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

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

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

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

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

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

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

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

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

The formation of a semi-ordered oxide passivation layer between hafnium oxide and In$_{0.53}$Ga$_{0.47}$As(001)-(4x2)/*c*(8x2) and InAs(001)-(4x2)/*c*(8x2) was studied using scanning tunneling microscopy/spectroscopy (STM/STS), and density functional theory (DFT) calculations. A passivation layer is needed to protect the surface from disruption during bulk amorphous oxide deposition for a high-κ gate insulator. Two methods of forming low coverage of HfO$_2$ were investigated: reactive oxidation of the e-beam deposited Hf metal and e-beam deposition from an HfO$_2$ target. STM results show that Hf atoms must cluster to be reactive to O$_2$. DFT suggests there is a high tendency for Hf to displace substrate atoms, which is undesirable. Direct deposition of the oxide is a better method. At submonolayer coverage, STM has identified individual bonding sites for the HfO$_2$ molecule; the HfO$_2$ forms small structures of mostly monolayer height with a high nucleation density. Density functional theory (DFT) calculations have been employed to assign the bonding structure. The DFT simulations show that for HfO$_2$/InAs(001)-(4x2), the most likely sites are stable by about -4.5 eV and the calculated density of states (DOS) shows no evidence of Fermi level pinning (no mid-gap states). At submonolayer coverage, the HfO$_2$ molecule bonds via group III-oxygen bonds and group V-hafnium bonds. STS measurements of clean InGaAs(001)-(4x2) reveal that the surface has significant band bending, showing p-type character for both n-type and p-type samples. Deposition of > 1 ML of HfO$_2$ is enough to move the Fermi level towards the conduction band for n-type InGaAs(001)-(4x2), as shown in results of STS vs. HfO$_2$ coverage. For p-type material, the Fermi level remains near the valence band after deposition of HfO$_2$. These results are consistent with the Fermi level remaining unpinned. In addition, annealing effects are studied. At temperatures of 300 °C and above, ordered oxide structures are seen in STM which form rows in the [-110] direction. However, lower annealing temperatures of 200 °C and below are preferable for good STS results. Hafnium oxide, evaporated via electron beam deposition, likely creates some O$_2$ and HfO, which may react in an undesirable way with the semiconductor surface. For this reason, a method is also proposed to protect the surface during e-beam deposition via a CO$_2$ protecting layer at low temperature (90 K), which does not appear to perturb the surface.

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

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

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

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

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

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

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

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

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

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

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

4:20pm SS1+EM-MoA8 Direct Atomic Scale Imaging and Spectroscopy of the Interior and Exterior of III-V Nanowires

A. Mikkelsen, Lund University, Sweden **INVITED**

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

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

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

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

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

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

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

5:00pm SS1+EM-MoA10 Passivation of Ge(100) Surface Studied by Scanning Tunneling Microscopy and Spectroscopy

J.S. Lee, *S.R. Bishop, A.C. Kummel*, University of California, San Diego

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

5:20pm SS1+EM-MoA11 Surface-driven Method for Incorporation of Mn into Ge Quantum Dots

C.A. Nolph, *K.R. Simov, P. Reinke*, University of Virginia

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

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