process, metal residues have been a killer defect that can cause significant decrease in the wafer yield. Residue remaining on the underlying surface may cause shorting of the conductive film and create defects that can affect planarity of the top film. Residues seen after tungsten etch back were due to incomplete tungsten etch back process in uneven areas. These residues can impact the metallization, patterning, and etch processes by causing broken metal lines or lines with defects. It is a known fact that during the tungsten etch back process; it is difficult to etch tungsten of the uneven surfaces due to under layer effects. Hence, high defects can be obtained after the WEB (tungsten etch back) step. If the CMP is performed to polish the remaining tungsten residue along with the barrier, most of the defects that were observed by the KLA after WEB step can be completely removed. The number of defects can be reduced drastically after CMP process. A considerable yield improvement due to CMP touch up process can be obtained. In this paper we show a short loop wafer yield map with high defects and compared to the KLA map performed after WEB process, the yield loss on the short loop wafer is directly correlated to the defects observed at the center of the wafer. This paper will show the defects before CMP and defects after CMP touch up step. Also it will discuss the impact on the electrical data and the SWEAT electromigration data due to Tungsten CMP touch up process.

4:20pm **EM1-ThA8 Etching and Cleaning of Silicon Wafers using HF Vapor Process in the Monolayer Etching Regime***, Y.-P. Han, **H.H. Sawin**,* Massachusetts Institute of Technology

We have studied the oxide etching mechanisms of a gas phase HF etching process in a condensed (liquid phase) and a non-condensed regime (gas phase). In the condensed regime, the etching rate of oxide is greatly affected by the flow rate of the reactant stream and the total pressure of reactor, which can change the mass transfer rates of both reactants and products. In the non-condensed regime, the oxide can be etched in both multilayer and monolayer adsorption states depending on process conditions. The gas phase mass transfer rate limits the etching rate in the multilayer adsorption regime while surface reactions are the rate limiting step in the monolayer regime. The rate limiting steps for etching have been studied at various conditions by changing the temperature of the reactor, the partial pressure of the reactants and the flow rate. In the monolayer etching regime, the etching kinetics can be described by a Langmuir-Hinshelwood adsorption mechanism with competitive adsorption between HF and water. The monolayer etching regime shows many advantages over other etching regimes. We have observed a smoother etched oxide surface, a low selectivity against TEOS, and uniform etching over entire 4" wafer. The native oxide grown on the silicon wafer is removed within a minute, as confirmed by contact angle measurement and XPS. Additionally, aluminum lines are not etched or corroded in the monolayer regime, which implies this process can be applied to metal layers. Since there is no condensed layer on the wafer and chamber wall, the pumping speed is rapid enough for use in a vacuum cluster tool under a hard vacuum environment. We believe that the monolayer HF vapor etching process is applicable to in situ contact cleaning and in situ polymeric residue removal process on metal layers.

4:40pm **EM1-ThA9 Chlorosilane Treatment of SiO@sub 2@-Covered Si Surfaces for Modification of their Chemical Reactivity in Si CVD***, **T. Yasuda**, M. Nishizawa, S. Yamasaki,* Joint Research Center for Atom Technology (JRCAT), Japan

SiO@sub 2@ surfaces are chemically inert against silane molecules. This nature has made SiO@sub 2@ the most preferred mask material for selective CVD of Si, while there are other device processes that require enhanced nucleation of Si on SiO@sub 2@. Thus a technique to control the chemical reactivity of the SiO@sub 2@ surface should be useful in many aspects of device processing. This paper shows that such control is possible by treating the SiO@sub 2@ surface with a proper chlorosilane gas, SiH@sub n@Cl@sub 4-n@. Experiments were carried out using Si(001) wafers covered by an ultrathin SiO@sub 2@ layer formed by plasma or UV-ozone oxidation. Our previous studies showed that this layer acts as a mask in Si CVD using Si@sub 2@H@sub 6@.@footnote 1@ An exposure of the SiO@sub 2@-covered sample to SiCl@sub 4@ at 500 K formed surface-SiCl@sub x@ groups as confirmed by on-line Auger electron spectroscopy. We have found that Si deposition is strongly suppressed on the SiCl@sub 4@-treated SiO@sub 2@ surface under our standard CVD condition (0.05 Pa Si@sub 2@H@sub 6@; 853 K). Density of the Si nuclei is much smaller (~10@super 8@ cm@super -2@) than those observed on the as-oxidized surfaces (~10@super 9@cm@super -2@). This indicates that the surface-SiCl@sub x@ group is inert against Si@sub 2@H@sub 6@. In contrast, Si nucleation is greatly enhanced by a SiH@sub 2@Cl@sub 2@ treatment, the nucleation density reaching 6 x 10@super 10@ cm@super -2@. We have also found that electron-beam irradiation of the chlorosilane-treated surfaces prior to the CVD processing enhances Si nucleation. The minimum electron dose to induce this effect was 10 mC/cm@super 2@. Taking advantage of this effect we have achieved "resistless" selective deposition on the beam-defined parts of the SiO@sub 2@ surface. This study, partly supported by NEDO, was carried out at JRCAT under the joint research agreement between NAIR and ATP. @FootnoteText@ @footnote 1@ T. Yasuda et al., Appl. Phys. Lett. 74, 653 (1999).

5:00pm **EM1-ThA10 The Passivation of Si(100)-2x1 with Alcohols***, **T. Bitzer**, A. Lopez,* St. Andrews University, United Kingdom*; N.V. Richardson,* St. Andrews University, United Kingdom, UK

Wet chemical etching is a fundamental process in the production of nanostructures on silicon wafers. It has been found that the addition of alcohols such as iso-propanol to an aqueous KOH etchant moderates the etching process, which improves the surface finish.@footnote 1@ In this study, we simulated the conditions at the silicon wafer/etchant interface inside ultra high vacuum (UHV) by the passivation of the Si(100)-2x1 with alcohols ((CH@sub 3@)@sub n@CH@sub 3-n@OH, n=1,2,3), such as ethanol, iso-propanol and tert-butyl alcohol, and post-exposure to H@sub 2@O. Vibrational spectra, taken with high resolution electron energy loss spectroscopy (HREELS), show that alcohol species chemisorb via a deprotonation of the OH group. The alkoxy species are bonded to the silicon dimer through a Si-O-C linkage. We found that post-exposure to H@sub 2@O does not result in a removal of alkoxy species but rather in an oxidation of the Si-Si bond of the silicon dimer. After prolonged H@sub 2@O exposure, 2x1 diffraction spots are absent in LEED. The findings will be compared with the reactivity of alcohols on hydroxylated Si(100)-2x1.@footnote 2@ @FootnoteText@ @footnote 1@ S. A. Campbell, K. Cooper, L. Dixon, R. Earwaker, S. N. Port and D. J. Schiffrin, J. of Micromech. and Microeng. 5, 209 (1995) @footnote 2@ T. Bitzer, N. V. Richardson and D. J. Schiffrin, Surf. Sci. Lett. 382, L686 (1997).

Electronic Materials and Processing Division
Room 611 - Session EM2-ThA

Silicon Carbide and Dielectrics on Si

Moderator: R.M. Feenstra, Carnegie Mellon University

2:00pm **EM2-ThA1 Silicon Carbide: Material of the 21st Century?***, **P.G. Soukiassian**,* Université de Paris-Sud/Orsay, France **INVITED**

Silicon carbide (SiC) is a refractory material belonging, with diamond and nitrides, to the wide band gap semiconductor class. SiC has a strong technological interest especially in high temperature, high speed, high voltage and high power semiconductor devices and sensors. Furthermore, rather inert chemically, its ability to resist to radiation damages makes SiC very suitable for hostile environments. In addition, SiC has very interesting mechanical properties and is one of the best biocompatible material. These exceptional properties are driving forces into the present fast growing interest in surfaces and interfaces of this advanced material. The surfaces and interfaces of cubic and hexagonal SiC are investigated by atom-resolved variable temperature scanning tunneling microscopy and spectroscopy and photoemission spectroscopies using synchrotron radiation.@footnote 1-3@ Such important issues as the atomic scale self-propagated surface oxidation and SiO2/SiC initial interface formation will be addressed.@footnote 4,5@ In addition, the discovery of highly stable self-organized Si and C atomic lines having fascinating characteristics and their dynamics will also be described.@footnote 6,7@ The Si nanostructure number and spacing could be mediated by annealing time and temperature leading to ordering ranging from a single isolated Si atomic line to large superlattices of "massively parallel" atomic chains.@footnote 6@ One discovers also a sp to sp3 temperature-controlled diamond-like transformation which could potentially be usefull in diamond growth.@footnote 7@ All these characteristics are unprecedented and show a very novel and interesting aspect of SiC in its ability to also be a very suitable material in nanoscience. @FootnoteText@ @footnote 1@F. Semond, P. Soukiassian, A. Mayne, G. Dujardin, L.Douillard and C. Jaussaud, Phys. Rev. Lett. 77, 2013 (1996). @Footnote 2@P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli and C. Joachim, Phys. Rev. Lett. 78, 907 (1997). @Footnote 3@V.Yu. Aristov, L. Douillard, O. Fauchoux and P. Soukiassian, Phys. Rev. Lett. 79, 3700 (1997). @Footnote 4@A. Mayne, F. Semond, G. Dujardin and P. Soukiassian, Phys. Rev. B 57, Rap. Comm., R 15108 (1998). @Footnote 5@F. Semond, L. Douillard, P. Soukiassian, D. Dunham, F. Amy and S. Rivillon, Appl. Phys. Lett. 68, 2144 (1996). @Footnote 6@P. Soukiassian, F. Semond, A. Mayne and G. Dujardin, Phys. Rev. Lett. 79, 2498 (1997). @footnote 7@V. Derycke, P. Soukiassian, A. Mayne, G. Dujardin and J. Gautier, Phys. Rev. Lett. 81, 5868 (1998).

2:40pm **EM2-ThA3 Characterization of PECVD SiC and its Application in Advanced Reticle Technology-SCALPEL Membrane***, **S. Han**, W.J. Dauksher, P.J.S. Mangat, K.D. Cummings, S.M. Smith,* Motorola, Inc.

The material which forms thin membrane layer (1000@Ao@) in Scattering with Angular Limitation Projection Electron Beam Lithography (SCALPEL) mask technology should satisfy a handful of rigid requirements such as stress controllability, high mechanical stiffness and good chemical etch resistance for wet processing. We have demonstrated that amorphous PECVD SiC can be an excellent choice of material that satisfies the criteria above. SiC potentially could be a better candidate for the membrane layer than silicon nitride, which is currently recommended. Furthermore, it has the possibility of better membrane yield and improved image placement because the elastic modulus for SiC is almost twice that for silicon nitride. Amorphous SiC films were prepared by PECVD using SiH4 and CH4 chemistries. The as-deposited intrinsic stress can be varied from mid-compressive to weak tensile depending on the deposition conditions. Furthermore, we have shown that the magnitude and sign of the as-deposited stress in the film can be modulated by RTA anneal cycle. Stress level in the films can be modified to our level of interest (about 1e9 dynes/cm2 tensile.) In addition, the etch resistance in KOH etchant, an important criteria, is improved after the post annealing cycle. This is associated with hydrogen evolution during the annealing, which reduces the density of hydrogen bonds with C and Si. Results will include the yield impact of controlling stress on the membrane by deposition conditions or by post annealing. In addition, characterization results of films using FTIR and RBS for hydrogen bonding and atomic ratio, respectively will be included. In summary, this paper addresses comprehensive information on a uniform, low stress PECVD SiC that can be used as a membrane material for SCALPEL mask technology.

3:00pm **EM2-ThA4 Contact Properties of Cerium Ultrathin Film on SiC***, W.J. Lu, D.T. Shi, **T. Crenshaw**, A. Burger, W.E. Collins,* Fisk University

Cerium (Ce) is well known as an excellent catalyst for NO@sub x@ conversion in environmental and automobile exhaust gas control. It has a strong adsorption capability for oxygen containing gases. Ce/SiC has a great potential as a chemical sensing materials for NO@sub x@ which can be operated at high temperature. To the best of our knowledge, the electrical contact properties of Ce/SiC on SiC have not been reported. In this work, the morphology and interfacial composition of Ce ultra-thin films on 6H-SiC and 4H-SiC are investigated after thermal annealing using atomic force microscopy and X-ray photoelectron spectroscopy. The Ce ultra-thin films of about 3 nm thickness are deposited by RF sputtering. The samples are annealed at the evaluated temperatures for 30 minutes in air. The Ce ultra-thin film on 6H-SiC and 4H-SiC has a good uniformity as deposited, and there are no significant morphological changes for both samples after annealing. The Ce on SiC contact is a Schottky contact, and the Schottky barrier heights for Ce/6H-SiC and Ce/4H-SiC as deposited are 1.43 eV and 1.77 eV, respectively. The Ce film is oxidized to be a Ce oxide film after thermal annealing in air. The morphology and the interfacial compositions after annealing will be presented. Key Words: SiC, Ce, AFM, XPS, and Schottky barrier height.

3:20pm **EM2-ThA5 A Thermodynamic Analysis of Silicide and Carbide Formation and Stability of W, Co, V, and Zr Thin Films on Single-Crystal SiC***, **W.F. Seng**, M.J. Bozack, P.A. Barnes,* Auburn University*; S.A. Catledge, Y.K. Vohra,* University of Alabama at Birmingham

Electronic devices capable of operation at elevated temperatures require understanding of the chemical reactions which occur at the metal-semiconductor interface. Phases predicted from equilibrium thermodynamics are presented in the forms of both Ellingham and Gibbs ternary diagrams to understand the temperature sequence of silicide and carbide formation and stability of the phases formed at the metal-SiC interface. W, Co, V, and Zr were deposited on single-crystal SiC by electron-beam deposition and annealed to temperatures approaching 1000 C. Resulting phases were identified by AES, XPS, and XRD and compared to the phases predicted by thermodynamic analysis. Limitations of the thermodynamic approach are also discussed.

3:40pm **EM2-ThA6 Deposition of Yttrium Oxide by Yttrium Sputter/Thermal Oxidation and Reactive Sputtering for Advanced High k Gate Dielectrics***, **J.J. Chambers**, G.N. Parsons,* North Carolina State University

The advent of 50nm MOSFET devices will require an equivalent SiO@sub 2@ thickness (t@sub ox,eq@) of 10Å. Direct tunneling through SiO@sub 2@ becomes problematic below about 15Å. To maintain low tunneling, the gate thickness must be >15Å, which requires an insulator with k>3.9. We form yttrium oxide on Si by: 1) yttrium sputtering followed by thermal oxidation; and 2) reactive sputtering of yttrium. Conditions for the sputter/thermal oxidation process were yttrium sputter in 4.3mTorr Ar at 25°C then ex-situ furnace oxidation in 1 atm N@sub 2@/O@sub 2@ at 900°C. Conditions for reactive sputtering of yttrium were 4.3mTorr, 25-500°C and an Ar/N@sub 2@O flow ratio of 0.5. Infrared absorption peaks from 400-600cm@super -1@ are present in the FTIR transmission spectra of the sputter/thermal oxidation and reactive sputtered films. These peaks are consistent with the 467, 562 and 698cm@super -1@ absorption peaks present in the spectrum of a 99.9% pure Y@sub 2@O@sub 3@ standard. CV and IV electrical measurements have been performed on films from both processes. Leakage current at 2V of 0.1µA/cm@super 2@ has been measured for sputter/thermal oxidation (t@sub ox,eq@=50Å) and reactive sputtered (t@sub ox,eq@=100Å) films. Using optical thickness measured with spectroscopic ellipsometry, effective dielectric constants are approximately 8.0 for films from both processes. Bulk Y@sub 2@O@sub 3@ has k=14-17, which suggests that the films described here have a reduced k in their thin film form, some yttrium silicate formation and/or an underlying SiO@sub 2@ layer. Under some deposition conditions, inert gas annealing increased inversion capacitance in the CV trace, possibly due to interfacial silicide formation. We will discuss the affects of pre-deposition N@sub 2@ and N@sub 2@O plasma surface treatments on the electrical properties of these films. The chemical and structural changes upon annealing will be investigated using XPS, AFM and RHEED.

4:00pm **EM2-ThA7 Bi@sub 4@Ti@sub 3@O@sub 12@ Ferroelectric Thin Films Deposited on Silicon by Pulse Injection Metal-Organic Chemical Vapor Deposition***, **S.K. Lee**, H.J. Kim,* Seoul National University, Korea

Bi@sub 4@Ti@sub 3@O@sub 12@ is one of the well-known bismuth-based layered perovskite materials. This compound has attracted much attention because of its characteristic anisotropic property. Especially, the low coercive field along c-axis, about 3.5 kV/cm, has made Bi@sub 4@Ti@sub 3@O@sub 12@ thin film a very promising gate dielectric for a ferroelectric field effect memory device. For this application, ferroelectric thin film has to be fabricated at low temperature in order to keep the abrupt interface with the semiconductor substrate and the composition of the film has to be uniform. By these requirements, metal-organic chemical vapor deposition (MOCVD) was taken as the fabrication method of Bi@sub 4@Ti@sub 3@O@sub 12@ thin film on p-type (100) silicon substrate. Solid Bi(C@sub 6@H@sub 5@)@sub 3@ and liquid Ti(OC@sub 3@H@sub 7@)@sub 4@ were chosen as precursors of bismuth and titanium, respectively, because of their good stability and complete decomposition ability. However, the great difference in formation kinetics of TiO@sub 2@ and Bi@sub 2@O@sub 3@ made it very difficult to control the Bi@sub 4@Ti@sub 3@O@sub 12@ /Si interface and the film composition. In order to overcome this problem, pulse injection method was introduced, in which input precursors were varied periodically during deposition for compensating the lower reactivity of Bi(C@sub 6@H@sub 5@)@sub 3@ with oxygen. By this pulse injection method, abrupt Bi@sub 4@Ti@sub 3@O@sub 12@ /Si interface was attained and the composition of Bi@sub 4@Ti@sub 3@O@sub 12@ thin film was also very uniform. The properties of Bi@sub 4@Ti@sub 3@O@sub 12@ thin films were strongly dependent on the substrate temperature and pulse injection conditions.

4:20pm **EM2-ThA8 Film-Formation Mechanisms and Step Coverage of (Ba,Sr)TiO@sub 3@ Films Grown by MOCVD***, **Y. Gao**, T.T. Tran, S. Thevuthasan, M.H. Engelhard,* Pacific Northwest National Laboratory*; P. Alluri,* Motorola, Inc.

Isotopic labeling experiments (@super 18@O@sub 2@) have been carried out to understand the film-formation reactions in the MOCVD growth of (Ba,Sr)TiO@sub 3@ (BST) thin films using Ba(thd)@sub 2@, Sr(thd)@sub 2@, and Ti(O-iPr)@sub 2@(thd)@sub 2@ as the metalorganic precursors. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) reveals both M@super 18@O and M@super 16@O (M= Ba, Sr, Ti) in the BST films, indicating that the oxygen in the BST films originates from both the gas phase oxidants (@super 18@O), and the precursor ligands (@super 16@O). The amount of @super 18@O and @super 16@O in these films was also determined by nuclear reaction analysis (NRA). The results are in agreement with the TOF-SIMS data. Thus, the isotopic labeling study reveals two film-formation reactions: oxidation and thermal decomposition of the precursor molecules during the MOCVD growth. The results show that about two thirds of M-O bonds in the original precursors are preserved in the BST films grown at 650 °C in O@sub 2@. However, more precursor molecules are oxidized by O@sub 2@ at 590 °C, indicating that the ligand substitution by O@sub 2@ plays an important role in the film-formation at lower temperatures. Use of a 50%@super 18@O@sub 2@-50%N@sub 2@@super 16@O mixture results in a reduction of @super 18@O incorporation in the BST film, indicative direct involvement of N@sub 2@O in the film-formation reactions. Addition of N@sub 2@O in O@sub 2@ also appears to improve film surface morphology and step coverage. The BST films deposited at 650 °C in the 50%O@sub 2@-50%N@sub 2@O mixture exhibit conformal step coverage, excellent crystallinity, and good dielectric properties. The correlation between the film-formation mechanisms, step coverage, crystallinity, and dielectric properties will be discussed in this presentation.

4:40pm **EM2-ThA9 Anhydrous Zirconium (IV) Nitrate as a CVD Precursor for ZrO@sub 2@***, R. Smith, N. Hoelien, C. Taylor, T. Ma, S. Campbell, W.L. Gladfelter, **J.T. Roberts**,* University of Minnesota*; M. Copel, D.A. Buchanan,* IBM T.J. Watson Research Center*; M. Gribelyuk,* IBM

We report the chemical vapor deposition (CVD) of ZrO@sub 2@ from the anhydrous metal nitrate, zirconium (IV) nitrate [Zr(NO@sub 3@)@sub 4@]. Zirconia films were deposited onto 100-oriented Si substrates using thermal CVD methods. Measurements of the ZrO@sub 2@ growth kinetics imply an exceedingly low barrier for ZrO@sub 2@ nucleation on a Si(100) surface, as there was essentially no induction period between the onset of CVD and the achievement of steady-state growth. The films were extensively characterized with respect to their suitability as high dielectric constant materials in advanced microelectronic devices. Ion beam methods (Rutherford backscattering, RBS, and medium energy ion scattering spectroscopy, MEIS) suggested that the films were close to the ideal stoichiometry or slightly oxygen-rich. X-Ray diffraction established that most films were monoclinic ZrO@sub 2@. Cross-sectional transmission electron microscopy (TEM) and MEIS measurements showed that the Si-ZrO@sub 2@ interface consists of a 10-15Å thick interlayerof nearly pure SiO@sub 2@. Finally, electrical characterization measurements established low leakage current densitites across the Si-ZrO@sub 2@ interface. This study adds to a growing body of work on the usefulness of volatile, anhydrous metal nitrates as precursors for high electrical quality metal oxide materials.

5:00pm **EM2-ThA10 A New Approach for the Fabrication of Device-Quality Ge/GeO@sub 2@/SiO@sub 2@ Interfaces Using Low Temperature Remote Plasma Processing***, **R.S. Johnson**, H. Niimi, G. Lucovsky,* North Carolina State University

It has been shown that low temperature (300°C) remote plasma enhanced processing can separately and independently control interface formation and bulk oxide deposition on silicon substrates. Plasma processing is followed by a low thermal budget thermal anneal, e.g., 30 s at 900°C. This process has been used for the formation of the device-quality gate dielectrics in both NMOS and PMOS devices. In the new results reported in this paper, this process has been modified and applied to germanium substrates to determine if it can provide a successful pathway to device-quality Ge-dielectric interfaces. The new process is similar low temperature (300°C) three-step process consisting of (i) an O@sub 2@/He plasma-assisted oxidation of the Ge surface to form a superficial germanium-oxide passivating film, (ii) deposition of a SiO@sub 2@ bulk film by remote plasma-enhanced CVD from SiH@sub 4@ and O@sub 2@, and (iii) a post-oxide deposition anneal for chemical and structural relaxation. We track the initial stages of the plasma-assisted oxidation of the germanium substrate using on-line Auger Electron Spectroscopy (AES). We then discuss why the O@sub 2@ /He plasma oxidation is critical for prevention of "subcutaneous" oxidation of GeO@sub 2@ -Ge interface during the deposition step. As in the case of Si deives, the oxidation step is required for formation of a device quality interface.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-ThA

Nanotubes: Functionalization and Metrology

Moderator: D. Herr, Semiconductor Research Corporation

2:00pm **NT+NS+EM+MS-ThA1 Opportunities and Challenges for Nanotubes in Future Integrated Circuits***, **R.R. Doering**,* Texas Instruments **INVITED**

We speculate about a few potential research opportunities that may be of mutual interest to both the microelectronics and nanotube communities. Perhaps the most evolutionary use of nanotubes in integrated circuits would be in the form of "thin films." Such use would capitalize on "bulk" material properties. For example, a layer of nanotubes (with "best metallic" conductivity) might serve as an interconnect film. Alternatively, an insulating nanotube layer (e.g, "modified" CNTs or other tube chemistries) might be used as a low-K dielectric. Even lower K might be achieved by using high-conductivity CNTs as "self-supporting wires," taking advantage of their inherent mechanical strength to eliminate the need for solid insulating layers. Another type of evolutionary use might involve nanotube structures for passive IC components. For example, the huge volume density of surface area looks appealing for DRAM capacitors. A significant amount of current nanotube research is aimed at active devices, which might ultimately replace today's silicon semiconductor switches. One of the most exciting prospects is the potential for more extensive and effective use of the "third-dimension" in integrated circuits. However, as with today's "planar" IC technology, the benefit/cost of "going 3D" will depend on details of the practical fabrication techniques. For nanotubes, this brings up "formation/place/route" issues. Nanotubes may also play a role in future "atomically perfect manufacturing," which may be needed to scale much below about 50-nm features regardless of the type of device technology employed.

3:00pm **NT+NS+EM+MS-ThA4 Simulations of Plasticity and Kink Catalyzed Functionalization of C and BN Nanotubes***, **D. Srivastava**,* NASA Ames Research Center*; M. Menon,* University of Kentucky

Routes to plasticity and kink catalyzed chemistry for functinlaization of C and BN nanotubes are investigated via classical molecular dynamics (MD) and generalized tight-bonding quantum molecular dynamics (QMD) methods. The critical strain for plasticity of BN nanotube is found to be more than that for the similar C nanotube. The structural collapse of nanotubes under compression is explored in which we find that the accumulated strain drives the tube in a plastic deformation in which four-fold coordinated tetrahedral bonds form at the location of the collapse. This lowers the elastic limit of compressed nanotubes to much less than what was predicted earlier with classical MD potential methods alone.@footnote 1@ The critical stress needed for this transition, as computed with QMD method, is in good agreement with experimental values observed for compressed nanotubes in polymer composites and graphite to diamond like transition in a bucky-onion pressure cell. Mechanical kink driven side-wall functionalization of C and BN nanotubes is also explored. We find that mechanical twisting and bending of the tube enhances the binding energy (and lowers the cohesive energy) at kink or edge sites by 1-2 eV as compared to the reactivity of undeformed tubes. Highly localized selective functionalization and etching of sidewalls could thus be possible through kink catalyzed chemical reactivity of nanotubes. A preliminary example of the experimental evidence will be shown.@footnote 2@ @FootnoteText@ @footnote 1@D. Srivastava, M. Menon, and K. Cho, submitted (1999). @footnote 2@D. Srivastava, D. W. Brenner, J. D. Schall, K. D. Ausman, M. F. Yu and R. S. Ruoff, to appear J. Phys. Chem. (1999).

3:20pm **NT+NS+EM+MS-ThA5 Nanoindentation and Nanotribology with Carbon Nanotubes***, B. Ni, A. Garg, **S.B. Sinnott**,* University of Kentucky

The mechanisms by which carbon nanotubule (CNT) proximal probe tips deform during the nanometer-scale indentation and scratching of surfaces are explored using classical molecular dynamics simulations. The forces acting on the atoms in the simulations are calculated using a many-body, reactive bond-order potential for hydrocarbons. The results show that single-walled and multiwalled CNT tips indented against hydrogen-terminated diamond and graphene surfaces buckle and slip to relieve the applied stress. However, in the case of reactive surfaces, tip-surface adhesion occurs on contact that ultimately destroys the tubule. Furthermore, while shell-shell interactions have little effect on the deformation mechanisms, the multiwalled tubule is stiffer than comparably sized single-walled tubules. Finally, the way in which the deformation of these tubules changes during scratching of diamond and graphene surfaces will be discussed and the results compared to available experimental data. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

3:40pm **NT+NS+EM+MS-ThA6 Quantum Chemistry Study of Carbon Nanotube Fluorination***, **R.L. Jaffe**,* NASA Ames Research Center

Quantum chemistry calculations are carried out to characterize the products of fluorination reactions of C@sub 60@, C@sub 70@ and carbon nanotubes. The calculations utilize density functional theory with a widely used hybrid nonlocal functional (B3LYP-DFT). C@sub 60@ is known to readily undergo reaction with molecular fluorine to form C@sub 60@F@sub n@ with n<44. C@sub 60@F@sub 18@ and C@sub 60@F@sub 36@ are the predominate products. C@sub 70@ also is known to undergo similar reaction, but the products have not been completely characterized. Less is known about the possibility of fluorinating nanotubes. However, it has been conjectured that highly fluorinated nanotubes may have attractive chemical and dielectric properties. Fluorination of C@sub 60@ and C@sub 70@ is used to benchmark the calculations for nanotubes. Previous studies have demonstrated that polycyclic aromatic hydrocarbons with an externally constrained curvature are good model molecules for studying the functionalization reactions of single-walled carbon nanotubes. Reaction is likely if the products are energetically stable and any activation energy barriers are small. Initial studies for C@sub 60@ and (10,10) nanotubes have shown that the difluoronated products are quite stable and the fluorination reaction is highly exothermic.

4:00pm **NT+NS+EM+MS-ThA7 Gear-like Rolling Motion of Carbon Nanotubes on HOPG***, **M.R. Falvo**, J. Steele, A. Buldum,* University of North Carolina, Chapel Hill*; D. Schall,* North Carolina State University*; R.M. Taylor II,* University of North Carolina, Chapel Hill*; D.W. Brenner,* North Carolina State University*; J. Lu, R. Superfine,* University of North Carolina, Chapel Hill

Though much work has been done in recent years in exploring nanometer and atomic scale sliding friction, little experimental or theoretical work has been done on rolling and its relation to sliding at this scale. We will present lateral force microscope investigations of frictional phenomena of multiwall carbon nanotubes (MWCNTs) on highly oriented pyrolytic graphite (HOPG), that include all the rigid body motions: sliding, rotating in-plane, and rolling. Using an advanced manipulation interface for AFMs, the nanoManipulator, we study these friction phenomena through sophisticated manipulation experiments where lateral forces are monitored during manipulations. We have manipulated MWCNTs into a state of atomic registry between the lattice of the tube and underlying substrate. Out of atomic registry the friction is smooth and uniform. As the CNT is rotated in the plane of the substrate, three discrete atomically registered orientations are observed marked by a 3-10 fold increase in the lateral force required to remove them from these orientations. Results of molecular statics calculations for this system show that the potential energy as a function of in-plane rotation angle has three deep minima spaced sixty degrees apart corresponding to atomic lattice registry. When the CNT locks into atomic registry, there is a transition from an in-plane rotational motion to a stick-slip rolling motion. Rather than being perfectly cylindrical, our lateral force data during rolling indicate that the CNT may be faceted (polygonal cross section). MS calculations indicate that faceting is to be expected for MWCNT depending on diameter and wall thickness. The calculated friction expected for rolling a faceted MWCNT agrees well with experimental lateral force data. Molecular dynamics calculations will be shown that lend insight into the energy loss mechanisms for both the sliding and rolling case. This work is supported by the NIH (NCRR), NSF, ONR (MURI), and ARO (DURIP).

4:20pm **NT+NS+EM+MS-ThA8 Selectivity and Diffusion of Binary Fluids in Carbon Nanotubes***, **Z. Mao**, S.B. Sinnott,* University of Kentucky

Carbon nanotube bundles have been proposed as good materials for the manufacture of tailored ultrafiltration membranes due to their uniform, porous structure. In contrast to conventional membranes produced by only partially sintering a ceramic or stretching a polymer, a nanotube membrane would offer the advantages of fewer blocked pores and a narrower distribution of pore sizes. To investigate the properties of a nanotube membrane, the adsorption of simple binary fluids within single tubules and tubule bundles are modeled using atomistic simulations. Specifically, classical molecular dynamics simulations are performed using a combined many-body, reactive bond-order and Lennard-Jones potential. The results show how the diffusion of these molecules proceeds at differing rates within the nanotubes as a function of the diameter and helical structure of the tubules, the density of the fluid, the size difference between the molecules, and temperature. An example of a binary fluid that has been studied is a mixture of CH@sub 4@ and C@sub 4@H@sub 10@ at room temperature. The simulations predict high selectivity in the diffusion of these molecules through the nanotubes. They also allow for the determination of the type of diffusion followed by each type of fluid molecule. Comparisons will be made between these simulation results and the results of similar studies in the literature of diffusion in zeolites and other molecular sieves. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

4:40pm **NT+NS+EM+MS-ThA9 Improved Tungsten Disulfide Nanotubes as Tips for Scanning Probe Microscopy*, A. Rothschild*,** *G. Frey, M. Homyonfer, M. Rappaport, S.R. Cohen, R. Tenne,* Weizmann Institute of Science, Israel

Synthesis and applications of long and hollow WS@sub 2@ nanotubes are described. Although synthesis of nanotubes from various inorganic compounds have been reported, the high yields of uncontaminated nanotubes reported here represents a significant improvement over past efforts by ourselves and others.@footnote 1@,@footnote 2@ The nanotubes are synthesized in a two-step process the first being the creation of WO@sub 3@ nanoparticles by heating a tungsten filament in the controlled presence of water. The second step, sulfidization, resulted in a 30 times increase in the length of these particles without change in width so that nanotubes up to 10 microns in length and 20-40 nm width were formed. These tubes were attached to scanning force microscope (SFM) tips and used to image deep and sharp features inaccessible by sharp silicon tips. Due to their sandwich S-W-S structure, these nanotubes are probably stiffer than the carbon analogs and hence less prone to instabilities under such rigorous scanning conditions. We propose application of these probes for nanophotolithography, aided by the facile excitation of these compounds by visible and infra-red light. Support by the Israel Ministry of Science, Israel Science Foundation, and Applied Materials-Weizmann Foundation are gratefully acknowledged. A.R. is a recipient of the Lavoisier fellowship (France). @FootnoteText@ @footnote 1@ Y. Feldman, E. Wasserman, D.J. Srolovitz, R. Tenne, Science 267, 222 (1995). @footnote 2@ N.G. Chopra, et al, Science 269, 966 (1995).

Surface Science Division
Room 606 - Session SS1+EM+NS-ThA
Metal/Metal Growth

Moderator: R.Q. Hwang, Sandia National Laboratories

2:00pm **SS1+EM+NS-ThA1 Dislocation Structures of Submonolayer Films near the Commensurate-Incommensurate Phase Transition: Ag on Pt(111)*, J.C. Hamilton*,** *R. Stumpf,* Sandia National Laboratories*; K. Bromann, M. Giovannini, K. Kern, H. Brune,* EPF Lausaane, Switzerland

We provide a theoretical explanation@footnote 1@ for unusual experimental observations@footnote 2@ of submonolayer Ag film growth on Pt(111). These films exhibit parallel partial dislocations with narrow hcp regions separated by much wider fcc domains. Using a 2D Frenkel-Kontorova (FK) model we show that this unusually large difference is primarily due to proximity to the commensurate-incommensurate phase transition, and only secondarily to stacking fault energies. We next consider the relationship between island energy, island dislocation structure, and island shape. Using the FK model we calculate the stability of islands with no dislocations, a single dislocation pair across the island, two parallel dislocation pairs across the island, and a "Y" shaped dislocation structure. The model is in excellent agreement with experiment in predicting the onset of dislocation structures in growing islands. It also suggests that the dislocations have little or no effect on the equilibrium island shape. Finally we discuss the relationship between these calculations and related experiments@footnote 3@ on the structure of the clean Pt(111) surface which reconstructs above 65% of the melting point. @FootnoteText@ @footnote 1@ J. C. Hamilton, R. Stumpf, Karsten Bromann, Marcella Giovannini, Klaus Kern and Harald Brune, Phys. Rev. Lett., in press@footnote 2@ Karsten Bromann, Harald Brune, Marcella Giovannini, and Klaus Kern, Surf. Sci. V388, L1107 (1997). @footnote 3@ A. R. Sandy, S.G.J. Mochrie, D.M. Zehner, G. Grubel, K.G. Huang and Doon Gibbs, Phys. Rev. Lett. 68, 2192 (1992).

2:20pm **SS1+EM+NS-ThA2 Non Capillarity Driven Grain Growth in a Strained Cu Ultrathin Film*, A.K. Schmid*,** *T. Giessel, N.C. Bartelt, J. de la Figuera, R.Q. Hwang,* Sandia National Laboratories

Properties of metal films are crucially influenced by details of their grain structure. To determine basic mechanisms of grain evolution we have investigated a prototypical granular thin film using LEEM and STM. In two monolayer thick films of Cu on Ru(0001) a uniaxial relaxation relieves the misfit strain (5.5%) with the substrate, leading to a two-dimensional grain structure consisting of three orientationally different domain types. We observed in-situ grain growth using LEEM in dark field imaging mode and took STM snap shots at several stages of the grain evolution. While on large scale of both time and area the total length of grain boundary decreases in order to reduce the free energy of the system an increase of boundary length has been observed locally and on smaller time scale. The observed behavior can not be described within the framework of a Q-state Potts model which has been widely used for the description of grain growth. We show that the long-ranged lateral interactions between the surface atoms in the strained Cu film which are not considered in Potts model are responsible for the observed behavior.

2:40pm **SS1+EM+NS-ThA3 Exchange Processes in Metal on Metal Growth Studied with High-resolution STM*, M. Schmid,*** Technische Universitaet Wien, Austria **INVITED**

In the early 1990's, after the first atomic-scale studies by field ion microscopy and related simulation calculations it became apparent that many processes in growth of thin films involve exchange of substrate and deposited atoms. It was concluded that interlayer diffusion at steps, the key process determining the growth mode, often occurs by replacing a substrate atom with a deposited atom, pushing the substrate atom onto the lower terrace. A new way to study such phenomena is scanning tunneling microscopy (STM) with atomic resolution and chemical contrast@footnote 1@. We have deposited a small amount of Co on a Pt(111) surface with a high density of steps. In the resulting structure, we can distinguish between substrate (Pt) and deposited material (Co) on an atom-by-atom basis. An analysis of the STM data shows that Co atoms do not descend Pt steps by diffusing over the step, but descend from the upper terrace to the lower by an exchange diffusion process at the step edge with the Pt atoms. The Co atoms descend a Pt step edge by this process neither at straight A nor at B steps, but rather at the corners or kinks of the vacancy islands. These results are in qualitative agreement with simulations based on embedded atom method (EAM) potentials. Other examples of exchange processes can lead to subsurface growth of the deposited material, with substrate atoms floating on top of it. Such phenomena were observed to occur already at or near room temperature when Co was deposited on the Pt(111) and Pt(110) surfaces. @FootnoteText@ @footnote 1@ E. Lundgren, B. Stanka, G. Leonardelli, M. Schmid, and P. Varga, Phys. Rev. Lett., accepted.

3:20pm **SS1+EM+NS-ThA5 Self-diffusion on Pt(110)-1x2: Ab-initio Barriers vs. Experiment@footnote 1@*, P.J. Feibelman,*** Sandia National Laboratories

Because it requires breaking more bonds, dimer diffusion by dissociation and recombination on clean Pt(110)-1x2 should cost more energy than the recently discovered@footnote 2@ "leapfrog" mechanism. Since cohesion per bond decreases with increasing coordination, the leapfrog mode should also have a lower barrier than monomer diffusion. Though first-principles calculations confirm these deductions, they are at odds with experiment, possibly signalling the influence of low-level surface contamination. @FootnoteText@ @footnote 1@ Work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy @footnote 2@ T.R. Linderoth, et al., Phys. Rev. Lett. 82, 1494(1999); F. Montalenti and R. Ferrando, Phys. Rev. Lett. 82, 1498(1999).

3:40pm **SS1+EM+NS-ThA6 Novel Temperature Dependence of the Morphology of Deposited Multilayer Ag/Ag(100) Films*, C.R. Stoldt*,** *A.R. Layson, C.J. Jenks,* Iowa State University*; M.C. Bartelt,* Sandia National Laboratories*; K. Caspersen, J.W. Evans, P.A. Thiel,* Iowa State University

Metal(100) homoepitaxy provides a natural testing ground for recently developed ideas on kinetic roughening and "mound formation" due to step-edge barriers. Non-monotonic variation of roughness with deposition temperature (T) has been predicted,@footnote 1@ but not observed. Here, we report comprehensive VT-STM studies for growth of Ag/Ag(100) films between 130K and 300K which reveal this behavior. Roughness of 25ML Ag/Ag(100) films at first increases "classically" below 300K due to inhibited downward transport, but then decreases below 220K, achieving a low plateau value below 170K. Unlike Pt/Pt(111) and Rh/Rh(111) growth, non-monotonic behavior is not associated with a dramatic change in 2D island morphology, but rather with enhanced downward funneling from (the more prevalent) step edges at lower T. We also characterize the mound morphology, noting the steepness of the mound sides and small lateral dimension at lower T. A breakdown of kinematic scattering behavior of the intensities observed in our HRLEED studies of these films is attributed to this feature. Monte Carlo simulations of a realistic model for growth@footnote 1@ are consistent with and elucidate observed behavior. @FootnoteText@ @footnote 1@M.C. Bartelt and J.W. Evans, Surf. Sci. 423 (98) 189; Phys. Rev. Lett. 75 (95) 4250.

4:00pm **SS1+EM+NS-ThA7 Edge Diffusion During Growth: Kink Ehrlich-Schwoebel Effect and Resulting Instabilities@footnote 1@***, O. Pierre-Louis,* Univ. J. Fourier (CNRS), France*; **T.L. Einstein,*** University of Maryland

In addition to the usual step Ehrlich-Schwoebel effect (SESE) on typical metal and semiconductor surfaces, there can also be a kink Ehrlich-Schwoebel effect (KESE), associated with asymmetries in barriers at kinks/corners encountered by atoms during transport along step edges.@footnote 2@ We take into account both phenomena to study the evolution of arbitrarily oriented surfaces during molecular beam epitaxy. We find that the heretofore rarely discussed@footnote 3@ KESE has a profound effect on growth morphology. Under the usual growth conditions, KESE induces a new instability of vicinal surfaces, supplanting the familiar Bales-Zangwill instability@footnote 4@ due exclusively to SESE. The possibility of stable kink flow growth is analyzed; fluctuations can shift the stability threshold. For some orientations, KESE can stabilize steps. KESE can also induce mound formation. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@ O. Pierre-Louis, M. R. D'Orsogna, and T. L. Einstein, Phys. Rev. Lett. 82 (1999) 3661; note also M. V. Ramana Murty and B. H. Cooper, preprint. @footnote 3@ See, however, I. L. Aleiner and R. A. Suris, Sov. Phys. Solid State 34 (1992) 809; Z. Zhang and M. G. Lagally, Science 276 (1997) 377; J. G. Amar, Bull. Am. Phys. Soc. 43 (1998) 851 and to be published. @footnote 4@ G.S. Bales and A. Zangwill, Phys. Rev. B 41 (1990) 5500.

4:20pm **SS1+EM+NS-ThA8 Atom-by-Atom Growth: Bonding and Rebonding on Metal Surfaces***, **A. Bogicevic,*** Sandia National Laboratories

The bond-order--bond-length concept put forth by Pauling almost 70 years ago has greatly added to our intuitive understanding of atomic-scale bonding in molecules. The basic idea is that the more bonds an atom makes, the weaker and longer each becomes [rebonding]. This concept has been extensively tested, and is routinely used in molecular chemistry today, so one would assume that a similar model for the gas-surface interface would prove useful. In an early first-principles study of Al/Al(100), strong and observable rebonding effects were predicted. Unfortunately, these results are an artifact of some severe modelling compromises imposed by computational limitations. New, fully converged (160-180 atom unit-cells, 36 k-points), first-principles density-functional calculations for a wide variety of homogeneous and heterogeneous metal systems show that, contrary to rebonding theory, addimers (adsorbed atom pairs) do not have longer surface bonds than adatoms, do not reside farther above the surface, and do not meet the rebonding arguments for augmented mobility. Rebonding does contribute to destabilize addimers, but does not explain inherently weak adatom-adatom interactions. I explain the absence of rebonding effects in terms of elastic and electronic contributions to the rebonding energy, and present an alternative explanation for the adatom-adatom bond weakness based on bond frustration. Implications for nucleation and growth of metals will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Work at Sandia National Laboratories is supported by the U.S. Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

4:40pm **SS1+EM+NS-ThA9 Diffusion of Lead on the Au(111) Surface Studied by Scanning Tunneling Microscopy and Embedded-Atom Method Molecular Dynamics***, **M.C. Robinson,*** Trent University and Queen's University, Canada*; K. De'Bell,* University of New Brunswick in Saint John, Canada*; A.J. Slavin,* Trent University and Queen's University, Canada

Low coverages of Pb deposited on the reconstructed Au(111) surface have been studied with STM and show that the reconstruction strongly influences diffusion and film morphology. Nucleation sites for Pb adatoms are found at the kinks of the reconstruction. For higher coverages, Pb atoms concentrate in the fcc and hcp regions; the elevated transition regions are much less populated. The reconstruction is lifted for some coverage between 0.05 and 0.3 monolayers (ML). For comparison, the Embedded Atom Method-Molecular Dynamics (EAM-MD) method has been used to study diffusion of Pb on both the unreconstructed (flat) and reconstructed surfaces. EAM-MD simulations show that diffusion is complicated by the reconstruction. Using both static and dynamic methods, the diffusion energies have been determined. They show that, for an adatom moving perpendicular to the compression direction, the energy barrier is 1.7 times greater than for motion in the parallel direction. Diffusion is slowed on the fcc part of the reconstructed surface, as compared to the unreconstructed, by a factor of about 2. No greater coverage than 0.07 ML could be forced onto the EAM-modelled reconstructed surface. However, the flat surface could be fully covered, suggesting that the reconstruction is not energetically stable at higher coverages, as has been observed experimentally.

5:00pm **SS1+EM+NS-ThA10 Low Energy Electron Microscope Investigation of Pb Overlayers on Cu(100)***, **G.L. Kellogg,*** Sandia National Laboratories

Pb overlayers on Cu substrates provide a model system for investigating epitaxial films exhibiting large lattice misfits and for studying two-dimensional phase transitions (e.g., disordering and surface melting). On Cu(100), room-temperature deposition of Pb follows classical Stranski-Krastanov growth with three well-defined overlayer structures forming at submonolayer coverages.@footnote 1@ In this investigation, low energy electron microscopy (LEEM) is used to (1) characterize the changes that occur to these structures resulting from annealing to various temperatures and (2) monitor the subsequent growth of 3-D islands. The low-coverage c(4x4) and high-coverage c(5@sr@2x@sr@2)R45 phases, both of which consist of rotationally inequivalent domains, are observed to disorder at temperatures of 270C and 215C, respectively. By forming images using selected low energy electron diffraction beams (i.e., dark-field LEEM), the domain structure that forms upon cooling from above the transition temperature is imaged directly with a spatial resolution of ~10 nm. Dark-field LEEM is also used to characterize the c(4x4) - c(2x2) co-existence structure that forms upon desorption of excess Pb from the high-coverage phase. The growth of three-dimensional Pb islands on top of the high-coverage phase and the coarsening of these structures at temperatures from 100-150C are measured to derive fundamental energetic parameters involved in the melting of 3-D Pb clusters. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000 @FootnoteText@ @footnote 1@ J. Henrion and G. E. Rhead, Surface Sci. 29(1972)20.

Electronic Materials and Processing Division
Room 608 - Session EM-FrM
In Situ Monitoring and Growth

Moderator: C.R. Abernathy, University of Florida

8:20am **EM-FrM1 Optical Techniques for Real-Time Measurement of Stress and Morphology During Thin Film Growth***, **J.A. Floro,*** Sandia National Laboratories **INVITED**

Mechanisms for the generation and relaxation of stresses in thin films during deposition have been subject to extensive scientific research and technological tweaking. Stress evolution during film growth can be quite complex, and is best measured in real-time during the deposition process. The primary focus of this talk will be on the use of substrate curvature measurements, since this approach has the greatest degree of flexibility in its implementation. The use, limitations, and extensions of the Stoney equation, which relates substrate curvature to film stress, will be discussed. Methods for curvature measurement will be surveyed, with emphasis on a recently developed laser-deflection technique that is currently being applied to a wide range of thin film systems. I will present several instructive examples on the interpretation of real-time stress data obtained during the deposition of heteroepitaxial and polycrystalline thin films. Finally, a new spectroscopic light scattering technique will be introduced that provides real-time measurement of surface morphological evolution. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

9:00am **EM-FrM3 Insitu Surface Stress Measurements during Contact Reaction of Ultrathin Overlayers of Cobalt on Si(100) and Si(111)***, **J.G. Nivison**, D.G. Waters, P.A. Bennett,* Arizona State University

We report insitu measurements of surface stress during the contact reaction of 10 Angstrom overlayers of cobalt on Si(111) and Si(100) using an optical deflection wafer curvature technique. The instrument features a feedback stabilized reference beam, which removes thermal drift to first order, allowing temperature dependent measurements. For Si(100), the surface stress during room temperature dosing is +0.2 N/m per Ml (tensile), saturating at 8Ml. Upon annealing, the stress increases monotonically to +0.6 N/m at 200C, which is attributed to a partially coherent CoSi2 overlayer. For Si(111), the stress during room temperature dosing is +0.6 N/m for the first Ml, changing to -4.5 N/m at 5Ml coverage. Upon annealing, the stress increases to +4.0 N/m at 450C, which is attributed to a fully coherent CoSi2 overlayer.

9:20am **EM-FrM4 Vibration Analysis of SiH@sub n@ Bending Modes on Hydrogenated Si(100) Surface Using Infrared Reflection Absorption Spectroscopy***, **H. Noda**, T. Urisu,* Institute for Molecular Science, Japan*; M. Hiramatsu,* Meijo University, Japan

Detailed analyses have been successfully made for the SiH@sub n@ stretching vibration mode on hydrogenated Si(100) surface, which is of great scientific and technological interest.@footnote1@ However, concerning the bending vibration region, which gives important information about SiH@sub 2@ and SiH@sub 3@ species, very little work has been done. Recent developments of buried metal layer infrared reflection absorption spectroscopy (BML-IRRAS) have made the high-resolution vibration analysis of bending region easy. In this work, adsorption and desorption of hydrogen on Si(100) surfaces have been investigated by measuring BML-IRRAS covering a wide spectral range (800-2200 cm@super-1@). In both 3x1 and 1x1 phases observed with reflection high-energy electron diffraction (RHEED), a doublet peak (902 and 913 cm@super -1@) has been clearly observed and assigned to the SiH@sub 2@ scissors mode. The splitting of the peak is most likely due to the frequency difference of SiH@sub 2@ scissors vibration between single SiH@sub 2@ (ordered 3x1 units ; H-Si-Si-H H-Si-H H-Si-Si-H) and neighboring SiH@sub 2@ (disordered 3x1 units ; H-Si-Si-H H-Si-H H-Si-H H-Si-Si-H). Coverage and annealing temperature dependence of this doublet peak have also been investigated. @FootnoteText@ @footnote 1@ Y. J. Chabal and K. Raghavachari, Phys. Rev. Lett. 54 (1985) 1055.

9:40am **EM-FrM5 Assessment of Various Sensors for in-situ Monitoring and Control of MBE***, **K.G. Eyink**,* Air Force Research Laboratory

Molecular Beam Epitaxy is a technique, which has been used to grow semiconductor thin film structures. In this process reactants fluxes are incident onto a substrate held at an elevated temperature. Typically the structure is grown by an appropriate shuttering sequence that is based on extensive pre-calibration. In this talk I am going to discuss the use of several sensors to monitor MBE in real-time. A discussion of the advantages and disadvantages of the various techniques will be given. The utilities of ellipsometry, desorption mass spectrometry, and atomic absorption for in-situ targeting of composition and growth rates will be given. As well as the advantage of integrating absorption band edge spectroscopy into substrate temperature control and its coupling to the various other sensors.

10:00am **EM-FrM6 Integrated Real-time SE, RDS and QMS to Characterize and Optimize OMCVD Growth***, **K.A. Bell**, M. Ebert, S.D. Yoo, K. Flock, D.E. Aspnes,* North Carolina State University

We combine spectroscopic ellipsometry (SE) and reflectance-difference spectroscopy (RDS) in a single optical path with quadrupole mass spectrometry (QMS) on an OMCVD reactor to probe bulk and surface properties as well as ambient composition in real time during growth. This unique system enables us to characterize the complex parameter space of OMCVD and optimize growth conditions. Monitoring the optical response of the sample and gas phase species enables us to determine ideal growth parameters for our reactor and to characterize growth mechanisms. The optical spectrometer is a multichannel, parallel acquisition and processing system built around a commercial rotating-spindle OMCVD reactor and a custom photodiode array (PDA) detector that allows us to extract sample optical properties over a spectral range of 200 to 800 nm at a repetition rate of 2 Hz. Together with time-resolved QMS, we determine system-specific parameters necessary to calibrate temperature and characterize gas flow dynamics. The former has been done using reciprocal space analysis of SE data to extract sample critical point energies in real time with an accuracy of 0.5 meV corresponding to +/-1 degree in sample temperature. Monitoring the growth of GaP on Si(001) in real time, we observe a SE sensitivity to 0.1 Angstrom changes in thickness and a QMS sensitivity of 0.1% changes in ambient composition.

10:20am **EM-FrM7 Real-time Thickness and Compositional Control of Ga1-xInxP Growth using P-Polarized Reflectance***, **V. Woods**, K. Ito, I. Lauko, N. Dietz,* North Carolina State University

Advances in the engineering and design of advanced electro-optical materials require sensors and control strategies that allow tight control over thickness and composition. In response to this demand, we developed p-polarized reflectance (PR) as a real time optical characterization technique, and demonstrate its sensitivity during heteroepitaxial GaP/GaInP growth under pulsed chemical beam epitaxy (PCBE) conditions. For closed loop control, we applied nonlinear control algorithms (based on nonlinear Kalman filtering) that utilizes the PR signals to control thickness and composition during heteroepitaxial growth of GaxIn1-xP on Si (001). A reduced order surface kinetics (ROSK) model has been formulated to describe the decomposition process of organometallic precursors and the time-dependency of the molar concentrations of the precursors fragments. These data are linked to compute the composition and thickness increase per time unit, utilizing the monitored PR signal for validation. This allows to establish feedback control algorithms, able to control both the growth rate and composition of GaxIn1-xP heterostructures.

10:40am **EM-FrM8 Migration-Enhanced Epitaxy of CuInSe@sub 2@***, **B.J. Stanbery**, S. Kincal, S. Kim, O.D. Crisalle, T.J. Anderson,* University of Florida

We describe a novel rotating-disc MBE reactor that implements a Migration-Enhanced Epitaxy (MEE) process@footnote 1@ and its application to the growth of Copper Indium Selenide (CIS) on GaAs and ZnTe single-crystal substrates. MEE is a process variant of conventional MBE and one of a general class of Modulated-Flux Deposition (MFD) processes that are based on cyclic alternation between deposition and relaxation steps, and the separation of cationic and anionic species fluxes. All of these measures are intended to achieve long surface diffusion lengths and promote adatom/substrate equilibration. Our reactor is divided by carefully designed shielding into four nominally isolated zones: metals (Cu+In) deposition, cooling, chalcogen (Se,S) deposition and heating. The fixed substrate heater in the latter zone combined with the rotating-disc design results in cyclic heating and cooling of the substrates. The direction of substrate rotation can be reversed, enabling two different growth cycles. The cooling zone includes a source for dosing the substrates with dopants or surfactants. We will present the results of our molecular and thermal flux modeling and discuss their implications for surface growth kinetics in our reactor. We will also present XRD, AFM, Auger, SIMS and PL data characterizing our successful epitaxial growth by MEE of (001)CuInSe@sub 2@ on (001)GaAs and (001)ZnTe. Our data also shows phase segregation of

Cu@sub 2-X@Se in copper-rich epilayers and a relative loss of crystal quality in indium-rich epilayers. We will discuss the relevance of these results to our free-energy thermochemical defect model of the Cu-In-Se ternary system. We show that these data provide evidence of a transition from Stranski-Krastonov to Frank-Van de Merwe growth mode when the surface is dosed with small quantities of sodium fluoride during the initial stages of epitaxy on (001)ZnTe, supporting our thesis@footnote 2@ that sodium behaves as a surfactant in this material system. @FootnoteText@ @footnote 1@ Y. Horikoshi, M. Kawashima, and Y. Yamahuchi, Jap. J. Appl. Phys. 25, 1986, p. L868. @footnote 2@ B.J. Stanbery, C.-H. Chang, and T.J. Anderson, 11th International Conference on Ternary and Multinary Compounds, 1997, Inst. of Phys. Conf. Series 152, pp. 915-922.

11:00am **EM-FrM9 Boron Nitride Thin Films for High Temperature Multilayer Ceramic Capacitor Chips (MLC3's)***, **N. Badi**, D. Starikov, N. Medelci, I.E. Berishev, A. Bensaoula,* University of Houston

There is a great need for miniaturized, high power density, low cost capacitors that operate at high frequency and can sustain high operating temperatures. In our laboratory we are investigating the use of boron nitride (BN) based materials for such devices. Advantages of BN include high temperature and chemical resistance which should result in more compact, and reliable devices. We investigate here, the temperature stability of different multilayer capacitor heterostructures (e.g. TiN/BN/TiN/Si, Cu/BN/Cu/quartz, Cu/AlN/Si). To study the interdiffusion between the dielectric and the electrodes at elevated temperatures, we performed secondary ions mass spectroscopy (SIMS) on two structures: (I) TiN/B/BN/Si and (II) B/TiN/Si. In this manner we minimize ion mixing effects in determining the quality of the relevant interfaces (TiN/B/BN and B/TiN/Si) at annealing temperatures up to 500 °C. High resolution SEM pictures from TiN/BN/TiN/Si samples showed dense boron nitride layers with sharp interfaces. However Cu/AlN/Si structures showed copper diffusion into the silicon substrate due to the columnar structure of the single crystal AlN films. I-V measurements revealed the highly insulating properties of TiN/BN/TiN/Si capacitor. In fact a breakdown voltage (BDV) of 400 V/mm was measured for a 2000 Å BN thin layer. C-V measurements from a 3mm x 4 mm planar structure, show a capacitance value of 1.1 nF at 10 KHz and 1 Vrms. Furthermore the temperature dependence of C-V characteristics, dissipation factor, insulation resistance, and reliability of the ceramic capacitor will be presented. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Technology Program Grant # 1-1-32061, and the Ballistic Missile Defense Organization/Science and technology and managed by William Shoup from The DTRA/CPTI. @FootnoteText@ *A. Bensaoula email address: Bens@jetson.uh.edu.

11:20am **EM-FrM10 The Deposition of Polycrystalline Si and SiGe by Ultra-high Vacuum Chemical Vapor Deposition System***, **K.M. Chen**, H.J. Huang,* National Chiao Tung University, Taiwan, R.O.C.*; L.P. Chen, G.W. Huang,* National Nano Device Laboratory, Taiwan, R.O.C.*; C.Y. Chang,* National Chiao Tung University, Taiwan, R.O.C.

The polycrystalline Si@sub 1-x@Ge@sub x@ (poly-Si@sub 1-x@Ge@sub x@) films have better properties than poly-Si for device fabrications, such as lower transition temperature and process thermal budget. For these reasons, the poly-Si@sub 1-x@Ge@sub x@ films have been utilized for low-temperature TFT fabrications and gate electrodes of MOS transistors. In this work, disilane and germane were used to grow poly-Si@sub 1-x@Ge@sub x@ films at low temperature (0.1). This implies that the growth mechanism of poly-Si@sub 1-x@Ge@sub x@ films is different from that of epitaxial Si@sub 1-x@Ge@sub x@ on Si. The uniformity of poly-Si@sub 1-x@Ge@sub x@ films depends on the Ge content, and it is improved by the addition of germanium. The result can be explained by the lower activation energy (< 0.25 eV) related to deposition of poly-Si@sub 1-x@Ge@sub x@, as compared to that of poly-Si (~2.1eV) in the surface-reaction limited growth mode. From the XRD and AFM analyses, the crystallinity and roughness of films are suitable to device fabrications.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-FrM

Nanotubes: Growth, Characterization and Properties II

Moderator: R.L. Jaffe, NASA Ames Research Center

8:20am **NT+NS+EM+MS-FrM1 Gas-phase Nanotube Production at High Pressure By Disproportionation of Carbon Monoxide***, **P. Nikolaev**,* G. B. Tech Inc. / NASA - JSC*; M. Bronikowski, K. Bradley, D. Colbert, K. Smith, R.E. Smalley,* Rice University

Single-wall carbon nanotubes (SWNTs) were produced in gas phase, in a flow tube reactor in 3 - 15 atm. of CO at 850@super o@ - 1200@super o@C. Nanotube growth was catalyzed by unsupported iron particles created in-situ by decomposition of iron pentacarbonyl vapor which was added to the CO feedstock at a few ppm level. We find that low Fe(CO)@sub 5@ concentration combined with fast heating rate of feedstock gas allows us to produce very small iron particles, while high pressure increases the rate of CO disproportionation, leading to effective nucleation and growth of SWNTs. Unlike pyrolysis of hydrocarbons, CO disproportionation is a "clean" process which proceeds only on the catalyst surface, resulting in essentially no amorphous carbon overcoating. Diameter distribution of the SWNTs is rather narrow and depends on CO pressure. Higher CO pressures (10 atm.) yield smaller nanotubes, with distribution centered at 0.7 nm (which is roughly the size of C@sub 60@ molecule). Nanotube yield relative to the amount of iron catalyst increases as the heating rate and mixing of Fe(CO)@sub 5@ are enhanced, indicating better catalyst utilization. In order to further increase nanotube yield, we have designed a "shower head" injector, in which cold CO/Fe(CO)@sub 5@ feedstock enters furnace through water-cooled injector, surrounded by "shower head" carrying CO pre-heated to 1200@super o@. Nanotube yield is also increased by addition of small amount of methane, while more CH@sub 4@ results in amorphous overcoating on the nanotube surface. In contrast to previously reported SWNT production methods, this scheme constitutes a continuous flow gas phase SWNT production process. It should therefore be readily amenable to scale up for bulk SWNT production.

8:40am **NT+NS+EM+MS-FrM2 The Optical Properties of Carbon Nanotubes and Their Use in the Characterisation of Bulk SWNT Material***, **M.S. Golden**, T. Pichler, R. Friedlein, M. Knupfer, J. Fink,* IFW Dresden, Germany*; O. Jost, A.A. Gorbunov, W. Pompe,* TU Dresden, Germany

The investigation of the optical properties of carbon nanotubes,@footnote 1,2@ either using UV-Vis or electron energy loss spectroscopies, offers insight into carbon nanotubes on two levels. Firstly, analysis of the energy positions of the characteristic electronic transitions between the singularities in the density of states enables a quick and easy determination of the overall NT yield, the diameter distribution and the ratio of semiconducting-to-metallic SWNTs in bulk samples. This represents an ideal express characterisation method to accompany tuning of the nanotube preparation process parameters. Secondly, the momentum dependence of the collective excitations of the @pi@-electron system in nanotubes measured using high resolution electron energy loss spectroscopy in transmission proves to be a sensitive probe of the effective dimensionality of the electron system and inter-tube interaction, both in bulk samples of SWNT and MWNT. @FootnoteText@ @footnote 1@ T. Pichler, M. Knupfer, M. S. Golden, J. Fink, A. Rinzler, R. E. Smalley, PRL 80 4729 (1998) @footnote 2@ T. Pichler, M. Sing, M. Knupfer, M. S. Golden, J. Fink, Solid State Commun., 109, 721 (1999).

9:00am **NT+NS+EM+MS-FrM3 Li Intercalated Carbon Nanotubes Ropes***, J. Lu, J. Zhao, **A. Buldum**, B. Gao, O. Zhou,* University of North Carolina, Chapel Hill **INVITED**

The electronic and electrochemical properties of Li intercalated single-wall nanotube ropes are studied theoretically using ab initio method@footnote 1@ and experimentally in an electrochemical cell.@footnote 2@ Complete charge transfer is found between Li atoms and nanotubes. The energetic and electrochemical potential of intercalated Li atoms on both the inside and the outside of tubes are investigated. The intercalated ropes are metallic with conduction band resides on C atoms. Both theoretical and experimental studies suggest that it is possible to achieve a Li intercalation density significant larger than that in the graphite, making the Li intercalated nanoropes a promising material for battery applications. @FootnoteText@ @footnote 1@ J. Zhao, A. Buldum, J. P. Lu, to be published. @footnote 2@ B. Gao and O. Zhou, to be published.

9:40am **NT+NS+EM+MS-FrM5 Mechanical and Electronic Properties of Carbon Nanotubes Under Bending*, L. Yang*, *M.P. Anantram, J. Han, R.L. Jaffe,* NASA

Bending, buckling and even collapsing of carbon nanotubes have been more frequently observed experimentally. They could be elastic or plastic deformations, and responsible for a variety of mechanical and electronic measurements. We systematically investigate mechanical and elecronical properties of carbon nanotubes under these deformations. They are correlated with tube configuration and stress - strain relations. Some interesting observations are made. For example, electron transport can be enhanced or suppressed, depending on the configuration and deformation of a tube. We also apply the simulation results in understanding some related experimental observations.

10:00am **NT+NS+EM+MS-FrM6 Effect of Strain on Electrical Properties of Carbon Nanotubes*, S. Paulson,*** *N. Snider, M.R. Falvo, A. Seeger, A. Helser, R.M. Taylor III, R. Superfine, S. Washburn,* University of North Carolina, Chapel Hill

We have used an advanced interface to an Atomic Force Microscope to apply strain to carbon nanotubes. Simultaneously, we measure the current voltage characteristics, and see how they change as a function of strain in the tube. We have applied enough strain to fracture nanotubes, causing the resistance to become infinitely large, and then reassembled the ends to form junctions. The characteristics of these junctions will be discussed, as well as other strain dependant effects.

10:20am **NT+NS+EM+MS-FrM7 Molecular Dynamics Simulation of the Thermal Conductivity of Carbon Nanotubes*, M.A. Osman,*** NASA Ames Research Center, US*; D. Srivastava,* NASA Ames Research Center

Carbon nanotubes (CNT) have very attractive electronic, mechanical, and thermal properties. Recently, measurements of thermal conductivity in single wall CNTs showed thermal conductivity magnitudes ranging from 17.5 to 58 W/cm-K at room temperature, which are better than bulk graphite.@footnote 1@ The cylinderical symmetry of CNT leads to large thermal conductivity along the tube axis which is an improvement over the strongly anisotropic nature of thermal conductivity of graphite. Additionally, unlike graphite, CNTs can be made into ropes that can be used as heat pipes. We have investigated the thermal concutivity of single wall CNTs Using non-equilibrium molecular dynamics (MD) with Brennar potential. The results of the simulation are in good agreement with the experimental results. We will discuss the results of our simluation and report on the effects of tube diameter and chirality on the thermal conductivity. @FootnoteText@ @footnote 1@ J. Hone, M. Whitney, C. Piskoti, and A. Zettl, Phys. Rev. B59, R2514 (1999).

10:40am **NT+NS+EM+MS-FrM8 Materials Applications of Carbon Nanotubes: Hydrogen Storage and Polymer Composites*, S.J.V. Frankland,*** *D.W. Brenner,* North Carolina State University

Simulations addressing two applications of carbon nanotubes will be presented. Nanotubes have been proposed as storage media for hydrogen in fuel cells. Experiments have shown that the nanotube samples contain more hydrogen than will fit densely packed into the tubules themselves. Therefore, the location of the hydrogen is in question. The Raman shift of the hydrogen may provide a useful indicator of its placement. So far, two qualitative trends have been identified with molecular dynamics simulation which should enable the distinction of internal versus intercalated hydrogen. For internal hydrogen a decreasing Raman shift is observed with increasing nanotube radius. For intercalated hydrogen, the simulations predict a broadened Raman band with relatively little dependence on nanotube radius. The second application being considered is the usage of nanotubes to strengthen polymer composites. Molecular dynamics simulations are in progress to understand the load transfer mechanism between the polymer and the nanotube.

Surface Science Division
Room 604 - Session SS3+EM-FrM

Reactions on Semiconductors

Moderator: S.F. Bent, Stanford University

8:20am **SS3+EM-FrM1 A Comparative Study of [2+2] Cycloaddition Reactions of Organic Alkenes on Group IV Semiconductor Surfaces*, R.J. Hamers,*** *J.S. Hovis, S.C. Coulter,* University of Wisconsin, Madison*; C.M. Greenlief,* University of Missouri, Columbia

Organic alkenes such as cyclopentene can bond to Si(001) and Ge(001) surfaces to produce monolayer organic films that are chemically homogeneous and structurally ordered. The bonding of these molecules to the dimerized Si, Ge, and C (diamond) surfaces is analogous to a class of ring-forming reactions known in organic chemistry as [2+2] cycloaddition reactions. While the bulk reactions involve the reaction of two alkene groups to form a four-member ring, the surface reactions involves two electrons from the organic alkene and two electrons from the ? orbital of the surface Si=Si, Ge=Ge, or C=C dimers. Solution-phase reactions of organic compounds via [2+2] processes are forbidden by orbital symmetry considerations and are therefore extremely slow. In order to better understand the nature of the analogous surface reactions, we have used infrared spectroscopy, scanning tunneling microscopy, X-ray photoelectron spectroscopy, and quantum chemistry methods to investigate the adsorption of cyclopentene and other simple alkenes on Si and Ge(001) semiconductor surfaces. Our results show that reactions of simple alkenes on Si(001) and Ge(001) surfaces are facile, producing ordered monolayers. Ab initio calculations for Si, Ge, and C clusters indicate that the reactions on Si and Ge surfaces are facile because of the ability of these surface dimers to tilt, facilitating a low-energy, low-symmetry pathway to adsorption on these surfaces. This talk will summarize our recent experimental and computational studies aimed at understanding the nature of cycloaddition reactions of organic alkenes on Group IV semiconductor surfaces. @FootnoteText@ This work was supported in part by the U.S. Office of Naval Research and the National Science Foundation.

8:40am **SS3+EM-FrM2 Novel Organic Monolayer Films on Si(100): Theoretical Studies of Cylocaddition Chemistry***, J.A. Barriocanal,* ***D.J. Doren,*** University of Delaware

A class of cycloaddition reactions will be described that can be used to attach monolayer organic films to Si(100). These reactions, known as 1,3-dipolar additions, can be performed with organic molecules containing a wide variety of organic functional groups. Examples include nitro compounds (R-NOO), azides (R-NNN) and their sulfur and phosporous analogs. Density functional theory calculations for prototypical cases show that the molecules chemisorb with negligible activation barrier. As in traditional organic synthesis, having a variety of functional groups that react in a similar way allows some control over the final product by proper choice of the reagent. A complication, in many cases, is that the product of the initial reaction is not the thermodynamic product, and rearrangements will occur. Some guidelines for predicting the most likely rearrangements, based on density functional theory calculations, will be discussed. Potential applications and comparisons to available experimental work will also be described.

9:00am **SS3+EM-FrM3 Formation of Si/Thiophene Hybrid System in UHV by a Hetero Diels-Alder Cycloaddition Surface Synthetic Strategy***, Y. Cao,* ***G.Q. Xu,*** National University of Singapore, Singapore

The formation of organic monolayer on semiconductor surfaces has great device applications in biosensors, field effect transistors as templates for the epitaxial layer growth on semiconductors. In this work, the covalent coupling of thiophene monolayer on a semiconductor surface has been attained by a facile way at room temperature in UHV. We demonstrate here a hetero Diels-Alder cycloaddition reaction strategy for chemical modification of a well-defined Si(111)-7x7 surface with thiophene molecules. The concerted [4+2] cycloaddition reaction of thiophene with adjacent rest atom-adatom pair, resulting the formation of a 2,5-dihydrothiophenelike cycloadduct on Si(111)-7x7, has been clearly demonstrated by combined STM and HREELS spectroscopic studies. Documented as the least reactive diene in Deils-Alder cycloaddition reaction due to its high aromaticity, however, the cycloaddition reaction of thiophene on Si(111)-7x7 is facile even under UHV conditions. In addition, the reactivity of thiophene toward the rest atom-adatom pairs on Si(111)-7x7 can be theoretically explained by correlation of the the HOMO and LUMO energy of thiophene molecule and the surface band level for the empty and filled states on Si(111)-7x7. The feasibility of such procedure provides a better understanding of the chemical reactions proceed through semiconductor surfaces, more significantly, offers a potential new methodology for functionalization the semiconductor surfaces with desired control.

9:20am **SS3+EM-FrM4 Kinetics of Abstraction of Monohydride and Dihydride D from Si(100) Surfaces***, A. Dinger, C. Lutterloh,* ***J. Küppers,*** Universität Bayreuth, Germany

The interaction of H(D) atoms with Si(100) surfaces and the abstraction of D adsorbed in the monohydride and dihydride phases on Si(100) by H was studied with thermal desorption spectroscopy and direct product rate measurements. H/D atoms were produced in W tube sources heated at 2000 K. H/D atom exposure to clean Si(100) surfaces at 380 K and 640 K lead to the formation of dihydride and monohydride phases with the characteristic desorption peaks at 690 K and 810 K. In addition, after application of high atom fluences, H@sub 2@ (D@sub 2@) peaks were seen at 910 K which are interpreted as a consequence of etching. Etch products were monitored in desorption and during reaction. H atom exposure to monohydride D covered surfaces at 640 K revealed HD and D@sub 2@ as gaseous products. At a saturated monohydride surface about 6% of the adsorbed D occurred in D@sub 2@ products. The kinetics of HD formation is not in accordance with the operation of an Eley-Rideal mechanism. This is most clearly apparent at small D coverages since then the HD rate is constant at decreasing D coverage. Abstraction of D from dihydride phases at 380 K exhibit an Eley-Rideal phenomenology in the HD rates, however a small contribution of D@sub 2@ products (<1%) illustrate that another mechanism also acts in abstraction of D from the dihydride. The results can be explained by the operation of hot-atom mechanisms, in which the probabilities of hot-atom sticking and reaction determine the kinetics of gaseous products formation.

9:40am **SS3+EM-FrM5 The Adsorption and Thermal Decomposition of Dimethylamine Adsorbed on Si(100)***,* ***S.M. Casey,*** *C.P.A. Mulcahy, A.J. Dennis,* University of Nevada, Reno

Dimethylamine (DMA) adsorption on the Si(100)-(2x1) surface has been studied using Auger electron spectroscopy (AES), low-energy electron diffraction, and temperature-programmed reaction spectroscopy (TPRS). It is shown that at room temperature DMA chemisorbs on this surface with a saturation coverage of about 0.5 monolayers. These experiments also show evidence for multilayer formation in this adsorbate system. For doses above the saturation dose level, intact DMA molecules begin to adsorb on top of the surface-bound adsorbate layer. TPRS data show that the decompostion of DMA adsorbed on the Si(100) surface proceeds via two different mechanisms in the monolayer vs. multilayer coverage regimes. The adsorbates directly bound to the surface are shown to decompose via reactions that form gaseous hydrogen and hydrogen cyanide products, while the intact multilayer DMA species decompose to form hydrogen and imine dehydrogenation products. Evidence for formation of both the cyclic ethylenimine species and the straight-chained N-methylmethanimine species in this multilayer regime is presented. Kinetic analysis of the TPRS data shows that the heats of desorption for the two products of the surface-bound adsorbate decomposition (hydrogen and hydrogen cyanide) are much higher than the heats of desorption for the products of multilayer decomposition. AES results show that repeated decomposition of DMA on Si(100) leads to the slow deposition of carbon- and nitrogen-based films, although the thermal deposition efficiency is relatively low and the overall stoichiometry of the resulting films could not be clearly established.

10:00am **SS3+EM-FrM6 Reactivity of Diamond (100) towards Cycloaddition Chemistry***,* ***G.T. Wang,*** *S.F. Bent,* Stanford University*; J.S. Hovis, R.J. Hamers,* University of Wisconsin, Madison*; J.N. Russell, Jr., J.E. Butler,* Naval Research Laboratory*; M.P. D'Evelyn,* General Electric

Diamond has a number of extreme material properties that make it an ideal candidate for a wide range of applications, including electronic devices, electron emitters, multispectral windows, and heat sinks. Similar to Si(100) and Ge(100), the diamond (100) surface undergoes a 2x1 reconstruction in which pairs of atoms are bonded into dimers via a strong sigma bond and a partial pi bond. Recent studies on 2x1 reconstructed Si(100) and Ge(100) have shown that the pi bond of the surface dimers can react with unsaturated hydrocarbons via [2+2] and [4+2] (Diels-Alder) cycloaddition reactions, forming covalently attached ring structures. In this study we investigate the viability of the diamond (100) surface to undergo cycloaddition reactions with cyclopentene and 1,3-butadiene using multiple internal reflection infrared spectroscopy and ab initio quantum chemistry calculations. While cyclopentene can react with the surface only via a [2+2] cycloaddition (which is formally forbidden for concerted reactions by symmetry considerations), 1,3-butadiene can potentially react via a [2+2] or [4+2] cycloaddition due to its conjugated double bond. It was found that both cyclopentene and 1,3-butadiene reacted with the diamond (100) surface at room temperature, although significantly larger exposures of cyclopentene were required. The greater reactivity of 1,3-butadiene versus cyclopentene may be attributable to 1,3-butadiene bonding via a lower-barrier [4+2] pathway not available to cyclopentene. Comparison of cycloaddition reactivity on diamond (100) versus Si(100) and Ge(100) provides insight into the mechanism of these reactions on semiconductor surfaces. These results also demonstrate the viability of organic synthetic routes for modifying the diamond surface.

10:20am **SS3+EM-FrM7 Surface Infrared Spectroscopy of CH@sub x@ Adsorbates during GaAs OMVPE***,* ***J.R. Creighton,*** *K.C. Baucom,* Sandia National Laboratories

We have used surface infrared spectroscopy (SIRS) to identify the adsorbates present on GaAs(001) during organometallic vapor phase epitaxy (OMVPE) and atomic layer epitaxy (ALE). The key advantage of SIRS, as compared to reflectance-difference spectroscopy (RDS) and related UV-vis reflectance techniques, is that the interpretation of infrared spectra is much more straightforward and less ambiguous. One example of the rich spectral information derived with SIRS is seen during the trimethylgallium (TMGa) ALE cycle. During the initial stages of TMGa exposure, methyl groups (CH@sub 3@) bonded to both gallium and arsenic can be detected and differentiated. With time, the methyl-arsenic species disappear and methylene (CH@sub 2@) species (the precursors to carbon incorporation) begin to cover the surface. During low-temperature OMVPE we also detect a significant methyl group coverage, and these results will be compared to the other in-situ optical measurements, e.g. RDS, at similar growth conditions. (Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.).

10:40am **SS3+EM-FrM8 Ab initio Study of Adsorption and Decomposition of NH@sub 3@ on Si(100)-(2x1)***,* ***Y. Widjaja,*** *M. Mysinger, C. Musgrave,* Stanford University

Deposition of silicon nitride thin films has become a key technology in the microelectronics industry. In silicon nitride deposition, NH@sub 3@ is typically used as the nitriding agent because of its high sticking coefficient and reactivity. In this study, we investigate the atomistic mechanisms for NH@sub 3@ adsorption and initial decomposition on the (2x1) reconstructed Si(100) surface using B3LYP density functional theory (DFT) and by utilizing the cluster model. We present a detailed investigation of the effects of cluster size on the reaction energetics. We find that the Si@sub 9@H@sub 12@ (1-dimer) cluster model does not describe the NH@sub 3@(a) adsorption state well due to the delocalized nature of the electron transfer in forming the NH@sub 3@(a) dative bond. We find that the Si@sub 21@H@sub 20@ (3-dimer) cluster is necessary to fully capture these non-local effects. The 3-dimer model is able to satisfactorily reproduce the results of larger cluster models. We then use the 3-dimer cluster model to study the adsorption and decomposition reactions of NH@sub 3@ on the Si(100)-(2x1) surface. Ammonia is found to adsorb on the down atom of buckled silicon dimers with no activation barrier. This adsorption is exothermic with an adsorption energy of 29 kcal/mol. This adsorption is then followed by dissociation to form NH@sub 2@(a) + H(a) with a low activation energy. Our calculated recombination desorption energy of 51 kcal/mol is found to be in good agreement with the TPD experimental result of 47 kcal/mol. In addition, we also calculate the vibrational spectra of the dissociated species. We find our results to be in good agreement with the experimental HREELS spectra.

11:00am **SS3+EM-FrM9 Reactions of Substituted Aromatic Hydrocarbons with the Si(001) Crystal Surface***,* ***S.C. Coulter,*** *J.S. Hovis, M.D. Ellison, R.J. Hamers,* University of Wisconsin, Madison

The surface chemistry of small aromatic molecular systems chemisorbed on the single domain Si(001)-(2x1) face has been investigated using Infrared and X-ray Photoelectron Spectroscopy. Both the [2+2] and the [4+2] Diels-Alder cycloaddition processes are possible. Substitued aromatic hydrocarbons, including toluene, benzonitrile and ortho-, meta- and para-xylene, have been studied to provide clues as to their possible steering effects into a favored bonding geometry. Our data indicates that these reactions are complex and, in some cases, involve multiple bonding configurations. Detailed analysis of the infrared spectra and comparisons with known compounds have been used to help identify the surface products and to provide new understanding of substituent effects during molecular bonding at silicon surfaces.

11:20am **SS3+EM-FrM10 Thermal Hydrogen Reactions with Boron-doped Si(100) Surface*, B. Gong,*** The University of Texas at Austin*; S.K. Jo,* Kyung Won University, South Korea*; J.G. Ekerdt,* The University of Texas at Austin

The reactions of hydrogen with boron-doped Si(100) have been studied with temperature programmed desorption, high resolution electron energy loss spectroscopy and low energy electron diffraction. Recent studies by our group have illustrated that in the boron concentration range from 0.002 to 0.1 monolayer (ML), SiH@sub 2@ (@beta@@sub 2@) formation is greatly suppressed at 400 K. This inability of the H-passivated Si(100) to undergo the 3x1 reconstruction is associated with the subsurface boron-induced bond strain and silicon dimer vacancy defects. At higher boron coverages (0.2-0.5 ML), H@sub 2@ desorption data show a new, broad desorption peak (@beta@@sub 3@) at ~ 400 K in addition to SiH (@beta@@sub 1@) and SiH@sub 2@ states. The @beta@@sub 1@ and @beta@@sub 2@ desorption energies are unchanged by boron. The new H@sub 2@ desorption peak is related to trihydride formation (SiH@sub 3@) on silicon sites that are associated with second layer boron atoms. Both SiH@sub 3@ and @beta@@sub 3@-H@sub 2@ desorption increase with increasing boron coverage. We propose that the enhanced silicon growth rate found during in situ boron doping is related to the new H@sub 2@ desorption channel that has its origin with SiH@sub 3@ formation. Extensive H-induced surface etching is also seen on intrinsic Si(100) surfaces at 180 K. SiH@sub 4@ desorption at ~600 K has been used as an indicator of H-induced etching, where SiH@sub 3@ forms as a result of H atoms breaking Si-Si back bonds; SiH@sub 2@ formation precedes the formation of the SiH@sub 3@ etch product. This surface etching is sharply reduced on lightly boron-doped Si(100) surfaces, which is in good agreement with the result that low coverage boron prevents SiH@sub 2@ formation on Si(100).

11:40am **SS3+EM-FrM11 Impact of Surface Structure on the Arsine Adsorption Kinetics on GaAs and InP (001)*, Q. Fu,*** *L. Li, C. Li, D. Law, R.F. Hicks,* University of California, Los Angeles

Arsine adsorption on the gallium-rich GaAs (001) (4x2) reconstruction and on the indium-rich InP (001) (2x4) reconstruction has been studied by internal-reflection infrared spectroscopy and scanning tunneling microscopy. It was found that AsH@sub 3@ adsorption on the (4x2) follows an autocatalytic mechanism, with the rate proportional to the fraction of occupied and vacant sites. By contrast, AsH@sub 3@ adsorption on the (2x4) follows a Langmuir adsorption mechanism, with the rate depending only on the fraction of vacant sites. We attribute these differences in the reaction kinetics to the impact of the semiconductor surface structure on the adsorption mechanism. The GaAs (4x2) reconstruction is terminated with 3 gallium dimers per unit cell, while the InP (2x4) contains one In-P heterodimer, and 4 In dimers per unit cell. An arsine molecule dissociatively adsorbs onto the group III dimers and transfers hydrogen to a group V dimer site. On the GaAs (4x2), only a few of these latter sites are present, and more are created by adsorption, so the reaction is autocatalytic. Conversely, on the InP (2x4), the latter sites are readily available, and Langmuir adsorption occurs. The decomposition mechanisms of arsine on these surfaces will be discussed in detail at the meeting.

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