

## Electronic Materials and Processing Division Room 316 - Session EM-MoM

### Processing for Advanced Technology

**Moderator:** D. Temple, Microelectronics Center of North Carolina

8:20am **EM-MoM1 SCALPEL: Projection Electron Beam Lithography, L.R. Harriott**, Bell Laboratories, Lucent Technologies **INVITED**

SCALPEL (SCattering with Angular Limitation Projection Electron beam Lithography) combines the high resolution and wide process latitude inherent in electron beam lithography with the throughput of a projection system. This approach has the potential to satisfy the lithographic requirements for many IC generations, down to the minimum feature sizes contemplated in the SIA roadmap. We believe that with solid industry support and resources, SCALPEL can be introduced in the 130 nm generation as a replacement for 193 nm lithography for critical levels with reduced cost. SCALPEL masks are expected to be considerably lower cost than optical masks which will require OPC and phase shift for the 130 nm generation. We see the evolution of lithography technology directly from 193 nm to SCALPEL. Throughput is usually thought of as the determining factor in determining the cost of ownership for a lithographic technology. As the limits of optical lithography are pushed toward and beyond sub-wavelength printing, strategies such as phase shifting and optical proximity effect correction (OPC) are required. These technologies add significantly to the cost of the masks and thus, contribute to the cost of wafer printing. The size of the mask factor depends strongly on the mask usage. The number of wafers printed for each mask varies according to the nature of an individual IC business with averages for ASIC at 1000 wafers or less printed per mask. The averages for logic and DRAM are roughly 2000 and 3000 respectively. The total cost of printing a wafer level can, particularly in cases of low mask usage, then be dominated by mask costs and less effected by throughput than has been the case in the past. For SCALPEL, technologies such as phase-shifting and OPC are not required and the resulting mask costs at a given design rule (such as 130 nm) can be significantly less than the corresponding photomask costs. Thus, even though SCALPEL throughput will be less than that for 193 nm optical lithography, the overall cost per level of lithography will be lower due to significantly lower mask costs. We believe that this factor will be a major driving force in determining the timing of the shift away from optical lithography to SCALPEL. We have recently completed our proof-of-lithography system which implements the step-and-scan writing strategy. Our recent data shows that we can write stripes over a 1 X 1 cm field and stitch them together with a raw accuracy of better than 50 nm three-sigma. These measurements were made using box-in-box type patterns at the joining of adjacent stripes across the field. Other errors such as those of the mask beam-writer have not been accounted for in this preliminary experiment. We expect that with further calibration and removal of mask errors that we can achieve stitching to the 10 nm level or less as we have seen in the static stitching data. In order to bring SCALPEL technology to the next step in its evolution, we are beginning a three-year development program aimed at the full-field high throughput system. The program will focus on larger format mask technology, a high throughput exposure tool, and resist and process development. In this talk, we will outline the status of SCALPEL technology as well as the plans for its continued development. This work has been supported in part by DARPA and SEMATECH

9:00am **EM-MoM3 Fundamental Issues in Wafer Bonding and SOI, U.M. Goesele**, Max Planck Institute of Microstructure Physics, Germany **INVITED**

During the last decade, wafer bonding has developed from an approach with a "black magic" image to a versatile technology which is partly already used industrially and which allows to avoid the restrictions usually imposed by epitaxy. The science and technology of wafer bonding has been advanced almost independently in three major areas: i) fabrication of SOI (Silicon-On-Insulator) substrates; ii) silicon based micromechanics (where wafer bonding is known as fusion bonding), and iii) bonding of III-V compounds for light-emitting devices and compliant substrates. Present day research aims at understanding and controlling the processes happening at the bonding interface especially for general material combinations and at developing low temperature bond strengthening approaches for already processed wafers and/or dissimilar materials with different thermal expansion coefficients. Versatile thinning methods for many different technologically relevant materials such as the smart-cut or related methods are also of special interest. The processes involved in atmospheric, low vacuum, or ultra high vacuum wafer bonding at room

temperature will be outlined. Hydrogen implantation-induced delamination and layer transfer (smart-cut and smarter cut procedures) will also be discussed for a number of materials including silicon, germanium, diamond, SiC, GaAs and sapphire.

9:40am **EM-MoM5 The Fundamental Mechanisms of Silicon Wafer Bonding and Layer Exfoliation, M.K. Weldon**, Bell Laboratories, Lucent Technologies **INVITED**

The fabrication of Silicon-On-Insulator (SOI) materials has progressed to such an extent over the past decade that the material specifications are approaching those of bulk silicon and many viable manufacturable processes are now in operation. Silicon wafer bonding is one such commercially-employed approach to SOI synthesis in which two (oxide-terminated) Si wafers are directly bonded under ambient conditions and then annealed to elevated temperatures (1100 C) to form a permanent chemical bond. In the conventional process, the device wafer is subsequently thinned to the required dimensions by extensive grinding/polishing. The limitations imposed by this latter step have recently been removed with the advent of a remarkable new process wherein H+ is pre-implanted into the device wafer at a critical concentration and depth, prior to bonding. Upon subsequent joining to the companion 'handle' wafer and annealing to ~400 C, complete lift-off (exfoliation) of the overlying Si occurs, so that the final SOI structure can now be formed in one elegant annealing step, with thickness uniformities of ~50 Å over the entire wafer. Research has played an important role in the advancement of this field, despite the inherent difficulties in obtaining spectroscopic information about the physics and chemistry of interfaces that typically lie ~500 microns below the surface. In this talk, I will describe how we have obtained@footnote 1@ unprecedented insight into the thermal evolution of the buried interfaces that comprise both the bonded and the exfoliation interfaces, using a wide variety of different experimental probes in combination. In particular, I will highlight the pivotal role of infrared spectroscopy in delineating the microscopic mechanisms that permit the intimate chemical bonding of two wafers and the transformation of isolated hydrogenated defects into extended internal cracks that ultimately lead to exfoliation of macroscopically large areas of Si. @FootnoteText@ @footnote 1@M.K. Weldon, V.E. Marsico, Y.J. Chabal, A. Agarwal, D.J. Eaglesham, J. Sapjeta, W.L. Brown, D.C. Jacobson, Y. Caudano, S.B. Christman and E.E. Chaban, J. Vac. Sci. Technol. B 15, 1065 (1997).

10:20am **EM-MoM7 DARPA High Definition Systems Program, B.E. Gnade**, Defense Advanced Research Projects Agency **INVITED**

The DARPA High Definition Systems (HDS) Program has the overall goal to meet the diverse, but specific, needs for information display for the Department of Defense. The goals of the HDS program include increasing power efficiency, reducing weight, and improving the overall ruggedness of display systems. The HDS program is also actively working to transition DARPA-funded display technologies into specific military applications. A brief review will be presented which shows how new display technologies are being used in the military, as well as examples of new technologies which are being supported under the DARPA HDS program.

11:00am **EM-MoM9 Field Emission Energy Distributions from Silicon Field Emitter Arrays, J.L. Shaw, H.F. Gray, K. Hobart**, Naval Research Laboratory

A great deal of work on field emitter array (FEA) surface coatings, treatments, and "conditioning" effects has been reported in hopes of improving the maximum current, robustness, and transconductance. However, the typical current-voltage diagnostic technique has limited utility in understanding the effects of such treatments. Field enhancement and work function effects are difficult to separate using I-V measurements and assuming the classical Fowler-Nordheim theory. Furthermore, the I-V characteristics typically vary with time and emission even in UHV. To better understand the emission process, we have measured FEA emission energy spectra. Our equipment includes a hemispherical analyzer and allows in-situ wafer probing and simultaneous I-V characterization. The spectra we obtain include structure at lower energies than reported from single, macroscopic, clean silicon tips. Since the emission energy relative to the bulk Fermi level represents a loss, such spectra are of considerable interest. The spectra change as a function of emission current, conditioning, and processing. In some cases we find energy losses in excess of 10 volts. Such losses may explain why failures can occur at emission levels below 1uA, even though calculations (that assume straightforward Joule and Nottingham heating) predict no temperature increase at emission currents below 100uA. Our measurements suggest that both the emission current and dissipated energy can be strongly influenced by the presence of surface states. Thus detecting such effects is

likely to prove useful in improving FEA emission uniformity and total current density.

**11:20am EM-MoM10 Effects of Oxygen on Silicon and Platinum-coated Silicon Field Emitter Arrays, W.D. Palmer, D. Temple, D.G. Vellenga, L.N. Yadon, G.E. McGuire, Microelectronics Center of North Carolina**

Field emission depends strongly on the work function of the emitter surface. At any vacuum level, molecules will adsorb on the emitter surface and change the work function by forming a chemical bond with the emitter material. This study addresses this problem and one possible solution by testing silicon and platinum-coated silicon field emitter arrays in oxygen over a wide pressure range similar to that expected in commercial field emission flat panel displays. Platinum is less likely than silicon to form these bonds, and so should exhibit less sensitivity to the ambient gases in the display panels. The experiments were undertaken using silicon and platinum-coated silicon gated field emitter arrays fabricated at MCNC. The arrays were initially operated at base pressure (5x10<sup>-9</sup> Torr) using an automated system to guarantee that all tests were performed consistently. After collecting current versus voltage (I-V) curves for each device at base pressure, a leak valve was used to introduce oxygen at the target pressure. The arrays were then operated with a constant voltage on the gate electrode until the emission current stabilized. In this study, the data is shown as a function of exposure, the product of pressure and time, to normalize the results. I-V curves were collected at the target pressure after stabilization, then the leak valve was closed and the chamber was pumped back to base pressure. Finally, I-V curves were again collected at base pressure to verify that the array had recovered to its initial level of performance. The data collected on silicon and platinum-coated silicon field emitter arrays will be shown and compared. This work was performed under the DARPA/ETO High Definition Systems program, contract number N00014-96-C-0283.

**11:40am EM-MoM11 Improved Performance in Thin Film Electroluminescent Phosphors by Fluxing, J.S. Lewis, K.E. Waldrup, M.R. Davidson, D. Moorehead, University of Florida, Gainesville, U.S.; S.S. Sun, Planar Systems, Inc.; P.H. Holloway, University of Florida, Gainesville**

The brightness and efficiency of AC thin film electroluminescent devices (ACTFELD's) which use ZnS:Mn as the thin film phosphor have been improved by the incorporation of various fluxes. The brightness of fluxed, sputter deposited films were doubled and the efficiencies are nearly tripled compared to unfluxed, sputter-deposited films. In addition, the improved brightness and efficiency values surpass those achieved by the standard evaporated or ALE (atomic-layer epitaxy) grown devices. The fluxes have been incorporated both during and after sputter deposition of the phosphor, and a post-deposition anneal is required. Data will be presented which demonstrate improved brightness and efficiency. The flux treatment gave significant improvement in the degradation of luminescence after accelerated device operation. Microstructural changes that result from fluxing as detected by X-ray diffraction, transmission electron microscopy, and scanning electron microscopy will be presented.

## Organic Electronic Materials Topical Conference Room 327 - Session OE+EM-MoM

### Organic Thin Film Devices I: Light Emitters

**Moderator:** A. Kahn, Princeton University

**8:20am OE+EM-MoM1 Polymers for Optoelectronics, N. Peyghambarian, University of Arizona**

**INVITED**

Tailoring of organic molecules and polymers has enabled the recent development of multifunctional materials such as photorefractive polymers and organic electroluminescent materials. This talk will review: (i) the development of thermally stable photorefractive polymers with infrared and their application to imaging through scattering media using holographic time-gating techniques; (ii) the fabrication of photorefractive polymer-dispersed liquid crystals; (iii) the demonstration of ultra-bright electroluminescent devices using new Al-based cathodes; (iv) the fabrication of micro-pixel arrays of organic light-emitting devices for displays; (v) the demonstration of optically pumped organic laser structures based on conjugated polymers.

**9:00am OE+EM-MoM3 High Efficiency Three Color Stacked Organic Light Emitting Devices, P.E. Burrows, G. Parthasarathy, G. Gu, S.R. Forrest, Princeton University; T. Zhou, Universal Display Corporation**

**INVITED**

Vacuum deposited organic light emitting devices (OLEDs) based on "small molecule" organic semiconductors have demonstrated adequate efficiency and lifetime for commercial monochrome flat panel display applications. For full color display applications, vertically stacked OLEDs (SOLEDs) offer increased resolution and aperture ratio over conventional, side-by-side patterned pixels. The SOLED consists of separate red, green and blue elements grown in a vertical stack by sequential vacuum deposition. The elements emit light co-axially through semi-transparent electrodes enabling any combination of three colors to be emitted from the entire area of the device. In this paper we present recent improvements in the color, efficiency and operating voltage of SOLEDs. A typical SOLED is a 13 layer device comprised of organic semiconductors, metal oxides and metal thin films. Understanding and controlling microcavity effects in the stacked device is therefore essential to generate a pixel with well separated and adequately saturated colors. We present an analytical model of weak microcavity effects in SOLEDs and apply the results to fabricate a three color pixel with minimal directionality and good color separation. We also discuss a highly transparent, metal-free cathode which defeats the microcavity effects by reducing reflections within the stack.

**9:40am OE+EM-MoM5 Excited-State Electronic Structure of Conjugated Polymers and Oligomers: Characterization of the Luminescence and Two-Photon Absorption Properties, J.L. Brédas, University of Mons-Hainaut, Belgium**

**INVITED**

Conjugated polymers and oligomers present remarkable semiconducting and nonlinear optical properties. They can for instance be incorporated as the active element in new generations of organics-based field-effect transistors, light-emitting diodes, or photovoltaic cells; much work is also devoted to designing chromophores with enhanced second-order or third-order optical response. In this talk, we discuss the results of correlated quantum-chemical calculations aimed at characterizing the electronic structure of these excited states that are responsible for the luminescence and nonlinear optical properties. We focus on polyparaphenylene vinylene and its derivatives; these polymers are widely exploited in polymer-based light-emitting diodes. We describe the nature of the lowest singlet excited states involved in the absorption and emission processes. We then discuss the major influence of interchain interactions; by considering polyphenylenevinylene chains carrying different substituents, we show that some combinations lead to exciton transfer (which is good for luminescence) and others to charge transfer (which is good for photovoltaics). The second (brief) part of the talk deals with the design of novel donor-acceptor phenylenevinylene oligomers which display unprecedented two-photon absorption cross-sections. Some examples of potential applications will be briefly described.

**10:20am OE+EM-MoM7 Gain, Amplified Spontaneous Emission and Lasing in Semiconducting Polymers, M.D. McGehee, R. Gupta, E.K. Miller, A.J. Heeger, University of California, Santa Barbara**

**INVITED**

Because of the high absorption coefficients, the high density of chromophores, and the Stokes-shifted luminescence, luminescent semiconducting polymers have potential as low threshold laser media. Optically pumped amplified spontaneous emission has been demonstrated in submicron films of  $\frac{1}{4}$ -conjugated polymers as the active materials. Resonant structures appropriate for photopumped lasers include microcavities, distributed feedback (DFB) substrates, and whispering gallery mode micro-discs and micro-rings. Photopumped stimulated emission and lasing have been observed in a growing number of highly luminescent polymers with emission wavelengths that span the visible spectrum. Progress in the areas of polymer lasers will be reviewed and the possibility of electrically pumped diode lasers (fabricated from semiconducting polymers) will be explored.

**11:00am OE+EM-MoM9 XPS and AFM Investigation of Stability Mechanism of tris-(8-hydroxyquinoline) Aluminium Based Light-Emitting Devices, Q.T. Le, F.M. Avendano, E.W. Forsythe, L. Yan, Y. Gao, University of Rochester; C.W. Tang, Eastman Kodak Company**

Stability is an essential issue in the application of organic light-emitting devices (OLEDs). We have investigated the indium tin oxide (ITO) surface for operated and un-operated OLEDs that consist of ITO/phenyl-diamine (NPB)/tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@)/Mg:Ag with NPB thickness varied from 0 to 300 Å using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques. The ITO surface was exposed by removing the organic and metal layers with dichloromethane,

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an organic solvent in which NPB and Alq@sub 3@ are highly soluble. Electroluminescence (EL) characterization demonstrates that the NPB layer substantially enhanced the stability. XPS analysis shows that for the device made without NPB and after 90 hours of operation, there exists an insoluble organic material on the ITO surface. This organic material is not observed on the ITO of un-operated cells nor of the operated NPB-containing devices. Lateral force AFM also shows a striking difference between the ITO surface of devices with and without NPB after operation. The XPS and AFM results suggest that the organic residue is the degradation product of Alq@sub 3@ that act as quenching sites at the ITO/Alq@sub 3@ interface, which may lead to the early failure of the single layer devices. This work was supported in part by DARPA DAAL 0196K0086 and NSF grant DMR-9612370.

11:20am **OE+EM-MoM10 A Comparison of the Change in the Valence Electronic Structure of p-sexiphenyl Thin Films upon Doping with K and Cs**, *N. Koch*, Technische Universität Graz, Austria; *J.-J. Pireaux*, *L.M. Yu*, Facultés Universitaires Notre-Dame de la Paix, Belgium; *R.L. Johnson*, Universität Hamburg, Germany; *G. Leising*, Technische Universität Graz, Austria

Thin films of the electroactive conjugated material para-sexiphenyl (6P) were doped with potassium and cesium under ultra-high vacuum conditions. The changes in the valence electronic structure of 6P upon increasing dopant exposure were followed with synchrotron ultraviolet photoelectron spectroscopy (UPS), and are compared subsequently. For doping with Cs, new occupied electronic states are only found in the energy gap at 5.8 and 3.6 eV (with respect to the vacuum level); they lie well below the Fermi level, and can be interpreted to negative bipolaron states in 6P. The experimental findings are different when doping with K; for very low doping levels, a finite density of valence states (DOVS) is observed at the position of the Fermi-level  $E_F$ . Higher doses of K lead to a shift of  $E_F$  closer to the vacuum level, and out of the DOVS. This observation could be interpreted in terms of a polaron to bipolaron transition of the charged species of 6P with progressive doping. But also a different interpretation will be proposed, in a manner that bipolarons are formed from the beginning of the doping experiment.

# Monday Afternoon, November 2, 1998

## Electronic Materials and Processing Division Room 316 - Session EM-MoA

### Future Issues in Electronics and Photonics

**Moderator:** H.A. Atwater, Caltech

2:00pm **EM-MoA1 Pathways Toward Chemically Assembled Electronic Nanocomputers**, *J.R. Heath*, University of California, Los Angeles; *R.S. Williams*, P.J. Kuekes, Hewlett Packard Corporation

**INVITED**

Many ideas for alternatives to CMOS-based VLSI manufacturing have been proposed as new paradigms for computer fabrication. These ideas include quantum computing, molecular computing, and chemically-assembled electronic nanocomputers. Of these three, only electronic nanocomputers can potentially build upon the foundation of CMOS architectures, and, as such, they hold the potential for relatively near-term realization. However, even the simplest of computational tasks have yet to be demonstrated for electronic nanocomputers. From a chemist's point of view, there are two major differences between anything fabricated chemically, and a current microchip. The current microchip is complex and is the result of manufacturing perfection, while anything that is chemically synthesized is likely to be ordered (crystalline) and imperfect. Thus, in many ways, the chemist's task is to design a system from which perfect complexity can be extracted from imperfect order. In this presentation, I will discuss an ongoing HP/UCLA project in which we are attempting to build an electronic nanocomputer. Architectural considerations will be stressed, and experimental progress towards building the nanocomputer will be discussed.

2:40pm **EM-MoA3 Room Temperature Silicon Single Electron Memory and Switch and Nanoimprint Lithography**, *S.Y. Chou*, Princeton University

**INVITED**

The paper presents two recent progresses in developing single electron devices that can operate at room temperature and one breakthrough in nanopatterning. The first is a single-electron MOS memory in crystalline silicon, that has a channel width (~10 nm) and a nanoscale polysilicon dot (~7 nm by 7 nm) as the floating gate embedded between the channel and a control gate. @footnote 1@ It is observed that storing one electron on the floating gate can significantly screen the channel from the potential on the control gate, leading to a threshold voltage shift. The second progress is a silicon single electron switch, that has a small silicon dot (~12 nm in diameter) inside the channel and separated from the source and drain by two thin tunneling barriers. @footnote 2@ As a gate modulates the electron population inside the dot, the drain current oscillates at room temperature. Each oscillation is attributed to electron tunneling through a discrete single electron level inside the dot. Finally, nanoimprint lithography is a new lithographic method that has achieved sub-10 nm feature size with high throughput and low cost, paving the road for manufacturing silicon single electron devices. @footnote 3@ @FootnoteText@ @footnote 1@ L. Guo, E. Leobandung and S.Y. Chou, Science, vol. 275, 649-651, 31 January, 1997. @footnote 2@ L. Zhuang, L. Guo, and S.Y. Chou, IEDM, Dec. 8-10, 1997. @footnote 3@ S.Y. Chou, P.R. Krauss, W. Zhang, L. Guo and L. Zhuang, J. Vac. Sci. Technol. B 15(6), 2897 (1997).

3:20pm **EM-MoA5 Terabit Integration: New Ideas, Need for New Materials**, *K.K. Likharev*, State University of New York, Stony Brook

**INVITED**

The electronics industry predicts that the current progress in scaling down silicon MOSFETs will lead eventually to dynamic random-access memories with a density of the order of 5 Gbits/cm<sup>2</sup> and integration scale up to 64 Gbits. Further progress in this direction is, however, in doubt, mostly because of problems with the storage capacitance scaling. The situation may be changed by the recently proposed @footnote 1@ "crested" tunnel barriers, with an electrostatic potential maximum in the middle. In these barriers, applied voltage increases the barrier transparency much more quickly. Calculations have shown that crested barriers may combine long retention time (say, 10 years) with fast write/erase time (below 10 nanoseconds). This radical improvement may be used, first of all, in nonvolatile random-access memories ("NOVORAM"). Using dual-gate, nanoscale MOSFETs with ballistic electron transfer along undoped channels, @footnote 2@ NOVORAM cells are scaleable to a minimum feature size about 6 nm, corresponding to a memory density of 100 Gbits/cm<sup>2</sup> and, and apparently integration scale up to 16 Tbits. Beyond this frontier, NOVORAM may be challenged by SET/FET hybrid memories @footnote 3@ with dynamic read-out using single-electron

transistors (SETs) in background-charge-insensitive mode. Analysis shows that these memories may be scaled to the 2 nm minimum feature size, enabling integration up to 64 Tbits. Moreover, there is an opportunity to combine crested barriers and SET/FET hybrids in a system for electrostatic data storage with density beyond 100 Gbits per square inch. In my presentation at the meeting, I will describe these encouraging prospects in detail, and also discuss the requirements to materials for their practical implementation. @FootnoteText@ @footnote 1@ K.K. Likharev, in: GOMAC'98 Technical Paper Digest, p. 35. @footnote 2@ F. Pikus and K. Likharev, Appl. Phys. Lett. 71, 3661 (1997). @footnote 3@ K.K. Likharev and A.N. Korotkov, in: Proc. of 1995 ISDRS, p. 355

4:40pm **EM-MoA9 Oxide-Confined Vertical Cavity Surface Emitting Lasers using Quantum Well and Quantum Dot Active Regions**, *D. Huffaker*, University of Texas, Austin

**INVITED**

There is increasing interest in low power optoelectronics including ultralow threshold semiconductor lasers for use in optical interconnect applications. The oxide-confined vertical cavity surface emitting laser (VCSEL) is a potential candidate for such applications because of the promising device results which have been demonstrated to date. At the University of Texas we have focused on minimizing optical loss from the lasing mode by lateral index confinement and high contrast mirrors. This talk will overview our device structures, the selective oxidation processing and low threshold quantum well VCSEL results. The low loss VCSEL cavity may be especially important in realizing 1.3 μm VCSELs grown on a GaAs substrate using an InAs/GaAs QD active region as the QDs have limited gain at this long wavelength. To date, we have achieved a 1.15 μm GaAs-based VCSEL using the InAs/GaAs QDs. We will also discuss very recent data characterizing ultranarrow electroluminescence spectra from a large ensemble of quantum dots at very low current densities.

## Nanometer-scale Science and Technology Division Room 321/322/323 - Session NS+EM+SS-MoA

### Cross-sectional Scanning Tunneling Microscopy of Semiconductors

**Moderator:** M. Weimer, Texas A&M University

2:00pm **NS+EM+SS-MoA1 Scanning Tunneling Microscopy Studies of Atomic-Scale Structure in Semiconductor Heterostructures**, *E.T. Yu, S.L. Zuo*, University of California, San Diego

**INVITED**

Engineering of advanced heterostructure and nanoscale semiconductor devices requires a detailed understanding of the structure and properties of semiconductor materials and devices at the atomic to nanometer scale. Cross-sectional scanning tunneling microscopy provides unique and powerful capabilities for characterization of structural morphology and electronic properties in semiconductor epitaxial and device structures with spatial resolution at or near the atomic scale. In conjunction with results obtained using complementary characterization techniques, such studies can provide valuable insights into the relationships among epitaxial growth conditions, atomic-scale compositional structure, and various aspects of device behavior. We will discuss a number of recent applications of cross-sectional scanning tunneling microscopy to the characterization of III-V compound semiconductor heterostructures. Studies of InAsP/InP heterostructures, currently of interest for optoelectronic devices operating at 1.3-1.55 microns, have revealed that extensive nanoscale compositional clustering occurs, with As-rich and P-rich clusters bounded preferentially by {111} planes forming in the InAsP alloys. Related studies of InNAsP/InP heterostructures, in which low concentrations (~1-2%) of N are incorporated, have provided information about the influence of N on heterojunction band alignments. And STM images of InAsP/InAsSb superlattices of interest for midwavelength infrared emitters have revealed nanoscale compositional fluctuations in these materials consistent with previously reported observations by electron diffraction of partial ordering in InAsSb alloys.

2:40pm **NS+EM+SS-MoA3 Growth Asymmetry in InGaAsP/InAsP Superlattices Studied by Scanning Tunneling Microscopy**, *B. Grandidier, H. Chen, R.M. Feenstra*, Carnegie Mellon University; *R.S. Goldman*, University of Michigan; *C. Silfvenius, G. Landgren*, Royal Institute of Technology, Sweden

InGaAsP based multiple quantum well structures are increasingly used to fabricate optoelectronic devices. However the strain can lead to lattice relaxation processes during the growth which degrades the optical properties of these structures. To understand the differences in the

photoluminescence efficiency of several superlattices composed of InGaAsP quaternary wells, we have investigated a series of InGaAsP/InGaP and InGaAsP/InAsP superlattices using cross-sectional scanning tunneling microscopy (xSTM). These superlattices were grown by metalorganic vapor phase epitaxy, with different number of periods and with or without InP interlayers inserted in the barrier. For InGaAsP/InGaP superlattices, the individual well and barrier layers are well resolved in the xSTM images. In contrast, for InGaAsP/InAsP superlattices, the InGaAsP quantum well and preceding InAsP barrier layers can be clearly seen, whereas the subsequent InAsP barriers are severely intermixed with the quantum wells. Possible mechanisms for this intermixing are described. In addition, the contrast observed in both types of superlattices has been related to the strain which exists in the layers; the compressively strained InAsP barrier protrudes outwards from the (110) cleavage plane whereas the tensilely strained InGaP barrier contracts inwards. Finite element computations are used to quantify these elastic relaxation effects of the cleavage surface.

3:00pm **NS+EM+SS-MoA4 Microstructure of Mixed-Anion Interfaces Examined with XSTM**@footnote 1@, *J. Harper, M. Weimer, Texas A&M University; D. Zhang, C.H. Lin, S.S. Pei, University of Houston*

The quality of the interfaces between the nearly-lattice-matched 6.1 Å materials (InAs, GaSb, and AlSb) is important for a number of applications, including the development of mid-IR lasers, long-wavelength photodetectors, and resonant-tunneling devices. Cross-sectional scanning tunneling microscopy (XSTM) is a powerful tool for characterizing the heterojunctions in these structures, which pose special challenges for molecular beam epitaxy (MBE) because of the mixed-anion nature of this material system. We have observed a white-noise component in the roughness spectrum of the GaSb-on-InAs interface with XSTM that is associated with the presence of interface point defects; these defects most likely arise from thermodynamically favored anion exchange reactions that occur during the crossover from arsenide to antimonide growth. Abruptness of the InAs-on-GaSb interface, on the other hand, is limited by antimony segregation that causes compositional grading within the arsenic layers. We have quantitatively characterized the Sb fraction as a function of distance from the arsenide-on-antimonide heterojunction, and find this compositional grading is well described by an exponential profile. @FootnoteText@ @footnote 1@ Work supported by the National Science Foundation (DMR-9633011).

3:20pm **NS+EM+SS-MoA5 X-STM Study of InAs/In@sub 1-x@Ga@sub x@Sb/InAs/AlSb Laser Structures**@footnote 1@, *W. Barvosa-Carter, M.J. Yang, L.J. Whitman, Naval Research Laboratory*

Strained-layer heterostructures involving the 6.1 Å family of III-V semiconductors (including InAs, GaSb, and AlSb) are being investigated for use in a growing number of high-speed and opto-electronic devices. Recently it was shown in InAs/In@sub 0.73@Ga@sub 0.28@Sb/InAs/AlSb mid-IR structures that the photoluminescence (PL) intensity and x-ray superlattice diffraction quality are strongly dependent on MBE growth temperature. These characteristics were shown to be optimized within a rather narrow growth temperature range (410-460°C) and much worse outside of that range. Although the quality of the interfaces in these structures is expected to play a crucial role in determining device performance, little is known about the actual atomic-scale structure of the interfaces. We present an atomic-resolution cross-sectional STM (X-STM) study of these laser structures in order to directly correlate atomic-scale features, such as interface roughness and layer intermixing, with material quality as measured by PL and x-ray measurements on the same samples. Two such laser structures have been examined, one grown at the optimum temperature and another grown at a higher temperature. Interface roughness appears to be larger in the higher temperature structure. In addition, intermixing occurs at the AlSb-on-InAs interfaces which results in electronic structure differences between the InAs-on-AlSb and AlSb-on-InAs interfaces as observed by X-STM. Based on our X-STM results, we will discuss the atomic-scale sources of device degradation, and present possible routes towards improvement of the growth of these laser structures. @FootnoteText@ @footnote 1@ Funded by the Office of Naval Research and the Air Force Research Laboratory.

3:40pm **NS+EM+SS-MoA6 Kinetics of Anion Cross Incorporation in Type-II Heterostructures Characterized with XSTM**@footnote 1@, *J. Steinshnider, J. Harper, M. Weimer, Texas A&M University; D. Zhang, C.H. Lin, S.S. Pei, University of Houston*

We have used cross-sectional scanning tunneling microscopy (XSTM) to examine MBE material quality in the mixed-anion InAs/GaSb/AlSb system under growth conditions (including the use of cracked arsenic and

antimony sources) similar to those presently employed for type-II quantum well and interband cascade lasers. Two apparently different anion defects are noted within the antimonide layers. The demonstration of a linear correlation between the defect densities observed with STM and the arsenic valve setting during antimonide-layer growth establishes background arsenic incorporation as the common origin for both of these defects. @footnote 2@ The distribution of As substitutional defects in a (110) cleavage plane is analyzed by way of the two-dimensional pair correlation function. We observe a pronounced attractive correlation in the [110] direction, parallel to the Sb dimer bonds of the (1x3) reconstructed growth surface, whereas the distribution in the orthogonal [001] direction is essentially random. This anisotropic correlation reflects the kinetics of arsenic dimer incorporation during growth and not the equilibrium distribution associated with strain-mediated repulsive interactions. @FootnoteText@ @footnote 1@ Work supported by the National Science Foundation (DMR-9633011). @footnote 2@ J. Harper, M. Weimer, D. Zhang, C.H. Lin, and S.S. Pei, JVST B 16, in press (1998).

4:00pm **NS+EM+SS-MoA7 Low Temperature Cross-Sectional Scanning Tunneling Microscope-Induced Luminescence of GaN**, *S. Evoy, C.K. Harnett, Cornell University; S. Keller, U.K. Mishra, S.P. DenBaars, University of California, Santa Barbara; H.G. Craighead, Cornell University*

The GaN system is of interest for applications in the green, blue, and UV spectral regions. Advances in device development have been made in spite of issues such as dislocation densities and defect induced visible luminescence. These issues prompted interest in spatially resolved luminescence studies of the material. Scanning tunneling microscope-induced luminescence (STL) offers nanometer scale resolution and control of the injection bias. In-situ cleaving and cross-sectional imaging is of particular interest for nanoscale luminescence studies of GaN heterostructures and interfaces. We recently reported the first low temperature STL of GaN, and the first STL images of this material. We now report the low temperature cross-sectional STL of MOCVD-grown GaN. Optical interference filters are used for semiquantitative spectral analysis. Room temperature top-view experiments reveal faint visible emission at tip biases above 1.5 V, with no clear evidence of UV luminescence. However, a sharp increase of emission in the 350±35 nm range is observed under liquid He cooling at biases above 3 V. The room temperature visible emission may be related to surface issues, suggesting that low temperature is required for the analysis of intrinsic bulk luminescence. Cross-sectional experiments are performed on in-situ cleaved samples. Incompatible cleaving planes between the GaN and the sapphire produce 200-400 nm wide vertical features, yielding an edge roughness of 30-50 nm. Behavior of luminescence is similar to what was observed in top-view. However, close to the sapphire interface, the 350±35 nm band-edge emission is undetected even at low temperature. Images show strong correlation between the remaining visible emission and the cleaved-induced artifacts. We are currently working on our cleaving technique in order to improve the quality of the edge. The technique will also be applied to the study of GaN heterostructures such as InGaN/GaN quantum wells.

4:20pm **NS+EM+SS-MoA8 Cross Sectional STM Study on MBE-grown Si/Ge(111) Interface**, *H. Hirayama, M. Ohmori, K. Takayanagi, Tokyo Institute of Technology, Japan*

We studied the (111) cross sectional surface of MBE grown Si/Ge(111) samples. Samples were cleaved in ultra-high vacuum, and their (111) cross section were investigated in-situ by using STM. On the as-cleaved surface, 2x1 reconstruction were observed at both Si and Ge side. After annealing, 2x1 reconstruction changed to 7x7 and c(2x8) on the Si and Ge layer, respectively. At around the interface, 7x7 reconstruction changed to c(2x8) reconstruction in moving from Si to Ge side. But, the transition from 7x7 to c(2x8) was not abrupt. The transient region of the width of c.a.200nm was observed. In the transient region, adatoms arranged with 2x2 and c(2x4) short range orderings. Patchy domains of 7x7 reconstruction, which was accompanied with (110)-oriented grooves and non-double layer height steps, were also observed in the sea of 2x2 and c(2x8) arrangement of adatoms. In a detailed analysis of adatom arrangement, we found that the non-double layer height step was caused by the glide in the (111) plane parallel to the substrate. The groove was triggered by partial dislocations at the edge of the glide region. The strain field with the glide-induced step and grooves modified the surface strain locally, and caused patchy 7x7 domains.

# Monday Afternoon, November 2, 1998

4:40pm NS+EM+SS-MoA9 Scanning Tunneling Microscopy

**Characterization of the Depletion Zone of a Si Lateral pn Junction, M.L.**

*Hildner, R.J. Phaneuf, E.D. Williams*, University of Maryland, College Park

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are used to characterize lateral pn junctions fabricated on silicon (100) surfaces. Two separate device structures, one with p<sup>+</sup>-n and the other with n<sup>+</sup>-p abrupt junctions, were examined. The STM images of the first set of devices show both an electronic feature and a structural groove on each side of the ion implanted p-type regions. The groove is an etching artifact of the implantation mask fabrication process and was easily avoided in making the second set of devices which show only a similar electronic feature. The electronic feature widens with applied reverse bias with a voltage dependence that closely matches that expected for the depletion zone. However, the width of the electronic feature is much smaller than that of the depletion zone. The STS measurements show that the tip-junction system can be modeled as a series of non-equilibrium metal-insulator-semiconductor (MIS) diodes formed with a semiconductor of spatially variable carrier density. From this model, we qualitatively describe the electronic feature as confined to that portion of the depletion region in which the biasing sense of the MIS junction is switched from the biasing sense when the junction is in the lightly doped neutral region. Thus, the electronic feature commences, as the tip is moved from the lightly doped neutral region into the depletion region, when the majority carrier changes (from electrons to holes for the lightly doped n devices). This work has been supported by the Laboratory for Physical Science, with partial support from the NSF-MRSEC.

## Electronic Materials and Processing Division Room 316 - Session EM+SE-TuM

### Critical Issues in Widebandgap Semiconductors

**Moderator:** M.R. Melloch, Purdue University

8:20am **EM+SE-TuM1 Gallium Nitride Structures for High Power Microwave Amplification, L.F. Eastman, K. Chu, N. Weimann, J. Smart, J.R. Shealy, Cornell University**

**INVITED**

Among the wide band-gap materials Gallium Nitride has yielded the best frequency response and efficiency for microwave amplifiers. Wurtzite Al<sub>x</sub>Ga<sub>1-x</sub>N/GaN/SiC HEMT structures, with  $x < .50$ , yield a high two-dimensional electron gas density of  $\sim 1 \times 10^{13} \text{ cm}^{-2}$  with no intentional doping, due to the piezoelectric effect. The drain-source breakdown voltage at pinchoff rises linearly with gate length, being  $> 200 \text{ V}$  for  $1 \mu\text{m}$  gates due to the  $3\text{-}4 \text{ MV/cm}$  breakdown field strength. Using SiC substrates having  $> 3 \text{ W/cm}^2\text{K}$  thermal conductivity, up to  $20 \text{ W/mm}$  periphery will be possible. The normalized drain current is  $> 1 \text{ A/mm}$ , yielding a high normalized optimum load of  $\sim 200 \text{ ohm-mm}$  for  $1 \mu\text{m}$  gates. Large periphery HEMT's with reasonable load resistances will allow power levels  $> 100 \text{ W}$ , with efficiency above 60%, for frequencies  $< 12 \text{ GHz}$ . The impact of dislocations, with density of  $.5 - 2.0 \times 10^9 \text{ cm}^{-2}$  for GaN on SiC, on electron mobility has been determined analytically, and is in the range of  $1,500\text{-}2,000 \text{ cm}^2/\text{V-s}$ . These dislocations line up in the growth direction and thus do not substantially limit the electron mobility in vertical FET's such as the Static Induction Transistor (S.I.T.) The theoretical value of the peak electron velocity for GaN is  $2.7 \times 10^7 \text{ cm/s}$  and is reached at  $150\text{-}200,000 \text{ V/cm}$ . Short gate ( $.15 \mu\text{m}$ ) HEMT's have unity current gain frequency of  $\sim 70 \text{ GHz}$ , and unity power gain frequency of  $140 \text{ GHz}$ . Due to the large bandgap, operation with channel temperatures  $> 200^\circ\text{C}$  is possible with no substantial reduction in performance.

9:00am **EM+SE-TuM3 HfN Films Grown on GaN by Reactive MBE using Ammonia@footnote 1@, A. Parkhomovskiy, B.E. Ishaug, A.M. Dabiran, P.I. Cohen, University of Minnesota**

Stoichiometric HfN has a sodium chloride structure which is lattice matched to GaN to within 1%, assuming a 45 degree rotation. It has a low work function and hence should be an abrupt ohmic contact to wide bandgap semiconductors that is stable at very high temperatures. In this work we report the epitaxial growth of HfN on the (000-1) plane of GaN thin films. Hf and Hf-N thin films of various nitrogen contents were grown by MBE using a Hf electron beam source and an ammonia leak. The films were studied using RHEED and AFM. It was found that epitaxial HfN could be grown on GaN even at room temperature. However, the surface morphology and structure are dependent upon the nitrogen content and on the substrate temperature. GaN films of about 0.2 microns thickness, also grown using ammonia, were used as the substrate for the HfN growth. The GaN was grown under conditions of excess ammonia. The surface was annealed in ammonia as the temperature was lowered, producing an N termination on this polarity. Hf and HfN were then deposited on top of GaN at temperatures between 20C and 730 C. Deposition of pure Hf at room temperature revealed an epitaxial, though bulk diffraction pattern. This was only slightly affected by annealing in vacuum to 700 C. Little change was observed when annealed in an ammonia flux. However, when Hf was deposited in an ammonia flux at room temperature, the diffraction pattern corresponding to HfN is observed. For this room temperature film, there is some evidence of faceting in the diffraction pattern. AFM indicated an rms roughness of 5 nm for 100 nm film. If HfN was deposited at substrate temperatures above 350 C, a polycrystalline diffraction pattern was observed. This consisted of arcs at the intersection of the Ewald sphere, which were not continuous, indicating some preferential ordering in the film. AFM indicated an rms roughness of 40 nm for a 100 nm film. The electrical properties of the contact as well as the role of the interfacial termination and the flux ratio on the film growth will be presented. @FootnoteText@ @footnote 1@Partially Supported by Air Force Office of Scientific Research and the Office of Naval Research.

9:20am **EM+SE-TuM4 Investigation of Metal / GaN Interface Properties using Photoemission Spectroscopy and I-V Measurements, C.I. Wu, A. Kahn, Princeton University**

We present a systematic investigation of the formation of Schottky barriers between n- and p-GaN grown by MOCVD and a series of high and low work function metals (Mg, Al, Ti, Au and Pt). We compare interface Fermi level

positions with measured transport characteristics (I-V). The interfaces are formed on well ordered (0001)-(1x1) surfaces. The initial band bending is 0.75 eV upward and 0.75 eV downward on clean n- and p-type surfaces, respectively. The chemistry and electronic properties of these interfaces are studied by x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). Al, Ti and Mg are found to react at room temperature with nitrogen, as indicated by the appearance of a free Ga component in the Ga 3d core level spectrum, whereas Au and Pt form abrupt, unreacted interfaces. The Fermi level movements on both n- and p-GaN are consistent with the metal work functions, but limited by surface or interface states. The maximum metal induced band bending is 0.9 eV downward for Mg on p-GaN and 0.8 upward for Pt on n-GaN. Upon annealing, the incorporation of Mg increases the density of acceptors as seen on both n- and p-GaN. In spite of similar work functions and chemical reaction with nitrogen, Ti and Al form drastically different Schottky barriers. Ti causes an additional band bending of more than 0.5 eV for both n- and p-GaN whereas the Al-induced band shift is less than 0.2 eV. The difference is due to very different products of reaction, i.e. AlN is a wide band gap semiconductor whereas TiN is a metallic compound. The Schottky barrier heights are 1.2 eV (1.45 eV) and 1.1 eV (0.7 eV) on n- and p-GaN, respectively, for Au (Pt). We will present on-going measurements on the comparison between Schottky barrier heights obtained by photoemission spectroscopy and I-V measurements.

9:40am **EM+SE-TuM5 Mg Doping Studies of ECR-MBE GaN Thin Films, I.E. Berishev, E. Kim, O. Kameli, D. Starikov, A. Bensaoula, University of Houston**

MBE of GaN is a rapidly progressing ultra high vacuum growth technique that allows the growth of high purity materials, at lower temperatures, in a clean and well characterized environment, and at high enough growth rates. Much of the recent work however was performed using RF nitrogen sources instead to previously popular ECR sources. Lower deposition rates for ECR sources being the major reason. In all growth technologies, p-type doping remains an issue for GaN device structures fabrication such as LED, LD, FET, etc. As grown p-type MBE GaN layers were however successively realized by several groups. In our study a modified ASTEX ECR source, allowing optically active GaN thin films at growth rates up to 1 micron per hour, was utilized in an MBE environment. Using this nitrogen source, Mg doping studies of GaN were undertaken. The effects of growth parameters and ECR source design on the Mg incorporation and its electrical activity were characterized by SIMS, electrochemical profiling, and photoluminescence. The background concentration and major impurities are identified by time of flight SIMS. A direct correlation exists between Mg incorporation and the ECR power, nitrogen flow, Mg cell temperature, growth temperature and ECR exit aperture size. Using an optimized process, SIMS show sharp profiles between doped and undoped layers can be obtained. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061.

10:00am **EM+SE-TuM6 Deposition of AlN Gate Dielectrics, B. Gila, S.M. Donovan, C.R. Abernathy, K.N. Lee, J.D. MacKenzie, F. Ren, S.J. Pearton, University of Florida, Gainesville; S.N.G. Chu, Bell Laboratories, Lucent Technologies**

The development of a suitable insulator for GaN is a critical step in developing a GaN MOSFET technology. Conventional dielectrics such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> have generally failed on III-V materials because of high interface state densities. AlN is an attractive alternative because of its large bandgap, high thermal conductivity and excellent thermal stability. Also, a high relative dielectric constant (8-9) alleviates the problem of high fields in the dielectric in high voltage applications. AlN has also been proposed as a potential replacement for silicon dioxide in high temperature MIS based silicon carbide device applications. In this study, 375Å AlN films were deposited in ultrahigh vacuum (UHV) using an RF nitrogen plasma and dimethylethylamine (DMEA) on Si, SiC and GaN/Sapphire at temperatures ranging from 325° to 525°C. Prior to deposition various surface cleans were employed including hydrogen plasma exposure, BOE (Si) high temperature exposure to ammonia and nitrogen plasma (GaN and SiC). Cross-sectional TEM (XTEM), Auger electron spectroscopy (AES), reflection high energy electron diffraction (RHEED), C-V and I-V analysis were used to characterize the films as functions of deposition temperature and surface preparation. In spite of the low deposition temperatures, none of the films were found to contain oxygen or carbon within the detection limit of AES. Consequently, the reverse breakdown characteristics of the layers were found to be excellent.

# Tuesday Morning, November 3, 1998

By contrast, the interface state density as measured by C-V was found to depend strongly on the nature of the initial substrate surface. Optimization of the initial starting surface via mass spectrometry and RHEED during in-situ chemical cleaning produced substantial reduction in the interfacial leakage current. As a result, initial GaN HIGFET devices show promising performance with improved breakdown and C-V behavior relative to conventional MESFET structures.

10:20am **EM+SE-TuM7 Progress in SiC: From Material Growth to Commercial Device Development**, *C.H. Carter, V.F. Tsvetkov, D. Henshall, O. Kordina, K. Irvine, R. Singh, S.T. Allen, J. Palmour*, Cree Research, Inc.

INVITED

Silicon carbide technology has made tremendous strides in the last several years, with a variety of encouraging device and circuit demonstrations in addition to volume production of nitride-based blue LEDs being fabricated on SiC substrates. The commercial availability of relatively large, high quality wafers of the 6H and 4H polytypes of SiC for device development has facilitated these exciting breakthroughs in laboratories throughout the world. These have occurred in numerous application areas, including high power devices, short wavelength optoelectronic devices, and high power/high frequency devices. This presentation will describe progress made in increasing the quality and size of SiC wafers, advances in SiC epitaxy and some of the resulting device demonstrations and commercialization by Cree Research. To meet the challenges required for commercialization of SiC semiconductors, we have made specific efforts towards larger diameter high quality substrates which have led to production of 50 mm diameter 4H and 6H wafers for fabrication of LEDs and the demonstration of 75 mm wafers. The latest results on micropipe reduction will be presented including a wafer which contains a total of 7 micropipes, yielding a density of 0.7 cm<sup>2</sup>/super-2@. High voltage P-i-N diodes have been fabricated from hot-wall grown epitaxy using junction termination extension (JTE) edge termination. The highest breakdown voltage achieved for these diodes is >5.5 kV, which is a new world record for blocking voltage for a SiC device. In the microwave device area, a SiC MESFET with 42 mm of gate periphery on a single die which had a maximum RF output power of 53 watts CW with 37% power-added efficiency (PAE) at 3.0 GHz has been demonstrated. This unprecedented power from a die with an area of only 3 mm<sup>2</sup>@ demonstrates the extremely high power handling capability of SiC microwave devices. Additionally, SiC MESFETs showing 2.5 W/mm with 41% PAE at 8 GHz, demonstrate the utility of this technology at X-band.

11:00am **EM+SE-TuM9 Critical Development Issues for Deep (10 to 100 μm) Etching of SiC**, *D.C. Sheridan*, Auburn University; *J.B. Casady*, Northrop Grumman; *C.E. Ellis*, Auburn University; *R.R. Siegiej*, Northrop Grumman; *J.D. Cressler*, Auburn University; *W.E. Urban, W.F. Valek, H. Buhay*, Northrop Grumman

Silicon carbide is a wide bandgap (3.2 eV for the 4H polytype) semiconductor gaining popularity in applications requiring high-power, high-frequency, and high-temperature performance@footnote 1@. Material quality improved significantly since the first commercial release of SiC substrates in 1991. Numerous SiC semiconductor devices have been developed, such as thyristors, diodes, JFETs, MESFETs, and static induction transistors. Because of its high bond strength, the etching of SiC has been quite difficult, performed almost exclusively using dry etching techniques. Most techniques have utilized fluorinated gas chemistries in reactive ion etch (RIE), electrocyclotron resonance (ECR) etch, or inductively coupled plasma (ICP) etch systems. Residue free etches have been developed with etch rates from 5 nm/minute up to 350 nm/minute@footnote 2,3@. For very deep etching of SiC, up to 75 μm, which would be required for selected applications, no suitable process has been reported on. The ideal process would optimize a combination of fast etch rate, good mask selectivity, and reproducibility. In this work, we compare five SiC etches used in commercial RIE systems with regard to the above criteria. The SiC etches examined are all residue-free, and possess etch rates ranging from 8 nm/minute up to 160 nm/minute. The etches utilize one or more of the following fluorinated gases: NF@sub 3@, SF@sub 6@, CHF@sub 3@, or CF@sub 4@. A more detailed characterization of the etch recipes will be given in the full paper, and partial details have been reported elsewhere@footnote 4,5,6@. Several inorganic and organic mask materials will also be evaluated. Each mask material is characterized and tabulated in terms of etch rate, selectivity, and residue-formation for each of the SiC etches. @FootnoteText@ @footnote 1@ J.B. Casady and R.W. Johnson, Solid-St. Elect., Vol. 39, No. 10, p. 1409, 1996. @footnote 2@ P.H. Yih, V. Saxena, and A.J. Steckl, Phys. Stat. Sol. (b) Vol. 202, p. 605, 1997. @footnote 3@ G. McDaniel, J.W. Lee, E.S. Lambers, S.J. Pearton, P.H.

Holloway, F. Ren, J.M. Grow, M. Bhaskaran, and R.G. Wilson, J. Vac. Sci. Technol. A, Vol. 15 @footnote 4@ J.B. Casady, E.D. Luckowski, M. Bozack, D. Sheridan, R.W. Johnson, and J.R. Williams, J. Electrochem. Soc., Vol. 143, No. 5, p. 1750, 1996. @footnote 5@ P.H. Yih and A.J. Steckl, J. Electrochem. Soc., Vol. 140, p. 1813, 1993. @footnote 6@ J.B. Casady, S.S. Mani, R.R. Siegiej, W. Urban, V. Balakrishna, P.A. Sanger, and C.D. Brandt, J. Electrochem. Soc., Vol. 145, No. 4, p. L58, 1998.

11:20am **EM+SE-TuM10 Thermochemical Stability of Plasma-Deposited Silicon Oxycarbide Thin Films Subjected to Post-Deposition Rapid Thermal Annealing**, *D.M. Wolfe, B. Ward, F. Wang, M. Xu, G. Lucovsky, R.J. Nemanich, D.M. Maher*, North Carolina State University

Low defect density gate dielectrics are of critical importance to maximize electrical performance/reliability in SiC high power devices. Under some growth conditions carbon atoms are trapped in thermally-grown oxides forming silicon oxycarbides@footnote 1@, and it has been suggested that these C-atoms degrade device performance. The bonding of C-atoms in silicon oxycarbides as well as their thermal stability is therefore addressed. Thin silicon suboxide (SiO@sub x@, x<2) and silicon oxycarbide (SiO@sub x@C@sub y@, x<2, y<<1) films were deposited at 250°C by remote-plasma enhanced CVD. Changes in the local chemical bonding and the onset of crystallization upon rapid thermal annealing at temperatures from 600-1100°C were investigated. XPS and RBS were used for compositional analysis; FTIR was used to track the extent of structural/chemical changes through shifts in Si-O and Si-C bond-stretching frequencies. Raman spectroscopy, and HRTEM/selective area diffraction were used to monitor crystallization products through the appearance of characteristic phonon modes and diffraction patterns, respectively. These studies showed a structural/chemical transformation occurred at about 900°C for silicon suboxide films. At this temperature, the end-product material was comprised of Si nanocrystals imbedded in an non-crystalline SiO@sub 2@ matrix. A similar structural/chemical transformation, in which Si nanocrystals were also formed, was observed between 1000 and 1050°C for the silicon oxycarbides. However, a siloxane-type Si-O-C bond was observed to form at intermediate temperatures (~900°C), and to disappear upon crystallization. No evidence for amorphous or crystalline C-C bonds, or other C-O bonding groups was found in the oxycarbide films before, or after annealing. Finally, concentrations of Si and O, and Si, O and C remained essentially the same for the respective as-deposited and fully-annealed films. @FootnoteText@ @footnote 1@ B. Hornetz, H.-J. Michel, J. Halbritter, J. Mater. Res 9, 3088 (1994).

## Organic Electronic Materials Topical Conference Room 327 - Session OE+AS+EM-TuM

### Organic Thin Film Interfaces

**Moderator:** J.L. Brédas, University of Mons-Hainaut, Belgium

8:20am **OE+AS+EM-TuM1 UV Photoemission Study of Interfacial Electronic Structures of Organic Materials**, *K. Seki, E. Ito, H. Oji, K. Sugiyama, D. Yoshimura, Y. Ouchi, H. Ishii*, Nagoya University, Japan

INVITED

The energy level alignment at organic/inorganic and organic/organic interfaces is a fundamental issue for understanding interfacial phenomena of organic-based electronic devices. Using UV photoemission spectroscopy (UPS), we have investigated the electronic structure and energy level alignment at the interfaces of various organic films on metal substrates prepared in ultrahigh vacuum (UHV). The observed results clearly demonstrated that the traditional picture which assumes vacuum level alignment at the interfaces is not valid: the vacuum level of organic layer is shifted from that of metal electrode. We report here our recent effort on the examination of the vacuum level shift at organic/metal, and organic/organic interfaces. At most organic/metal interfaces so far studied, downward shifts of vacuum level were observed (i.e. the vacuum level of organic layer is below that of the metal). At acceptor/metal interface, upward shift was often observed, depending on metal electrode. From the relation between the observed shift and the work function of the metal, we discuss the possible origins of the vacuum level shift such as the polarization of organic molecule by image effect, charge transfer, and mid-gap state. We will also present the results of 'sexiphenyl(6P) on metal' and 'metal on 6P' by UPS, X-ray photoemission (XPS), and metastable atom electron spectroscopy (MAES). At organic/organic interface such as Alq@sub 3@/(tris(8-hydroxyquinolino)aluminum) /TPD(N-N'-diphenyl-N-N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine), the observed vacuum level shift was less than 0.1eV, leading to an apparent applicability of the



traditional model. However, finite shift of 0.2 eV was observed at donor/acceptor interface such as TTN(tetrathianaphthalene)/TCNQ(tetracyanoquinodimethane) due to electron-transfer.

## 9:00am OE+AS+EM-TuM3 Electronic Structure of Molecular Organic Semiconductor Metal Interfaces, A. Kahn, I.G. Hill, Princeton University

It is now well known that the traditional assumption of vacuum level alignment at metal-organic semiconductor interfaces is incorrect.<sup>1,2</sup> Large interface dipoles shift the vacuum level at the interface by more than 1 eV in some cases. The electron injection barrier therefore cannot be reliably estimated as the difference between the metal work function and the organic electron affinity. Furthermore, it has been found that the magnitude of this barrier varies significantly with the metal work function on some organic materials, and not at all on others. To illustrate these properties, we present a comprehensive investigation of metal-organic semiconductor interfaces. Many of these interfaces have been studied both in the organic on metal and metal on organic systems, which in general are not equivalent. The metals studied range in work function from 3.7 eV (Mg) to 5.2 eV (Au). The organic materials studied include the hole transport materials, PTCDA and  $\alpha$ -NPD, the electron transport material Alq<sub>3</sub>, and the cathode interface material, CBP. Using ultraviolet photoelectron spectroscopy, we have measured the relative positions of the metal Fermi level and the organic HOMO, as well as the offset of the vacuum level at each interface. We show that the dependence of the barriers on the metal work function is very small with PTCDA and Alq<sub>3</sub>, and increases with  $\alpha$ -NPD and CBP. All of these organic-metal pairs exhibit substantial interface dipoles which compensate for the restricted range of interface Fermi level positions. Implications for contact performances are discussed.<sup>1</sup> H. Ishii and K. Seki, IEEE Trans. on Elect. Dev., 44, (1997) 1295.<sup>2</sup> I. G. Hill, A. Rajagopal, A. Kahn and Y. Hu, Submitted to Appl. Phys. Lett.

## 9:20am OE+AS+EM-TuM4 Interface Dipoles and Band Bending in Organic Semiconductor Interfaces, R. Schlaf, M.W. Nelson, P.G. Schroeder, B.A. Parkinson, Colorado State University; P.A. Lee, K.W. Nebesny, N.R. Armstrong, University of Arizona

The fast paced development in the field of organic light emitting diodes (OLED) and thin film transistors (OTFT) has sparked intense efforts to determine the electronic structure at organic interfaces and to understand the rules governing it. Photoemission spectroscopy (PES) measurements offer direct information about the HOMO alignment, interface dipole and band bending at such interfaces. We performed multistep growth experiments with insitu PES characterization on a variety of organic/organic, organic/inorganic semiconductor and organic/conductor interfaces. We used combined X-ray and UV photoemission spectroscopies (XPS, UPS) which allow the separate determination of the band bending across the interface. This procedure, which is well established in the field of inorganic semiconductor heterojunctions, allows the measurement of HOMO alignment and interface dipoles with high precision. High precision results from avoiding the problem of the superposition of substrate and overlayer emissions in UP-spectra where elaborate curve fitting procedures are needed to distinguish between band bending and HOMO alignment. Our measurements indicate that band bending and interface dipoles play a significant role in the electronic structure at these interfaces similar to effects known from inorganic semiconductor interfaces. The interface dipoles are discussed in terms of quantum and structural dipoles caused by tunneling of charge carriers and permanent molecular dipoles at the interface.

## 9:40am OE+AS+EM-TuM5 Molecular Level Offsets at Organic Semiconductor Heterojunctions, I.G. Hill, A. Rajagopal, A. Kahn, Princeton University

Organic light emitting devices typically consist of two or more organic layers between hole and electron injecting contacts. The interface between the two organics can provide a barrier to either holes or electrons, which may increase device efficiency by reducing the leakage current through the device (leakage current does not contribute to light production). Most of the exciton formation and subsequent light emission occurs near this interface because of the resulting high carrier densities. Knowledge of the relative positions of the organic highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular (LUMO) orbitals at the interface is required to predict the transport or blocking characteristics for holes and electrons, respectively. The assumption of vacuum level alignment at organic heterojunctions is usually used to predict the size of carrier

injection barriers, but it has been shown that this model breaks down at organic-metal interfaces.<sup>1</sup> We have addressed the validity of this assumption by performing the most comprehensive direct measurement of the HOMO-HOMO offsets at key organic-organic interfaces using ultraviolet photoelectron spectroscopy. Five molecular solids are considered: PTCDA,  $\alpha$ -NPD, Alq<sub>3</sub>, CBP and CuPc. In general, the assumption of a common vacuum level at the interface was found to be valid. A few heterojunctions, such as PTCDA/Alq<sub>3</sub> and  $\alpha$ -NPD/Alq<sub>3</sub>, do show substantial discontinuities of the vacuum level, however, indicating the formation of an interface dipole.<sup>2</sup> The molecular level offsets are discussed in terms of the Fermi level positions observed at interfaces between these organics and various metals.<sup>1</sup> H. Ishii and K. Seki, IEEE Trans. on Elect. Dev., 44, (1997) 1295.<sup>2</sup> A. Rajagopal, C. I. Wu and A. Kahn, J. Appl. Phys., 83, (1998) 2649.

## 10:00am OE+AS+EM-TuM6 Interface Analysis of Naththyl-substituted Benzidine Derivative and tris-8(hydroxyquinoline) Aluminum Using Ultraviolet and X-Ray Photoemission Spectroscopy, E.W. Forsythe, V.-E. Choong, University of Rochester; C.W. Tang, Eastman Kodak Company; Y. Gao, University of Rochester

The interface energy level alignment is a decisive factor in producing highly efficient organic light emitting diodes (OLEDs). We have studied the interface between naththyl-substituted benzidine derivative (NPB) and tris-8-(hydroxyquinoline) aluminum (Alq), a prototypical system used in OLEDs. The combination of ultraviolet photoemission and x-ray photoemission spectroscopy (UPS, XPS) allows us to distinguish contributions from NPB and Alq and obtain a detailed picture of the interface formation. The NPB coverages were deposited onto a 150 Å thick Alq film prepared insitu at 1x10<sup>-9</sup> Torr. The Alq and NPB HOMO levels are -1.7 eV and -1.4 eV, relative to the Fermi level, respectively. From the UPS difference spectrum, the gradual modification of the HOMO levels of NPB and Alq are revealed. The Alq HOMO level increases from -1.7 eV in the bulk to -1.8 eV with 2 Å of NPB. Likewise, the NPB HOMO level increases from -1.1 eV for the 5 Å coverage to -1.4 eV with 55 Å of NPB. The increases observed for the Alq and NPB HOMO levels are consistent with the vacuum level shift as well as the observed core level shifts from XPS. Further, the XPS results show no chemical interactions at the interface. This observed local interface formation region may contribute additional traps and energy barriers for carrier transport across the Alq/NPB interface. This work was supported by DARPA DAAL01-96-K-0086 and NSF DMR-9612370.

## 10:20am OE+AS+EM-TuM7 Vapor Deposition Polymerization of 4-fluorostyrene and Pentafluorostyrene, B. Bartlett, L.J. Buckley, D.J. Godbey, Naval Research Laboratory; M.J. Schroeder, U.S. Naval Academy

Solventless deposition of thin, uniform dielectric films is of considerable interest and importance in the microelectronics industry, due to increasing wafer sizes and environmental concerns. This work demonstrates a solvent-free method for atmospheric pressure chemical vapor deposition polymerization of thin dielectric films on a variety of substrates, including Si, Mo, Pt, and Cu. The films are characterized using transmission FTIR, and XPS. Depth profiling is performed using XPS, ellipsometry, and step profilometry. Film growth is found to be independent of substrate, and proceeds with an activation energy of 15 kcal/mol between 450K and 500K. Films are shown by GPC (gel permeation chromatography) to consist of low molecular weight polymer and oligimer species (between 3 and 165 repeat units). AFM analysis indicates that the RMS thickness variation along the surface is < 0.2%, verifying film uniformity.

## 10:40am OE+AS+EM-TuM8 Growth and Characterization of Polyaniline Thin Films on Metal Substrates, K. Lee, R.V. Plank, J.M. Vohs, University of Pennsylvania; Y. Wei, N.J. DiNardo, Drexel University

Polyaniline (PANI) thin films have potential for use as conductive layers in organic-based electronic devices. In a series of experiments, the near-surface sensitivity of High Resolution Electron Energy Loss Spectroscopy (HREELS) was used to probe interfacial and thin film properties of insulating and conducting forms of PANI grown on metal surfaces. PANI was deposited on Ag, Cu, and Au surfaces by evaporative-deposition in vacuum using an emeraldine source and from solution. The fully-resolved vibrational spectra and electronic excitation spectra of PANI films as a function of thickness and modes of preparation reveal clear trends regarding film quality and conductivity upon doping. Specific interface interactions observed in the vibrational spectra at the outset of growth of ultrathin vapor-deposited PANI correlate with increased ordering and an oxidation state similar to the starting emeraldine powder. A relatively high (microscopic) conductivity is indicated by the observation of a split-off far-

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IR plasmon loss upon HCl doping; this has been compared to the bulk (macroscopic) conductivity of similarly prepared films. In contrast, thicker vapor deposited and solution cast films exhibit a greater degree of branching and lower conductivities. Studying the evolution of polymer thin film properties from the polymer-substrate interaction to the polymer surface demonstrates a general approach with great potential, and the data suggests several aspects of preparation and modification to better control the properties of PANI films in particular.

**11:00am OE+AS+EM-TuM9 Tapping Mode Near-Field Scanning Optical Microscopy of Molecular Crystals and Thin Films, H. Stadniychuk, A. Kosterin, C.D. Frisbie, University of Minnesota**

We describe near-field optical imaging experiments to probe fluorescence and birefringence in molecular crystals and polymeric thin films. These experiments utilize a near-field microscope that employs tapping mode feedback to scan the sample underneath a cantilevered optical fiber probe, facilitating imaging of soft organic samples. In one set of studies, we have focussed on fluorescence and transmission imaging of 30-400 nm thick crystals of tetracene grown by vacuum sublimation onto transparent substrates. These well-defined crystals are excellent samples for investigating quantitative aspects of near-field imaging, and we seek to determine the spatial extent of the near-field by quantifying the relationship between fluorescence intensity and crystallite thickness. A second set of studies exploits polarization modulation techniques to investigate birefringence from thin films of polymers, such as polyethylene oxide. A key aspect of these investigations is comparison of the near-field birefringence images with birefringence images obtained by confocal microscopy. This comparison facilitates understanding of contrast mechanisms in near-field characterization of organic thin films.

**11:20am OE+AS+EM-TuM10 Morphology and Relaxation Dynamics in Thin Organic Films Probed by Femtosecond Time-Resolved Photoemission Spectroscopy, A.J. Mäkinen, S. Xu, S. Diol, A.R. Melnyk, D.A. Mantell, M.G. Mason, A.A. Muentner, Y. Gao, University of Rochester**

We have studied for the first time the lifetimes of the excited electron states of thin N,N'-bis(phenethyl)-perylene-3,4:9,10-bis(dicarboximide) (DiPe) films, prepared in situ, using femtosecond time-resolved photoemission spectroscopy. DiPe is an organic compound similar to photoreceptor materials widely used in many imaging applications. By controlling the evaporation conditions, we have been able to grow films of different morphologies, and found that the relaxation dynamics depends on the morphology. We have investigated two distinct films characterized by very different absorption spectra. We have found that for the film with absorption maximum at 500 nm, a typical lifetime is 45 fs at 2.1 eV above the molecular HOMO level. For the other film with absorption maximum at 630 nm, the relaxation rate is almost twice as fast, resulting a lifetime of 25 fs at the same energy. We attribute the extremely short lifetimes to a rapid charge transfer reaction from the high energy sites to the low energy sites. This mechanism is further enhanced by the presence of disorder, which prevents the conservation of crystal momentum in the films. The dependence of the lifetimes on the morphology can be explained by the difference of crystallinity of the films, which affects the density of states and the localization of the excited electrons.

**11:40am OE+AS+EM-TuM11 XPS and ISS Studies of Cu Deposited onto Acid-terminated Self-Assembled Monolayers, L.S. Dake, D.E. King, A.W. Czanderna, National Renewable Energy Laboratory**

Metal/self-assembled monolayer (SAM) systems serve as models for more complex metalized polymers. Often the adhesion of metals to polymers is a problem, and the metal/polymer interface can be the critical weak link in such a system. We have studied the interactions of Cu deposited onto an acid-functionalized (COOH) SAM surface to improve our understanding of the fundamental metal/organic interactions. We are interested in the chemical interactions of the Cu with the SAM surface, the growth mode of the deposited metals, and the penetration of the metal. Copper deposited onto SAMs with different organic functional endgroups exhibits a wide range of behavior ranging from no surface interaction and rapid penetration (for methyl-terminated SAMs) to weak interactions followed by slow penetration (for methyl-ester terminated SAMs). In this work, we have characterized the interactions of Cu with a carboxylic acid-functionalized alkanethiol SAM, using XPS to examine the chemical interactions, and a combination of XPS and ISS to deduce the growth mode and penetration rate of the deposited Cu. Of particular interest is whether a chemical reaction with the acid surface suppresses penetration, and if there is a limit to the amount of Cu that penetrates the SAM. We find that small amounts of Cu react with the acid surface group, whereas the rest of

the Cu penetrates beneath the SAM. Considerable amounts of Cu (10 nm or more) will diffuse beneath the SAM layer, despite the presence of small amounts of reacted Cu at the surface. The penetration rate depends strongly on the deposition rate, with much more rapid penetration occurring at deposition rates of 0.1 nm/min or less. Cooling the sample during Cu deposition, and more rapid Cu deposition rates result in slower or even completely suppressed penetration of the Cu through the SAM layer. This work was performed under DOE contract DE-AC36-83CH10093 @FootnoteText@ After Aug. 1, address for Dr. L. S. Dake is Susquehanna University, Selingsgrove, PA 17870-1001

## Electronic Materials and Processing Division Room 316 - Session EM+PS+SE-TuA

### Plasma Processing of Compound Semiconductors

Moderator: C. Eddy, Boston University

2:00pm **EM+PS+SE-TuA1 Thermally Induced Improvements on SiN@sub x@:H/InP Devices**, *E. Redondo, N. Blanco, I. Mártel, G. González Díaz*, Universidad Complutense de Madrid, Spain; *R. Peláez, S. Dueñas, H. Castán*, Universidad de Valladolid, Spain

The electron cyclotron resonance (ECR) plasma technique has been recently proved to be optimum as insulator deposition method in Al/SiN@sub x@:H/InP devices. In this communication we present a study of the influence of rapid thermal annealing (RTA) treatments on the interface characteristics of Al/SiN@sub x@:H/InP devices. The insulator was obtained by the ECR plasma method at 200°C-deposition temperature. The films were deposited in two steps: we deposited first a film with  $x=1.55$  and then another with  $x=1.43$ . Total film thickness was 500Å in one set of samples and 200Å in other. RTAs were conducted in Ar atmosphere during 30s in a temperature range between 400 and 800°C. The electrical characteristics of the devices have been obtained by capacitance-voltage (C-V) and deep-level transient spectroscopy (DLTS) measurements. Those films annealed between 400 and 500°C/30s in Ar atmosphere give structures with the minimum interfacial trap density. The interface trap density behavior with the annealing temperature has been observed to show the same trend with both CV and DLTS measurements, reaching lower values in the latest ones. The minimum interfacial trap density value achieved with the best annealing is of  $3 \times 10^{11}$  cm<sup>-2</sup> eV<sup>-1</sup>, obtained for 400°C/30s annealing on the thinnest structure (200Å). Besides, DLTS measurements show the presence of features in the spectrum that are characteristic of phosphorus vacancies, V@sub p@, and deep centers. The annealing at 400°C/30s reduces the V@sub p@ content. This suggests that the nitrogen from the insulator is filling these vacancies so InP surface is being passivated. @FootnoteText@ @footnote 1@ S.García, I.Mártel, G.González Díaz, E.Castán, S.Dueñas, M.Fernandez. J.Appl.Phys, 83 (1), 1998, pp 600-603.

2:20pm **EM+PS+SE-TuA2 Damage to III-V Devices During Electron Cyclotron Resonance Chemical Vapor Deposition**, *F. Ren*, University of Florida, Gainesville; *J.W. Lee, D. Johnson, K. McKenzie*, Plasma-Therm, Inc.; *T. Maeda, C.R. Abernathy, Y.-B. Hahn, S.J. Pearton*, University of Florida, Gainesville; *R.J. Shul*, Sandia National Laboratories

GaAs-based metal semiconductor field effect transistors (MESFETs), heterojunction bipolar transistors (HBTs) and high electron mobility transistors (HEMTs) have been exposed to ECR SiH@sub 4@/N@sub 2@, SiH@sub 4@/N@sub 2@/O and SiH@sub 4@/NH@sub 3@ discharges for deposition of SiN@sub x@ or SiO@sub 2@ passivating layers. The effect of source power, rf chuck power, pressure and plasma composition have been investigated. Effects due to both ion damage and hydrogenation of dopants are observed. For both HEMTs and MESFETs there are no conditions where substantial increases in channel sheet resistivity are not observed, due primarily to (Si-H)@super o@ complex formation. In HBTs the carbon-doped base layer is the most susceptible layer to hydrogenation. Ion damage in all three devices is minimized at low rf chuck power, moderate ECR source power and high deposition rates.

2:40pm **EM+PS+SE-TuA3 Anisotropic Etching of InP using CAIBE (Cl@sub 2@/Ar): Importance of the Sample Temperature Stability and the Reactive Gas Distribution**, *B. Lamontagne, M. Gagnon, J. Stapledon, P. Chow-Chong, M. Davies*, National Research Council, Canada

Process development has been performed for the dry etching of InP using our Chemically Assisted Ion Beam Etching (CAIBE) system (Ionfab 300 from Oxford Inst.). We studied the etching mechanisms in order to obtain vertical, deep and smooth InP sidewalls. Such etching profiles are essential for optoelectronic discrete devices such as turning mirrors, reflector gratings, deeply etched waveguides, etc. The CAIBE system has a 15 cm diameter R-F driven ion source, the ion beam is usually composed of argon while chlorine is introduced through the gas ring located in front of the heated platen. The sample temperature - a critical parameter when etching InP with chlorine - has been calibrated and monitored using a non-contact sensor: a diffuse reflectance spectrometer (DRS 1000 Thermionics Northwest Inc.). It gives an accurate temperature measurement of the sample itself using the shifting effect of the temperature on the absorption

edge position of semiconductors. This diagnostic tool allowed us to monitor the sample temperature increase under ion bombardment (CAIBE process) for various conditions; sample heating and mounting technique, ion beam current and energy. In some extreme process conditions the sample temperature has increased from 20° C to 300° C in less than one minute. Our results point out the need to use a stable process temperature in order to obtain vertical sidewalls. The influence of the reactive gas distribution has also been investigated, for example, by modifying the gas ring design. Etching conditions characterized by vertical (>89°) and long (up to 15 µm) sidewalls and SiO@sub 2@ mask selectivity of 30 were obtained.

3:00pm **EM+PS+SE-TuA4 Hydrogen in Compound Semiconductors**, *M.D. McCluskey, N.M. Johnson*, Xerox Palo Alto Research Center **INVITED**

Hydrogen can be inadvertently introduced at any of several steps in the fabrication of optoelectronic devices. In particular, incorporation of hydrogen can occur during growth, wet chemical processing, or dry etching. The most common consequence of hydrogenation is the passivation of dopant impurities, which leads to a decrease in the electrical conductivity of the material. The most successfully applied experimental technique for directly determining the involvement of hydrogen has been infrared-absorption local vibrational mode (LVM) spectroscopy, which will be illustrated with representative examples. In GaN:Mg grown by metalorganic chemical vapor phase deposition, hydrogen passivates Mg acceptors during the growth. Through experimental and computational studies it has been determined that hydrogen incorporated during growth forms electrically inactive complexes with Mg, and that a furnace anneal dissociates these complexes to activate the acceptor dopant. LVM spectroscopy was essential in the identification of the Mg-H complex. The observed frequency of the hydrogen LVM verified the theoretical prediction that hydrogen attaches to a host nitrogen atom. Recently, large hydrostatic pressures have been applied to compound semiconductors to probe the vibrational properties of hydrogen-related complexes. In GaAs, the pressure dependent shifts of hydrogen stretch modes provide clues about the location of hydrogen in the complexes. In AlSb, pressure was utilized to resolve a mystery as to why the Se-D complex gives rise to one stretch mode peak while the Se-H stretch mode splits into three peaks. This anomalous splitting is explained in terms of a new resonant interaction between the stretch mode and combination modes involving a wag mode harmonic and extended lattice phonons.

3:40pm **EM+PS+SE-TuA6 The Interaction of Electrons with Hydrogenated GaN(0001)**, *V.J. Bellitto, B.D. Thoms*, Georgia State University; *D.D. Koleske*, Naval Research Laboratory

Although Group III nitrides have recently been used to produce blue LEDs and laser diodes, many surface properties and processes have yet to be fully understood. One issue important to many applications of these materials is the effect of hydrogen during growth and processing. For example, hydrogen has been reported to significantly affect incorporation of dopants, Group III constituents, and contaminants. We have studied GaN(0001) using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). The ELS spectrum of GaN is seen to be particularly sensitive to exposure to atomic hydrogen (produced by a tungsten filament heated to 2073 K). A new peak appears at a loss energy of approximately 12 eV after atomic-hydrogen exposure but is not seen after exposure to molecular hydrogen alone. However, this peak is strongly affected by low energy electron irradiation of the surface. Substantial reduction in the 12 eV peak intensity is observed following exposure to 1.8 microamps of 90 eV electrons for two minutes. After 10 minutes of electron impingement on the hydrogen-atom-exposed surface, ELS spectra appear identical to those taken with no hydrogen atom exposure. Heating to 690 K is also seen to remove the hydrogen-related peak from ELS spectra. Recently, Gillis et al. have shown that simultaneous exposure of GaN to hydrogen atoms and low energy electrons results in anisotropic etching. Implications of these data for both surface science and etching of GaN will be discussed.

4:00pm **EM+PS+SE-TuA7 III-V Surface Plasma Nitridation: A Challenge for III-Nitride Epigrowth**, *G. Bruno, M. Losurdo, P. Capezzuto*, MITER-CNR, Italy; *E.A. Irene*, University of North Carolina, Chapel Hill

A challenge in the growth and processing of III-V nitrides is the control and optimization of the substrate/epilayer interface. It has been reported that high quality epilayers of GaN and related materials can be obtained by nitridation of the sapphire and GaAs substrates before the film growth. Substrate nitridation allows to accommodate the lattice mismatch between substrates and GaN epilayers and crucially affects the crystalline quality and

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structure of both the buffer and epitaxial GaN layers. In this contribution, the focus is on the nitridation process of GaAs and GaP (100) substrates to form GaN layers and of (0001) sapphire surfaces to form thin AlN. In order to elucidate the chemistry and kinetics of these solid state anion exchange reactions, the nitridation of (100) InP is also investigated. Nitridations are performed in a remote radiofrequency plasma metalorganic chemical vapor deposition (MOCVD) apparatus by exposing surfaces to the downstream flow of N@sub 2@ and N@sub 2@-H@sub 2@ plasmas, taking the advantages of low process temperatures and minimal surface damage. In situ optical diagnostics such as optical emission spectroscopy (OES) and spectroscopic ellipsometry (SE) are used to fingerprint in real time the gas phase and surface modifications, respectively. Thus, the chemistry and kinetics of the plasma-surface interactions are described together with the surface/interface composition and morphology. AFM analysis has been used to measure the surface roughness and to validate the effectiveness of plasma nitridation with respect to the conventional thermal nitridation by NH@sub 3@. Transmission electron microscopy (TEM) is used to highlight the different structural aspects of the nitride layers obtained by N@sub 2@ and N@sub 2@-H@sub 2@ mixtures. Optimizing the surface temperature and the N@sub 2@/H@sub 2@ ratio the formation of an interfacial As-rich layer in the GaAs/GaN growth is minimized, the nitridation depth is increased up to 15nm and compact and chemically stable GaN layers are obtained.

**4:20pm EM+PS+SE-TuA8 III-Nitride Dry Etching - Comparison of Inductively Coupled Plasma Chemistries, H. Cho, Y.-B. Hahn, D.C. Hays, C.R. Abernathy, S.M. Donovan, J.D. MacKenzie, S.J. Pearton, University of Florida, Gainesville; J. Han, R.J. Shul, Sandia National Laboratories**

A detailed comparison of etch rates, etch yields, surface morphology and sidewall anisotropy has been performed for GaN, InN and AlN etched in Inductively Coupled Plasma discharges of BCl@sub 3@, BI@sub 3@, BBr@sub 3@, ICl and IBr. Etch selectivities of 100:1 for InN over GaN and AlN are obtained in BI@sub 3@ due to the relatively high volatility of the InI@sub x@ products and the lower bond strength of InN. The selectivities are much lower in the other chemistries. The etched surfaces of the nitrides are smooth over a broad range of source and chuck powers, pressures and discharge compositions, and there is typically a slight deficiency of N@sub 2@ in the near-surface (@<= 100Å) region. The etch yields for all of the chemistries are relatively low (@<= 2), indicating that the high ion flux in the ICP tool is a critical factor in obtaining practical etch rates for the nitrides.

**4:40pm EM+PS+SE-TuA9 Photoenhanced RIE of III-V Nitrides in BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ Plasmas, A. Tempez, N. Medelci, N. Badi, I. Berichev, D. Starikov, A. Bensaoula, University of Houston; A. Chourasia, Texas A&M University**

Boron nitride (BN) and gallium nitride (GaN) are known as superior semiconductor materials for UV optoelectronic and high power, high temperature applications. As a consequence of their high molecular bond strength, these materials are extremely difficult to etch. In order to address the device processing issue, reactive ion etching (RIE) tests were performed on BN and GaN thin films. Our experiments show that optimum etching occurs using BCl@sub 3@/Cl@sub 2@/Ar chemistries for GaN and Cl@sub 2@/Ar for BN. In the case of GaN, the BCl@sub 3@/Cl@sub 2@/Ar mixture results in the highest reported RIE GaN etch rates. @footnote 1@ Auger and x-ray photoelectron spectroscopy analyses of the etched surfaces always show a depletion of the surface nitrogen atomic composition which increases with the dc bias (rf power). The impurity incorporation, C and Cl also shows the same trend. In order to improve the etch rates at lower powers, a photoenhanced RIE process was investigated. A BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ plasma in combination with a xenon arc lamp was utilized. Preliminary results show a 33% increase in GaN etch rates for a -220 V dc bias (100 W rf power). The dependence of etch rates, surface composition and chemistry, and surface morphology on dc bias (rf power) and photo-irradiation flux will be presented. In addition, the energy and angle distribution of the reaction species from nitride materials exposed to well characterized reactive beams were investigated. The results will be compared to those from RIE and Photo-RIE data and a model for the possible surface etch reactions will be discussed. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061. This material is also based upon work supported by the U.S. Civilian Research and Development foundation under Award No. REI-247. @FootnoteText@ @footnote 1@ N. Medelci, A. Tempez, E. Kim, N. Badi, I. Berichev, D. Starikov and A. Bensaoula, 1998 MRS Spring Meeting (in print).

**5:00pm EM+PS+SE-TuA10 Characteristics of Cl@sub 2@-based Inductively Coupled Plasmas during the GaN Etching, H.S. Kim, J.W. Jang, Y.H. Lee, G.Y. Yeom, Sungkyunkwan University, Korea; J.W. Lee, T.I. Kim, Samsung Advanced Institute of Technology, Korea**

Planar inductively coupled Cl@sub 2@-based plasmas have been used to etch GaN and etch properties having smooth and nearly vertical etch profiles with the etch rates close to 850 nm/min could be obtained with Cl@sub 2@-rich gas combinations. To understand the effects of plasma conditions on the GaN etch properties, The quadrupole mass spectrometry(QMS), optical emission spectroscopy(OES), and an electrostatic probe have been used. Especially, the quadrupole mass spectrometer system we used in the analysis of the plasmas was configured with ion optics, energy filter, and integral electron impact ion source for plasma diagnostics. Therefore, not only the radical densities but also positive and negative ion densities and their energy distributions were also measured. As process conditions used to study the effects of plasma characteristics on the GaN etch properties, Cl@sub 2@ was used as the main etch gas and Ar, BCl@sub 3@, and CH@sub 4@ were used as additive gases. Operational pressures were varied from 5mTorr to 30mTorr while other conditions such as inductive power, bias voltage, and substrate temperature were fixed at 600 watts, -120 volts, and 70 centigrade, respectively. The relative amounts of reactive ions (Cl@super +@, Cl@sub 2@@super +@, Cl@super -@, etc.), Ga-containing etch products(GaCl, GaCl@sub 2@, and GaCl@sub 3@ for Cl@sub 2@ plasma), and nitrogen-containing etch products ( N, N@sub 2@, NH@sub 3@, etc. ) were estimated by the plasma mass spectrometric measurements. The results showed that the enhancement of GaN etch rate was related to the increase of Cl radical and reactive ion such as Cl@super +@, Cl@sub 2@@super +@, etc. measured by the QMS and OES during the Cl@sub 2@-based inductively coupled plasma etching. Therefore, chemical reactions between Ga in GaN and Cl and Cl@sub 2@@super +@ from Cl@sub 2@, under the sufficient ion bombardments to break GaN bonds, appear to be important in the GaN etching. More detailed analysis of plasmas and their relation to GaN etching will be given in the presentation.

## Electronic Materials and Processing Division Room 316 - Session EM-WeM

### Fundamentals of Si Cleaning and CMP

**Moderator:** Y. Ma, Bell Laboratories, Lucent Technologies

#### 8:20am EM-WeM1 Surface Preparation and Contamination Control for Advanced CMOS Processing, S.C. O'Brien, Texas Instruments, US INVITED

Advanced CMOS device manufacturing requires levels of contamination which 20 years ago would have been considered science fiction. Particulates, metals, organics, haze, and residue from sacrificial films represent critical yield issues for DRAM and logic devices. Accurate and precise measurement of these species also represents an incredible challenge. The use of TRXRF, SIMS, EDX, and XPS as surface contaminant metrology techniques will be discussed. In many cases the contrast between metrology and analysis has not yet been fully explored. The use of non-destructive inline contaminant metrology is becoming much more important as the wafer size increases from 200 to 300mm. Quick turnaround time is needed for fast problem solving, while the ability to send a wafer for subsequent processing after measurement is valuable for superior problem solving. In addition, correlation of inline measurements with end of line yield is the only relevant method of discovering problems. Any inline defects which do not correlate with end of line yield are usually irrelevant. Specific areas of cleaning technology to be discussed are pre-cleans for thin gate oxides, pre-furnace cleans for metal gates and other metal gate technology, sidewall polymer removal for polysilicon gates, self-aligned cobalt and titanium silicides, sidewall polymer removal for aluminum lines, corrosion of copper and aluminum lines, contamination from new materials (such as ruthenium or BST), and copper processing.

#### 9:00am EM-WeM3 Dissolution of Cu and Au into Aqueous Semiconductor Processing Solutions, I. Suni, D. Chopra, A.A. Busnaina, Clarkson University

Dissolution of Cu into 50:10:1 H<sub>2</sub>O:H<sub>2</sub>O<sub>2</sub>:O<sub>2</sub> from p-type Si wafers was studied by total reflection x-ray fluorescence spectroscopy (TXRF). Starting from an initial surface coverage of approximately 1.2x10<sup>13</sup> atoms/cm<sup>2</sup>, Cu dissolution was seen to be first order in Cu surface coverage, although slight deviations from this behavior are seen at longer times. The rate constant for this dissolution process was about 2.7x10<sup>-2</sup> sec<sup>-1</sup>. Prior literature results indicate that Au dissolution into acidic solutions is also 1st order when dissolution is slow, but deviates from 1st order when dissolution is rapid. One possible explanation for these phenomena is that metal dissolution is a reversible reaction which slows down as the concentration of metal ions in solution increases and diffusion is slow. This explanation is consistent with recent results published by Sony Corp. The dissolution process in a wafer cleaning tank was modeled using experimentally determined constants through finite difference solution of the convective diffusion equation by the ADI method, including a 1st-order surface reaction as a boundary condition. The results demonstrate the transition between rate-limitation by surface reaction and rate-limitation by product diffusion as the dissolution rate is increased. This can be done by raising the temperature, increasing the solution strength, or using a more active oxidizing agent. The possibility is demonstrated of large removal gradients on the wafer surface arising from the coupling of convection, diffusion, dissolution and redeposition.

#### 9:20am EM-WeM4 A Reduced Carbon Contaminant, Very Low-Temperature Silicon Substrate Preparation for Defect-Free Homoepitaxy, P.J. Taylor, W.A. Jesser, University of Virginia; M. Martinka, K. Singley, J. Dinan, US Army CECOM-Night Vision and Electronic Sensors Directorate; R. Lareau, M. Wood, W.W. Clark III, US Army Research Laboratory

A low-temperature cleaning technique incorporating an ultraviolet light/ozone treatment with conventional hydrogen-passivation techniques is shown to yield record-low concentrations of surface contaminants: <= 0.01 monolayer (ML). An additional advantage is that no Atwater-type<sup>1</sup> UHV prebaking treatments are required for substrates receiving this treatment prior to epitaxy. Low-temperature silicon molecular beam epitaxy (MBE) on such substrates is characterized by a threading dislocation density on the order of 10<sup>4</sup>/cm<sup>2</sup> (Schimmel etching<sup>2</sup>) which is a reduced threading dislocation density compared to that measured from films receiving more conventional hydrogen-passivation preparation techniques: typically between 10<sup>5</sup>/cm<sup>2</sup> and 10<sup>6</sup>/cm<sup>2</sup>.<sup>3</sup> The interfacial contamination was measured before

homoepitaxy by in-situ Auger electron spectroscopy (AES) and after homoepitaxy using secondary-ion-mass spectroscopy (SIMS). The results of this study suggest that aqueous solutions are a significant source of surface carbon and that an ultraviolet light-ozone treatment before hydrogen passivation is particularly efficacious for removing residual carbon on the silicon surface which would otherwise contribute to the generation of threading dislocations in Si homoepitaxial films. <sup>1</sup>@FootnoteText@<sup>2</sup>@Footnote 1@Nikzad, S., Wong, S., Ahn, C., Smith, A., Atwater, H., Appl. Phys. Lett. Vol. 63(10) p. 1414 (1993). <sup>3</sup>@Footnote 2@Schimmel, D., Journ. Electrochem. Soc., Vol. 126 p. 479 (1979). <sup>3</sup>@Footnote 3@Eaglesham, D., Higashi, G., Cerullo, M., Appl. Phys. Lett., Vol. 59(6) p. 685 (1991).

#### 9:40am EM-WeM5 The Modeling of Excimer Laser Particle Removal From Silicon Surfaces, X. Wu, E. Sacher, M. Meunier, École Polytechnique de Montréal, Canada

The interaction of an excimer laser with a silicon surface can lead to the removal of submicrometer-sized contaminant particles. This technique is efficient, simple, fast and is chlorofluorocarbon-free, a considerable environmental advantage over standard cleaning techniques. In addition, the laser cleaning approach is compatible with cluster tools. Laser cleaning may be dry, meaning that no water was present on the sample surface during laser exposure. However, to increase removal efficiencies, the "steam" laser cleaning technique may be used, where the pulsed laser beam is coupled to a liquid energy transfer medium, such as water, which is condensed on the silicon surface. We found that organic particles, such as polystyrene and carboxylate modified latices, with dimensions as low as 0.1 micrometers, can easily be removed by dry cleaning. However, inorganic particles, such as alumina and silica, of the same dimensions, can only be removed by steam cleaning. We have performed a detail analysis of the comparison between particle adhesion forces (van der Waals with deformation, capillary and chemical) and removal forces (thermoelastic, and bubble pressure when water is used) to understand laser particle removal efficiencies with respect to particle size and nature, as well as the effect of water. Our calculations show that, for organic particles during dry cleaning, the van der Waals deformation term is predominant for adhesion, and the dominant removal force is thermoelastic. However, for inorganic particles, the dominant adhesion force is that due to hydrogen bonding. Our calculations show that the presence of water greatly reduces the adhesion forces. This, coupled with the bubble pressure created by the explosive evaporation of water when exposed to the laser, leads to the higher efficiency found for steam cleaning.

#### 10:00am EM-WeM6 Chelating Agents for Dry Removal of Metals, A. Shah, L. Ford, L. Nigg, Y. Wang, R. Masel, University of Illinois, Urbana

We and others have found that various diketones can be used to remove metals from a variety of surfaces under dry conditions. In this paper we use a variety of surface spectroscopic techniques to characterize the process for the removal of copper, nickel and palladium from various surfaces. We find that there are two regimes with different reactivities, a regime where the metal is (reduced) metallic and a regime where the metal is oxidized. In the oxidized regime, the rate desorption step is volatilization of the metal. In this case, the metal removal rate goes as the volatility of the metal chelate, with hexafluoropentanedione (Hf<sub>2</sub>fac) showing the highest removal rate followed by trifluoropentanedione (Htf<sub>2</sub>ac), Hexafluorooctanedione (HFOD), 2,4-pentanedione (Hacac), Tetramethylheptanedione (TMHD). In contrast in the reduced condition, oxidation is rate determining, and the removal rate follows almost the opposite trends. We have also found some unusual effect in the intermediate oxidation conditions. For example, if we work under conditions where Cu<sup>1+</sup> forms, we observe much lower removal rates than under conditions where Cu<sup>0</sup> or Cu<sup>2+</sup> forms. Htf<sub>2</sub>ac is the best etchant under minimal oxygen conditions. Finally, we have also discovered that some of the intermediates can polymerize and decompose on the surface, leading to carbon contamination. The main contamination pathway seems to be enhanced by impurities in the source gases. Details are still unclear, but it appears that we need purer source gases than are presently available to do clean etching.

#### 10:20am EM-WeM7 Process Optimization of CMP of Dielectrics for ULSI Multilevel Metallization, H.W.A. Treichel, OnTrak Systems, Inc.; R. Frausto, A. Meyer, R. Morishige, S. Srivatsan, B. Withers, Lam Research Corporation INVITED

The push of leading edge ULSI manufacturing technologies toward the formation of sub 0.1 µm feature sizes places extreme performance demands on the processes and equipment used. At submicron line widths, the depth-of-focus was limiting technology and CMP emerged as an

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essential enabling technology for feature sizes of 0.35  $\mu\text{m}$  and below to meet the stringent DOF requirements for next generation devices. Thus, CMP emerged quickly and has become quite sophisticated. @footnote 1@ Current CMP systems are adaptations from existing glass and silicon polishing tools. These platforms are based on a rotating head and a circular platen. Lam Research recently introduced a new revolutionary linear track system (Aurora), an automated CMP machine which has a belt platen module that is capable of linear speeds up to 120 to 150 m/min, especially designed for planarization. This results in less pattern sensitive planarization, very high removal rates, and excellent uniformities at low head pressures. CMP is a very complex process. Its performance is determined not only by machine controlled parameters like belt speed, down force, and more, but also by consumables, pad conditioning and wear. @footnote 2,3@ In order to clarify the role of numerous factors as control parameters, extensive evaluations have been performed. This article reports on specific improvements in LPT technology. It also describes the major dependencies of machine parameters versus experimental results and finally highlights selected optimized CMP processes. @FootnoteText@ @footnote 1@R. DeJule, Semiconductor Int., 11, 15 (1996) @footnote 2@S. Sivaram, H. Bath, R. Leggett, A. Maury, K. Mennig, and R. Tolles Solid State Technology, 5, 87 (1992) @footnote 3@L.M. Cook, J.F. Wang, D.B. James, and A.R. Sethuraman Semiconductor Int., 11, 141 (1995)

11:00am **EM-WeM9 Nanoscale Corrosive Wear of Ionic Materials: A Model System for Chemical Mechanical Polishing**, J.T. Dickinson, L. Scudiero, S.C. Langford, Washington State University

Fundamental studies of chemical mechanical polishing (CMP) are needed to improve and extend CMP to new applications. In CMP, surfaces experience simultaneous tribological loading and corrosive chemical exposure, which together produce high wear rates and favorable topography. We employ scanning probe microscopy (SPM) of single crystal surfaces in mildly corrosive solutions, where the SPM tip provides the mechanical stimulation in a controlled fashion. The applied normal force, the location of the contact, and lateral motion are readily controlled. For simplicity we choose model systems where the corrosive agent is water (properly buffered) and the single crystals are slightly soluble. These include calcite [ $\text{CaCO}_3$ ] and brushite [ $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ] (a model biomaterial). Silicon nitride tips are used with applied normal loads from 0-300 nN, tip radii 30 nm and tip velocities from 1-200  $\mu\text{m/s}$ . Quantitative data on the role of normal force, lateral velocity, surrounding surface topography, and solution chemistry can be obtained from images of the wear of atomic steps. The wear rate is a highly non-linear function of applied normal force (essentially exponential). Our results are interpreted in terms of stressed enhanced dissolution of steps, where double kink nucleation is the rate limiting process. We present a model which fits data for all systems examined to date. Careful analysis of step stability explain the observed sensitivity of certain step orientations to the enhanced wear induced by stress. Studies of atomically flat planarization of surfaces produced by controlled scanning are presented. This work is supported in part by the National Science Foundation under Grant CMS-9414405.

11:20am **EM-WeM10 Studies on Passivation Behavior of Tungsten in Application to Chemical Mechanical Polishing**, D. Tamboli, S. Seal, A. Kale, V. Desai, University of Central Florida; Y. Obeng, A. Maury, Bell Laboratories, Lucent Technologies

Chemical mechanical polishing (CMP) is considered to be the enabling technology for meeting the planarization requirements in < 0.35 micron feature sized multi-level devices and interconnects in semiconductor industries. Considerable importance is given to the role played by the passive oxide film formation on the surface in CMP process. @footnote 1@ However, there are very few studies available in open literature regarding the characterization of surface reaction products in terms of chemistry and thickness of the reaction layers. @footnote 2@ In this research study, X-ray Photoelectron Spectroscopy is used to understand modification of surfaces (i.e. oxide layers) during the CMP process. Tungsten wafers are treated in static solutions with varying pH, oxidizer levels, temperature and applied potential in order to determine the effect of these parameters on the chemistry of the passive oxide layers. XPS measurements are employed to probe the chemical and stoichiometric changes (e.g.  $\text{WO}_3/\text{WO}_2$  ratio, presence of any hydroxides, etc.) in these surface films treated under various conditions. Valence band XPS studies on W(4f) and O (2p) states are performed to determine the electronic structure of the oxide layer and its relevance to passivation. These results are compared with the electrochemical studies carried out both ex-situ and in-situ during

polishing. @FootnoteText@ @Footnote 1@F.B. Kaufman, et al., J. Electrochem. Soc., 138, 3460, 1991 @Footnote 2@E.A. Kneer, et al., J. of the Electrochem. Soc., 143, 4095, Dec 1996

11:40am **EM-WeM11 Studies of the Pad-Slurry-Surface Interactions in Chemical-Mechanical Polishing of Copper Thin Films and Patterned Structures**, J. Hernandez, P. Wrschka, G.S. Oehrlein, State University of New York, Albany; J. King, Cybeq Nano Technologies

Chemical mechanical polishing (CMP) of copper is a key technology for producing sub-micrometer Cu lines in multilevel metallization structures. In this work, blanket copper, tantalum and silicon dioxide thin films as well as copper damascene structures were polished using different pads and slurries. Selectivities of  $\text{Cu/SiO}_2$  as high as 200:1 were observed after polishing at low pressures and velocities utilizing slurries consisting of alumina abrasive particles. Examination of planarized Cu damascene microstructures by scanning electron microscopy allowed us to investigate critical issues in CMP such as  $\text{SiO}_2$  spacer erosion, copper line recess, corrosion of sub-micron copper lines, slurry contamination, and removal selectivity of the Ta diffusion barrier. Finally, surface chemical studies of Cu, Ta, and  $\text{SiO}_2$  thin films and the pad after CMP by x-ray photoelectron spectroscopy were undertaken to assist in the identification of the controlling factors of the CMP process.

**Magnetic Interfaces and Nanostructures Technical Group**  
**Room 324/325 - Session MI+EM-WeM**

**Spin-dependent Devices: Technology and Processing**

**Moderator:** B.A. Everitt, Seagate Technology

8:20am **MI+EM-WeM1 Limiting Factors in Dense Pseudo Spin Valve and Spin Dependent Tunneling Memory Arrays**, A.V. Pohm, M.C. Tondra, C.A. Nordman, J.M. Anderson, Nonvolatile Electronics **INVITED**

For pseudo spin valve or spin dependent memory technology to persist for the coming decades, they must be able to exploit the evolving sub-micron semiconductor technology and adjust to the diminishing conductor widths. However, as pseudo spin valve and spin dependent memory arrays are scaled to 0.1 micron widths or less, a number of factors play a role in limiting ultimately the memory array densities which can be achieved. An analysis has been performed which shows that to achieve adequate stability against thermal agitation for half selected cells, the shape anisotropy in the 25 Angstrom storage layer must be at least 300 Oe for 0.1 x 0.3 micron cells. Half select fields of 100 to 150 Oe are required for the write operation. This necessitates current densities in the GMR sandwich in the 10<sup>8</sup> A/cm<sup>2</sup> range for the sense lines and 10<sup>7</sup> A/cm<sup>2</sup> in the word lines. Although GMR sandwiches can tolerate the high current densities, thin dielectrics and careful use of heat sinks are required to keep the temperature rise modest. Materials such as tungsten must be used for the word line in order to have adequate electro-migration limits. Because of the high resistance and capacitance in the spin dependent tunneling memory cells, semiconductor isolation is necessary for high performance. As a consequence, maximum array density is about 1/2 of that for pseudo spin valve cells.

9:00am **MI+EM-WeM3 New Aspects of GMR Spin Valves: Enhancing Specular Electron Scattering and Using Surfactants for Improved Growth**, W.F. Egelhoff, Jr., National Institute of Standards and Technology

We have investigated the deposition and processing of a variety of giant magnetoresistance (GMR) spin valves with the aim of optimizing their properties. We have found that many of the magnetic and magnetoresistive properties of spin valves are strongly influenced by surface and interface effects occurring during growth. These effects include the balance of surface and interface free energies, surface diffusion, interdiffusion at interfaces, low temperature deposition, the use of surfactants to modify growth, and specular electron scattering at surfaces. In some cases, it is possible to control these factors or to use them to manipulate the growth or improve post-growth processing of spin valves to improve their magnetic and magnetoresistive properties. For example, specular scattering is particularly important for achieving the largest possible GMR values in simple spin valves. For symmetric (or dual) spin valves GMR values as large as 24.8% have been achieved, and for simple spin valves (containing only one Cu layer) GMR values as large as 19.0% have been achieved. The best hope for someday achieving GMR values in simple spin valves as large as those reported for GMR superlattices appears to be increasing the degree of specular scattering and reducing the bulk defect scattering. The author would like to acknowledge his collaborators

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in this work, including P. J. Chen, C. J. Powell, M. D. Stiles, R. D. McMichael, J. H. Judy, K. Takano, A. E. Berkowitz, and J. M. Daughton.

## 9:20am **MI+EM-WeM4 High Temperature Pinning Properties of IrMn vs. FeMn in Spin Valves, M.C. Tondra, D. Wang, Nonvolatile Electronics**

The antiferromagnetic pinning properties of IrMn and FeMn have been observed by building spin valve samples with the structure NiFeCo / CoFe / Cu / CoFe / NiFeCo / (IrMn or FeMn) and measuring their magnetoresistive properties. The pinning strength was evaluated in terms of the break field, defined as the field applied in the direction opposite to the magnetization of the pinned layer at which the pinned layer switches. At room temperature, the break fields for both the IrMn and FeMn samples were about 250 Oe. But as the temperature increased, the break field for samples pinned with IrMn held up considerably better than for those pinned with FeMn. Specifically, the pinning of the FeMn spin valves was gone at 150°C while the pinning of the IrMn spin valves persisted to temperatures above 225°C. The IrMn spin valves performed as well as the FeMn spin valves in terms of magnetoresistance and lithographic process compatibility.

## 9:40am **MI+EM-WeM5 Magnetisation Reversal Studies by TEM of Continuous and Patterned GMR Films, J.N. Chapman, University of Glasgow, United Kingdom**

**INVITED**

A highly modified transmission electron microscope has been used to study magnetisation processes in a range of GMR films suitable for application in devices. Films were deposited onto silicon nitride "window" substrates suitable for study in the TEM directly after growth or following patterning. Application of fields in-situ allowed the evolution of the magnetic domain structure to be followed in real time in both continuous films and elements. The latter frequently had dimensions in the sub-micron regime. Reversal of the free layer in spin-valve films is found to depend on the strength of coupling between free and pinned layers and the orientation of the applied field, the latter being readily under the control of the experimenter. Conditions under which quasi-coherent rotation of magnetisation takes place have been established. However, very significant changes take place as the dimensions of the films are reduced and magnetostatic energy contributions play an enhanced role. Domain nucleation at corners can lead to undesirable reversal modes and for elements with micron-sized dimensions the reversal depends critically on size, shape and the nature of the pinning layer. Examples will be given of how shape modification can change the characteristic of the reversal to suit sensing or storage application. In the case of Co/Cu multilayers reversal mechanisms quite different from those in spin-valves are observed and depend critically on the nature of the coupling between the layers. Thus films with strong biquadratic coupling tend to reverse in a relatively simple manner resembling processes in single layer films whilst films with weak antiferromagnetic coupling reverse through the formation and evolution of complex sub-micron "patch" domains. Irreversible processes are prevalent in the latter case but can be effectively suppressed in the former making films with biquadratic coupling suitable for applications where low hysteresis is essential.

## 10:20am **MI+EM-WeM7 Deposition and Processing of Novel GMR Structures @footnote 1@, J.R. Childress, University of Florida, Gainesville**

**INVITED**

Optimized GMR devices may require the development of magnetic multilayer film structures combining binary and ternary alloys, composition gradients, composites, and metal/insulator interfaces. The structural and magnetic optimization of individual components within these multilayers often require specialized deposition and/or processing parameters which may be mutually incompatible, or incompatible with other necessary processing. Additionally, the interfacial structural and magnetic properties of alloys may be different from bulk, further complicating the interpretation of experimental data. Several current examples and experimental approaches will be discussed, such as the development of 100% spin-polarized magnetic films using NiMnSb and other compounds, metallic and insulating antiferromagnets for exchange biasing, and metal/insulator interfaces. @FootnoteText@ @footnote 1@ Author present address: IBM Almaden Research Center, 650 Harry Rd, San Jose, CA 95120

## 11:00am **MI+EM-WeM9 Direct-Measurement of Spin-Dependent Transport Across Ferromagnetic and Non-Magnetic Thin Films, S.K. Upadhyay, R.N. Louie, Cornell University; R.A. Buhrman, Cornell University, US**

We have used superconductor-ferromagnet nanocontacts to directly measure a>spin-polarization of the current in ferromagnets (Co and Ni) and b>spin dependent transmission rates of thin ferromagnetic (Co, Ni) and non-magnetic (Cu) films. Since the size of the contact (3-10nm) is smaller than other scattering lengths in the system, our measurements can selectively probe the scattering at interfaces of dissimilar metals. We will discuss our results in the context of giant magnetoresistance in thin film magnetic multilayers and their significance in understanding the role of interfacial versus bulk scattering.

## 11:20am **MI+EM-WeM10 Effect of Noble Gas Addition (He,Ar,Xe) on Cl@sub 2@-Based Etching of NiFe and NiFeCo, K.B. Jung, H. Cho, Y.-B. Hahn, E.S. Lambers, Y.D. Park, S.J. Pearton, University of Florida, Gainesville; J.R. Childress, IBM Almaden Research Center; M. Jenson, A.T. Hurst, Jr., Honeywell, Inc.**

The mechanism for high rate dry etching of NiFe, NiFeCo and other components of multilayer magnetic thin film devices such as read/write heads and magnetic random access memories depends on formation of chlorinated etch products, and their efficient desorption by ion-assisted sputtering. A systematic study of the dependence of noble gas species (He, Ar, Xe) additive to high-density Inductively Coupled Plasma Cl@sub 2@ discharges has been performed. The etch rates of the NiFe and NiFeCo increase in direct proportion to the atomic weight of the noble gas species, which is the dominant factor controlling etch product desorption. Increasing the weight of the additive also leads to a decrease in residual chlorine on the etched surface, as determined by Auger Electron Spectroscopy. The effect of altering the noble gas species on etch selectivity over common mask materials (SiO@sub 2@, SiN@sub X@ and photoresist) has also been studied. Facetting of the mask edges is a particular problem with Cl@sub 2@/Xe discharges.

## 11:40am **MI+EM-WeM11 Magnetoresistance Properties in Granular Silicide Thin Films Formed by High Dose Iron Implantation, M.F. Chiah, W.Y. Cheung, S.P. Wong, I.H. Wilson, The Chinese University of Hong Kong, Hong Kong**

High dose iron implantation into silicon wafer has been performed with a metal vapor vacuum arc ion source (MEVVA) to doses ranging from 1\*10@super 16@ to 2\*10@super 17@ cm@super -2@ at various beam current densities. The magnetoresistance (MR) effects in these implanted granular layers were studied at temperatures from 15K to 300K. A positive MR effect, i.e, an increase in the resistance at the presence of a magnetic field, was observed at temperatures lower than about 70K in samples prepared under appropriate implantation conditions. The magnitude of the MR effect, defined as @DELTA@R/R@sub o@ = (R(H)-R@sub o@)/R@sub o@ where R(H) and R@sub o@ denote respectively the resistance value at a magnetic field intensity H and that at zero field, was found to depend on the implantation dose, the beam current density. This is attributed to the beam heating effect during implantation which affects the formation of the microstructures. The ratio @DELTA@R/R@sub o@ was found to attain high values larger than 500% for some samples at low temperatures. The dependence of the MR effects on temperature, implantation dose, substrate dopant concentration and beam current density will be presented and discussed in conjunction with results of Transmission Electron Microscopy and Mössbauer Spectroscopy. The phase of iron silicide, composition and depth of damaged layer were determined by spreading resistance, Rutherford backscattering and XRD measurements. This work is supported in part by a grant from the Research Grants Council of Hong Kong (Ref. No.: CUHK 374/96E)

## Electronic Materials and Processing Division Room 314/315 - Session EM1-WeA

### Si Surface Chemistry

**Moderator:** M.K. Weldon, Bell Laboratories, Lucent Technologies

**2:00pm EM1-WeA1 Understanding the Evolution of Surface Morphology during Chemical Etching.** *M.A. Hines*, Cornell University; *J. Flidr*, Y.-C. Huang, T.A. Newton, Cornell University, US

**INVITED**

In this talk, I will discuss the evolution of surface morphology during the etching of Si(111) by  $\text{NH}_4\text{F}$ . By combining STM measurements of surface morphology with kinetic Monte Carlo simulations of the etching process, we are able to obtain microscopic information on surface reaction mechanisms. We find that long-range surface roughness can be suppressed by a low density of monolayer-deep etch pits on an otherwise "perfect" surface. On surfaces miscut in the direction, Si(111) etches via a step-flow mechanism that is nucleated by slow etching into the step and then propagated by rapid etching of the nucleated kinks -- the steps "unzip" in a direction parallel to the step. Without terrace etching, individual steps would etch independently, and the long-range surface roughness, which is reflected in the terrace width distribution, would be comparable to that expected of an equilibrium surface. If there is a small probability of terrace etching, the steps repel one another through a kinetic feedback effect that we term dynamic step-step repulsion. This effect is mediated by the anisotropic distribution of terrace pits -- wide terraces have a higher density of pits than narrow terraces. We also find that steps can self-pin during etching. This type of pinning is independent of contamination and is due to the formation of a relatively unreactive structure on the etching step. Once formed, this structure reacts slowly and acts as a self-propagating pinning site to further etching. Self-pinning can drive a morphological transition that leads to chemically induced step faceting. In spite of this pinning, the steps still etch by step-flow.

**2:40pm EM1-WeA3 Structure of a Passivated Ge Surface Prepared from Aqueous Solution.** *P.F. Lyman*, Northwestern University; *D.T. Keane*, Northwestern University and DND CAT; *D.L. Marasco*, T.-L. Lee, Northwestern University; *M.J. Bedzyk*, Northwestern University and Argonne National Lab

We investigated the local structure and order of a aqueously sulfided Ge(001) surface using x-ray standing waves. The adsorption of a group VI element on the Ge(001) surface could satisfy all of the substrate dangling bonds by occupying a bridge site. Such a surface would be expected to be both chemically and electronically passivated, perhaps suppressing surface carrier recombination. In the present study, S/Ge(001) surfaces prepared in aqueous ( $\text{NH}_4\text{S}_2\text{O}_8$ ) solution (diammonium sulfide) exhibited a S coherent position  $\Delta z$  of  $0.90 \pm 0.01$ , implying that the S adsorption height is  $1.27 \pm 0.01$  Å. This closely corresponds to the expected adsorption height for S residing in a bridge site. This finding supports the local geometry inferred for aqueously sulfided Ge(001) by previous workers. That study concluded that a single atomic layer of S binds to the surface, residing in the a (1x1) bridge-bonded configuration. However, the present studies showed a low, repeatable value of 0.15 for the coherent fraction. The simplest explanation for these observations is that, in addition to an ordered S monolayer at the interface, a ~5 ML sulfided Ge layer is formed during the chemical passivation treatment. Although this model conflicts with the conclusions of Ref. 1, such an interface is not unlike the native oxide of Si, where several atomic layers of passivating silicon oxide readily form. We are presently conducting other tests of the S/Ge(001) surface to determine the nature of this interface more completely. @FootnoteText@ @footnote 1@G. W. Anderson, et al., Appl. Phys. Lett. 66, 1123 (1995).

**3:00pm EM1-WeA4 Reflectance Difference Spectroscopy of Ge / Si(001).** *V. Zielasek*, S.G. Jaloviar, M.G. Lagally, University of Wisconsin, Madison

Reflectance difference spectroscopy (RDS) has proven to be an easy-to-use tool to monitor semiconductor epitaxy, especially of III-V systems. The origins of the surface optical anisotropy, however, are not yet fully understood. Several calculations for dimerized Si(001) terraces and lately for Ge / Si(001) have been reported and compared with experimental RD spectra from highly vicinal surfaces with the conclusion that steps do not produce an RD signal. @footnote 1@ Recent experiments, however, demonstrate that on vicinal Si(001) with miscut angles even as low as  $1^\circ$  the steps contribute significantly to the RD signal. @footnote 2@ From this, we expect that other morphological features, such as dimer vacancy lines

formed during the epitaxy of Ge on Si(001), leave their fingerprint in RD spectra as well. We present a combined RDS and scanning tunneling microscopy (STM) study of Ge / Si(001) using both vicinal and superflat wafers as substrates. STM provides an accurate measure of step density and step structure. A macroscopic anisotropy of the superflat Si(001) surface is obtained by applying uniaxial elastic strain to the sample, leading to step movement and favoring domains with dimer rows oriented in the direction of lowest external compression. We find a shift in energy of RD spectral features with increasing Ge coverage in the sub-monolayer regime. Reversal of the surface stress anisotropy with increasing Ge coverage around 1 monolayer leads to a reversal in sign of the RD signal in the 2 - 4 eV range after applying external strain. For superflat and vicinal Si(001)  $4^\circ$  [110] with similar Ge coverages and annealing temperatures both the RD spectra and the morphologies of the growing films differ. We discuss the relationship of stress induced by Ge adsorption and external strain effects, focussing on their influence on the RD spectra. Supported by NSF, ONR, and Alexander von Humboldt-Stiftung (V.Z.) @FootnoteText@ @footnote 1@J.R. Power et al., Phys. Rev. Lett. 80 (1998) 3133. @footnote 2@S.G. Jaloviar, J.-L. Lin, M.G. Lagally, submitted.

**3:20pm EM1-WeA5 Second Harmonic Study of Ge/Si(100) and Si@sub 1-x@Ge@sub x@ (100) Films.** *P.S. Parkinson*, D.E. Brown, M.C. Downer, J.G. Ekerdt, University of Texas, Austin

Second harmonic generation (SHG) allows real-time, in-situ measurement of hydrogen coverage on intrinsic silicon. Thus, SHG has been used by this group to perform hydrogen desorption measurements and growth rate calculations on intrinsic silicon. @footnote 1@ Our current challenge is to develop SHG as a tool to study the Si@sub 1-x@Ge@sub x@ (100) alloy surface. We present studies of the SiGe/Si(100) and the Ge/Si(100) systems in vacuum around the E@sub 1@ critical point using SHG. In Ge@sub 2@H@sub 6@ atomic layer epitaxy (ALE) on Si(100), the SH intensity increases linearly with Ge coverage; below 5 ALE cycles (approximately 1.5 ML). Further deposition causes a continuous decrease in the signal intensity and a blue shift in the spectra. Hydrogen passivation of the surface leads to substantial quenching of the signal which reveals the sensitivity of the SH response to the near-surface Ge composition. Monitoring the growth of Si@sub 1-x@Ge@sub x@ (100) films, with SHG we observed an initial rise in the SH intensity and then a decrease as the films became rougher and thicker. The time constant for the initial rise became shorter with increasing Ge film composition. Spectra of strained smooth SiGe films showed that the SH intensity at the peak maxima increased with increasing Ge film composition. Also, hydrogen saturation of the film surfaces led to an order of magnitude decrease in the SH response, similar to the Ge/Si(100) system. Thus, the initial rise in SH intensity during growth may correspond to the development of the near-surface Ge composition profile at the leading edge of growth. SH intensity decreased with increasing atomic hydrogen coverages on the SiGe/Si(100) surface; the same trend observed on intrinsic Si(100). Therefore, the SH response to hydrogen coverage in the alloy system might be explainable within the framework of models proposed for the H/Si(100) system. @footnote 2@ @FootnoteText@ @footnote 1@ Xu et al., Appl. Phys. Lett., 71, 1376, (1997). @footnote 2@ Dadap et. al., Phys. Rev. B, 56, 1, (1997).

**3:40pm EM1-WeA6 Silicon Epoxide: Fundamental Intermediate in Si(100) Oxidation.** *A.B. Gurevich*, Columbia University; *M.K. Weldon*, *Y.J. Chabal*, *B.B. Stefanov*, *K. Raghavachari*, Bell Laboratories, Lucent Technologies

Understanding the growth and formation of thin oxides is critical to the development of high quality gate oxides. However, obtaining a detailed structural picture of interfacial  $\text{SiO}_2$  poses a formidable scientific challenge due to the lack of long-range order and the critical dependence on processing parameters. We have therefore investigated with infrared absorption spectroscopy the water-induced oxidation of Si(100)-(2x1) under ultra-high vacuum conditions, as a prototypical silicon-oxide system: the water is initially dissociated into H and OH on each surface dimer; as the temperature is increased to 675K, the Si-Si dimer becomes the first target for oxygen insertion into the surface, facilitating in turn the subsequent incorporation of O into the Si backbonds. @footnote 1@ We show here that, upon dehydrogenation at higher temperatures (900K), a surprising structure is formed. The combination of high resolution IR spectroscopy and density functional cluster calculations can, for the first time, identify this triangular  $\text{SiOSi}$  sub-unit, termed silicon epoxide, based on substantially lower Si-O stretch frequencies (780-990  $\text{cm}^{-1}$ ) and smaller isotopic shifts (20-30  $\text{cm}^{-1}$ ) compared to those of known oxide structures. These silicon epoxides are similar to COC structures well-known in organic chemistry and characterized by a shorter Si-Si bond (2.4Å). We demonstrate that epoxides are the



thermodynamically favored product upon dehydrogenation when three or more oxygen atoms are agglomerated. These epoxide structures are stable at intermediate annealing temperatures (800-1000K) and are observed upon pure oxygen exposure as well. They therefore constitute a metastable intermediate in the growth of thermal gate oxides, and are expected to be preferentially formed both in small molecules and at silica interfaces. @FootnoteText@ @footnote 1@ M.K. Weldon, B.B. Stefanov, K. Raghavachari and Y.J. Chabal, Phys. Rev. Lett. 79, 2851 (1997).

4:00pm **EM1-WeA7 Structure of Ultrathin Silicon Oxide - Silicon Interfaces Studied by Ultraviolet Photoelectron Spectroscopy**, J.W. Keister, J.E. Rowe, North Carolina State University; J.J. Kolodziej, Rutgers University; H. Niimi, North Carolina State University; T.E. Madey, Rutgers University; G. Lucovsky, North Carolina State University

Device-grade ultrathin (9-18 Å) films of silicon dioxide, prepared from crystalline silicon by remote-plasma oxidation, are studied by the surface-sensitive method of ultraviolet photoelectron spectroscopy. The 2p core-level spectra for silicon (at ~100 eV binding energy) show evidence of five distinct states of Si. These peaks are attributed to the five oxidation states of silicon between 0 (the Si substrate) and +4 (the thin SiO<sub>2</sub> film), although the precise configuration has recently been called into question. @footnote 1@ We find that the peaks for Si<sup>0</sup> through Si<sup>+4</sup> are shifted relative to the Si<sup>0</sup> bulk peak to higher binding energy by 0.92 eV, 1.90 eV, 2.51 eV and 3.86 eV. The relatively weaker signal found for the three intermediate states (+1, +2, and +3) is attributed to silicon atoms at the interface between these two materials. Estimates of the interface thickness from the intermediate valence signal agree with the value reported earlier of 3-5 Å (~2 ML). @footnote 2,3@ In this work, the position and intensity of the five peaks are measured as a function of post-growth annealing temperature (700 - 900 °C), crystal orientation, and incorporation of N<sub>2</sub> in the reactant gas flow. One result we have found is that annealing produces more abrupt interfaces, but never more abrupt than about one or two monolayers. This comes from the observation of a sudden drop in the interface thickness (in particular the Si<sup>+2</sup> peak intensity) upon reaching 800-900 °C annealing temperature. A more complete and quantitative analysis will be presented which explores the effects of the other sample parameters and takes advantage of nonlinear least-squares fitting routines. @FootnoteText@ @footnote 1@ McFeely, Zhang, Banaszak-Holl, Lee, Bender J. Vac. Sci. Tech. B 14(4), 2824-2831 (1996). @footnote 2@ Himpel, McFeely, Taleb-Ibrahimi, Yarmoff, Hollinger, Phys. Rev. B 38, 6084-6096 (1988). @footnote 3@ Himpel, Meyerson, McFeely, Morar, Taleb-Ibrahimi, Yarmoff Core Level Spectroscopy at Silicon Surfaces and Interfaces, in Campagna and Rosei, eds. Photoemission and Absorption of Solids and Interfaces with Synchrotron Radiation (Proceedings of the International School of Physics "Enrico Fermi", Course CVIII, Varenna, Italy. 1988.) North-Holland/Elsevier Science Publishers: 1990, pp. 203-236.

4:20pm **EM1-WeA8 Influence of Rapid Thermal Annealing on Vicinal Si(111)/SiO<sub>2</sub> Interfaces Investigated by Optical Second Harmonic Generation**, J.F.T. Wang, G.D. Powell, D.J. Stephens, R.S. Johnson, B.R. Solazzo, Y. Wu, D.E. Aspnes, G. Lucovsky, North Carolina State University

We have studied optical Second Harmonic Generation, SHG, from Si/SiO<sub>2</sub> interfaces formed by 800°C thermal oxidation of vicinal Si(111) surfaces off-cut approximately 5 degrees in the 112-bar direction. Changes in the rotational anisotropy of the SHG were observed when interfaces were annealed at temperatures between about 800 and 1000°C. We have analyzed the rotational anisotropy by including harmonic functions that reflect the C<sub>2v</sub> and C<sub>3v</sub> symmetry of the vicinal Si(111) surface corresponding respectively to steps and terraces of the vicinal surfaces. The relative phase difference, @phi@@sub 13@, between the C<sub>2v</sub> and C<sub>3v</sub> harmonic contributions is strongly influenced by the Rapid Thermal Annealing, RTA, temperature. In this paper we compare our results with an incident wavelength of 800 nm (or 1.55 eV) from a Ti:sapphire laser to previous reported work with incident wavelength of 1053 nm (or 1.17eV) using a Nd:YLF laser. The largest change in @delta@@phi@@sub 13@, ~72 degrees, using the 1.55 eV laser source is between 800°C and 900°C which is consistent with the previously reported studies using the Nd:YLF laser. @footnote 1@ However, @delta@@phi@@sub 13@ is larger for a pump beam of 800 nm compared to that of 1053 nm, ~72° compared to ~38°. These results are consistent with the anharmonic oscillator model if the laser energy is less than about one-half of the resonance energy of the anharmonic oscillator. @footnote 2@ Finally, it is important to note that annealing at 900°C has been shown to reduce sub-oxide interfacial bonding introduced at the Si/SiO<sub>2</sub> interface during thermal and plasma-assisted

oxidation processes @footnote 3@ suggesting that changes in @delta@@phi@@sub 13@ between 800 and 900°C anneals in the SHG response are associated with changes in interface bonding that include a reduction of the extent of transition regions with the sub-oxide bonding arrangements. @FootnoteText@ @footnote 1@ C. H. Bjorkman, C. E. Shearon, Jr., Y. Ma, T. Yasuda, G. Lucovsky, U. Emmerichs, C. Meyer, K. Leo, and H. Kurz, J. Vac. Sci. Technol. A11(4), 964 (1993) @footnote 2@ Y. R. Shen, The Principles of Nonlinear Optics (John Wiley & Sons, New York, 1984) @footnote 3@ G. Lucovsky, A. Banerjee, B. Hinds, C. Clafin, K. Koh and H. Yang, J. Vac. Sci. Technol. B15, 1074 (1997), and references therein.

4:40pm **EM1-WeA9 The Initial Stages of Si(100) Oxynitridation by NO: An Infrared Study**, J. Eng, Jr., K.T. Queeney, Y.J. Chabal, B.B. Stefanov, K. Raghavachari, Bell Laboratories, Lucent Technologies; X. Zhang, E. Garfunkel, Rutgers University

The oxynitridation of Si(100) by N<sub>2</sub>O has been studied extensively because the electrical properties of thin silicon oxynitride films are superior to those of silicon oxide films with the same thickness. Although the oxynitridation mechanism is not completely understood, it is generally believed that N<sub>2</sub>O decomposes to form NO under industrial processing conditions, and that NO is the species ultimately responsible for oxynitridation. On this basis, we have chosen to study the initial reaction of NO with clean Si(100) by using infrared spectroscopy, Auger electron spectroscopy, and low energy electron diffraction. We conclusively show that NO dissociatively adsorbs on Si(100) at room temperature, thereby resolving an existing debate in the literature. @footnote 1@ Heating the NO/Si(100) surface to 650 °C causes the formation of SiO<sub>2</sub> xN<sub>y</sub> structures which have strong characteristic modes at 858, 989, and 1057 cm<sup>-1</sup>. These modes have been assigned based on isotopic labeling studies involving <sup>15</sup>N<sub>2</sub>O and <sup>14</sup>N<sub>2</sub>O, as well as ab-initio density functional calculations. Auger studies show that heating to 850 °C removes oxygen, but the nitrogen 379 eV KLL feature is not attenuated. However, the Si-H vibrational features observed in H atom post-dosing experiments designed to probe the surface after heating to 850 °C are similar to those obtained by exposing clean Si(100) to H atoms, indicating that the N atoms reside in subsurface sites. Additional information about the Si-N modes is obtained by studying the adsorption and thermal decomposition of ammonia on Si(100) surfaces. @FootnoteText@ @footnote 1@ Y. Taguchi, M. Fujisawa, and M. Nishijima, Surf. Sci. Lett., 233 (1990) L251-252

5:00pm **EM1-WeA10 Growth and Analyses of Silicon Nitride Thin Films on Si(111) and Si(100)**, X.-S. Wang, Hong Kong University of Science & Technology, China; N. Cue, Hong Kong University of Science & Technology, China, Hong Kong, China

Silicon nitride is attractive for applications as dielectric and wide bandgap semiconductor materials. Using LEED, SPM, AES and XPS, we have analyzed geometric, thermodynamic and electronic properties of silicon nitride thin films grown on Si(111) and Si(100) substrates. The nitride films are prepared in two ways: (a) nitridation of Si substrates, i.e., by exposing clean Si samples to NH<sub>3</sub> or NO of various dosage and at substrate temperatures about 1150 K; (b) Si deposition under a flux of NH<sub>3</sub> or NO. In the second method, the substrate temperature can be kept significantly lower than 1150 K. On Si(111), the nitride thin films show a clear 8/3x8/3 superstructure. On nitrided Si(100), LEED shows a weak 1x2 + 2x1 pattern sometimes. Analysis of lattice structure of Si<sub>3</sub>N<sub>4</sub> film epitaxy on Si(111) is feasible, while on Si(100) this is much more difficult. The nitride films show a remarkable thermal stability in comparison with silicon oxide films. Desorption of oxide films starts at about 1075 K, whereas the nitride films remain stable at a substrate temperature as high as 1350 K. Furthermore, surface crystalline order of the nitride films is preserved after air exposure and even after going through system baking. The implication of these results on application of nitride, oxide and oxynitride thin films in microelectronics will be discussed.

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## Electronic Materials and Processing Division

### Room 316 - Session EM2-WeA

#### Application of Scanning Probes to Electronic Materials

Moderator: A. Smith, Ohio University

**2:00pm EM2-WeA1 Oscillating Contrasts Surrounding Charged Defects and Dopant Atoms in (110) Surfaces of III-V Semiconductor at Room-Temperature, Ph. Ebert, C. Domke, M. Heinrich, K. Urban, Forschungszentrum Jülich, Germany**

Positively and negatively charged defects and dopant atoms in n-doped GaAs(110) surfaces give rise, at room temperature, in occupied-state scanning tunneling microscope images to a bright elevation, which is surrounded by a dark depression ring. This oscillating contrast is not observed in empty-state images. A similar effect is found on n-doped GaP(110) surfaces. In order to explain the origin of this contrast behavior we simulated the spatial variation of the tunnel current as a function of the tunneling voltage, the polarity of the charge, and the doping of the material. The calculation of the tunnel current takes into account the tip-induced band bending, the local potential change induced by the screening of the charge, and the extension of the Tersoff-Hamann model for larger voltages. The results suggest that the oscillation in room-temperature STM images can be explained as the image of the local potential change (screened Coulomb potential) induced by the presence of the charge on (110) surfaces of III-V semiconductors. It is found that the oscillating contrast behavior occurs only if competing contributions to the tunnel current from the valence and conduction bands exist. The simulation also reproduces qualitatively all presently known contrast features of charged defects and dopant atoms on III-V and II-VI compound semiconductor cleavage surfaces in STM images.

**2:20pm EM2-WeA2 Two-Dimensional Carrier Profiling of III-V Structures using Scanning Spreading Resistance Microscopy, P. De Wolf, T. Hantschel, IMEC, Belgium; M. Geva, C.L. Reynolds, Bell Laboratories, Lucent Technologies; W. Vandervorst, IMEC, Belgium; F. Bysma, Bell Laboratories, Lucent Technologies**

Scanning Spreading Resistance Microscopy (SSRM) is a powerful tool originally developed for measuring two-dimensional (2D) carrier distributions in Si device structures with nm-spatial resolution.<sup>1</sup> It is in essence based on an Atomic Force Microscope equipped with a conductive tip that is biased relative to the sample. From the current flowing through the tip one deduces the local spreading resistance value. The spreading resistance value is determined primarily by the resistivity of the material in the small semi-hemispherical volume at the surface region where the tip contacts it. The resistivity is closely related to the local carrier concentration (and mobility) in this surface region. The spatial resolution thus mainly depends on the tip radius and pressure. Since SSRM measures resistance, a material property that depends upon carrier concentration, rather than detecting the carriers directly, it is capable of producing images of both high spatial resolution and wide dynamic range of carrier concentration. We have demonstrated spatial resolution values as small as 20 nm, and dynamic ranges of  $10^{15}$ – $10^{20}$  atoms/cm<sup>3</sup> in analyses of Si devices.<sup>1</sup> Whereas its application has been explored in detail on Si structures,<sup>1</sup> we report here for the first time on the application of SSRM for the analysis of III-V semiconductor structures, and in particular MOCVD-grown InP-based structures. We found that the application of SSRM to InP-based structures is much simpler than to Si. A minimal surface preparation is required in the cross sectioning process, much lower tip forces are needed, and metal tips instead of diamond tips can be used. When imaging complex multilayer epi-structures (containing p, n, and semi-insulating layers), close agreement between the SSRM profile and SIMS profiles can be obtained. More importantly is the capability of SSRM to image and determine 2D structures in actual devices, such as mesas and trenches common in semiconductor laser devices. SSRM also proved very valuable in characterizing with high spatial resolution 2D dopant and implant distributions. In this presentation we will present SSRM analysis of lateral Zn-diffusion into a semi-insulation layer in a mesa-like InP structure.<sup>1</sup> P. De Wolf, T. Clarysse, W. Vandervorst, L. Hellemans, Ph. Niedermann, and W. Hänni, J. Vac. Sci. Technol. B16, 355 (1998).

**2:40pm EM2-WeA3 The Structure of InAs/AlSb/InAs Surfaces and Interfaces Grown by MBE, B.Z. Nosh, W.H. Weinberg, University of California, Santa Barbara; B.V. Shanabrook, B.R. Bennett, W. Barvosa-Carter, L.J. Whitman, Naval Research Laboratory**

We have used in-situ plan-view scanning tunneling microscopy to study the surfaces and interfaces within an InAs/AlSb/InAs resonant tunneling diode-like structure grown by molecular beam epitaxy. The nanometer and atomic-scale morphologies of the surfaces have been characterized following a number of different growth procedures. When InAs(001)-(2x4) is exposed to Sb at a bilayer surface is produced, with one monolayer-deep (3 Å) vacancy islands covering approximately 25% of the surface. Both layers exhibit a (1x3)-like reconstruction characteristic of an InSb-like surface terminated with >1 ML Sb, indicating that there is a significant amount of Sb on the surface. When 5 ML of AlSb is deposited on an Sb-terminated InAs surface, the number of layers observed on each terrace increases to three. Growth of an additional 22 ML of InAs onto the AlSb layer, followed by a 30 s interrupt under Sb, further increases the number of surface layers observed. The rms roughness is found to increase at each subsequent interface; however, on all the surfaces the roughness is  $\leq 2$  Å. The surface roughness is attributed to a combination of factors, including reconstruction-related stoichiometry differences and kinetically-limited diffusion during growth. To begin to elucidate these various factors and help distinguish between kinetic and thermodynamic effects, we have examined the initial stages of Sb deposition on InAs(001)-(2x4) under various growth conditions. Possible methods to reduce the roughness of the interfaces will be discussed.

**3:00pm EM2-WeA4 In-Situ STM of MBE Growth Quality for GaAs(001) and InP(001)\*, G. Lengel, F.G. Johnson, W.T. Beard, R.J. Phaneuf, Laboratory for Physical Sciences; E.D. Williams, University of Maryland**

As heterostructure-based devices continue to shrink in size, the roughness of the interface between two materials plays a larger role in determining the performance of the final product. Characterization of the lateral length scales of the roughness as well as the root-mean-square roughness is important for understanding the impact of interface quality on device performance. To address this problem, In-Situ Scanning Tunneling Microscopy (STM) has been used to study the geometry of freshly prepared MBE samples. The evolution of roughness as a function of the initial condition of the surface before growth, the thickness of the buffer layer, as well as the role of the growth temperature on both GaAs and InP will be presented. The relative quality of these surfaces has been quantified by calculation of the height-height correlation function from the measured images. The physical significance of the measured parameters, and their usefulness as criteria for judging growth quality will be discussed.<sup>1</sup> This work has been supported by the Laboratory for Physical Sciences.

**3:20pm EM2-WeA5 Structural and Morphological Studies of GaN Heteroepitaxy on SiC(0001), V. Ramachandran, A.R. Smith, R.M. Feenstra, D.W. Greve, Carnegie Mellon University**

Heteroepitaxial growth of GaN on SiC has been studied using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and high resolution x-ray diffraction. Growth was performed by molecular beam epitaxy (MBE) on hydrogen etched SiC(0001) substrates that show a  $\sqrt{3} \times \sqrt{3}$  R-30° reconstruction. Significant differences are seen in the growth morphology in different growth temperature regimes, both at low and high film thicknesses. At a coverage of a few monolayers, STM observation of GaN grown at temperatures around 550°C shows layer-by-layer growth. Terraces show sub-Å corrugation corresponding to the formation of misfit dislocations at the heterointerface, indicating that the film has relaxed. Films grown at around 650°C with a similar thickness show columnar, flat-topped islands of uneven heights with deep crevices between them. This difference in morphology may be understood in terms of the different strain relaxation mechanisms in the two temperature regimes. At higher temperature, films prefer to relieve strain by forming 3-D islands, which can be distorted to relieve strain. Alternatively, at lower temperature, the films remain pseudomorphic and grow in a layer-by-layer manner both before and after the formation of misfit dislocations. AFM measurements also show remarkable morphological differences between thicker (200 nm) films grown in the two temperature regimes mentioned above. Films grown at 550°C show a large number of spiral growth fronts while films grown at 650°C show a stepped layer-by-layer structure. Based on the growth model outlined above, it is apparent that in the low temperature 2-D growth mode, misfit dislocations at the interface are associated with screw dislocations which extend up to the surface and act as a source for the spiral growth. In 3-D growth, misfit dislocations can

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form at the edges of islands without the need for as many screw dislocations. X-ray rocking curve measurements on GaN films 200-400 nm thick show decreasing FWHM with increasing growth temperature. This would agree with the above model, where, as the growth temperature rises, the film requires fewer screw dislocations in order to create the necessary number of misfit dislocations at the interface.

**3:40pm EM2-WeA6 Impact of Deposition Method on the Microstructural and Electrical Properties of Thin Film Silica Aerogels, C. Caragianis-Broadbridge, L. Carmona, M. Farag, M. Guillorn, F. Stellabotte, Trinity College**

Aerogels are nanoporous materials with unique optical, thermal and electrical properties. Silica thin film aerogels demonstrate great potential as low dielectric constant insulators for interlevel dielectric applications. The focus of this research is the fabrication of thin film silica aerogels through a sol-gel process in conjunction with low-temperature supercritical extraction of CO<sub>2</sub>. The microstructural and electrical properties of the aerogel were studied as a function of deposition method, using non-contact atomic force microscopy (nc-AFM), scanning and transmission electron microscopy (SEM and TEM) and capacitance-voltage (C-V) instrumentation. Alcogels, aerogel precursors, were prepared by hydrolysis and condensation of metal alkoxide, tetraethyorthosilicate, and were catalyzed by both acids and bases, according to a standard reaction. Before gelation, the solution was deposited on two substrates (bare Si and SiO<sub>2</sub> coated Si) by two techniques (dipping and spin coating). After supercritical extraction of the CO<sub>2</sub>, the resulting aerogels were characterized using AFM, SEM and TEM to obtain film uniformity, thickness and pore size. C-V data were acquired from metal insulator semiconductor (MIS) capacitors fabricated using the aerogel-coated wafers. This study reveals a correlation between deposition technique and uniformity of the aerogel. Thin films deposited by the spinning technique yield consistently smaller pore sizes, ranging between 150 and 440nm while producing a more uniform film thickness. C-V characterization of the aerogel MIS devices (for both substrates) indicates a high quality dielectric with minimal mobile, fixed and interface state charge. These measurements also reveal that these aerogel MIS capacitors possess a substantially lower dielectric constant (1.5-3.5 vs. 3.9) when compared with standard control SiO<sub>2</sub> MOS devices.

**4:00pm EM2-WeA7 UHV STM Nanofabrication and the Giant Deuterium Isotope Effect: Applications to CMOS Technology, J.W. Lyding, M.C. Hersam, G.C. Abeln, E.T. Foley, J. Lee, Z. Chen, D.S. Thompson, J.S. Moore, S.-T. Hwang, H. Choi, K. Hess, University of Illinois, Urbana-Champaign**

**INVITED**

The use of the UHV STM to selectively desorb hydrogen with atomic scale precision from Si(100)-2x1:H surfaces<sup>1</sup> has opened new opportunities for creating nanoelectronic device structures. The chemical contrast between H-passivated and clean Si has enabled the development of nanoscale selective chemical schemes including oxidation,<sup>2</sup> nitridation,<sup>3</sup> and molecular functionalization.<sup>4</sup> Using a high temperature STM these schemes are also being extended to include nanoscale metallization by UHV chemical vapor deposition. A key aspect of this work is the establishment of an electronic interface between nanoelectronic device structures and macroscopic contacts to enable testing. We will report on several schemes that are being developed for this purpose. In a parallel set of experiments it was found that the desorption of deuterium from Si(100)-2x1:D surfaces is much more difficult than hydrogen desorption.<sup>5</sup> Using this as a basis, we discovered that deuterium treatment can dramatically prolong the lifetime of CMOS transistors by factors of 10 to 50.<sup>6</sup> Recent low temperature STM desorption experiments<sup>6</sup> have shed additional light on the CMOS degradation problem and the giant isotope effect. <sup>1</sup>J.W. Lyding, T.-C. Shen, J.S. Hubacek, J.R. Tucker, and G.C. Abeln, Appl. Phys. Lett. 64, 2010 (1994). <sup>2</sup>J.W. Lyding, T.-C. Shen, G.C. Abeln, C. Wang, E.T. Foley, and J.R. Tucker, Mat. Res. Soc. Symp. Proc. 380, 187 (1995). <sup>3</sup>G. C. Abeln, S. Y. Lee, J. W. Lyding, D. S. Thompson, and J. S. Moore, Appl. Phys. Lett. 70, 2747 (1997). <sup>4</sup>Ph. Avouris, R.E. Walkup, A.R. Rossi, T.-C. Shen, G.C. Abeln, J.R. Tucker, and J.W. Lyding, Chem. Phys. Lett. 257, 148 (1996). <sup>5</sup>J.W. Lyding, K. Hess, and I.C. Kizilyalli, Appl. Phys. Lett. 68, 2526 (1996). <sup>6</sup>E. T. Foley, A. F. Kam, J. W. Lyding, and Ph. Avouris, Phys. Rev. Lett. 80, 1336 (1998).

**4:40pm EM2-WeA9 Scanning Probe Microscopy Imaging of IC Cross Sections, K.-J. Chao, R.J. Plano, J.R. Kingsley, X. Lu, I. Ward, Charles Evans & Associates**

Various Scanning Probe Microscopy (SPM) techniques have been applied to investigate the cross sections of modern integrated circuit (IC) devices. The IC devices were prepared by polishing using common Scanning Electron Microscope (SEM) sample preparation methods. Some of the samples were further etched to delineate the various oxides. Atomic force microscope (AFM) was used to simultaneously acquire both topography and phase images of these surfaces. The topography images reveal height information about the sample while the phase images are sensitive to material differences and show edges clearly. Different metal layers and device structures are clearly resolved. To verify the results, these samples were coated with a thin layer of metal and then imaged with an SEM. AFM and SEM results show a close agreement, with the AFM topography image having additional height information and the phase image showing sharper detail than the SEM images. Also, the doping regions of IC devices were investigated by the scanning capacitance microscope (SCM) and low voltage SEM. A detail comparison will be presented.

**5:00pm EM2-WeA10 Silicon Nitride Islands as Oxidation Masks for the Formation of Silicon Nano-Pillars, J.S. Ha, K.-H. Park, W.S. Yun, E.-H. Lee, ETRI, Republic of Korea**

We have used nanometer-scale silicon nitride islands as oxidation masks for the formation of silicon nano-pillars. For the growth of silicon nitride islands on Si(111)-7x7 surface, two different methods were used; N<sub>2</sub> exposure at temperatures between 700 and 800 °C and 100 eV N<sup>+</sup> ion exposure at room temperature followed by subsequent post-annealing at 980 °C. Scanning tunneling microscope (STM) images taken from the two differently prepared surfaces showed a submonolayer coverage of nanometer-sized silicon nitride islands. On these surfaces, O<sub>2</sub> was exposed at high temperatures where silicon etching was dominant over oxide formation. It was found that N<sub>2</sub>-induced silicon nitride islands work as successful oxidation masks to form silicon nano-pillars as high as several nanometers via selective oxygen etching of silicon. On the other hand, oxygen exposure to the silicon surface covered with N<sub>2</sub>-induced silicon nitride islands resulted in the increase of lateral size and density of pillars, compared to the initially formed islands. Such difference can be explained in terms of the segregation of extra nitrogen species which had migrated into subsurface region when N<sub>2</sub> had been exposed at high temperatures. Optimum conditions for the formation of silicon nano-pillars could be obtained by controlling the nitridation temperature, annealing time, and oxidation temperature. In this paper, we will propose a successful way to form silicon nano-structures using silicon nitride islands and also discuss underlying mechanisms of the island growth.

## Electronic Materials and Processing Division Room 314/315 - Session EM+PS-ThM

### Processing of High K Dielectrics for DRAMs

**Moderator:** K.R. Milkove, IBM T.J. Watson Research Center

**8:20am EM+PS-ThM1 Growth and Characterization of Ba@sub 0.6@Sr@sub 0.4@TiO@sub 3@ Thin Films on Si with Pt Electrodes, L. Kinder, I.L. Grigorov, C. Kwon, Q.X. Jia, Los Alamos National Laboratory; L. Luo, J. Zhao, Applied Materials, Inc.**

The application of high dielectric constant materials like barium strontium titanate in dynamic random access memories requires the integration of these materials into the existing Si technology. In this study, pulsed laser deposition was used to grow Ba@sub 0.6@Sr@sub 0.4@TiO@sub 3@ (BST) thin films on Si with Pt electrodes. Through scanning electron microscopy, x-ray diffraction, and electrical characterization, the Pt/BST/Pt capacitor processing on Si has been optimized. BST films on Pt sputtered at high power tends to show high leakage current. However, high leakage current is prevented if the Pt is sputtered at low powers. Low power deposition leads to not only smooth Pt film but also less hillocks. The smoother Pt electrodes allow the BST to grow with greater crystallinity. 150 nm BST on Pt shows a dielectric constant over 400 and dielectric loss of 0.01 at 10 kHz. The quality of the dielectric can be further improved by first depositing a thin seed layer of BST at lower temperatures. We have successfully used 20 nm BST deposited by metal-organic chemical vapor deposition as a seed layer to improve the over all device performance. The influence of interface and of initial nucleation of BST films on the structural and dielectric properties of the thin film capacitors will be also discussed.

**8:40am EM+PS-ThM2 Synthesized Single Crystalline Ba@sub (1-x)@Sr@sub x@TiO @sub 3@ Thin Films for DRAM Application, F.F. Feng, University of Houston; C.L. Chen, Z.H. Zhang, University of Houston, U. S. A.; Y. Liou, P. Jin, University of Houston; W.K. Chu, University of Houston, U. S. A.; C.W. Chu, University of Houston**

Perovskite Ba@sub (1-x)@Sr@sub x@TiO@sub 3@ thin films have been synthesized on (001) LaAlO@sub 3@ and (001) SrTiO@sub 3@ substrates with SrRuO@sub 3@ or Pt bottom electrodes by pulsed laser ablation. Extensive X-ray diffraction, rocking curve, and pole-figure studies suggest that the as-grown films are (001) oriented with single crystalline quality. RBS studies indicate that the epitaxial films have excellent crystalline quality with an ion beam minimum yield of only 2.6 % or less, suggesting that the crystallinity of the as-grown films can be compared with the single crystal silicon. Atomic force microscopy studies indicate that the as-epitaxial films are atomic smooth under the selected growth conditions. The dielectric property measurements show room temperature values of the relative dielectric constant and loss tangent of larger than 750 and 0.005, respectively.

**9:00am EM+PS-ThM3 Scanning Capacitance Imaging for Evaluation of High-k Dielectric Oxide Materials, Y. Yamaguchi, K.P. Wiederhold, B.D. White, N.E. Wittry, H.C. Galloway, Southwest Texas State University**

We have used scanning capacitance imaging to measure the dielectric properties of oxide materials such as BST which have large dielectric constants (high-k). These materials are of interest as potential replacements for the dielectric in memory devices due to their increased capacitance per unit area. Several scanning capacitance methods have been developed using modified atomic force microscopes and they are actively used to measure quantities such as the thickness of SiO@sub 2@ layers or the doping levels across a p-n junction. We will discuss how this technique can be used as a diagnostic tool when applied to the high-k oxides. First, the measurement of the dielectric properties on a local scale may help to identify the causes of failure modes in materials. As an example, we will report on local variations of the dielectric constant observed in films of BST grown by RF planar magnetron sputtering. Second, we have used scanning capacitance to evaluate films of novel oxide materials grown by Dual Ion Beam Sputtering.@footnote 1@ The advantage of Scanning Capacitance Microscopy is that the relative merits of different growth conditions can be rapidly assessed and compared to each other or to a reference standard. This allows us to investigate new materials or deposition conditions without having to form complete devices for analysis. By identifying the most promising growth conditions that yield high dielectric constants, uniform films, and low leakage currents we can speed up the process of testing new growth methods and materials.

@FootnoteText@ @footnote 1@P. Perera, R. Selestino, and C.J. Gutierrez, Department of Physics, Southwest Texas State University

**9:20am EM+PS-ThM4 Characterization of Thermal Annealing of Tantalum Pentoxide for High-k Dielectric Applications, R.L. Opila, J.P. Chang, G.B. Alers, Bell Laboratories, Lucent Technologies**

Tantalum pentoxide is being studied as an alternative high dielectric constant material for storage capacitors or gate dielectrics. Since the oxide layers are thin, even for high dielectric constant materials, interfaces between the tantalum pentoxide and other thin film materials can greatly affect device electrical properties. This paper focuses on analyzing the bulk properties of the Ta@sub 2@O@sub 5@ film and the Ta@sub 2@O@sub 5@/TiN interface to assess a new TiN/Ta@sub 2@O@sub 5@/TiN storage capacitor structure that has lower contact resistance and higher specific capacitance than conventional poly-Si based capacitors. The effect of thermal annealing on the electrical performance of the capacitor will be presented. Angular Resolved X-ray Photoelectron Spectroscopy (ARXPS) has been used to characterize the interfacial composition and stoichiometry of tantalum pentoxide deposited by CVD processes at low temperatures. The amount of carbon incorporated in the film during the CVD process decreases with increasing process temperature. Reduced leakage current has been observed as the concentration of carbon in the film increases. Formation of TiO@sub 2@ was observed at the Ta@sub 2@O@sub 5@/TiN interface at an RTA temperature of 450°C. Significant amounts of titanium suboxides are also observed at the Ta@sub 2@O@sub 5@/TiN interface. The imperfect interface is thought to reduce the specific capacitance and increase leakage currents, perhaps through partial reduction of the Ta@sub 2@O@sub 5@. Correlation between the interface chemical states and the electrical performance will be presented.

**9:40am EM+PS-ThM5 Structural Properties of Ultrathin Films of High Dielectric Constant Materials on Silicon, E. Gusev, IBM T.J. Watson Research Center; H.C. Lu, T. Gustafsson, E. Garfunkel, Rutgers University; G.B. Alers, Bell Laboratories, Lucent Technologies**

The high tunneling rates in ultrathin gate oxides is driving the search for higher-K replacement dielectrics in silicon microelectronics. Ta@sub 2@O@sub 5@ and several other metal oxides are now attracting the attention of the device community. One problem that plagues the use of metal oxides on Si is the formation of an interfacial SiO@sub 2@ layer; such layers limit the capacitance and can degrade the electrical properties of the gate structures. We have examined the composition of interfacial layers of several high dielectric constant oxide systems using high resolution medium ion energy scattering. We find that the interfacial region is best described as neither Si/SiO@sub 2@/metal-oxide nor Si/metal-oxide, but can be viewed as a compositionally graded oxide with a dielectric constant significantly higher than that of pure SiO@sub 2@ (as inferred from electrical measurements). Annealing changes the near-interfacial composition substantially. When post anneal temperatures are kept low, stable composite oxide structures (with physical thickness greater than 7nm) can be obtained that demonstrate good electrical properties and an effective SiO@sub 2@ thickness of less than 2 nm.

**10:00am EM+PS-ThM6 Etching of High Dielectric Constant Materials for DRAMs and Ferroelectric Materials for FeRAMs, L.G. Jerde, A. Cofer, K. Olson, P. Rajora, S.P. DeOrnellas, Tegal Corporation**

**INVITED**

The introduction of ferroelectric and high dielectric constant films and their associated metals, barrier materials and adhesion layers for DRAM, embedded DRAM and FeRAM applications are driving some of the most challenging etch requirements in the IC fabrication industry. The specifications resulting from these requirements range from very aggressive profile and critical dimension control, to etch selectivities, contamination and damage, defects and chamber cleaning frequency. Some of the most difficult of these requirements are a result of the design rules that will be used in production for the DRAM applications (i.e., 0.15  $\mu$ m and below). The inherent involatility of the etch products of these materials is another key factor contributing to the difficulty in meeting the requirements. In this paper we will present and discuss the etch requirements for these materials, the reactor technology we use to etch them, selected process and manufacturability results for these materials and future directions for this work.

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10:40am **EM+PS-ThM8 Patterning of Reactively Sputtered Tantalum Pentoxide, a High Epsilon Material, by Plasma Etching**, *L.B. Jonsson, F. Engelman, J. Du, C. Hedlund*, Uppsala University, Sweden; *U. Smith*, Ericsson Components AB, Sweden; *H.-O. Blom*, Uppsala University, Sweden  
The large size of integrated capacitors is a problem today. The capacitors can easily cover a major part of the total chip area. By using a high epsilon material as the dielectric material in the capacitor the size can be reduced significantly. One very promising candidate is Tantalum pentoxide ( $\text{Ta@sub2@O@sub5@}$ ) which has an epsilon of 25 compared to Silicon dioxide which has 3.9. In order to make integrated capacitors the Tantalum pentoxide must be patterned. We have investigated and optimized dry etching processes for realizing a complete capacitor structure. One process for etching the Tantalum pentoxide on a back contact made of poly-silicon and one process for etching contact holes, in silicon dioxide, down to the Tantalum pentoxide. Data from Reactive Ion Etching (RIE) as well as for Inductively Coupled Plasma (ICP) processes will be presented.

11:00am **EM+PS-ThM9 The High Temperature Platinum Etching Using Titanium Layer**, *H.-W. Kim, B. Ju, B. Nam, W. Yoo, C.J. Kang, T.-H. Ahn, J. Moon, M.Y. Lee*, Samsung Electronics, Co., Korea

1. Introduction: It is necessary to use the platinum as a bottom electrode material of the BST capacitor in highly integrated devices, however, the Pt etching of the fine patterns is difficult due to the inherent non-reactivity of platinum. It is revealed that the Pt etch slope of  $80^\circ$  was attained by  $\text{O@sub2@Cl@sub2@}$  chemistry by elevating the substrate temperature up to  $160^\circ\text{C}$ . This result is thought to be due to the reaction of O species with Ti layer and analyzed by TEM, XPS and AES. 2. Experimental & Results: As an experimental setup for high temperature etching, the modified chiller using Galden HS260 (B.P.= $270^\circ\text{C}$ ) was chosen. The oxide  $5000\text{\AA}/\text{Ti}600\text{\AA}/\text{Pt}2000\text{\AA}$  structure was used and the  $\text{O@sub2@Cl@sub2@}$  ( $\text{O@sub2@} = 80\%$ ) gas was chosen as an etchant combination in MERIE system. The change of the Pt etching profile at  $100^\circ\text{C}$ ,  $130^\circ\text{C}$ ,  $160^\circ\text{C}$ , respectively was investigated. The Pt etch slope does not depend on the substrate temperature up to the just etch time, the etch slope of the  $160^\circ\text{C}$ -sample was about  $80^\circ$  after 100% overetch and the Ti mask was not eroded significantly. It appeared that the titanium mask of  $100^\circ\text{C}$ ,  $130^\circ\text{C}$  samples were eroded considerably. The Pt etching results of  $160^\circ\text{C}$  with Ti, TiN and  $\text{TiO@sub2@}$  layer were compared (not shown). TiN and  $\text{TiO@sub2@}$  layer does not help attaining high Pt etch slope even with the thermal heating. From the above result, it is surmised that the change or stabilization of Ti layer through the reaction/diffusion of O atoms during plasma etching plays a major role in attaining the higher Pt etching slope. From the XTEM investigation of the  $160^\circ\text{C}$ -etched one, the center of the Ti layer stays crystalline, however, the edge of the Ti layer became amorphous and the oxygen content increased up to more than 50%, by EDX analysis. The XPS analysis of 100-Ti layer showed that the considerable amount of Ti-Ti bond changed to the Ti-O bond during the  $\text{O@sub2@Cl@sub2@}$  plasma treatment. The AES analysis confirmed the above phenomena. 3. Conclusions: The etching slope of Pt was improved by the reaction of the mask material with the etching species, not by the reaction of Pt itself. The optimal overetching helps to attain the higher etch slope as long as the Ti mask stays. High temperature processing helped the duration of the titanium mask by activating the reaction of Ti with O-species.

11:20am **EM+PS-ThM10 Removal of Sidewall Re-depositions Formed by Reactive Ion Etching of Platinum for Embedded DRAM Applications**, *H.M. Ranpura, D.H. Butler, S.P. Beaudoin*, Arizona State University; *C.J. Tracy, L. Chang*, Motorola Semiconductor Products Sector

Removal of platinum sidewall re-depositions (SRDs) formed due to patterning of electrodes due to reactive ion etching (RIE) for an embedded dynamic random access memory (DRAM) project has been investigated. A serious problem in integrating these devices is the re-deposition of non-volatile etch products onto the pattern sidewall. Removal of these SRDs without damaging other exposed materials is a challenging process. A mixture of argon (Ar) and chlorine ( $\text{Cl@sub2@}$ ) plasma was used to etch the platinum electrodes. Following the etching step the wafers were processed in an oxygen plasma to remove the photoresist on the wafer. Results are presented for post-ashed wafers that were heated at different temperatures for varying times in different ambients. Following heating wafers were cleaned in aqueous hydrochloric acid (HCl). Results are also presented for ultrasonic cleaning of wafers in HCl.

11:40am **EM+PS-ThM11 Study on Surface Reaction of  $(\text{Ba,Sr})\text{TiO@sub3@}$  Thin Films by High Density Plasma Etching**, *S.B. Kim, C.I. Kim, E.G. Chang*, Chung-ang University, Korea

Ferroelectric devices are attractive for dynamic random access memories (DRAMs) applications because of high dielectric constant. Using ferroelectric device structure, manufacturing cell capacitance of highly integrated memory device is possible. Small feature size requires anisotropic etching. Since research of  $(\text{Ba,Sr})\text{TiO@sub3@}$  thin films etching is not widely, we studied on surface reaction of  $(\text{Ba,Sr})\text{TiO@sub3@}$  thin films by high density plasma etching.  $(\text{Ba,Sr})\text{TiO@sub3@}$  thin films were etched with an Inductively coupled plasma (ICP) by varying the etching parameter such as  $\text{BCl@sub3@}/\text{C@sub2@F@sub6@}/\text{Ar}$  gas mixing ratio, RF power, and pressure. Etching effect were investigated in terms of etch rate, selectivity. In this study,  $(\text{Ba,Sr})\text{TiO@sub3@}$  etching mechanism was investigated with XPS (X-ray photoelectron spectroscopy) and OES (Optical emission spectrometry) and QMS (Quadrupole mass spectrometry). Ion current density was measured by using single Langmuir probe. Surface of etched  $(\text{Ba,Sr})\text{TiO@sub3@}$  investigated with SEM (Scanning electron microscopy).

## Electronic Materials and Processing Division Room 316 - Session EM-ThM

### Compound Semiconductor Surface Chemistry

Moderator: R.S. Gold, University of Michigan

8:20am **EM-ThM1 Air-Stable Sulfur-Based Passivation of III-V Compound Semiconductor Surfaces**, *C.I.H. Ashby, K.R. Zavadil, A.G. Baca, P.-C. Chang, B.E. Hammons*, Sandia National Laboratories

Although the surface state density can be greatly reduced by sulfur bonding to III-V surfaces, this improvement is transient due to rapid oxidative loss of S from the surface. We have developed a method for stabilizing the improved properties of the semiconductor surface in the presence of S by stabilizing the S against air-oxidation. We employ a two-step process that forms an air-stable metal-S-semiconductor structure. A monolayer of S is applied by UV photodissociation of sulfur vapor. The sulfided surface is then reacted with a metal salt to form an insoluble metal-S overlayer on the semiconductor. XPS characterization of this overlayer shows the presence of the metal, S, and O in the overlayer. Photoluminescence (PL), and Raman spectroscopies have been employed to characterize the effect of the overlayer on surface-recombination-sensitive properties of the interface. For  $7\times10^{16}/\text{cm}^3$   $\text{n-GaAs}$ , a 15-fold increase in PL intensity results with the metal-S overlay, which is double the improvement obtained with S-treatment alone. Unlike photosulfidation or the more conventional sulfidation with  $\text{NH@sub4@S@subx@}$ , PL intensity following metal-S overlayer deposition does not degrade rapidly in air at room temperature. Passivation of  $1.8\times10^{18}/\text{cm}^3$   $\text{n-GaAs}$  produces a 20-30% increase in PL intensity that is retained after more than 10 months in air. In addition, the PL improvements due to the metal-S overlayer are retained following low-temperature deposition of  $\text{SiNx}$  dielectric coatings. Application of the metal-S passivation layer to GaAs HBTs followed by  $\text{SiNx}$  encapsulation has produced an increase in dc current gain from 40 to nearly 100 for  $2.5\times5\text{ }\mu\text{m}$  devices and from 90 to over 100 for large-area ( $100\times100\text{ }\mu\text{m}$ ) devices, consistent with a large reduction in surface recombination in these devices. 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.

8:40am **EM-ThM2 Development of Surface Morphology During  $\text{H@sub2@}$  Plasma Processing of  $\text{GaAs(001)}$** , *S.W. Robey*, National Institute of Standards and Technology, US

There is interest in hydrogen plasma etching as a route to low temperature, dry processing for oxide removal from semiconductors. The surface morphology that develops is a determining factor in the success of subsequent device fabrication, making it important to understand surface processes that can influence morphology development during plasma exposure. In situ Auger spectroscopy and RHEED were used in conjunction with ex situ AFM to investigate the development of surface morphology on  $\text{H@sub2@}$  plasma etched  $\text{GaAs(001)}$  surfaces. Etching of the GaAs, subsequent to the oxide removal, at temperatures above 600 K led to Ga-rich surfaces with a tendency for [11n]-type facet formation. Initial attack on the GaAs surface typically occurred in a localized manner leading to the formation of etch pits. Aligned rows of etch pits are often observed due to preferential etching at mis-cut steps. The preferential attack significantly

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influences subsequent morphology development. Height-difference correlation functions suggest scaling at small lengths with a roughness exponent in the range of 0.7 - 0.8. A crossover occurs for separations of ~ 30 nm to 60 nm, depending on substrate temperature. The crossover length appears to correlate with typical etch pit dimensions. For larger separations, the slope is much smaller, with some evidence of additional structure in the 100 nm to 200 nm range. Correlations between diffraction and AFM data, connections to continuum models for surface etching including processes such as diffusion, redeposition, etc., and comparison to other experimental work will be discussed.

9:00am **EM-ThM3 Thermal Chemistry and Photochemistry of Organothiols Chemisorbed on GaAs(110), N. Camillone, III, K.A. Khan, R.M. Osgood, Jr.,** Columbia University

Self-assembled monolayers of organothiols and related compounds hold promise for use in the semiconductor industry as ultrathin electron beam resists, atomic-layer-epitaxy precursor layers, and monolayer adhesives. We have recently begun fundamental studies of the surface chemistry and photophysics of small organothiols [CH@sub 3@SH, (CH@sub 3@S)@sub 2@ and CH@sub 3@SCH@sub 3@] on GaAs. Temperature programmed desorption measurements indicate that each of these species interact strongly with the GaAs surface. The first monolayer of CH@sub 3@SH desorbs near 300 K, compared to approximately 100 K for the second layer, indicating a chemical interaction between the thiol and the surface, despite the fact that the molecule predominantly appears to desorb intact. The behavior of (CH@sub 3@S)@sub 2@ is quite different; the disulfide decomposes upon adsorption (or during the TPD temperature ramp) and desorbs predominantly as CH@sub 3@SCH@sub 3@ at approximately 500 K, perhaps as the result of a concerted associative/dissociative desorption process which leaves sulfur at the surface. In addition, we will report on UV photoreaction cross section measurements and photoreaction products for these thiol, sulfide and disulfide compounds. For example, the measured cross section for photodissociation of an annealed (CH@sub 3@S)@sub 2@ monolayer at 193 nm is orders of magnitude smaller than that for CH@sub 3@SH.

9:20am **EM-ThM4 The Surface Structures of In@sub x@Ga@sub 1-x@As@sub y@P@sub 1-y@ (001) Films Grown by Metalorganic Vapor-Phase Epitaxy, L. Li,** University of California, Los Angeles; *B.-K. Han, M.J. Bergarney,* University of California, Los Angeles, US; *D. Law, Q. Fu, R.F. Hicks,* University of California, Los Angeles

Strained films of In@sub x@Ga@sub 1-x@As@sub y@P@sub 1-y@ were grown on GaAs and InP (001) substrates by metalorganic vapor-phase epitaxy (MOVPE). The film thickness and composition, and the degree of strain were determined by analysis of high-resolution x-ray diffraction spectra. In addition, the large-scale morphology, the atomic structure and the composition of the film surfaces were characterized after growth by low-energy electron diffraction, x-ray photoelectron spectroscopy, infra spectroscopy of adsorbed hydrogen, and scanning tunneling microscopy. All the surfaces immediately following MOVPE are composed of atomically flat terraces that are separated by double height steps. The steps exhibit smooth, gradual undulations along the terrace edges. Close-up images of the terraces reveal a disordered (2x1) or c(4x4) structure, which arises from a random mixture of group V atoms and alkyl groups adsorbed on top of the surface. Annealing in vacuum desorbs the alkyl groups and then the group V atoms, generating a variety of reconstructions at progressively higher group III coverages. Many new reconstructions are observed on these films, including (2x3), (3x2) and other (nx2) unit cells, where n is an odd integer. Evidently, these surfaces do not obey the electron counting scheme that holds for unstrained GaAs (001), and therefore, they may be positively or negatively charged. The structure and properties of some of these new surfaces will be described at the meeting.

9:40am **EM-ThM5 Low Induced Damages Dry Etching of III-V Materials for HBT Applications using ICP in Chlorinated Plasma, J.J. Etrillard, J.F. Bresse, C. Daguet, M. Riet, J. Mba,** CNET, France Telecom, France

Etching of InGaAs and InP in ICP using SiCl<sub>4</sub> was studied for HBT application. Low sample temperature was used to minimize the etching isotropy and to reduce the element V desorption. The low ion energy etching process results in a damaged layer thickness of a few angströms. AES results on InP demonstrate a very thin layer of non-stoichiometric material. The nature of the etching mask impacts on the surface contamination: local contamination effects due to sputtering are observed. For such low ion energy processes, the sample preparation before ICP etching is shown to be very important for the surface roughness, as observed by AFM. Various preparation schemes have been investigated,

before ICP etching, aiming at a reduction of the surface degradation resulting from ICP etching. It is shown that the best results in terms of roughness and etch-rate are obtained with a silicon nitride mask and a surface oxidation before a wet desoxidation immediately preceding the ICP etching. An ICP process was used successfully for partly etching the base mesa of HBT structures. No significant difference was observed in terms of induced damages and HBT current gain.

10:00am **EM-ThM6 Variable Substrate Temperature for Precise Growth of II-VI Interfaces, Y. Luo, M. Han, J.E. Moryl, R.M. Osgood, Jr.,** Columbia University

This paper describes the use of variable substrate temperature for the controlled growth of compound semiconductor hetero-interfaces. The investigation uses UHV surface probes to show that choice of surface temperature and temperature ramping during each half of bilayer growth, can lead to a precisely controlled interface composition. The emphasis on the investigation thus far is controlled interface abruptness, composition and crystallinity. The experiment uses sequential dosing of a ZnSe(100) substrate with dimethylcadmium and H@sub 2@S, respectively, in a UHV system. The substrate temperature is controlled by a temperature controller system and may be raised from 100K to 700K at 4K/sec. In situ surface analysis is accomplished with TPD, AES, LEIS and LEED. The experiments showed that, when DMCD was dosed onto a well ordered c(2x2) ZnSe substrate, the composition of surface growth varied dramatically with the substrate temperature. AES and TPD measurements show that this variation is directly dependent on the chemical interaction of the organic ligands at the surface at differing substrate temperatures. For example, within the temperature range from 250 K to 370 K, the Cd growth mode can change from a simple 0.5 monolayer Cd insertion, to a self-terminating one monolayer deposition or even a thick multilayer of Cd with significant Zn depletion near the interface. In the presence of a hydrogen sulfide flux the percentage of sulfur growth at the surface is directly dependent on the surface-coverage of existing methyl groups due to previous dosing of DMCD. Finally we have found that by selection of dosing temperature and the following temperature ramping one can accurately manipulate the interface composition on a monolayer scale, e.g. a mixture of a half monolayer Zn and a half monolayer Cd, or an abrupt full monolayer of Cd or intermediate layers of Zn@sub 1-x@Cd@sub x@Se@sub 1-y@S@sub y@.

10:20am **EM-ThM7 Effect of Surface Interactions on Band Offsets at Buried Semiconductor-Insulator Interfaces, B.R. Schroeder, S. Meng, M.A. Leskovic, M.A. Olmstead,** University of Washington

Once an interface between two materials is buried, it is generally assumed to be stable. However, when a CaF@sub 2@/Si film is exposed to atmosphere, the interface spacing increases by 1.7 Å and the band offset decreases by 0.5 eV. The mechanism for this modification of a buried interface is not understood. We have investigated the effect of surface exposure on the band offset at a buried CaF@sub 2@/Si(111) interface. Thin films (4-6 monolayers) of CaF@sub 2@, grown by molecular beam epitaxy on Si(111) substrates, were exposed to atmospheric pressure of various atmospheric constituents and the change in band offset was measured by core level photoemission spectroscopy. Exposure to nitrogen had a negligible effect, while exposure to water vapour (+ nitrogen) had the same result as atmosphere. Exposure to oxygen also reduced the band offset, but by a smaller amount. The decrease in band offset was partially reversible upon annealing at 450 °C. Besides the decrease in band offset, exposure to water or atmosphere also leads to the disappearance of the interface photoemission satellite. This may indicate a structural change in bonding at the interface, which in turn would alter the interface dipole. The magnitude of the band offset and decay of the interface satellite scale roughly with the amount of oxygen present in the film. To test this correlation, silicon was deposited at room temperature on (unexposed) CaF@sub 2@/Si(111). The band offset at the lower interface again decreased by about 0.5 eV, but in this case no additional oxygen was observed. This indicates that oxygen is sufficient to change the band offset but not necessary.

10:40am **EM-ThM8 Comparison of Morphology and Interfacial Composition of Pd Ultra-thin Films on 6H- and 4H-SiC at Different Annealing Temperatures, W.J. Lu, D.T. Shi, E. Bryant, A. Burger, W.E. Collins,** Fisk University

Pd/SiC has been applied as a chemical sensor for hydrogen and hydrocarbon gases at high temperatures. The diffusion and interfacial reaction between the thin film and SiC substrate alter the electrical properties of the device. In this work, the morphology and interfacial

composition of Pd ultra-thin films on 6H- and 4H-SiC substrates are studied at different annealing temperatures using atomic force microscopy and X-ray photoelectron spectroscopy. The Pd ultra-thin films were deposited by RF sputtering with about 3 nm thickness. The SiC substrates are 3.5° tilted, Si-face and n-type 6H and 4H-SiC, and the Pd thin film deposition and annealing conditions are the same for both samples. The samples were annealed at 100 to 400°C for 30 minutes in air. The Pd ultra-thin films on both SiC substrates have a good uniformity. The morphology of the Pd ultra-thin films on 6H- and 4H-SiC are very similar for unannealed and annealed samples at 100 and 200°C, and the Pd diffusion on SiC has occurred at 200 °C. As the annealing temperature increases, the surface of the Pd film becomes rougher. At 300°C, the Pd islands, 40 to 70 nm in diameter, are found on 4H-SiC substrate by atomic force microscopy. The diameter of Pd islands on 6H-SiC are about 20-40 nm. At 400°C, the irregular shaped holes on the Pd ultra-thin film are formed on 4H-SiC substrate, while the morphology of the Pd thin film on 6H-SiC is unchanged. Using XPS measurements, at 300°C, more Pd on 4H-SiC has reacted with the SiC substrate to form Pd silicates than on 6H-SiC, thus 4H-SiC is more reactive with Pd than 6H-SiC. No significant changes in Schottky barrier height were found for both Pd/6H-SiC and Pd/4H-SiC samples. The relationships between the structural factor in SiC and the behavior of Pd diffusion and reaction on 6H- and 4H-SiC will be presented. Keywords: Pd thin film, SiC, atomic force microscopy, X-ray photoelectron spectroscopy.

11:00am **EM-ThM9 Field Emission Studies of BN Overlayers on Various Substrates, N. Badi, A. Tempez, D. Starikov, A. Bensaoula**, University of Houston; V.P. Ageev, S.V. Garnov, M.V. Ugarov, S.M. Klimentov, E. Loubnin, V.N. Tokarev, General Physics Institute, Russia; K.L. Waters, A. Shultz, Ionwerks

We have studied electron field emission from BN films deposited on various substrates (flat and tip shaped) by End Hall ion source and electron cyclotron resonance plasma source-assisted physical vapor deposition. The chemical bonding states of B, C, N and the valence band structures were investigated by x-ray photoelectron spectroscopy XPS. Post-growth annealing, thermal processing and surface laser modification effects on the field emission properties were investigated. Thin carbon doped BN films exhibited a turn-on voltage as low as 30 V and a maximum current density of 1A/cm<sup>2</sup>. The field emission nature was verified using Fowler-Nordheim plot studies. A significant difference between the initial I (E)-behavior and that measured during subsequent cycles, with a noticeable stepwise jump of the emission current by orders of magnitude, was observed. Similarly, features in the peak current variation with applied voltage were measured and are probably due to a resonance tunneling emission effect. To that end, the valence band distribution of both the acceptor and donor's energy levels in these BN thin films were investigated under a variety of excitations. In addition, the field emission and conductivity properties of the BN surfaces have been performed using scanning tunneling emission microscopy (STFEM). The total spatial resolution of this technique was as high as a few nm. The experiments were conducted in the emission mode under negative and positive bias. The 3-D surface topography mapping and its correlation to the field emission properties were investigated and the results will be presented and discussed. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061. This material is also based upon work supported by the U.S. Civilian Research and Development Foundation under Award No. REI-247

11:20am **EM-ThM10 Influence of Ammonia Surface Reactions in GaN Chemical Vapor Deposition, M.E. Bartram**, Sandia National Laboratories

UHV thermal desorption mass spectroscopy measurements of N<sub>2</sub> chemisorbed on GaN(0001) have demonstrated that ammonia undergoes both reversible and irreversible decomposition on the surface. Overall, N<sub>2</sub> fragments and surface hydrogen from ammonia dissociation either (I) recombined to liberate N<sub>2</sub> or (II) decomposed further to enrich the surface with nitrogen. This was accompanied by the desorption of N<sub>2</sub> at a temperature below that required for congruent GaN sublimation. These reactions are the "crossroads" for the other important reaction avenues on the surface. Considering case I, production of surface hydrogen from ammonia decomposition suggests that this rate may be sensitive to hydrogen coverage and hence be influenced by the H<sub>2</sub> carrier gas used commonly in GaN CVD. Case II suggests that in addition to supplying the nitrogen for GaN growth, ammonia decomposition can also lead to the extraction of nitrogen from the surface when the nitrogen

coverages are sufficiently high. This catalytic removal of surface nitrogen in the form of N<sub>2</sub> and not N<sub>2</sub>H<sub>4</sub> indicates further that N-H bond formation as an initial step in potential hydrogen etching reactions can be overwhelmed by the tremendous driving force of the NN bond energy (226 kcal/mol). Therefore, while the nitrogen feed to the surface in the form of ammonia is necessary to compensate for congruent GaN sublimation and also contribute to GaN growth, it can also provide a low energy reaction pathway for the removal of nitrogen from a nitrogen enriched surface. This suggests that the overall nitrogen incorporation rate must be well-matched to the Ga deposition rate to maintain the proper stoichiometry and a reproducible overall growth rate. We have also observed that ammonia lowers the temperature for the desorption of TMG from surface defects. This decrease in the TMG-surface bond energy which can also lower the TMG residence time on the surface, suggests ammonia surface reactions have the potential to inhibit TMG reactions during GaN CVD. (Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the USDOE under DE-AC04-94AL85000.)

11:40am **EM-ThM11 Optimization of the Nitridation of Sapphire Substrates Using a Fractional Factorial Designed Experiment, T.J. Kropewnicki, P.A. Kohl**, Georgia Institute of Technology

Future advances in the performance of wide bandgap microelectronic devices depend on further improvements in the quality of the materials from which these devices are fabricated. Nitridation of the substrate is an important step that promotes the growth of high quality Group III nitride semiconductors; however, very few systematic studies of the nitridation process have been done. Herein, we report on a fractional factorial designed experiment to optimize the nitridation of sapphire substrates for the subsequent growth of GaN by plasma assisted molecular beam epitaxy (MBE). The sapphire substrates were nitridated with hydrazine using a process described elsewhere. Single replicates of a 2<sup>4</sup>-1 fractional factorial design were performed. The investigated factors were the pretreatment of the sapphire substrate with a 3H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O:H<sub>2</sub>PO<sub>3</sub> etch prior to introduction into the reactor, an in situ H<sub>2</sub> cleaning step prior to nitridation, the substrate temperature, and the nitridation time. Four center points were included in the design to test for nonlinearity and to yield an estimate of the experimental error. The material properties used to assess the quality of the nitridated surfaces were the nitrogen content of the surface (as measured by x-ray photoelectron spectroscopy) and the surface roughness (as measured by atomic force microscopy). Bulk GaN films were then grown on each of the nitridated sapphire substrates by r.f. plasma assisted MBE. The bulk growth conditions were determined with a separate designed experiment, and these conditions were held constant for each of the growths. The influence of the nitridated surfaces on the quality of the bulk GaN films was studied by photoluminescence and x-ray diffraction. The results of this fractional factorial designed experiment as well as their impact on the growth of GaN on sapphire substrates will be discussed. T.J. Kropewnicki and P. Kohl, "Hydrazine Cyanurate as a Nitrogen Source for Thin Nitride Film Growth," Journal of Vacuum Science and Technology A, 16 (1), 139 (1998). T.J. Kropewnicki and P. Kohl, "Nitridation of Substrates with Hydrazine Cyanurate for the Growth of GaN," Proceedings of the 1998 Spring MRS Meeting, San Francisco, CA, April 1998. K. Lee and G. May, unpublished.



## Electronic Materials and Processing Division Room 314/315 - Session EM1-ThA

### Dielectrics

**Moderator:** E. Garfunkel, Rutgers University

**2:00pm EM1-ThA1 Short Range Order and Electronic Structure of Amorphous Silicon Oxynitride, V.A. Gritsenko,** Siberian Branch of Russian Academy of Science, Russia; *R.W.M. Kwok, Y.H. Ng, J.B. Xu,* The Chinese University of Hong Kong, China; *I.H. Wilson,* The Chinese University of Hong Kong, Hong Kong

The short range order and electronic properties (electronic structure, energy diagram, and charge transport) of bulk amorphous silicon oxynitride ( $\text{a-SiO}_x\text{N}_y$ ) were reviewed for the further understand of  $\text{a-SiO}_x\text{N}_y$  the properties of gate oxynitride of MOS devices on the atomic scale. Amorphous  $\text{SiO}_x\text{N}_y$  consists of Si-O and Si-N bonds and involves five types of tetrahedra:  $\text{SiO}_4$ ,  $\text{Si}_3\text{O}_7$ ,  $\text{Si}_2\text{O}_5$ ,  $\text{Si}_3\text{N}_7$ , and  $\text{Si}_2\text{N}_5$ . The local bonding in  $\text{SiO}_x\text{N}_y$  is governed by the Mott rule as shown in the equation  $4=2x+3y$ . From x-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, x-ray emission spectroscopy and the simulation of the electronic structure, we concluded that Si-O bonds in  $\text{a-SiO}_x\text{N}_y$  are created by O 2s, 2p and Si 3s, 3p, 3d bonding states, and Si-N bonds are created by N 2s, 2p and Si 3s, 3p, 3d bonding states. Barriers for electron and hole injection at Si- $\text{SiO}_x\text{N}_y$  interface also gradually change with composition. The nature of the removal of hole traps from the  $\text{SiO}_2/\text{Si}$  interface during oxide nitridation was understood from the removing of Si-Si defects. The origin of Si-Si bond creation near the top surface of gate oxynitride after re-oxidation are understood on the basis of the Mott rule through the oxidation of nitride species  $\text{Si}_3\text{N}_4$  to form Si-Si bonds.

**2:20pm EM1-ThA2 Cathodoluminescence Spectroscopy of Nitrided Si-SiO<sub>2</sub> Interfaces, R. Bandhu, J. Schäfer, A.P. Young, L.J. Brillson,** The Ohio State University; *H. Niimi, G. Lucovsky,* North Carolina State University We use cathodoluminescence spectroscopy (CLS) to probe the electronic states at ultrathin gate dielectrics with nitrided Si-SiO<sub>2</sub> interfaces, known to improve reliability in advanced CMOS devices. The 5 nm-thick oxide at plasma-processed interfaces were: i) as-deposited (at 300 °C) structures, ii) 400 °C 30 min post-metallization annealed (PMA) in H<sub>2</sub>/N<sub>2</sub>, iii) 30 s 900°C rapid thermal annealed (RTA) in argon, and iv) a combination of both anneals. CLS emission energies and relative intensities vs. excitation energy (0.6-4.5 keV) were essentially unchanged for the as-deposited interface as reported for non-nitrided plasma-processed interfaces. In the near-IR (Ge detector), peaks appear at 0.8 and 1.0 eV, with the 1.0 eV peak intensity increasing with increasing electron energy. In the visible and near-UV (S-20 photocathode), features were observed at 1.9, 2.7 and 3.4 eV. From the depth variations, the 2.7 eV peak is generated near the surface of the oxide film, the 3.4 eV peak arises from the Si substrate, and the 1.9 eV feature comes from the near-interface region. After the PMA, CLS is essentially the same as for non-nitrided interfaces, except for an increase of the relative intensity of the 1.9 eV feature; after the RTA, analogous spectral features appear. However, the combination of the RTA and PMA does not completely suppress the 1.9 eV feature as for non-nitrided interfaces. CLS for as-deposited structures parallels optical second harmonic generation (OSHG); there are no differences with and without nitridation. However, as with OSHG, after the combined RTA/PMA, CLS reveals a substantial difference between nitrided and non-nitrided interfaces. The behaviors of the CLS features clearly distinguishes between interfacial defects (0.8 and 1.0 eV) and bulk defects (2.7 eV) which are significantly reduced by the combined RTA/PMA, and features that are intrinsic to the bonding chemistry, such as the 1.9 eV nitrided interface feature and the 3.4 eV Si substrate feature. *P. Young, J. Schäfer, G. Jessen, R. Bandu, L. J. Brillson, H. Niimi, and G. Lucovsky, J. Vac. Sci. Technol. B, submitted. G. Lucovsky, A. Banerjee, B. Hinds, C. Claffin, K. Koh and H. Yang, J. Vac. Sci. Technol. B15, 1074 (1997).*

**2:40pm EM1-ThA3 Reliability of Ultra-thin Gate Dielectric formed with Nitrogen Implantation and Thermal Oxidation, Y. Ma, M.S. Carroll, F. Li,** Bell Laboratories, Lucent Technologies; *C.T. Liu,* Bell Laboratories, Lucent Technologies, US; *C.Y. Sung, M.M. Brown,* Bell Laboratories, Lucent Technologies

Traditionally nitrogen was incorporated into oxide through oxidation or post-oxidation annealing in  $\text{N}_2\text{O}$  or  $\text{NO}$ . With a well engineered process, a thin layer of oxide containing nitrogen forms at  $\text{SiO}_2/\text{Si}$  interface. The gate oxide reliability can be improved in terms of device lifetime. Recently, nitrogen incorporation with nitrogen implantation has been studied. In this paper, ultra-thin gate dielectric was thermally grown on nitrogen implanted silicon substrates. The advantages of this technique are (i) the oxide growth rate can be significantly suppressed and (ii) a multiple gate dielectric thickness on same chip can be realized. However, previous reports showed that gate oxide quality is degraded. In this paper, we demonstrated that higher thermal budget is needed to remove the implantation induced damage and to improve the gate oxide reliability. The gate oxides were either grown or post-oxidation annealed at higher temperature. We also will present that the gate oxide reliability are nitrogen dose dependent. Gate oxide quality was evaluated with three different techniques: current ramp breakdown, time dependent dielectric breakdown and hot carrier aging test. Both current ramp and TDDB indicate that the gate oxide was degraded with nitrogen implant. However, the hot carrier aging test showed that the device lifetimes were longer for the nitrogen implanted ones. CMOS transistors were also fabricated. Device performances such as channel mobility, drive current, device yield will also be reported.

**3:00pm EM1-ThA4 Effect of Substrate Temperature in SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> Films Deposited By Electron Cyclotron Resonance, A. del Prado, F.L. Martinez,** Universidad Complutense de Madrid, Spain; *M. Fernandez,* Instituto de Ciencia de Materiales, Spain; *I. Martil, G. Gonzalez Diaz,* Universidad Complutense de Madrid, Spain

High quality silicon oxynitride films for ULSI applications can be deposited at low temperatures using plasma assisted processes like the ECR-CVD technique. Physical properties of  $\text{SiO}_x\text{N}_y$  films have been studied. The films have been deposited from mixtures of  $\text{SiH}_4$ ,  $\text{O}_2$  and  $\text{N}_2$ , using the ECR-CVD technique, with substrate temperature ranging from room temperature to 200°C. FTIR spectroscopy, AES and ellipsometric measurements have been performed in order to characterize the films. Low bonded hydrogen content is observed along the entire composition range from  $\text{Si}_3\text{N}_4$  to  $\text{SiO}_2$ . N-H bonds are present in all the films, while Si-H bonds are detected only for those films deposited under high  $\text{SiH}_4$  partial pressure. No O-H bonds are detected. When substrate temperature is increased, a slight decrease in total bonded H concentration is observed. A small shift (7-20  $\text{cm}^{-1}$ ) in the main FTIR absorption peak (Si-N/Si-O stretching band) is detected. This behavior is attributed to hydrogen release from N-H bonds due to the substitution of H for Si, with no significant change in the film composition. FWHM of the main FTIR peak decreases as temperature is increased for all the composition range, indicating an improvement in the film quality, as this parameter is related to the structural order of the film. Silicon oxide films ( $\text{SiO}_2$ ) deposited at 200°C show improved properties with respect to those deposited at room temperature. FWHM decreases from 96  $\text{cm}^{-1}$  to 88  $\text{cm}^{-1}$ , and shoulder-to-peak ratio from 0.30 to 0.25. The position of the Si-O stretching band (1072  $\text{cm}^{-1}$ ) is unaffected. These values are very close to those obtained for thermally grown oxides while the thermal budget of the process is reduced. *S. V. Hattangady, H. Niimi, G. Lucovsky, J. Vac. Sci. Tech. A 14 (6) 3017 (1996) D. Landheer, Y. Tao, J. E. Hulse, T. Quance, D. -X. Xu, J. Electrochem. Soc. 143 (5) 1681 (1996)*

**3:20pm EM1-ThA5 Roughness at Si/SiO<sub>2</sub> Interfaces and Silicon Oxidation, X. Chen,** Argonne National Laboratory; *J.M. Gibson,* University of Illinois, Urbana

**INVITED**

Roughness at  $\text{Si/SiO}_2$  interfaces and silicon oxidation With a plan-view transmission electron microscopy technique to directly image buried  $\text{Si/SiO}_2$  interfaces, we studied the interface roughness resulting from the oxidation process. Our results show that thermal annealing in nitrogen at 900 °C can dramatically remove the interface roughness for  $\text{Si(100)/SiO}_2$  interfaces. (Xidong Chen and J. M. Gibson Appl. Phys. Lett. 70, 1462 (1997)) In contrast,  $\text{Si(111)/SiO}_2$  interfaces, which tend to be smoother than  $\text{Si(100)/SiO}_2$  interfaces, are not affected by annealing. A model to link interface roughness and silicon oxidation



kinetics was developed. This model not only qualitatively explains the difference between Si(111) and Si(100) interfaces that we saw but also shows that oxidation kinetics is the origin of the interface roughness. Hence, it might be a new approach to understand oxidation kinetics by studying interface roughness.

**4:00pm EM1-ThA7 Energy Dispersion of the Conduction Band Mass in Ultrathin SiO<sub>2</sub> Gate Oxides, R. Ludeke**, IBM T.J. Watson Research Center; A. Schenk, Swiss Federal Institute of Technology, Switzerland

The effective conduction band mass  $m_{ox}$  of a-SiO<sub>2</sub> has been the subject of extensive studies and considerable controversy, with a default value of 0.5  $m_0$  having been adopted by most researchers. The STM based technique of Ballistic Electron Emission Spectroscopy (BEEM) has recently been used to obtain a value of  $m_{ox} = (0.63 \pm 0.09)m_0$ , which was deduced from quantum interference (QI) oscillations in the BEEM current through a 2.8 nm oxide. However, the more fundamental issue of the energy dependence of  $m_{ox}$  has not yet been properly addressed experimentally or theoretically. We report here pronounced QI effects in the BEEM current through 2.2 nm oxides and an assessment of the energy dependence of  $m_{ox}(E)$  obtained from simulations of the transport process. Up to five QI peaks were observed over a kinetic energy range of 2 eV relative to the conduction band minimum (CBM). Peak positions were reproducible to within 0.1 eV for injections at sites previously not exposed to the electron beam. Transmission coefficients (TC) for over-the-barrier injection were calculated by numerically solving the Schrödinger equation, which included both image force effects and an energy dependent  $m_{ox}(E)$ . The gradients of  $m_{ox}(E)$  at the energies of the TC maxima were adjusted until a match to the maxima in the data was obtained. With the assumption of a 2.2 nm oxide thickness (measured by ellipsometry, with other measurements in progress), the fits show that  $m_{ox}$  increases rapidly from 0.6  $m_0$  near the CBM to 0.86  $m_0$  2 eV above the CBM. An expected trend toward  $m_{ox} = 1m_0$  for larger energies is suggested as well by the results. FootnoteText@ footnote 1@ A. Schenk and G. Heiser, J. Appl. Phys. 81, 7900 (1997) and references therein. Footnote 2@ H.J. Wen, R. Ludeke and A. Schenk, J. Vac. Sci. Technol. B 16, to be published

**4:20pm EM1-ThA8 Ultra Thin Silicon Oxide Film on Si(100) Fabricated by High Purity Ozone at Atmospheric Pressure, K. Nakamura, S. Ichimura, A. Kurokawa**, Electrotechnical Laboratory, Japan; K. Koike, G. Inoue, T. Fukuda, Iwatani International Corporation, Japan

Microstructure of electronic devices requires much thinner silicon oxide film so that alternative oxidants must be developed to lower substrate temperature during oxidation. High purity ozone is expected as one of such oxidants because of its higher reactivity not only for adsorption on surfaces but also for thin film growth in comparison with that of molecular oxygen. However, lowering oxidation temperature also needs high dose of ozone to compensate decreasing oxidation rate. We investigated growth kinetics of oxide film under different ozone pressure conditions and succeeded in formation of oxide with the thickness >2nm at room temperature. First we fabricated oxide by exposing Si(100) with the substrate temperatures between 300°C and 700°C to 8x10<sup>-4</sup> Pa ozone for 90 min. in an UHV chamber. Etching rates by 0.1wt% hydrofluoric acid solution of these SiO<sub>2</sub> films are equivalent to that of device-grade thermally grown oxide. Etching rate is so sensitive to film density that oxide films made by use of high purity ozone at lower substrate temperatures are expected to be as dense as thermally grown oxide. However, the oxidation rate, especially at oxide thickness >5Å, decreased as oxidation temperature decreased. So we utilized another ozone generator system giving an atmospheric pressure for much higher ozone dose. In this processing, oxide film >2nm was successfully grown on Si(100) even at room temperature. Etching rate of SiO<sub>2</sub> fabricated on Si(100), for example, at 350°C by this method is almost the same as that of thermally grown oxide or as those with lower ozone dose mentioned above. Effects of such treatment as preoxidation or hydrogen termination on oxidation kinetics and film quality will also be discussed. FootnoteText@ footnote 1@ K. Nakamura, A. Kurokawa and S. Ichimura, J. Vac. Sci. Technol. A 15, 2441 (1997). Footnote 2@ K. Nakamura, A. Kurokawa and S. Ichimura, Surf. Interface Anal. 25, 88 (1997). Footnote 3@ A. Kurokawa, S. Ichimura and D. W. Moon, Mat. Res. Soc. Symp. Proc. 477, 359 (1997).

**4:40pm EM1-ThA9 Mixed Silicon Dioxide / Tantalum Oxide Layers for High k MOS Gate Dielectrics Formed by Plasma Oxidation of Si and Ta Using a rf Remote N<sub>2</sub>O Plasma Source, J.J. Chambers**, North Carolina State University, U. S. A.; G. Lucovsky, G.N. Parsons, North Carolina State University

High dielectric constant gate insulators will be needed to minimize gate tunneling in sub-100 nm integrated circuit devices. High k will allow the gate capacitance to scale with gate length without a significant reduction in gate dielectric thickness. Mixing SiO<sub>2</sub> with high k metal oxides (including Ti or Ta oxides) is expected to increase the dielectric constant without losing the beneficial properties of the Si/SiO<sub>2</sub> system. We have developed a rf plasma source capable of concurrent remote plasma CVD and separately controlled d.c. sputtering of metals. The motivation of this work is to establish an in-situ process for controlled silicon/high-k interface formation that will be stable during subsequent high-k dielectric deposition. Using an Ar plasma, Ta was sputtered for 1 to 10 minutes leading to controlled coverage onto a cleaned silicon surface. The Ta target was removed from the plasma zone, and the surface was exposed to a remote N<sub>2</sub>O plasma for 10 minutes. After oxidation, XPS and AES were used to characterize Ta, Si and O bonding on the surface. XPS of the oxidized surface shows Ta 4f peaks at 28.4 and 30.3 eV indicative of Ta-O bonds. Si 2p peaks at 101.1 and 104.7 eV are also observed, indicating Si and Si-O bonding. As the surface coverage of tantalum increases, XPS of the oxidized surface shows the O 1s peak at 533.9 eV developing a shoulder at lower binding energy characteristic of O-Ta bonding. This data indicates, for the studied range of small tantalum surface coverage, that the tantalum is completely oxidized forming tantalum oxide and silicon oxide layers. Ellipsometry results indicate the oxide thickness is less than 20 Å. We will discuss the effect of initial Ta layer thickness on oxide formation, and experiments of co-deposition of metal and SiO<sub>2</sub> to form thin mixed metal oxide / silicon dioxide high dielectric constant films.

**5:00pm EM1-ThA10 Thermal Stability of a-SiNx:H Films Deposited by Plasma Electron Cyclotron Resonance, F.L. Martinez, A. del Prado**, Universidad Complutense de Madrid, Spain; D. Bravo, F.J. Lopez, Universidad Autonoma de Madrid, Spain; I. Martil, G. Gonzalez-Diaz, Universidad Complutense de Madrid, Spain

Amorphous hydrogenated silicon nitride is widely used in semiconductor devices. Its higher dielectric constant compared to silicon dioxide results in a larger gate insulator capacitance, which in its turn means a larger transconductance and a smaller threshold voltage shift for a given defect charge concentration. A Rapid Thermal Annealing (RTA) post-treatment can improve significantly the properties of the dielectric and the interface. We have analyzed the influence of RTA on Al/SiN<sub>x</sub>:H/Si structures with x=1.55. The silicon nitride is deposited by the Electron Cyclotron Resonance plasma method and the films were annealed at temperatures ranging from 300°C to 1050°C. Determination of the dangling bond density in the insulator was done with Electron Paramagnetic Resonance, while the density of interface states was obtained from the high-low frequency capacitance method. Resistivity and breakdown field were deduced from current measurements in accumulation. A pronounced dip in the density of dangling bonds is obtained for moderate annealing temperatures, from 1.85E18 cm<sup>-3</sup> for the as-deposited film down to 9.58E16 cm<sup>-3</sup> at the point of inversion of the trend between 500 and 600°C. The density of interface states is also reduced in this range of temperatures from 3.6E11 eV<sup>-1</sup>cm<sup>-2</sup> to 1.2E11 eV<sup>-1</sup>cm<sup>-2</sup>. Resistivity and breakdown field are maintained in the range 5E14-5E15 Ωcm and 6.4-6.6 MV/cm respectively up to a temperature of 600°C. We attribute the improvement of the film properties and interface characteristics to a thermal relaxation and reconstruction of the silicon nitride lattice and its interface with the silicon substrate. In this range of temperatures we did not observe hydrogen evolution from the SiN<sub>x</sub>:H lattice. For temperatures above this threshold the electrical properties suddenly deteriorate and the density of dangling bonds increase. At even higher temperatures (above 800°C) a release of hydrogen from N-H bonds takes place.

# Thursday Afternoon, November 5, 1998

## Electronic Materials and Processing Division

### Room 316 - Session EM2-ThA

#### Non-destructive Testing and In-situ Diagnostics

**Moderator:** C.J. Palmstrom, University of Minnesota

#### 2:00pm EM2-ThA1 In-Situ IR Spectroscopic Study of the Chemical Process of Si-Related CVD Thin Films, *T. Wadayama*, Tohoku University, Japan **INVITED**

A comprehensive understanding of the molecular process of thin films growing under the chemical vapor deposition (CVD) conditions is quite of importance from a technological point of view. In-situ molecular vibrational study of the dynamic behavior of surface species under such conditions should give us an important clue to the understanding of the process and, further, a useful guide in developing new thin film devices. However, there exist few techniques available for the in-situ observation of the process. The polarization modulation IR spectroscopy (PM-IR), which is based on the difference in absorption intensity of surface species upon the change in the polarization state of the incident IR light, is a powerful tool for detecting signals from surface species over wide ranges of the substrate temperature and gaseous pressure. We have been successful in applying this method to observing in-situ the photo-CVD process of the Si-related thin films as well as the reaction of the films with the metal-organic and the etchant molecules. In the present talk, we will mention (1) the basis of the PM-IR method, the results obtained through the in-situ IR observation of (2) the growing process of the a-Si:H and the a-SiN<sub>x</sub> thin films, and (3) the reaction of the a-Si:H/dimethylaluminum hydride ((CH<sub>3</sub>)<sub>3</sub>AlH) and the a-SiN<sub>x</sub>/F<sub>2</sub> film. The results suggest that the hydrogen-rich and the Si-rich layers are present on the growing surface of the a-Si:H and the a-SiN<sub>x</sub> film, respectively, illustrating the feasibility of the PM-IR method to the in-situ molecular vibrational study of the chemical process of the CVD thin films.

#### 2:40pm EM2-ThA3 Integrated Real-Time Spectroscopic Ellipsometric and Reflectance Difference Measurements on a Commercial OMCVD Reactor, *M. Ebert*, Technical University Berlin, Germany; *K.A. Bell*, *S.D. Yoo*, *G.D. Powell*, *D.E. Aspnes*, North Carolina State University

Comprehensive monitoring of epitaxial growth by organometallic chemical vapor deposition (OMCVD) requires not only near-surface measurements for compositional analysis of the most recently deposited material and bulk measurements for determining layer thicknesses, but also surface analysis for information about growth chemistry. Here, we describe the first unified optical system that meets all 3 needs simultaneously. This system is a multichannel, parallel acquisition and processing, combined reflectance-difference (RD) spectrometer and rotating-polarizer spectroscopic ellipsometer (SE). It is built around a commercial rotating-spindle OMCVD reactor and a state-of-the-art high-speed 16-bit photodiode array (PDA) and allows data to be taken from 200 to 800 nm at a repetition rate of 600 ms to a precision of  $\pm 0.0001$ . These capabilities are realized by the PDA detector, synchronization of the spindle to the polarizer in a 3-to-1 ratio, and a spindle design that allows wobble to be reduced to less than 0.02° during rotation. RD measurements on a test (011) Si wafer, when transformed to normal incidence, are in excellent agreement with normal-incidence data. In addition to the diagnostic capabilities of SE, updating complete RD spectra at 0.6 s intervals allows surface reconstructions to be interpreted by pattern recognition as in RHEED.

#### 3:00pm EM2-ThA4 Real-Time Optical Control of Ga<sub>1-x</sub>In<sub>x</sub>P Film Growth by P-Polarized Reflectance, *N. Dietz*, *K. Ito*, *V. Woods*, North Carolina State University

The engineering of advanced optoelectronic integrated circuits implies the stringent control of thickness and composition. These demands led to the development of surface-sensitive real-time optical sensors that are able to move the control point close to the point where the growth occurs, which in a chemical beam epitaxy process is the surface reaction layer (SRL), built up of physisorbed and chemisorbed precursor fragments between the ambient and film interface. In this contents, we explored the application of p-polarized reflectance spectroscopy (PRS) for real-time monitoring and control of pulsed chemical beam epitaxy (PCBE) during low temperature growth of epitaxial Ga<sub>1-x</sub>In<sub>x</sub>P heterostructures on Si(001) substrates by PCBE. Using a 'reduced order kinetic model' we demonstrate the linkage of the PRS response towards surface reaction chemistry, composition, film growth rate, and film properties. Mathematical control algorithms are introduced and applied that link the PR signals to the growth process control parameters to control composition and growth rate of epitaxial Ga<sub>1-x</sub>In<sub>x</sub>P heterostructures.

#### 3:20pm EM2-ThA5 Electron Cyclotron Resonance Induced Surface and Subsurface Defects in GaAs Exposed to a Chlorine/Ar Plasma, *O.J. Glembocki*, *R.T. Holm*, *W.E. Carlos*, *D. Leonhardt*, Naval Research Laboratory; *C.R. Eddy*, Boston University; *K.K. Ko*, *S.W. Pang*, University of Michigan; *D.S. Katzer*, Naval Research Laboratory

The detection and control of dry etched induced electronic damage is critical to the formation of high quality semiconductor devices. In order to avoid ambient contamination, we have used in-situ photoreflectance (PR) to study the behavior the surface electric fields and surface photovoltage in both n-type and p-type GaAs exposed to a chlorine/Ar plasma generated by an electron resonance cyclotron source. By monitoring the desorption of the Ga and As chlorides, we find that the removal of Ga is the rate limiting step. This leads to a surface that is Ga rich and decorated by Ga vacancies which change the surface pinning position in both n- and p-GaAs. In addition, the etched surfaces show a decreased surface photovoltage. By using in-situ chemical etching/passivation with chlorine, we are able to uncover subsurface damage and show that it is distinctly different from the Ga vacancies formed on the surface. We find that the bulk etch damage has an exponential profile and that it is amphoteric, behaving as a very deep donor in n-GaAs and a deep acceptor in p-GaAs. Our experiments further indicate that both states of this defect lie below midgap. Possible candidates are point defects such as interstitials. Spin resonance results will be used in discussing the nature of the defects.

#### 3:40pm EM2-ThA6 Reciprocal-Space Analysis of Optical Spectra, *S.D. Yoo*, *N.V. Edwards*, *D.E. Aspnes*, North Carolina State University

Reciprocal-space analysis of optical spectra yields significant improvements in determining critical point energies in comparison to conventional real-space analysis. Enhanced diagnostic power is realized because, among other aspects, baseline effects, spectral information, and noise are localized in the low, middle, and high Fourier coefficients, respectively, allowing information to be extracted largely independent of baseline and noise artifacts. We use reciprocal-space analysis to address several issues regarding spectroscopy of electronic materials, both in real-time and off-line applications. Among these are the determination of optimal slit widths and numbers of data points that allow data to be taken at the fastest rate for a given signal-to-noise ratio and a simple analytic expression that describes the apparent shift of apparent critical point energies with overlayer thickness. We apply reciprocal-space analysis to various problems in electronic materials. The binding energies of the A, B, and C excitons of various GaN layers epitaxially grown on sapphire and SiC substrates have been determined to within 1 meV from low temperature reflectance data, which allows the in-plane strain and upper valence band parameters to be determined to similar accuracy. Apparent bulk critical point energies and broadening parameters of (110) Ge samples with and without a thin (~30 Å) Ni overlayer show substantial (~10 meV) differences, providing further evidence of photon-induced localization of optically excited electron and hole states. Finally, analysis of photoluminescence and photoluminescence excitation (PLE) spectra of GaAs/AlGaAs single quantum wells shows that exciton energies can be obtained independent of baseline artifacts to a wavelength uncertainty of 0.1 Å, which is particularly important for PLE where baselines cannot be determined unambiguously.

#### 4:00pm EM2-ThA7 Observation of Adsorption and Reaction of NH<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>, AlN and AlON Under Steady-State Conditions Using IRRAS, *V.M. Bermudez*, Naval Research Laboratory

The surface chemistry of Al<sub>2</sub>O<sub>3</sub>, AlN and Al oxynitride ("AlON") with NH<sub>3</sub> is important in the MOCVD growth of GaN on these substrates. Thin films of Al<sub>2</sub>O<sub>3</sub>, AlN and AlON have been grown by reacting a NiAl(111) surface with O<sub>2</sub>, NH<sub>3</sub> or NO, respectively.<sup>1</sup> The resulting buried-metal-layer structures have then been employed as substrates for studies of NH<sub>3</sub> adsorption under steady-state conditions, at 300 K and up to 200 Torr, using polarization-modulated fourier-transform infrared reflection absorption spectroscopy. For Al<sub>2</sub>O<sub>3</sub> evidence is seen, in the form of a change in the LO phonon, for incorporation of N into the surface to form a dilute "AlON-like" phase. The  $\delta_s$  symmetric deformation mode of adsorbed NH<sub>3</sub> is easily detected under high (>25 Torr) static pressures. For AlN, no evidence of adsorbed NH<sub>3</sub> is seen in a 200 Torr ambient. For AlON, distinct surface and volume LO phonon modes are seen, with the former responding reversibly to chemisorbed NH<sub>3</sub>. The  $\delta_s$  frequency indicates a lesser degree of Lewis acidity on AlON vs. Al<sub>2</sub>O<sub>3</sub> surfaces, which may favor 2D GaN growth on AlON by increasing the surface mobility of NH<sub>x</sub> species. For each of the

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three materials, IRRAS also provides useful information about the structural quality of the films prior to NH<sub>3</sub> exposure. @FootnoteText@ @footnote 1@Franchy et al., Appl. Phys. A 65 (1997) 551.

4:20pm **EM2-ThA8 Time of Flight Mass Spectroscopy of Recoiled Ions Comparative Studies of Gallium Nitride Thin Film Deposition By Various Molecular Beam Epitaxial Methods**, E. Kim, I.E. Berishev, A. Bensaoula, University of Houston; K.L. Waters, J.A. Schultz, Ionwerks

GaN thin films were successfully grown by electron cyclotron resonance molecular beam epitaxy (ECR-MBE), gas source MBE (GSMBE), and chemical beam epitaxy (CBE). Time of flight mass spectroscopy of recoiled ions (TOF-MSRI) and RHEED were used in-situ to determine the surface composition, the crystalline structure, and the growth mode of GaN thin films deposited by the three MBE methods. The substrate nitridation and the buffer layers were characterized by TOF-MSRI and RHEED. In GSMBE, the Ga/N ratio is found to correlate well with ex-situ optical properties. In the case of CBE, the carbon incorporation determines the surface morphology, the crystalline quality and the optical activity of the epilayers. In the case of CBE, no nucleation was possible until a combination of ECR nitrogen and TEG was used for the low temperature buffer. The carbon and oxygen levels were found to depend greatly on the TeGA flow and substrate temperature. A model describing the main experimental observations will be presented. The model explains both the chemical dissociation of ammonia at low temperatures and the Ga to N TOF-MSRI peak ratio for various Ga and ammonia fluxes. Our study shows that under optimized conditions crystalline epilayers with good optical and surface morphologies can be obtained with all three methods. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061.

4:40pm **EM2-ThA9 Near-Surface Variation of Gallium Nitride Cathodoluminescence with Annealing**, T. Levin, J. Schäfer, A.P. Young, L.J. Brillson, The Ohio State University; J.D. MacKenzie, C.R. Abernathy, University of Florida, Gainesville

Er-doped GaN with its promising luminescence yield is of considerable importance for optical communications. However, interfaces can induce significant changes in Er efficiency for optical pumping. Here we report on low energy cathodoluminescence spectroscopy (CLS) to probe the emission of GaN:Er as a function of distance from the semiconductor surface. CLS reveals order-of-magnitude emission variations of Er dopants and related Er-defect complexes vs. depth. Variable incident beam energies (0.5 - 5 keV) provided a strongly depth-dependent excitation from ca. 4 to 40 nm. GaN was grown by metal-organic molecular beam epitaxy at 925°C and doped to  $3 \times 10^{18}$  cm<sup>-3</sup>. The primary spectral feature observed was the 0.8 eV (1554 nm) Er emission, which increases by over an order of magnitude with increasing excitation depth. Relative to the broad 'yellow' luminescence between 1.5 and 2.5 eV, which exhibits little or no increase away from the GaN surface, the variation in 0.8 eV emission suggests a depletion of Er within the outer 10 nm. The CLS also reveals three sharp spectral lines at 1.8, 2.2, and 2.3 eV which have been associated with Er 4f transitions from excitation spectroscopy. @footnote 1@ However, the intensities of these features do not scale directly with the 0.8 eV line as a function of depth or processing, but reflect the sensitivity of these additional transitions to near-surface defects and impurities. Annealing the GaN:Er to 500°C for 5 min extends the otherwise bulk emission from these levels to a more uniform distribution extending to within 10 nm of the surface. Further annealing to 700°C promotes even stronger near-surface as well as bulk emission from these lines. However, it produces no significant change in the depth distribution of the 0.8 eV emission but enhances its yield by over a factor of two. Overall, the contrast in intensity variation of specific Er 3+ emission lines with depth reveals the sensitivity of dopant intra-shell transition strengths to near-surface defects. @FootnoteText@ @footnote 1@M. Thaik, U. Hommerich, R.N.Schwartz, R.G.Wilson, and J.M.Zavada, Appl. Phys. Lett. 71, 2641 (1997).

5:00pm **EM2-ThA10 In-situ Formation, Reactions, and Electrical Characterization of MBE Grown Metal/Semiconductor Interfaces**, L.C. Chen, D.A. Caldwell, University of Minnesota; T.G. Finstad, University of Oslo, Norway; C.J. Palmstrom, University of Minnesota

An in-situ probe station is used for the determination of the electronic properties of interfaces being modified in an MBE system. After MBE growth of the semiconductor structures, contacts were formed by metal deposition through a removable molybdenum shadow mask. An abrupt

change in doping profile serves as a marker layer to allow doping density versus depth profile measurements obtained from capacitance-voltage (C-V) to be used to measure the position of the electrical metal/semiconductor interface relative to the marker layer, allowing metal/semiconductor reaction kinetics to be determined electrically in-situ. C-V measurements on n/n<sup>+</sup> GaAs structures were used to monitor the Ni/GaAs reaction and subsequent GaAs regrowth. The measurements indicated that 500Å of Ni consumes 700Å of GaAs during Ni<sub>3</sub>GaAs formation, which is in excellent agreement with RBS and cross-sectional TEM measurements. Exposure of Ni<sub>3</sub>GaAs to As<sub>4</sub> at 300°C results in the formation of NiAs at the surface and epitaxially regrown GaAs at the Ni<sub>3</sub>GaAs/GaAs interface. The doping profiles indicated the complete regrowth of the 700Å GaAs beneath the contact. In-situ current-voltage (I-V) measurements of the NiAs/regrown-GaAs interfaces showed good Schottky behavior (V<sub>bn</sub>=0.87 V, n=1.08). C-V measurements showed further that the net electrically active donor density 2000Å beneath the contact changed during the different stages of reaction; it was  $9.0 \times 10^{16}$  (after Ni deposition),  $6.5 \times 10^{16}$  (after complete Ni<sub>3</sub>GaAs formation),  $5.0 \times 10^{16}$  (after subsequent GaAs regrowth), and  $9.0 \times 10^{16}$  (after an additional 585°C anneal). This results from the formation of point defects in the underlying GaAs during the reactions, which are eliminated by a 585°C anneal. In-situ electrical measurements on MBE-grown epitaxial metallic compound/Ga<sub>1-x</sub>Al<sub>x</sub>As heterostructures grown on various surface terminations before and after annealing with emphasis on Sc<sub>x</sub>Er<sub>1-x</sub>As structures will also be presented.

# Thursday Evening Poster Sessions, November 5, 1998

## Electronic Materials and Processing Division Room Hall A - Session EM-ThP

### Electronic Materials and Processing Poster Session

**EM-ThP1 Synthesis and I-V Characterization of Tin Dioxide Varistors, A. Kale**, University of Central Florida; *R.N. Barve*, College of Engineering, India; *S.K. Date*, National Chemical Laboratories, India; *P.N. Santhosh*, Indian Institute of Science, India; *S. Seal*, University of Central Florida

Tin dioxide varistors are novel semiconducting ceramics having interesting non-ohmic current-voltage characteristics. They are widely used in consumer and military electronics, industrial protection, communications, transportation, data processing and other applications like medical devices. An overview of the steady state time dependent electrical properties of Tin dioxide varistors is presented. For a quantitative agreement with the experimental data the electronic defect states in the bulk of the Tin dioxide grains and at the interfaces between the grains were studied. The varistors were fabricated in two ways. The normal physical process (ceramic route) of mixing and compaction of Tin dioxide powder with various dopants and the second method being that of sol-gel processing in which dopants were taken in their aqueous solutions. Samples prepared by both the processes were studied for the dopant densification using Scanning Electron Microscope and X-ray diffraction. The effect of various sintering temperatures on their non-ohmic or non-linear characteristics was also studied. The varistors prepared by the sol-gel method showed high non-linearity, high density and high threshold voltage properties than the ceramic route owing to their finer grain structure and better densification of dopants around the grain boundaries. It was shown that the Tin dioxide non-linear properties are a function of grain size and depend upon the factors that influence the course of events at the sintering temperature. It is hoped that in coming years, the research efforts are likely to have path breaking impacts in design and development of better varistors

**EM-ThP2 First Principles Calculations of Ge (100) Covered by Up to One Monolayer of Pb, N. Takeuchi**, Universidad Nacional Autonoma de Mexico, Mexico

We have performed first principles total energy calculations to determine the atomic structure of the Ge(100) surface covered with different amounts of Pb. For low coverages, Pb starts growing parallel to the underlying Ge dimers (without breaking them), and it forms asymmetric dimers. This situation continues up to half a monolayer. At this coverage, several structures are possible: (2x2), p(4x2), etc. They are also formed by asymmetric Pb dimers on top of the Ge(100) surface. They differ from each other by the orientation of the buckled dimers. When the coverage is larger, the Ge dimer bonds start to break. >From this coverage, and up to one monolayer, the stable surface shows a c(4x8) reconstruction, similar to the one found in Sn on Si(100) and Pb on Si(100). It consists of rows of Pb ad-dimers, with one missing row out of every four, yielding a coverage of 0.75 of a monolayer. The dimers are also asymmetric. Calculated local density of states are in excellent agreement with scanning tunneling microscope images. Surface formation energies show that this configuration is more stable than the full monolayer (2x1) structure.

**EM-ThP3 TEM Study of TiAl@sub3@ Formation, C.C. Pace**, University of North Carolina, Chapel Hill and MCNC; *M.K. Lamvik*, *M.A. Ray*, Microelectronics Center of North Carolina; *A. McTeer*, Micron Technology Metallizations consisting of Al-Cu alloys and Ti layers are widely used in microelectronic device fabrication, because of their low contact resistance and resistance to electromigration and hillock formation. As device dimensions are reduced, reaction mechanisms between layers must be understood at the atomic level to develop device structures that minimize failures due to resistive heating and stress induced voiding. Structures consisting of 350nm Al-0.5% Cu on 20nm Ti sputter deposited onto SiO@sub2@/Si substrates have been studied using a Philips EM 430 transmission electron microscope (TEM) equipped with a heating stage. TEM specimens of as-deposited samples were prepared and annealed in situ in the TEM. The temperature was varied up to 450 °C and times up to several hours. Within this temperature range the reaction rate for the formation of TiAl@sub3@ in the in-situ experiments agree with the published literature, although the range in published values is quite broad. Cross-sectional TEM micrographs reveal a non-uniform TiAl@sub3@/AlCu interface. The roughness revealed by TEM contradicts interpretations of Rutherford backscattering spectra (RBS). RBS suggest a layer-by-layer growth mechanism, which would produce a TiAl@sub3@ layer of uniform

thickness. To show the equivalence of an in situ anneal and a furnace anneal, TEM samples were prepared from a wafer annealed in a furnace at 400 °C for 50 minutes. Cross-sectional micrographs revealed similar interface roughness. For both anneals, less than 10nm of Ti was consumed. An unreacted Ti layer remained even after extended annealing. In-depth profiling with Auger electron spectroscopy (AES) was utilized to confirm the presence of unreacted Ti. A model of the reaction mechanism that results in a non-uniform TiAl@sub3@ layer in contact with unreacted Ti will be proposed. It is critical that this mechanism be understood and controlled as device dimensions are scaled to ever smaller sizes.

**EM-ThP4 Side-Wall Damage in a Transmission Electron Microscopy Specimen of Crystalline Silicon Prepared by a Focused-Ion-Beam, N. Kato**, IBM, Japan; *H. Saka*, Nagoya University, Japan; *Y. Kohno*, IBM, Japan

Focused ion beam (FIB) milling has recently been widely used for the preparation of cross-sectional transmission electron microscopy (TEM) specimens. Inevitably, however, such specimens are caused a certain amount of damage by highly accelerated ion beams. The damage to the side-wall of a specimen is visible under TEM as amorphization, and the structure of the undamaged intermediate layer can be observed through the damaged layers. Nevertheless, these damaged layers do pose a serious problem for TEM observation, especially when high-resolution observation is required. Many techniques have been developed for reducing the damage, such as gas-assisted etching. In this study, we experimentally investigated the depth of the side-wall damage in silicon, and the effect of the damaged layer on TEM observation. The depth of damage caused by a 30-keV FIB without gas-assisted etching was 20 nm, which was reduced to 10 nm by lowering the acceleration voltage to 10 kV. Gas-assisted etching with iodine does not markedly reduce the damage, as would be expected from the enhanced etching ratio. We also investigated several methods for reducing the damage after FIB fabrication. Broad-argon-ion-beam milling reduced the damaged layer to 12 nm, and wet-etching the specimen with a mixture of nitric and hydrofluoric acid removed most of the damage. Removal of the amorphous silicon layer significantly improved TEM observation. No amorphous ring such as that observed in the diffraction pattern (DP) of the specimen immediately after FIB fabrication was seen in the DP of the wet-etched specimen, in which a silicon lattice fringe was clearly observed.

**EM-ThP5 Heat-Transfer in UHV-Scanning Thermal Microscopy, W. Müller-Hirsch**, *J.P. Parisi*, *M.T. Hirsch*, *A. Kittel*, University of Oldenburg, Germany; *L.V. Govor*, *A.Yu. Olevanov*, The State University of Belarus

Scanning thermal microscopy (STHM) offers the capability to map temperature distributions of samples with subµm resolution. A wide variety of microscope configurations and sensor designs have been described in literature. However, most experiments have been performed under ambient conditions and the heat-transfer between sensor and sample was attributed to be mostly due to a liquid film-bridge between sensortip and sample.@footnote 1@ In this study we use a Scanning Thermal Microscope to investigate the heat transfer under ultra-high vacuum (UHV) conditions. A needle-shaped Au/Ni-thermocouple-sensor is brought into close proximity of a liquid nitrogen cooled sample. We find an almost linear increase of the heat-transfer with decreasing tip-sample distance on a length-scale in the range of 10nm. Since our experiments are performed at a base-pressure of 10@super -10@ mbar, the heat conduction path via a liquid film-bridge can be excluded. We discuss other mechanisms like electron-, phonon- or photon-coupling between tip and sample as an origin of the heat-transfer in the near-field regime of the sample. Additionally, the observed near-field heat-transfer is sensitive with respect to the sample topography. Measurements of the plateau structure of Au-samples with a homogeneous temperature distribution will be presented and explained by a simple geometric model. Further measurements investigate the joule-heating of a MIS-diode array with diode-dimensions of 2µm. The inhomogeneous temperature distribution due to the joule-heating of the diodes is clearly resolved in the thermal image of the sample. @FootnoteText@ @footnote 1@K. Lou et.al. J. Vac. Sci. Technol B 15(2) p.349 (1997)

**EM-ThP6 Boron Phosphide Films Grown by Solid-Source Molecular Beam Epitaxy, D. Buchenauer**, *D. Dibble*, *K.F. McCarty*, *J.C. Lund*, *R.J. Anderson*, *M. Clift*, *D.L. Medlin*, *J.A. Schneider*, Sandia National Laboratories

A significant improvement in the detection of thermal neutrons could be made through the use of zinc blende boron phosphide (BP) as the detection medium in a solid-state neutron detector. Earlier work on the growth of BP using vapor transport,@footnote 1@ flux growth,@footnote 2@ and chemical vapor deposition@footnote 2@ has produced crystalline

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material of the required thickness, however, autodoping of the BP has been too high to allow their use in neutron detection. Recent progress on the growth of amorphous films using Molecular Beam Epitaxy (MBE) has led to nearly stoichiometric films with improved electrical properties. @footnote 3@ Here we report on the first growth of BP films using electron beam evaporation of boron and thermal cracking of phosphorus vapor by a three-cell EPI cracker. Stoichiometric films have been grown at substrate temperatures as low as 300°C. The relationship between the electronic and microstructural properties of the BP films and their performance as solid-state neutron detectors will be examined. @FootnoteText@ @footnote 1@T. L. Chu, J. M. Jackson, and R. K. Smeltzer, J. Crystal Growth 15 (1972) 254. @footnote 2@Y. Kumashiro, J. Mater. Res. 5 (1990) 2993. @footnote 3@Y. Kumashiro, T. Yokoyama, T. Sakamoto, and T. Fujita, J. Solid State Chemistry 133 (1997) 269.

**EM-ThP7 Effects of Various Configured Magnets on the Characteristics Of Inductively Coupled Plasmas, S.W. Hwang, Y.J. Lee, SungKyunKwan University, Korea; S.W. Joe, Kyoungki University, Korea; K.H. Kim, Hanyang University, Korea; G.Y. Yeom, SungKyunKwan University, Korea**

Although high density plasma(HDP) sources have been employed for dry etching in microelectronics, their scale-up to process larger wafer size such as the substrates used in flat panel display(FPD) technology is not that easy due to the uniformity problem over a large area wafer size. In this study, to enhance plasma uniformity and density of an inductively coupled plasma source, the effects of variously configured magnets on the characteristics of the plasmas were investigated. As the magnets, Helmholtz type axial electromagnets and multi-dipole magnets composed of 8sets of permanent magnets around the chamber wall were used. The chamber was designed as a square mainly for the FPD application such as liquid-crystal display(LCD), plasma display panel(PDP), etc. To characterize the plasmas as a function of magnetic field strengths and the combination of the magnets, electrostatic probe(Hiden Analytical Ltd.), optical emission spectroscopy(OES: SC Tech. PCM402), and quadrupole mass spectrometer(QMS: Hiden Analytical Ltd. PSM) were used. Ion density, plasma potential, and electron temperature were measured along the chamber diameter and axial direction for Ar and Cl@sub 2@/HBr gas combinations using the electrostatic probe. The results showed that high density plasma(10@super 11@-10@super 12@/cm@super 3@) with excellent uniformity(@<=3%) near the wafer surface could be achieved along the chamber diameter by the combination of the axial magnets and multi-dipole magnets. Optical emission spectra and mass spectra (positive and negative ions, radicals, and neutrals) were also studied as a function of axial magnetic strengths and with/without multi-dipole magnets for Cl@sub 2@/HBr gas combinations, and showed enhanced ionization and dissociation with the combined magnets. We believe that a suitable combination of axial magnets and multi-dipole magnets would also improve etch uniformities and etch rates of the large size wafers used in FPD.

**EM-ThP8 Atomic Order and Electron Affinity at AlN(0001) Surfaces, C.I. Wu, A. Kahn, Princeton University; E.S. Hellman, D.N.E. Buchanan, Bell Laboratories, Lucent Technologies**

We have used Auger electron spectroscopy (AES), low energy electron diffraction (LEED), x-ray and ultraviolet photoemission (XPS and UPS) and inverse photoemission spectroscopy (IPES) to investigate the preparation, atomic order and electron affinity of AlN(0001) surfaces. AlN films 0.2µm thick were grown by molecular beam epitaxy on Si(111) substrates. Following ambient transfer to the surface analysis chamber, repeated cycles of nitrogen sputtering (1 keV) and annealing (10 min., 1050 °C) were necessary to obtain ordered surfaces with only a few percent of a monolayer of O contaminant. The resulting surfaces exhibited sharp 1x1 LEED patterns. The UPS (Hel and Hell) spectra exhibited sharp features allowing a clear identification of the valence band maximum (E@sub v@). The position of E@sub v@ was confirmed by XPS measurements of the Al 2p core level and using the known binding energy of this level with respect to E@sub v@.@footnote 1@ The UPS-IPES combination showed the Fermi level at 4.8 eV above EV and 1.6 eV below the conduction band minimum at the surface of our AlN. Given these numbers and in spite of the concomitant observation of a sharp feature at the onset of photoemission, generally associated with the occurrence of negative electron affinity, the electron affinity was calculated to be +2.3 eV. Finally, the deposition of 1-2 monolayer of Al on the (1x1) surface followed by a 5 min. 1250°C anneal led to a structure characterized by a (@sr@3 x @sr@3)-R30° diffraction pattern. This LEED pattern is consistent with RHEED observations for increasing Al surface concentration during growth. @FootnoteText@

@footnote 1@J.R. Waldrop, and R.W. Grant, Appl. Phys. Lett. 68, 2879 (1996).

**EM-ThP9 Enhanced Electrical Performance of Au/n-GaN Schottky Diodes by Novel Processing, L. He, Northern Illinois University; X.J. Wang, University of Maryland at Baltimore County**

GaN has attracted great attention recently for its application in electronic and optoelectronic devices. Applications including in blue lasers, visible light emitting diodes (LED), metal-semiconductor field-effect transistor (MESFET), high electron mobility transistors(HEMT), ultraviolet photodetectors, have been demonstrated. Metal/GaN contacts, both ohmic and Schottky, are of important for device applications. Studies of Schottky contacts on GaN were especially interested. Schottky barrier height is expected to be dependent on the metal work function due to the ionic nature of GaN, though the work function of the contact metal is not the exclusive factor determining the Schottky barrier height. In this study, the low temperature (LT = 77K) metal deposition technique was used to improve the electrical characteristics of Au/n-GaN Schottky diode. The LT deposition technique has been successfully used to fabricate high quality Schottky contacts on InP, GaAs and InGaAs. A comparison of the barrier heights is conducted with previously reported results. The same chip of GaN epitaxial layer was used for room temperature (RT) and LT Schottky diodes. The LT Schottky diodes exhibit excellent performance. The leakage current density as low as 2.55x10@super -11@A@cm@super -2@ was obtained from the LT diodes. The linear region in the I-V curve of the LT diodes at forward bias could extend more than eight orders in the magnitude of the forward current. Current-voltage-temperature (I-V-T) measurements were carried out to study the characteristics of the LT diodes. A typical barrier height of 1.32eV for the LT diode was obtained, which is the highest value ever reported. The obvious enhancement in electrical performance makes the LT processing a high promising technique for GaN device application. Analysis through photoluminescence (PL) and x-ray diffraction measurements were conducted to collaborate with the electrical characteristics.

**EM-ThP10 W-Based Ohmic Contacts on p- and n-Type GaN, X. Cao, F. Ren, S.J. Pearton, University of Florida, Gainesville; A. Zeitouny, M. Eizenberg, Technion-Israel Institute of Technology, Israel; J.C. Zolper, Office of Naval Research; C.R. Abernathy, University of Florida, Gainesville; R.J. Shul, Sandia National Laboratories; J.R. Lothian, Bell Laboratories, Lucent Technologies**

W and WSi ohmic contacts on both p- and n-type GaN have been annealed at temperatures from 300-1000@degree@C. There is minimal reaction (@<=100@Ao@ broadening of the metal/GaN interface) even at 1000@degree@C. Specific contact resistances in the 10@super -5@ ohm cm@super 2@ range are obtained for WSi@sub x@ on Si-implanted GaN with a peak doping concentration of ~5x10@super 20@cm@super -3@, after annealing at ~750@degree@C. On p-GaN, leaky Schottky diode behavior is observed for W, WSi@sub x@ and Ni/Au contacts at room temperature, but true ohmic characteristics are obtained at 250-300@degree@C, where the specific contact resistances are typically in the 10@super -2@ ohm cm@super 2@ range. The best contacts for W and WSi@sub x@ are obtained after 700@degree@C annealing for periods of 30-120 secs. The formation of @BETA@-W@sub 2@N interfacial phases appear to be important in determining the contact quality.

**EM-ThP11 Redistribution and Activation of Implanted S, Se, Te, Be, Zn and C in GaN, R.G. Wilson, Consultant; J.M. Zavada, U.S. Army Research Office; X. Cao, S.J. Pearton, R.K. Singh, University of Florida, Gainesville; M. Fu, J.A. Sekhar, V. Sarvepalli, Mycropyretics Heaters International; R.J. Shul, J. Han, D.J. Rieger, Sandia National Laboratories; C.R. Abernathy, University of Florida, Gainesville**

We have previously found that implanted Si in GaN shows minimal redistribution after annealing at 1500@degree@C, with an effective diffusion coefficient of @<=2x10@super -13@cm@super 2.s@@super -1@ at this temperature. In this experiment, common donor (S, Se and Te) and acceptor (Be, Zn and C) dopants were implanted at a typical dose of ~5x10@super 14@cm@super -2@, with a projected range of ~1500@Ao@. Annealing was performed with AlN encapsulation on the GaN, at temperatures up to 1500@degree@C in a novel rapid thermal furnace utilizing intermetallic heating elements. After selective removal of the AlN cap in hot KOH solution, Secondary Ion Mass Spectrometry profiling was performed to measure the redistribution of the different dopant species. Effective diffusion coefficients were obtained from the broadening at full-width-half-maximum of the implanted profile.

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**EM-ThP12 Etch Characteristics of GaN using Chemically Assisted Ion Beam Etching(CAIBE) and Its Effects on Ohmic Contact Formation to n-type GaN, W.J. Lee, G.Y. Yeom, Sungkyunkwan University, Korea; J.W. Lee, Y.J. Park, T.I. Kim, Samsung Advanced Institute of Technology, Korea**

Currently, GaN facets required for GaN laser devices are fabricated using dry etching due to the difference in the cleavage planes of sapphire substrates and GaN epitaxial layers grown on them. Fabrication of GaN facets using dry etching not only requires high GaN etch rates, high selectivity over mask layers, and vertical etch profile with a smooth sidewall, but also requires damage-free etch surface which could be induced due to the energetic ion bombardment during the etching. This induced damage could degrade the electrical performance of the device. Therefore, in this study, we investigated the etch properties, etch-induced damage, and resistances of contacts formed on etched n-type GaN. The GaN samples used in the experiment were grown by metalorganic chemical vapor deposition on sapphire substrates and GaN etching was performed using CAIBE system(RF-350 Etching System, Veeco) having a 210mm diameter ion source, a Meissner trap, and a load-lock chamber. Ar was introduced into the ion source while  $\text{Cl}_{\text{sub}2}$ ,  $\text{BCl}_{\text{sub}3}$ , and HCl were distributed around the substrate through the nozzle. GaN samples patterned with PR or  $\text{SiO}_{\text{sub}2}$  were loaded on the rotational fixture which could be tilted between  $0^\circ$  and  $60^\circ$  and also could be heated up to 300 C or cooled down to 0 C. To determine the etch characteristics, GaN samples were etched as a function of Ar ion beam parameter, gas chemistry, tilt angle, and substrate temperature. Etch characteristics such as etch rates, selectivities, and etch profiles were estimated using a profilometer and scanning electron microscopy(SEM). Variation of surface composition of the etched GaN samples was investigated using X-ray photoelectron spectroscopy(XPS). Contact resistances of the etched n-type GaN samples were measured by transmission line measured(TLM) and physical damage on the etched GaN surface was observed using HRTEM. The relations of surface composition and physical damage on GaN surface to the ohmic contact resistances were also studied.

**EM-ThP13 Growth of  $\beta$ -SiC Thin Films on Si (100) at Low Temperature using Ultra-high Vacuum Electron Cyclotron Resonance Chemical Vapor Deposition, J.H. Pyo, Seoul National University, Korea; K.W. Whang, Seoul National University, Korea, South Korea**

$\beta$ -SiC thin films were grown on Si (100) at low temperature using ultra-high vacuum electron cyclotron resonance chemical vapor deposition with gas mixtures of  $\text{H}_{\text{sub}2}$  /  $\text{CH}_{\text{sub}4}$  /  $\text{SiH}_{\text{sub}4}$  and their properties such as crystallinity and stoichiometry were investigated. Care was taken to prepare the clean, damageless Si surface prior to the growth. In situ  $\text{H}_{\text{sub}2}$  plasma cleaning, as well as conventional wet cleaning, were performed to confirm Si (2X1) reconstruction structure, which seemed to be an essential process to grow the  $\beta$ -SiC thin films at low temperature. In addition, Si surface was carburized with  $\text{H}_{\text{sub}2}$  /  $\text{CH}_{\text{sub}4}$  plasma at 700 °C before the growth of the film. After the in situ cleaning and the carburization, SiC thin films were grown on the carburized surface with the various ranges of microwave input power,  $\text{SiH}_{\text{sub}4}$  to  $\text{CH}_{\text{sub}4}$  flow ratio, and substrate temperature. Reflection high energy electron diffraction (RHEED) patterns of the films which were deposited at the substrate temperature 600 °C showed the changes from textured to ring pattern as the microwave power increased or the flow ratio decreased. Analyses of the films using XPS and spectroscopic ellipsometry showed that the ring and textured patterns were polycrystalline  $\beta$ -SiC and Si-rich films, respectively. These results implies that stoichiometry of the film is affected by the microwave power and the flow ratio which presumably cause modification of the chemistry in plasmas. On the other hand, the crystallinity was affected by the substrate temperature. As the temperature increased up to 750 °C, the crystallinity was improved.

**EM-ThP14 Study of Pulsed versus Continuous Wave Plasma Deposition of Amorphous, Hydrogenated Silicon Carbide ( $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ ) from Silane/Methane Mixtures, P.M. McCurdy, J.M. Truitt, E.R. Fisher, Colorado State University**

Hydrogenated amorphous silicon carbide ( $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ ) is an important material because of its current use as a window coating for amorphous Si solar cells and its potential applications in photoelectronics and as a hard coating. Equivalently powered, pulsed and continuous wave (cw) radio-frequency discharges (13.56 MHz) were used to deposit  $\text{a-Si}_{1-x}\text{C}_x\text{:H}$  films from silane and methane. Deposited films were studied using FTIR, XPS, Raman scattering spectroscopy, scanning electron microscopy and profilometry. Deposition parameters investigated included pulsed plasma power, duty cycle (d.c.) substrate temperature, substrate bias, and addition of a carrier gas ( $\text{H}_{\text{sub}2}$ , or

He). Films deposited from pulsed plasmas show a large decrease in hydrogen incorporation compared to films deposited in equivalently powered CW systems. Notably, there is a significant decrease in modes associated  $\text{CH}_{\text{sub}3}$  moieties.  $\text{CH}_{\text{sub}3}$  groups have been associated with electrical and mechanical instabilities of  $\text{a-Si}_{1-x}\text{C}_x\text{:H}$  films. Grounding the silicon substrate is shown to have a significant effect on both the CW and pulsed plasma deposited films.

## Electronic Materials and Processing Division Room 316 - Session EM-FrM

### Fabrication and Characterization of Semiconductor Device Layers

**Moderator:** A. Bensaoula, University of Houston

**8:20am EM-FrM1 Optical, Structural, and Morphological Properties of Epitaxial Al<sub>x</sub>Ga<sub>1-x</sub>N(0001) Films Grown by Gas-Source Molecular Beam Epitaxy, J.E. Van Nostrand,** Air Force Research Laboratory; *R.L. Hengehold*, Air Force Institute of Technology; *K.D. Leedy*, *M.L. Seaford*, *D.H. Tomich*, *C.E. Stutz*, *Q.-H. Xie*, Air Force Research Laboratory

Al<sub>x</sub>Ga<sub>1-x</sub>N(0001) is a material system of great interest due to its potential for optoelectronic and high temperature electronic applications. However, published studies on the growth and characterization of Al<sub>x</sub>Ga<sub>1-x</sub>N films are limited, and the structural and optical properties of Al<sub>x</sub>Ga<sub>1-x</sub>N films are not well understood. We present optical, microstructural, and morphological results for 0.5 μm thick Al<sub>x</sub>Ga<sub>1-x</sub>N thin solid films on 2.0 μm thick GaN on Al<sub>2</sub>O<sub>3</sub>(0001) grown by gas source molecular beam epitaxy. Films are deposited at 800 °C with a 0.5 μm hr@super -1@ growth rate, and ammonia is used for the nitrogen source. High-resolution X-ray diffraction results show deformation of the unit cell in the Al containing layers for x<0.15 due to tensile biaxial strain. Measurement of the evolution of surface morphology as a function of Al mole fraction using atomic force microscopy shows a large increase in surface roughness with increasing Al mole fraction for x<0.15, followed by an order of magnitude decrease in roughness for relaxed films. Microstructural properties such as dislocation type and density as a function of Al mole fraction are systematically evaluated using cross-sectional transmission electron microscopy. Finally, low temperature (6K) cathodoluminescence is used to evaluate the location of the donor-bound exciton in the Al<sub>x</sub>Ga<sub>1-x</sub>N bandgap as a function of Al mole fraction. An approximately linear dependence on x is observed, suggesting the Al<sub>x</sub>Ga<sub>1-x</sub>N bandgap also exhibits a linear dependence on x.

**8:40am EM-FrM2 Investigation of High Temperature Characteristics of Metal-Insulator-Semiconductor Diode Structures Fabricated Using BN Layers Grown on GaN and SiC, D. Starikov, N. Badi, I. Berichev, N. Medelci, A. Tempez, V. Zomorrodian, A. Bensaoula,** University of Houston

Dielectric materials commonly used for fabrication of silicon-based semiconductor devices did not prove their viability when applied on wide band gap materials for high temperature applications, such as GaN and SiC. Boron nitride layers grown by physical vapor deposition have several advantages over conventional dielectrics due to their high thermal and chemical stability, mechanical and radiation strength, and excellent surface morphology. In this work we will describe the basic technological processes for fabrication of Metal-Insulator-Semiconductor (MIS) structures on GaN and SiC using insulating BN layers. I-V curves measured in a temperature range up to 700 °C will be presented for MIS-structures based on GaN grown on sapphire, epitaxial 3-C SiC films grown on silicon, and 6H-SiC single crystal wafers. These data will be compared with results obtained from MIS-structures fabricated using similar technology on silicon wafers. The potential barrier height for all structures will be calculated using C-V and I-V measurements at different temperatures. Preliminary results show that GaN-based MIS structures rectify up to 600 °C, while those based on silicon lose their rectification characteristics only at 250 °C. The dependence of the potential barrier height on the thickness of the dielectric (BN) layer and its stability under high temperature vacuum annealing will be discussed and presented. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061

**9:00am EM-FrM3 Chemical Beam Epitaxy of GaAsN on GaAs (100), J.W. Rogers, Jr., C.L. Aardahl, H.K. Yun, T.P. Pearsall,** University of Washington  
Chemical beam epitaxy (CBE) has been used to deposit GaAsN on GaAs (100) at a growth pressure of order 5e-5 mbar and a substrate temperature of order 500C. Triethyl gallium, arsenic dimers, and an electron cyclotron resonance (ECR) nitrogen plasma were used as the Ga, As, and N sources, respectively. Secondary-ion mass spectrometry (SIMS) showed a maximum nitrogen content of 15% in the films grown in this study. Thermodynamic

arguments predict that GaAs and GaN are immiscible due to the large discrepancy in atomic radii between As and N which leads to a positive heat of mixing for GaN and GaAs alloys. X-ray diffraction measurements show that higher nitrogen content does indeed result in phase segregation to a mixture of zinc-blende GaAs, zinc-blende GaN, and wurzite GaN depending on the growth conditions. However, unstrained alloys were deposited with a nitrogen content of up to 3%. Transmission electron micrographs and selected area diffraction patterns are used to discuss the orientation of segregated phases and ordering in the films. The effect of these morphological features on the band gap bowing parameter of the GaAsN system is discussed.

**9:20am EM-FrM4 InP Photocathode Surface Preparation by Atomic Hydrogen Cleaning, K.A. Elamrawi, M.A. Hafez, H. Elsayed-Ali,** Old Dominion University

III-V semiconductors are efficient photocathodes. They provide a high quantum efficiency (QE), defined as the number of emitted electrons per incident photon. The QE is strongly reduced if the surface is contaminated with oxides and carbon compounds. For InP, the cleaning temperature is about 530 °C. At this temperature, incongruent evaporation occurs, and phosphorous evaporates preferentially leaving indium droplets on the surface. This heat cleaning process produces a surface that cannot be activated to Negative Electron Affinity (NEA). We use a low temperature cleaning process at 360 °C under atomic hydrogen irradiation. This process produces a phosphorous stabilized surface free of contaminants that can be activated to NEA. RHEED patterns acquired before the atomic hydrogen cleaning process show a halo indicating a thick oxide layer on the surface. However, the patterns acquired after cleaning show clear (2x4) reconstruction features. QE more than 6.5% is obtained after atomic hydrogen cleaning for InP photocathodes activated with cesium and oxygen. InP photocathodes revived by heating with atomic hydrogen irradiation produce higher QE than photocathodes revived by heating only.

**9:40am EM-FrM5 Deposition and Electroluminescent Properties of Sputter Deposited Zn(x)Mg(1-x)S:Mn, M.R. Davidson, K.E. Waldrip, J.S. Lewis, D. Moorehead, B. Speck,** University of Florida, Gainesville, U.S.; *P.H. Holloway*, University of Florida, Gainesville; *S.S. Sun*, Planar Systems, Inc.

Alternating current thin film electroluminescent devices (ACTFELD) have been prepared using a Zn<sub>x</sub>Mg<sub>1-x</sub>S:Mn phosphor. The phosphor films were deposited by RF magnetron sputter deposition. The composition of the films was varied by adjusting the substrate temperature causing the relative sticking coefficient of the ZnS and MnS to vary. It was found that the Mg gives a green shift of the peak emission of up to 17 nm. This shift is due to the increased crystal field on the Mn due to the smaller Mg ion substituting on a Zn site. The effects of the Mg on the crystal structure and emission have been characterized using XRD, TEM, and UV-Visible band-edge absorption spectroscopy. The effects of post-deposition anneal and fluxes on the ZnMgS:Mn ACTFELDs will be discussed.

**10:00am EM-FrM6 Small Area XPS Analysis of Silicon Wafers Employing Cu Line Technology, E. Principe, R. Brigham, T.J. Schuerlein,** Charles Evans & Associates

Shrinking device sizes are requiring semiconductor manufacturers to change the materials they use in their processes. The semiconductor industry is becoming aware that the future generations of devices will no longer be able to utilize aluminum as a conductor. As a fundamentally new technology, the development of copper metallization using Damascene processes have undergone a great deal of investigation. It is understood that the chemical and physical states of the copper and surrounding silicon can alter device performance, and therefore these states must be controlled. X-Ray Photoelectron Spectroscopy (XPS, also known as Electron Spectroscopy for Chemical Analysis, ESCA) can provide information that is difficult, if not impossible, to obtain by other methods. XPS will be shown to provide chemical state identification of copper, as well as measure the copper oxide thickness. Residual copper concentrations on the silicon surface at various process steps will be reported.

**10:20am EM-FrM7 Epitaxial Ferroelectric Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> Thin Films for Tunable Microwave Devices, C.L. Chen,** University of Houston, U. S. A.; *F.F. Feng*, University of Houston; *Z.H. Zhang*, University of Houston, U. S. A.; *A. Brazdeikis*, University of Houston; *F.A. Miranda*, Lewis Research Center; *Y. Liou*, University of Houston; *W.K. Chu*, University of Houston, U. S. A.; *C.W. Chu*, University of Houston  
Perovskite Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> thin films have been synthesized on (001) LaAlO<sub>3</sub> substrates by pulsed laser ablation. Extensive X-ray diffraction, rocking curve, and pole-figure studies suggest

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that the films are (001) oriented and exhibit good in-plane relationship of SBTO//LAO. RBS studies indicate that the epitaxial films have excellent crystalline quality with an ion beam minimum yield of only 2.6 %. Atomic force microscopy studies indicate that the as-epitaxial films are atomic smooth under the selected growth conditions. The dielectric property measurements by the interdigital technique at frequency up to 1.0 GHz show room temperature values of the relative dielectric constant and loss tangent of 1000 and 0.007 with no bias, and 500 and 0.001 with 35 V bias, respectively. The obtained data suggest that the as-grown BSTO films can be used for development of room temperature high frequency tunable elements and DRAM applications.

## 10:40am EM-FrM8 Reaction Pathways/Energetics for Chemical Attack of Amorphous Si-O-F and C-F-(H,OH) Low-k Dielectric Thin Films by Water Molecules, H. Yang, G. Lucovsky, North Carolina State University

Amorphous films of Si-O-F and C-F-(H,OH) are being considered for low-k inter-metal dielectrics in advanced CMOS devices. The relative stabilities of these different types of dielectrics with respect to chemical attack by water molecules are discussed. FTIR studies have provided the basis for a pseudobinary alloy model for Si-O-F with F-atoms incorporated solely in Si-F bonds. Network bonding statistics have been used to calculate the probability for F-atoms being i) isolated<sup>1</sup> on Si-atoms separated by one or more O-Si-O groups, ii) paired<sup>1</sup> on Si-atoms connected through at most one O-atom, and iii) more strongly clustered. Ab initio calculations are used to study reaction pathways for attack of Si-F bonds by water. For isolated Si-F bonds, the energy of attachment,  $E_{\text{sub a}}$ , of a water molecule through one H-bond is  $\text{Si-OH} + \text{HF}$ , is exothermic by  $\sim 0.1$  eV, whereas the reaction between a pair of Si-F bonds and a water molecule,  $\text{HOH} + 2\text{Si-F} \rightarrow 2\text{HF} + \text{Si-O-Si}$ , is exothermic by 0.7 eV. Based on the alloy model statistics, the ab initio calculations predict good stability against attack by water extending to  $\sim 10$  at.% F, corresponding to a dielectric constant of 3.2 to 3.4. The situation is quantitatively different for the C-F materials. Reaction pathways for attack of C-F bonds by water have also been studied by the same ab initio approach. The attachment energies of water for isolated, and near-neighbor C-F bonds are each significantly lower,  $\sim 0.1$  eV, and reaction pathways are endothermic: e.g.,  $\text{HOH} + 2\text{C-F} \rightarrow 2\text{HF} + \text{C-O-C}$  is endothermic by 1.6 eV. This suggests that initial attack of C-F low-k materials by water must be through other bonding groups such as C-H or C-OH. Ab initio calculations are being extended to C-F-(H,OH) materials to study reaction pathways and reaction energetics. Supported by ONR, NSF and INTEL Corporation.

## 11:00am EM-FrM9 Carbon Incorporation in SiGeC Alloys Grown by UHV/CVD, A.C. Mocuta, D.W. Greve, Carnegie Mellon University

We report on growth and carbon incorporation in  $\text{Si}_{1-x}\text{yGe}_x\text{C}_{\text{sub y}}$  alloys with up to 2% carbon concentration grown by Ultrahigh Vacuum Chemical Vapor Deposition using silane, germane and methylsilane as Si, Ge and C precursors. Alloy growths have been performed at temperatures ranging from 550 °C to 650 °C. Carbon incorporation has been studied for alloys with Ge content of about 5%, 10% and 20%. The  $\text{Si}_{1-x}\text{yGe}_x\text{C}_{\text{sub y}}$  layers grown on Si(100) substrates have been analyzed by High Resolution X-ray Diffraction (HRXRD) and Secondary Ion Mass Spectrometry (SIMS). For low methylsilane flow and growth temperature of less than 600 °C carbon is incorporated on substitutional positions in levels of up to 0.3%. With increasing methylsilane flow carbon begins to occupy interstitial positions as well but also, the germanium fraction in the layer begins to increase. For carbon concentrations of 1% or higher the crystal quality of the alloy is degraded. Thermal stability and critical thickness for layers with about 10% Ge and low carbon levels (0.2%) has also been studied. Addition of small amounts of carbon to SiGe layers greatly improves the thermal stability of the layer. Upon annealing for 1 hour at 900 °C no significant strain relaxation occurs in  $\text{Si}_{1-x}\text{yGe}_x\text{C}_{\text{sub y}}$  single layers or multiple quantum well structures while in similar SiGe structures with comparable strain and thickness strain relaxation is observed.

## 11:20am EM-FrM10 XPS Study of the Role of Ti and TiN Caps on the Cobalt / SiO<sub>2</sub> Interface, T. Conard, IMEC, MAPFCA, Belgium; E. Kondoh, W. Vandervorst, IMEC, Belgium

Continuous downscaling of devices features and increases in operation frequency of ICs requires a low electric resistance of interconnects to transistors. Due to its low resistivity, high thermal stability and small lattice mismatch with Si, the integration of  $\text{CoSi}_2$  into ultra large scale ICs is becoming the main stream. The role of metal caps layer (Ti, TiN) on the Si/Co interface chemistry has already been described but its effect on insulation dielectric such as  $\text{SiO}_2$  has not yet been widely studied. In this

study, a 20 nm Co film was grown on a 150 nm LPCVD  $\text{SiO}_2$  and Ti or TiN top layers were deposited on the Co layer without breaking the vacuum. The samples were annealed for 90 sec at 850 °C in  $\text{N}_2$  ambient and the specimens were analyzed by X-ray Photoelectron Spectroscopy (XPS) in depth profile mode using Ar<sup>+</sup> sputtering. Significantly different depth profiles were obtained depending on the nature of the cap layer. The multilayer with a top TiN layer presents a profile corresponding to sharp interfaces with only a limited diffusion of Ti inside the Co layer and no differences in chemistry of the interfaces due to the annealing procedure. The Co depth profile has a very symmetric shape. On the contrary, the presence of a Ti cap layer induces very strong modification of the interface reactions. First, an important diffusion of the Ti is observed through the Co layer is observed and an accumulation of Ti occurs at the Co/ $\text{SiO}_2$  interface. At the interface, Ti is observed in an oxidized form and reduces the  $\text{SiO}_2$  top layer. The effect of the annealing temperature will also be presented.



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 Zhang, X.: EM1-WeA9, **17**  
 Zhang, Z.H.: EM+PS-ThM2, **20**; EM-FrM7, **31**  
 Zhao, J.: EM+PS-ThM1, **20**  
 Zhou, T.: OE+EM-MoM3, **2**  
 Zielasek, V.: EM1-WeA4, **16**  
 Zolper, J.C.: EM-ThP10, **29**  
 Zomorrodian, V.: EM-FrM2, **31**  
 Zuo, S.L.: NS+EM+SS-MoA1, **4**