

## Surface Science

Room: 208 - Session SS+EM+NC-FrM

## Semiconductor Surfaces

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **SS+EM+NC-FrM1 From Nanochemistry to Active Nano-Objects at Semiconductor Surfaces, P.G. Soukiasian**, Commissariat à l'Energie Atomique and Université de Paris-Sud/Orsay, France **INVITED** Silicon carbide (SiC) surfaces/interfaces are studied by atom-resolved scanning tunneling microscopy and spectroscopy (STM/STS) using electrons and/or photons, synchrotron radiation-based photoelectron spectroscopies (XPS, UPS,  $\mu$ -spot XPS) and/or diffraction, low energy electron microscopy (LEEM) experimental techniques and density functional theory. Such important issues as self-organized active metal nano-objects, defects and an amazing nanochemistry will be presented and discussed. It includes: The 1st example of H/D-induced clean/pre-oxidized semiconductor surface metallization, with an isotopic effect occurring using D; Selective formation of ultra-thin nitride layer at Si-SiC interface; Atomic crack defects developing at SiC surfaces; Anisotropic metal diffusion, metal atom pairs, chains and wires formation; Massively parallel active architecture based on metal/Si nanowires exhibiting a negative differential resistance behavior. These findings impact some important issues such as i) metallization of wide band-gap chemically passive semiconductor surfaces which is of particular interest in interfacing with biology, ii) selective SiC interface passivation especially useful in limiting dopant diffusion, iii) identifying and understanding some unusual defects most likely involved in the high density of interface states recurrent at SiC interfaces, and iv) achieving a massively parallel active architecture in the solid state.

9:00am **SS+EM+NC-FrM3 Chemistry of the Si-rich  $\beta$ -SiC(100) Surface Compared to the Si(100) Surface, S.M. Casey, L.N. Adhikari**, University of Nevada, Reno

The chemistry of the Si-rich  $\beta$ -SiC(100) surface has been studied using density functional theory (DFT) computational methods and small clusters to model the surface reactivity. Results for the reactions of the cluster models of the silicon carbide surface with ammonia and small alcohols and amines will be presented and the energetics compared to the corresponding pathways on the Si(100) surface. The computational results generally show that the silicon-rich silicon carbide surface exhibits stronger interactions with these types of adsorbates by 5-10 kJ/mol relative to the clean silicon surface. The major difference is that the silicon carbide surface has no closely bordering reactive silicon surface dimers, and, thus, the "intrinsic" reactivity of the silicon surface dimer can be examined without complicating multi-dimer reactions. The computational results will also be compared to experimental thermal desorption studies on these surfaces. The thermal desorption results are in general agreement with the DFT results.

9:20am **SS+EM+NC-FrM4 Surface Band Bending in GaN, M. Ruchala, M. Foussekis, H. Morkoc, M.A. Reshchikov, A.A. Baski**, Virginia Commonwealth University

In spite of tremendous progress in the development of nitride semiconductors, the detrimental effects of surfaces and interfaces on the electrical and optical properties of devices based on these semiconductors is often underestimated. We have investigated band bending at the surface of undoped GaN and its change caused by illumination (photovoltage) with scanning Kelvin probe microscopy (SKPM) in ambient and with a Kelvin probe attached to an optical cryostat in high vacuum. In the microscopy set-up, we charged the surface and increased band bending by several eV using conductive atomic force microscopy (CAFM), and then used SKPM to observe discharge transients of the surface band bending in dark from room temperature (RT) to 35 °C, as well as under sub-bandgap illumination. In the Kelvin probe set-up, we measured the photovoltage spectrum and its transients after UV illumination at temperatures from RT to 125 °C in vacuum and air ambient. These two complementary techniques provide independent information about surface band bending and its transient behavior after charge injection or illumination. The rate of restoration of the initial band bending in dark for both experiments (after CAFM charging or after flattening of band bending due to illumination) increased at higher temperatures and typically exhibited a quasi-logarithmic time dependence. The results indicate that the restoration of band bending disturbed from equilibrium occurs primarily by means of adsorption of some species from air, and not by thermionic emission of electrons over the surface potential barrier. Indeed, transients of the photovoltage (PV) caused by UV illumination in the Kelvin probe strongly depended on the ambient. In air

ambient under illumination, the PV signal increased to its maximum of 0.65 V in a few seconds and then gradually decayed by 0.3 V over 3 h, whereas in vacuum the signal quickly increased to 0.55 V and then slowly increased by 0.1 V over 3 h. This behavior indicates the photo-induced adsorption of negatively charged species in ambient or the photo-induced desorption of such species in vacuum. With regard to temperature, the initial band bending increased by 0.2 V from RT to 125 °C due to more bulk electrons overcoming the surface barrier and becoming trapped at surface states. Experiments are now in progress in the Kelvin probe to investigate the band bending behavior as a function of introduced gas species such as oxygen or water vapor.

9:40am **SS+EM+NC-FrM5 An Accelerated Molecular Dynamics Study of Diffusion on the GaAs (001)  $\beta$ 2(2x4) Reconstruction, M.H. Mignogna, K.A. Fichthorn**, The Pennsylvania State University

The GaAs (001)  $\beta$ 2(2x4) reconstruction is the most commonly used substrate for growth in GaAs homoepitaxy by molecular beam epitaxy. Kinetic Monte Carlo (KMC) simulations based on first-principles calculations<sup>1</sup> have illuminated the mechanisms for recovering this reconstruction during growth. However, the KMC simulations are based on rates of processes that occur on perfect  $\beta$ 2(2x4) unit cells. In experimental studies with reflection high-energy electron diffraction and scanning-tunneling microscopy, the surface is observed to exhibit domains of perfect  $\beta$ 2(2x4) unit cells, but long-range disorder persists and a possible origin is out-of-phase  $\beta$ 2(2x4) domains.<sup>2</sup> To examine the atomic-scale processes that lead to long-range disorder, as well as to characterize diffusion and the early stages of homoepitaxy on this surface, we employ accelerated molecular dynamics (MD). Our simulations are based on a semi-empirical, Tersoff-type potential that exhibits good agreement with a variety of bulk and surface properties of GaAs. Using accelerated MD we can probe long time scales, extending into the microsecond range and beyond. On the bare surface, we observe breaking, re-forming, and shifting of As row and trench dimers, that promotes the formation of out-of-phase domains of  $\beta$ 2(2x4) unit cells and leads to long-range disorder of the surface. The kinetic processes of the As dimers affect the surface diffusion of Ga adatoms, as well as the initial morphologies that occur during growth.

<sup>1</sup> P. Kratzer, E. Penev, M. Scheffler, *Appl. Phys. A* 75, 79 (2002)

<sup>2</sup> D.W. Pashley, J.H. Neave, B.A. Joyce, *Surf. Sci.*, 582, 189 (2005).

10:00am **SS+EM+NC-FrM6 First Principles Investigation of Dimer Ordering on III-V Semiconductor Surfaces, J.C. Thomas, J.E. Bickel, J.M. Millunchick, A. Van der Ven**, University of Michigan

Surface disorder can contribute significantly to optoelectronic, thermodynamic, kinetic and interfacial properties of epitaxial thin films, especially at the nano-scale. Surface reconstructions, which decrease surface free energy relative to bulk configurations via a reduction in unfavorable bonding and increase in configurational entropy, play a vital role in the determination of these properties. In this work, the effect of finite temperature on the free energy of surface reconstructions is investigated in order to determine the role of entropy in surface dimer concentration and ordering. As a model system, we consider the  $\alpha$ 2(2x4) and  $\beta$ 2(2x4) reconstructions on the (001) surface of homoepitaxial InAs, as these reconstructions are not only well studied, but are also stable within a continuous interval of chemical potential. A first principles model Hamiltonian is developed within the cluster expansion formalism and applied to equilibrium Monte Carlo simulations to obtain accurate thermodynamic quantities, as well as configurational trends. For example, fitting to energies for seven different dimer configurations of these 2x4 reconstructions, calculated via density functional theory show that there is an energetic preference for third nearest neighbor pairing (along the diagonal), giving rise to a "zig-zag" ordering of dimers, referred to as the z(4x4). Evidence of this structure has been previously reported. Monte Carlo simulations show the  $\alpha$ 2(2x4) to be stable within an intermediate range of chemical potentials, giving way to the  $\beta$ 2(2x4) at higher chemical potential. The transition between configurations shows a step-like behavior at low temperatures, smoothing out at higher temperatures. The fraction of the  $\alpha$ 2(2x4) that possesses the z(4x4) ordering was determined from averaged correlations. The coverage is about 60% at room temperature, and decreases to approximately 50% at typical growth temperatures, in reasonable agreement with published results. We show that size mismatch strain in ternary III-V alloys drives In surface segregation in GaAs and locks in a zig-zag ordering of As surface dimers.

10:20am **SS+EM+NC-FrM7 Hydroxyl Termination and Passivation of the Group III-rich (4x2)/c(8x2) Surfaces of InAs(001) and InGaAs(001) Surface Studied by STM, STS, and DFT, J.B. Clemens, T. Song, A.C. Kummel, University of California, San Diego**

Atomic Layer Deposition requires the substrate to have a chemical passivation/termination layer consisting of reactive groups that initiate the ALD reaction. A suitable passivation/termination layer would have ligands that mimic the surface during growth, such as hydroxyl (OH).<sup>1,2</sup> Scanning tunneling microscopy was used to study the initial bonding configuration of hydroxyl onto the group III-rich InAs(001)-(4x2)/c(8x2) surface, which is almost identical to the InGaAs(001)-(4x2)/c(8x2) surface. These surfaces are more resistant to oxidation than group V-rich surfaces, which is true of many III-arsenide semiconductors, and therefore is a better starting template for ALD.<sup>3</sup> Aqueous (30%) hydrogen peroxide vapour is used as the OH source. After annealing, the surface reaction forms well-ordered interfaces that terminate at about one ML indicating that this process is self-limiting. Substrate lattice disruption is minimal following OH desorption after annealing at 350° C. If pure water vapour is used as a control dose, less surface reaction occurs and it centers at surface defect sites. Density functional theory was used to model the interaction of InGaAs(001)-(4x2) with OH, H, and H<sub>2</sub>O. Energies and kinetics of adsorption and desorption of OH, H, and H<sub>2</sub>O are presented, which compares the stability of the HOOH/H<sub>2</sub>O vs the H<sub>2</sub>O only termination/passivation methods. DFT results show that the OH passivation method using HOOH is stable at high temperatures that are typically found under ALD growth conditions, while the passivation method using only water is not. The electronic structure was probed using scanning tunneling spectroscopy. On the clean as-prepared substrates, both n- and p-type InAs(001)-(4x2)/c(8x2) show n-type behavior, consistent with literature.<sup>4,5</sup> Upon OH termination, both surfaces exhibit n-type behavior, with the Fermi level about 0.1 eV below the CB minimum. This shows no evidence for midgap Fermi level pinning, suggesting that this method has potential for high-k gate oxide ALD on III-V semiconductor surfaces.

<sup>1</sup> K. Kukli, et al., J. Appl. Phys., 92, 1833 (2002).

<sup>2</sup> J. Aarik, et al., Appl. Surf. Sci., 161, 385 (2000).

<sup>3</sup> D. Winn, et al., J. Chem. Phys., 127, 134705 (2007).

<sup>4</sup> L. Olsson, et al., Phys. Rev. Lett., 76, 3626 (1996).

<sup>5</sup> P. De Padova, et al., Surf. Sci., 482-485, 587 (2001).

10:40am **SS+EM+NC-FrM8 Pit Nucleation in the Presence of (nx3) and β(2x4) Surface Reconstructions on In<sub>0.81</sub>Ga<sub>0.19</sub>As/InP Films, L.E. Sears, A. Riposan, J.M. Millunchick, University of Michigan - Ann Arbor**

The growth of heteroepitaxial films with high misfit strains on the crystallographic surface such as InGaAs/GaAs usually occurs in the Stranski-Krastanov mode, whereby coherent islands form on a planar wetting layer as a way to relieve strain due to a lattice mismatch. Theory has shown that both islands and pits can relieve strain on high misfit, low temperature films,<sup>1</sup> but experimentally only islands are typically observed as the initial mechanism of strain relief. We have discovered a growth regime in which pits relieve strain rather than islands due to a decrease in surface energy with increasing indium content. Models have predicted that altering the growth conditions, such as growth rate and temperature, or materials properties, such as surface energy or lattice mismatch, can lead to the nucleation of pits initially on the surface instead of islands,<sup>1,2</sup> but little experimental data exists to support those claims. We examine the growth of In<sub>0.27</sub>Ga<sub>0.73</sub>As/GaAs(001) and In<sub>0.81</sub>Ga<sub>0.19</sub>As/InP(001), which both have the same lattice mismatch strain, and show that In composition is important in determining the type of 3D features that nucleate on the surface. As the critical thickness is exceeded, low indium composition films have a tendency to form 3D islands as the primary strain relief mechanism. On the other hand, pits are the preferred strain relief mechanism in high In composition films grown with the same growth conditions and lattice mismatch. Increasing the indium content results in a more metallic surface that has a lower surface energy ( $\gamma$ ) and models have predicted that at sufficiently low  $\gamma$  pit nucleation is favored over islands as the initial strain relief mechanism.<sup>2</sup> Models have suggested that the presence of  $\beta(2x4)$  reconstructions may also act as strain relief mechanism in In<sub>0.81</sub>Ga<sub>0.19</sub>As/InP(001) films.<sup>3</sup> Analysis of the atomic surface structure of these films using scanning tunneling microscopy show that the reconstructions are also affected by the presence of pits, lending more evidence to surface reconstructions as a mechanism for strain relief.

<sup>1</sup> Lung MT, Lam CH, and Sander LM, Phys. Rev. Lett. 95 (086102) AUG 18 2005

<sup>2</sup> Bouville M, Millunchick JM, Falk ML, Phys. Rev. B 70 (235312) DEC 10 2004

<sup>3</sup> Riposan A, C. Pearson, and JM Millunchick, J. Vac. Sci. Technol. A 24 (2041) OCT 10 2006.

11:00am **SS+EM+NC-FrM9 In-situ ALD Studies of Al- and La-oxide on In<sub>0.53</sub>Ga<sub>0.47</sub>As, M. Milojevic, University of Texas at Dallas, B. Brennan, Dublin City University, Ireland, H.C. Kim, University of Texas at Dallas, F.S. Aguirre-Tostado, The University of Texas at Dallas, J. Kim, R.M. Wallace, University of Texas at Dallas, G. Hughes, Dublin City University, Ireland**

The combination of high k dielectric materials on high mobility III-V semiconductors offers the potential for MOSFETs with larger transconductance at lower operating voltages than are currently achievable with silicon based devices. Arsenic and gallium oxidation states are suspected to be the cause of Fermi level pinning, and therefore the removal or minimization of such states is required in order to develop practical devices. This study investigates the atomic layer deposition (ALD) of aluminium and lanthanum oxide based high-k dielectrics on the ammonium sulphide (NH<sub>4</sub>)<sub>2</sub>S and ammonium hydroxide NH<sub>4</sub>OH treated In<sub>0.53</sub>Ga<sub>0.47</sub>As surface grown by metal organic vapour phase epitaxy (MOVPE) on lattice matched InP substrates using in-situ surface chemical analysis. Monochromatic, in-situ X-ray photoelectron spectroscopy (XPS) and ex-situ atomic force microscopy (AFM) were used to determine optimal (NH<sub>4</sub>)<sub>2</sub>S conditions based on varying the sulphur concentration, temperature and treatment time. The ALD of the high-k films carried out at 300°C consists of a metal precursor pulse followed by a water pulse with an high purity N<sub>2</sub> carrier gas and was sequentially examined with in-situ XPS after every half cycle of the deposition process to determine the initial interfacial oxide and substrate reactions taking place during the growth. A 'clean up' effect, whereby the ALD process reduces native oxides at the surface during high-k deposition, is well known for thin dielectric films. In the case of TMA/water based deposition of Al<sub>2</sub>O<sub>3</sub>, we have found that the first TMA pulse is responsible for the removal of virtually all of the arsenic oxide left on the surface after the pre-treatments, especially with (NH<sub>4</sub>)<sub>2</sub>S, to within the detection limits of XPS. Gallium oxide bonding is reduced to approximately a monolayer consistent with a Ga-O-Al bond at the interface. Similar results for La-based precursor reactions will also be presented. Capacitance-voltage measurements were also carried out on metal oxide semiconductor MOS devices formed after the high-k dielectric growth. Supported by MARCO MSD Focus Center, Science Foundation Ireland, and FUSION.

11:20am **SS+EM+NC-FrM10 Atomic Scale Investigation of Mn Impurities on the InAs(110) Surface, Y.J. Song, University of Maryland, College Park and NIST, G.M. Rutter, P.N. First, Georgia Institute of Technology, N. Zhitenev, J.A. Stroscio, National Institute of Standards and Technology**

Increased interest in spin-based electronics as a replacement for charge-based electronics has led to significant scientific attention to dilute magnetic semiconductors (DMS). One of the main dilute magnetic semiconductors involves doping III-V semiconductors with Mn acceptors with the aim of achieving high Curie temperatures. In the present work, we studied Mn deposited on the InAs(110) surface with low temperature scanning tunneling microscopy and spectroscopy (STM/STS). Single Mn atoms were deposited onto a cleaved n-InAs(110) surface at cryogenic temperatures. The as-deposited Mn adatoms were found to be in two distinct configurations. About 10% of the Mn adatoms appear in the topographic images to be positively charged. The other 90% appear to be in a neutral configuration. Both types of adatoms can undergo an exchange process whereby the surface Mn atom substitutes for an In atom in the top surface layer. This process involves raising the sample tunneling voltage beyond a certain threshold voltage of approximately -0.6 eV for both types of Mn adatoms. This process is similar to that seen in the Mn/GaAs system.<sup>1</sup> And we also studied that in-situ deposition of Mn onto a cleaved n-doped InAs(110) substrate at low temperature produces an adsorbate-induced 2DEG at the InAs surface. Spatial properties of Landau level quantization<sup>2</sup> in high magnetic fields of both the 2D sub-bands and 3D conduction bands were studied in relation to the configuration of Mn atoms on the surface.

<sup>1</sup> D. Kitchen et al, Nature 442, 436 (2006)

<sup>2</sup> M. Morgestern et al, Phys. Rev. Lett. 90, 56804 (2003).

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Adhikari, L.N.: SS+EM+NC-FrM3, 1  
Aguirre-Tostado, F.S.: SS+EM+NC-FrM9, 2

## — B —

Baski, A.A.: SS+EM+NC-FrM4, **1**  
Bickel, J.E.: SS+EM+NC-FrM6, 1  
Brennan, B.: SS+EM+NC-FrM9, 2

## — C —

Casey, S.M.: SS+EM+NC-FrM3, **1**  
Clemens, J.B.: SS+EM+NC-FrM7, **2**

## — F —

Fichthorn, K.A.: SS+EM+NC-FrM5, 1  
First, P.N.: SS+EM+NC-FrM10, 2  
Foussekis, M.: SS+EM+NC-FrM4, 1

## — H —

Hughes, G.: SS+EM+NC-FrM9, 2

## — K —

Kim, H.C.: SS+EM+NC-FrM9, 2  
Kim, J.: SS+EM+NC-FrM9, 2  
Kummel, A.C.: SS+EM+NC-FrM7, 2

## — M —

Mignogna, M.H.: SS+EM+NC-FrM5, **1**  
Millunchick, J.M.: SS+EM+NC-FrM6, 1;  
SS+EM+NC-FrM8, 2  
Milojevic, M.: SS+EM+NC-FrM9, **2**  
Morkoc, H.: SS+EM+NC-FrM4, 1

## — R —

Reshchikov, M.A.: SS+EM+NC-FrM4, 1  
Riposan, A.: SS+EM+NC-FrM8, 2  
Ruchala, M.: SS+EM+NC-FrM4, 1

Rutter, G.M.: SS+EM+NC-FrM10, 2

## — S —

Sears, L.E.: SS+EM+NC-FrM8, **2**  
Song, T.: SS+EM+NC-FrM7, 2  
Song, Y.J.: SS+EM+NC-FrM10, **2**  
Soukiassian, P.G.: SS+EM+NC-FrM1, **1**  
Stroscio, J.A.: SS+EM+NC-FrM10, 2

## — T —

Thomas, J.C.: SS+EM+NC-FrM6, **1**

## — V —

Van der Ven, A.: SS+EM+NC-FrM6, 1

## — W —

Wallace, R.M.: SS+EM+NC-FrM9, 2

## — Z —

Zhitenev, N.: SS+EM+NC-FrM10, 2