

# Wednesday Afternoon, October 31, 2012

## Surface Science

Room: 22 - Session SS+EM-WeA

## Semiconductor Surfaces

Moderator: M.A. Hines, Cornell University

2:00pm **SS+EM-WeA1 Local Characterization of Laterally Patterned GaN Polar Surfaces.** *J.D. Ferguson*, Virginia Commonwealth University, *J.K. Hite, M.A. Mastro, C.R. Eddy, Jr.*, U.S. Naval Research Laboratory, *A.A. Baski*, Virginia Commonwealth University

Using scanning probe microscopy techniques, we have investigated the topographic and electrical properties of lithographically defined Ga- and N-polar regions grown on the same surface of a GaN epilayer. These unique structures were created on N-polar substrates grown by either hydride vapor phase epitaxy (HVPE) or metalorganic chemical vapor deposition (MOCVD). A patented selective epitaxy process [1,2] was used to prepare the alternating polarity surfaces on the two separate substrate types. To produce adjacent stripes of alternating polarity on a single substrate, a thin inversion layer comprising AlN was selectively grown inside a nitride mask. After removing the mask, Ga- and N-polar GaN were simultaneously grown over the inversion layer and bare N polar substrate, respectively, using MOCVD. Atomic force microscope (AFM) topography images reveal that Ga-polar regions are smoother than N-polar ones by about two orders of magnitude (rms of ~0.5 nm and ~50 nm, respectively). Local current/voltage (*I/V*) spectra obtained by conductive AFM indicate a lower turn-on voltage and higher conductivity for N polar regions, whereas Ga polar regions are insulating. Scanning Kelvin probe microscopy (SKPM) data show a surface potential drop of ~0.5 V across the interface domain boundary (< 200 nm lateral resolution) from the N- to the Ga polar regions on the HVPE substrate. A lower potential drop (~0.2 V) is seen across the N- to Ga- interface on the template, as well as inconsistent surface potential values (+/-0.1 V) for Ga-polar stripes. Using SKPM, the surface photovoltage (SPV), or the change in surface potential upon exposure to above-bandgap light, may also be measured for both surfaces simultaneously. Both samples show similar characteristics to previously studied polar GaN surfaces, where Ga-polar regions have higher initial SPV values (~0.3 V for HVPE, ~0.5 V for MOCVD) than N-polar regions (~0.2 V for HVPE, ~0.3 V for MOCVD). Restoration of the SPV signal after illumination is faster for Ga-polar regions, which is not consistent with previously studied bulk Ga-polar films. In summary, scanning probe methods can be used to distinguish Ga- versus N-polar GaN surface regions grown on the same GaN epilayer.

1. J.K. Hite, M.E. Twigg, M.A. Mastro, C.R. Eddy, Jr. and F.J. Kub, "Initiating Polarity Inversion in GaN Growth Using an AlN Interlayer", *Physica Status Solidi A* 208, 1504-1506 (2011).

2. J.K. Hite, N.D. Bassim, M.E. Twigg, M.A. Mastro, F.J. Kub and C.R. Eddy, Jr., "GaN Vertical and Lateral Polarity Heterostructures on GaN Substrates", *Journal of Crystal Growth* 332, 43-47 (2011).

2:20pm **SS+EM-WeA2 Systematic Prediction of Entropic Surface Reconstruction Stabilization on GaAs(001) from First Principles.** *J.C. Thomas, A. Van der Ven*, University of Michigan, *N.A. Modine*, Sandia National Laboratories, *J.M. Millunchick*, University of Michigan

Increasing evidence linking bulk material properties to surface structure has made critical the development of a comprehensive understanding of atomic-scale surface structure. This is particularly true in low-temperature-grown (LTG) GaAs, where As anti-site defects are incorporated at the As-rich growth surface. Unfortunately, GaAs(001) reconstruction stability is poorly characterized in this regime, where, in addition to the well-studied  $\beta_2(2\times 4)$  and  $c(4\times 4)$  reconstructions, a " $\times 3$ " reconstruction is also observed. This " $\times 3$ " reconstruction has been difficult to characterize experimentally, and theoretical calculations have failed to identify a stable " $\times 3$ " reconstruction on GaAs(001). We have developed a systematic, rigorous procedure for predicting equilibrium surface structure and ordering behavior at finite temperature. By combining new and established techniques, our method overcomes difficulties of studying multicomponent surfaces from first principles, which has traditionally followed a painstaking trial-and-error approach.

Using our approach of directed structural enumeration and density functional theory calculation, we can efficiently identify stable and near-stable reconstructions of the GaAs(001) surface in order to identify the structure of the missing " $\times 3$ " reconstruction. Accounting for lattice vibrations and configurational entropy from first principles, we predict finite-temperature stability of a  $(4\times 3)$  reconstruction over a range of  $A_s$  partial pressure at low temperature. Our results reveal a competition

between vibrational entropy of the  $(4\times 3)$  reconstruction and configurational entropy of the  $c(4\times 4)$  reconstruction, which becomes entropically stabilized at higher temperatures. We find that this same  $(4\times 3)$  reconstruction features prominently in calculated reconstruction phase diagrams for the wetting layer systems Bi/GaAs(001) and InAs/GaAs(001).

2:40pm **SS+EM-WeA3 3D Atomic Scale Structure Analysis of Semiconductor Nanostructures by Atom Probe Tomography and Cross-Sectional STM.** *P.M. Koenraad*, Eindhoven University of Technology, Netherlands **INVITED**

Present day semiconductor science depends heavily on the construction of precise nanostructures in which atomic scale details are of key importance in the understanding and utilization of such nanostructured semiconductor materials. It is thus of key importance to have techniques that allow such details to be assessed by novel microscopy techniques that can obtain, preferable in 3D, atomic resolution. In this presentation I will present recent results that we have obtained by two exciting techniques that allow for an atomic scale resolution. We have used cross-sectional Scanning Tunneling Microscopy (X-STM) and Atom Probe Tomography (APT) on a range semiconductor nanostructures such as quantum dots and rings. The X-STM technique offers a superb 2D true atomic resolution in a single atomic plane intersecting the nanostructure. Atom Probe Tomography is a technique that has recently become available for the analysis of semiconductor nanostructures. Laser induced field emission is used to get a full atomically resolved 3D map of the composition of semiconductor nanostructure. In the presentation I will apply and compare these techniques on quantum dots and rings that have been obtained by various growth procedures such as the traditional Stransky-Krastonow process, droplet epitaxy or by applying Sb during the dot formation process.

4:20pm **SS+EM-WeA8 Coverage-dependent Adsorption of a Bifunctional Molecule with a Rigid Spacer on the Ge(100)-2  $\times$  1 Surface.** *B. Shong, S.F. Bent*, Stanford University

Direct chemical functionalization of semiconductor surfaces with organic molecules has been gaining attention, in part due to its potential applications based on forming organic-inorganic interfaces with tailorable properties. Attachment of bifunctional molecule is important because of the possibility for manipulating the chemical properties of the surface to allow for successive reaction, for example by molecular layer deposition (MLD). Whether dual or single reaction occurs during adsorption of a bifunctional molecule is of critical interest. It is known that more singly-tethered adsorbates typically form at higher coverages, but most previous studies focused only on a few discrete coverages.

In this study, we investigate coverage-dependent adsorption behavior of resorcinol (1,3-benzenediol) on the Ge(100)-2  $\times$  1 surface. *In situ* X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy experiments along with density functional theory calculations are combined to determine the products and reaction pathways. First, the results support our previous conclusion that molecular geometry is an important factor in the reactivity and stereoselectivity of rigid bifunctional adsorbates.<sup>1</sup> Resorcinol is found to dually and singly attach on Ge(100) through its two hydroxyl groups, and the dually reacted adsorbate assumes only one configuration due to geometrical restrictions. Moreover, a detailed study with respect to coverage shows that the product distribution is strongly dependent on coverage in a nonlinear fashion with two distinct adsorption regimes. In the low coverage regime, a constant fraction of singly-attached adsorbates is observed, independent of coverage. On the other hand, the fraction of singly-bound adsorbates increases with coverage in the high coverage regime. The increase in singly-bound species at higher coverages is explained by surface crowding, with existing adsorbates blocking reactive sites. This study provides fundamental knowledge about the reactivity of bifunctional molecules on semiconductor surfaces.

<sup>1</sup>B. Shong, K. T. Wong, and S. F. Bent, *J. Phys. Chem. C* **116**, 4705 (2012).

4:40pm **SS+EM-WeA9 2012 AVS Medard Welch Award Lecture: Chemical Functionalization of H-terminated Silicon Surfaces.** *Y.J. Chabal\**, The University of Texas at Dallas **INVITED**

Silicon is best known for its oxide because of its propensity to oxidize and the remarkable properties of the Si/SiO<sub>2</sub> interface. Yet, oxidation is ill-defined and hard to control. Moreover, modification of chemically stable oxide surfaces mostly involves silanization, typically characterized by disorder and poor chemical stability in solution. The ability to functionalize oxide-free Si surfaces opens new opportunities for a broader range of

\* Medard W. Welch Award Winner

applications. Precise modification of clean Si surfaces in an ultra-high vacuum environment leads to interesting chemistry but is not widely applicable. In contrast, wet chemical preparation of well-defined H-terminated Si surfaces provides a platform for both fundamental science and further applications. Much work has been done to functionalize H/Si using well known chemical procedures, such as UV- or catalyst-induced hydrosilylation with alkene molecules or halogens followed by Grignard chemistry. Relatively little attention has been placed on the role of structure in H-terminated surfaces for selective modification. Yet, just as structure is important in etching, it also plays a role during chemical modification of surfaces, as illustrated by the reaction of ammonia on stepped Si(111) surfaces.<sup>1</sup> Understanding the role of structure during HF etching is also critical to devise new methods for expanding the functionality of H-terminated surfaces. This talk illustrates this concept and shows that thermal chemistry is well suited to explore such effects. It discusses, for instance, the use of methoxylation of H-terminated Si(111) surfaces to provide a well-defined template for interesting surface chemistry and a broader range of functionalization,<sup>2</sup> such as the grafting of phosphonates, amines, and metal complexes.

<sup>1</sup> Dai, M., Y. Wang, J. Kwon, M.D. Halls, and Y.J. Chabal, *Nitrogen interaction with hydrogen-terminated silicon surfaces at the atomic scale. Nature Materials* 8, 825 (2009).

<sup>2</sup> Michalak, D.J., S.R. Amy, D. Aureau, M. Dai, A. Esteve, and Y.J. Chabal, *Nanopatterning Si(111) surfaces as a selective surface-chemistry route. Nature Materials* 9, 266 (2010).

5:20pm **SS+EM-WeA11 Wet Chemical Approach for Amino Functionalization of Oxide-free Si(111) Surfaces, T. Peixoto, P. Thissen, Y.J. Chabal, University of Texas at Dallas**

The ability to functionalize H-terminated Si surfaces with NH<sub>2</sub> groups is crucial for a number of applications, such as biomedical (bio-sensors), solid diffusion barrier films, single electron devices, MOSFETs and MEMS. The Si-N bond provides a versatile functionality for chemical modification. Although the creation of a well-defined and stable interface for the Si-N bonds has remained elusive, chlorosilanes have been shown to easily react with gas-phase or liquid ammonia and primary and secondary amines to achieve a stable silicon nitride bond.

For fluorosilane surfaces, we have performed DFT calculations indicating that the kinetic barrier for the NH<sub>3</sub> reaction with Si-F surfaces is only slightly higher than for Si-Cl surfaces, suggesting the reaction should occur at moderate temperatures (<70°C). The 1/3 ML Si-F and 2/3 ML Si-H nanopatterned model surface has a tailorable distance between Si-F groups (from 6.8 Å for 1/3ML to 3.9 Å at higher coverages) allowing the adsorption mechanism to be investigated in detail (and evaluated by DFT calculations) and the role of NH<sub>x</sub>-NH<sub>x</sub> interactions explored. We further show that the Si-F surface reacts with amino containing molecules (NH<sub>2</sub>-R-NH<sub>2</sub>), as evidenced by the reaction between Si-F and ethylenediamine at room temperature. Using these reactions we demonstrate that the amidation for the nanopatterned surface takes place for both small molecules (NH<sub>3</sub>) and larger amino chains (NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>) with similar kinetics. The surfaces were characterized using Fourier-transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) to verify reaction mechanisms.

These results provide a fundamental understanding of the amidation reaction mechanism for achieving stable Si-N bonds using fluorosilanes surfaces. Achieving a well-defined and stable Si-N interface is significant for a number of important technological applications.

References:

[1] Tian, F.; Taber, D.F.; Teplyakov, A.V. *J. Am. Chem. Soc.* **2011**, *133*, (20769)

[2] Michalak, D. J.; Amy, S. R.; Aureau, D.; Dai, M.; Esteve, A.; Chabal, Y. J. *Nat. Mater.* **2010**, *9*, (266).

5:40pm **SS+EM-WeA12 Ammonia- and Amine-based Chemical Modification of Silicon Surfaces, A.V. Teplyakov, University of Delaware**  
Stable silicon-nitrogen bonds on surface of single crystalline silicon substrates can serve a variety of practical purposes. The main problem is that creating and controlling the formation of these bonds is done predominantly in the controlled ultra-high vacuum conditions. Here the formation of stable Si-N-based interfaces will be compared for vacuum procedures and for the wet chemistry-based methods. A number of compounds, including ammonia, amines, azides and nitro- and nitroso-compounds, dosed onto a clean silicon surface can yield stable Si-N bonds. However, designing surface reactions leading to contaminant-free interfaces that contain these bonds by wet chemistry methods has been a challenge. We will use multiple spectroscopy and microscopy techniques supplemented by density functional theory investigations to build interfacial systems based on Si-N bonds with ammonia and amines reacting with Cl-

covered single crystalline silicon surfaces in a solvent at room temperature. Further transformations of the produced functionalized surfaces will also be discussed.

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