Monday Morning, October 28, 2013

Surface Science
Room: 201 A - Session SS+AS+NS-MoM

Nanostructures: Growth & Characterization
Moderator: F.P. Netzer, Karl-Franzens University, Austria

8:20am SS+AS+NS-MoM1 Measuring Homogeneity of Nanocluster Size Distributions using Charge Resolved Low Energy Alkali Ion Scattering, *A.B. Arjad, J.A. Yarmoff*, University of California, Riverside
Gold nanoclusters on silicon dioxide are interrogated by charge-state resolved Low Energy Ion Scattering (LEIS). The LEIS data are analyzed in a novel way that quantitatively reveals information about the homogeneity of the clusters' size distribution. The method utilizes the fact that the neutralization probability and the probability of multiple scattering (MS) both depend on the cluster size, but in different ways. Smaller nanoclusters are more likely to neutralize scattered alkali ions [1], while larger nanoclusters lead to more MS. Thus, in a system with a bimodal distribution of cluster sizes, multiply scattered ions are less likely to be neutralized. This leads to a difference in the spectral shapes of the scattered ions and neutrals. In contrast, a system with a homogeneous cluster size distribution yields identical spectral shapes. LEIS has advantages over the use of STM for measuring cluster size distributions, as it is easier to deploy over a wide range of preparation conditions and STM cannot probe disordered materials.

We collected time-of-flight LEIS spectra for 2 keV Na^+ ions scattered from Au nanoclusters formed by deposition onto SiO_2 at room temperature and after annealing to increasing temperatures. The inhomogeneity in the cluster size distribution is quantified with a metric obtained by analyzing spectra collected for different charge states of the scattered projectiles. It is found that the cluster sizes are fairly uniform after the initial deposition, but a heterogeneous distribution, presumably due to Ostwald ripening, develops after annealing above 700 K.

[1] G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. **92**, 216801 (2004).

8:40am SS+AS+NS-MoM2 Surface Hydrogen Stabilized Semiconductor Nanowire Growth, *S. Sivaram, N. Shin, L.-W. Chou, M.A. Filler*, Georgia Institute of Technology
Semiconductor nanowires exhibit tunable optoelectronic properties that are attractive for applications in energy conversion, electronics, and photonics. A fundamental knowledge of the chemical bonding that governs nanowire synthesis is essential for the *a priori* manufacture of nanowires with enhanced complexity and functionality. To that end, we studied the role of sidewall hydrogen during germanium nanowire synthesis with real-time *in situ* infrared spectroscopy. We show that covalently bonded hydrogen atoms are essential for stable <111> oriented growth and strongly influence sidewall morphology. Nanowire arrays with fixed diameter distributions and areal densities were synthesized via the vapor-liquid-solid (VLS) technique at a range of process conditions ($210 - 280$ °C, $5.0 \times 10^{-5} - 1.5 \times 10^{-4}$ Torr). Our spectra exhibit two intense absorption bands, at 1980 cm^{-1} and 1965 cm^{-1}, whose intensities are a function of substrate temperature, precursor pressure, and nanowire elongation time. Planar adsorption studies suggest that these bands result from hydrogen bonded at Ge(100)-like and Ge(111)-like surface sites, respectively. We also demonstrate that the *in situ* delivery of atomic hydrogen modifies the nanowire sidewall taper, which unambiguously confirms the importance of surface chemistry on nanowire growth.

9:00am SS+AS+NS-MoM3 Analyzing Capture Zone Distributions (CZD) in Growth: Theory and Applications, *T.L. Einstein*, University of Maryland, *A. Pimpinelli*, UMD and Rice Univ., *D.L. Gonzalez*, UMD and Univ. del Valle, Colombia, *R. Sathiyanarayanan*, IBM Semiconductor R&D, India
In submonolayer epitaxial island growth, it is fruitful to consider the distribution of the area of capture zones, i.e. Voronoi (proximity) cells constructed from the island centers. For random nucleation centers (Poisson Voronoi diagrams) the CZD is expected to follow a Gamma distribution, but more generally we have argued [1], drawing from experiences analyzing the terrace-width distributions of vicinal surfaces, that the CZD is better described by the single-parameter generalized Wigner distribution (GWD). Painstaking simulations by Amar's and Evans's groups showed inadequacies in our mean field Fokker-Planck argument relating the characteristic GWD exponent β to the critical nucleus size (conventionally called i+1), i.e. the size of the smallest cluster assumed not to decay. We refine our derivation to retrieve their finding that β is nearly $i + 2$ [2]. While the GWD describes the CZD in the regime in which there is significant data in experiments (i.e. between half and twice the mean), it has shortcomings in the tails at both high and low areas. For large areas, the distribution may decay exponentially rather than in gaussian fashion. We discuss several treatments of this issue, emphasizing the fragmentation model we developed [3], which depends on two physically motivated scaling exponents.

We discuss applications of this formula and methodology to experiments involving Ge/Si(001), various organics on SiO_2, and para-hexaphenyl (6P) films on amorphous mica. We report a series of studies by Fanfoni et al. of InAs quantum dots on GaAs and very recent applications to metallic droplets by Millunchick's group, also on GaAs. (The former also shows that the more-often-probed island-size distribution is comparable the CZD at lower temperatures but not at higher temperatures when detachment--and consequent coarsening--becomes important.)

We have also used the GWD framework to elucidate kinetic Monte Carlo studies of homoepitaxial growth on Cu(100) with codeposited impurities of different sorts. Finally, we have applied this approach to the distribution of metro stations in Paris [3] and to the distribution of of the areas of French districts (arrondissements) [3,4] , counties in southeastern US states [4], and other such secondary administrative units.

[1] Alberto Pimpinelli and TLE, Phys. Rev. Lett. 99, 226102 (2007)

[2] Alberto Pimpinelli and TLE, Phys. Rev. Lett. 104, 149602 (2010)

[3] Diego Luis González and TLE, Phys. Rev. E 84, 051135 (2011)

[4] Rajesh Sathiyanarayanan, Ph.D. thesis, U. Maryland, 2009; RS et al., preprint.

9:20am SS+AS+NS-MoM4 Novel Behavior in Droplet-Mediated Growth of III-V Nanostructures, *J. Tersoff*, IBM Watson Center **INVITED**
A variety of self-assembled nanostructures can be grown from either group IV or III-V semiconductors, including nanowires, quantum dots, and more complex structures. In many ways, the behavior of different semiconductors is surprisingly similar. However, the growth of III-V nanostructures has an additional degree of freedom, the III/V ratio; and in important respects III-V growth can be very different than group IV. This talk will present recent results for two widely-studied III-V systems: nanowire growth, and droplet epitaxy. In each case, theoretical modeling explains some surprising results of recent experiments. Using in-situ microscopy to study growth of GaP nanowires, Chou, Ross et al. have found remarkable differences in kinetics depending on III/V ratio. In particular, the presence of crystal defects causes dramatic fluctuations in growth rate in one regime, but not the other. For droplet epitaxy, Zhou, Jesson et al. used in-situ microscopy of GaAs to observe how different structures form. In particular, for the exotic double-ring structures, they found that the outer ring grows in an extended zone outside the droplet. For both nanowire growth and droplet epitaxy, the surprising experimental behavior is reproduced and explained theoretically, as arising from the competition between evaporation and diffusion on the surface, with very different kinetics for the group V vs group III species.

10:00am SS+AS+NS-MoM6 Size-effects in Photoemission and Optical Second Harmonic Generation Spectroscopy of Ge Nano-dots on Si(111), *K. Pedersen, J. Rafaelsen*, Aalborg University, Denmark
Silicon and germanium nano-dots self-organized on silicon surfaces are interesting from the point of view of silicon-based optoelectronic devices. In the size range from a few nm to a few tens of nanometers such structures show size-dependent electronic and optical properties [1].

Ge nano-dots have been grown on Si(111) covered by a thin oxide layer (~0.8 nm) using a wedge shaped deposition profile, resulting in varying nano-dot size along the sample profile. The prescense of the thin oxide triggers growth of nano-dots rather than flat Ge domains.

Samples were investigated by optical second harmonic generation (SHG) and photoemission spectroscopy (PES). Characterization of the growth of nano-dots with core level PES showed the decaying Si2p signal from the substrate and the increasing Ge3d signal from the growing amount of deposited Ge along the sample. The core level spectra confirm the growth mode discussed in the literature where it is suggested that contact is created between the Ge nano-dots and the Si substrate through the tin oxide [1]. Scanning electron microscopy on focused ion beam cut cross sections of the sample show that the nano-dots are largely spherical. Valence band PES shows that the position of the valence band maximum depends on nano-dot size in agreement with previous results in the literature [1].

Investigations of this system with SHG show that this technique provides a coherent surface sensitive optical probe of Ge nano-crystals on a Si surface. The signal from the nano-crystals is clearly separated from that of the substrate. It is found that the Si substrate resonance grows with Ge deposition, probably due to charges causing field induced SHG. The resonance in the Ge SHG signal can be ascribed to interband transitions at the L-point of the Ge band structure, usually referred to as the E1 critical point. With increasing particle size the Ge SHG resonance shifts towards lower energy and approaches the position expected for a plane surface. It should thus be noted that while size effects in valence band PES originate from states close to the Fermi level at the Γ- point the initial states for the SHG resonance are ~1.8 eV further down in energy at the L- point.

[1] A. A. Shklyaev and M. Ichikawa, Surface Science **514**, 19 (2002).

10:40am SS+AS+NS-MoM8 Study of the Coupling of Ultra-thin CdSe Double Quantum Wells, *J.A. Lorenzo-Andrade, F. Sutara, **I. Hernández-Calderón***, Cinvestav, Mexico

The degree of coupling between adjacent quantum wells (QW) will depend on the sample structure and electronic properties of the QW and barrier materials. The design of heterostructures containing multiple QWs requires the precise knowledge of the minimum barrier thickness to couple/uncouple the neighboring QWs. In this work we present the results obtained from calculations employing the matrix transfer method (MTM) and the analysis of the excitonic spectra of heterostructures containing two CdSe ultra-thin quantum wells (UTQWs). The thickness of each quantum well, in the range from 1 to 3 monolayers (ML), was identical (symmetrical structure) or different (asymmetrical structure). The UTQWs were grown by atomic layer epitaxy (ALE) within ZnSe barriers onto GaAs(001) substrates. Due to the finite confinement the wave function of electron and holes will penetrate the ZnSe barriers, the degree of coupling of the CdSe QUTWs will depend on the thickness of the separating barrier. Then, a practical approach to determine the thickness to uncouple the pair of symmetrical QWs is the analysis of the evolution of the energy levels of the QWs as a function of the separating barrier thickness: as soon as the energy levels present a negligible change (and then identical values), we have uncoupled the QWs. We observed that, the thinnest the quantum well the largest the penetration of the electron and hole wave functions into the ZnSe barrier. From the MTM calculations barriers in the range from 12 to 26 ML are necessary to uncouple symmetrical UTQWs with thickness in the range from 5 to 1 ML. These results are also useful to explain the behavior of the FWHM of the UTQWs as a function of their thickness. A similar approach was employed for the case of asymmetrical UTQWs. The coupling/uncoupling of asymmetrical structures was experimentally verified by the analysis of the excitonic spectra at low and room temperature: in the case of coupling only the lowest energy transition is observed; for the case of uncoupled UTQWs the photoluminescence spectrum presents two peaks, one for each independent UTQW.

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11:00am SS+AS+NS-MoM9 Fine Tuning of the Self-Ordered Nanostructured O/Cu(110) Surface, ***F. Wiame***, *C. Poulain, Z. Budinska, V. Maurice, P. Marcus*, Chimie ParisTech, France

Self-organized nanostructured surfaces have been the object of much interest in recent years due to their potential applications as possible alternative to standard lithography techniques. Kern *et al.* [1] demonstrate that a submonolayer coverage of oxygen deposited on Cu(110) may form periodic stripes aligned along the [001] direction and that the periodicity of the system depends on the coverage. However, although this method appears very promising for the growth of nanostructured materials, the practical applications are limited due to the relatively small domains of periodicity and size as defined by the Marchenko-Vanderbilt (MV) model [2]. For oxygen coverage θ_O ranging from $0.1 < \theta_O < 0.4$ (the full coverage corresponds to $\theta_O = 0.5$), the periodicity only varies from 6.5 nm to 11 nm and the oxide band width from 2 nm to 9 nm. We will show that these ranges can be significantly increased by the co-adsorption of small amounts of sulphur at the surface.

The new preparation method presented here, which consists in the partial coverage of the surface by sulphur before annealing of the oxidized surface, enables us to significantly enlarge the domain of accessible periodic structures. Periodicity up to 200 nm and oxide band width up to 30 nm can be reached in a straightforward, reproducible and controlled way. The band width and periodicity dispersions are not modified by the sulphur adsorption. Moreover, while the structure of the O/Cu(110)-(2×1) is fully determined by the surface coverage, our method allows us to define the periodicity independently of the oxygen coverage by adjusting the sulphur amount at the surface. A new model has been proposed in order to take into account the effect of the sulphur on the elastic constant of the system. This model allows a reinterpretation of results from the literature [3].

This new system may be used as a template for the growth of nanostructures as well as more fundamental purposes. Indeed, the use of such a versatile structure should enable to gain information e.g. on the elastic and electrostatic properties that are responsible for the nanostructuration of the surface or on the effect of quantum confinement by quasi-one-dimensional structure and how it is influenced by structural modification at the nanometer scale. Moreover, it may be seen as an ideal playground to test the change in the reactivity of a surface as a function of its structure.

[1] K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. Goerge, G. Comsa, Phys. Rev. Lett. 67, 855 (1991).

[2] V. I. Marchenko, JETP Lett 55, 73 (1992) ; D. Vanderbilt, Surf. Sci. 268, L300 (1992).

[3] K Bobrov, L. Guillemot, Surf. Sci. 604, 1894 (2010).

11:20am SS+AS+NS-MoM10 DFT Studies on the Adsorption and Diffusion of Small Rh and Au Clusters on Graphene/Ru(0001), ***D. Teng***, *D. Sholl,* Georgia Institute of Technology, *B. Habenicht, L. Semidey-Flecha, Y. Xu,* Oak Ridge National Laboratory

Stable metal nanoparticles grown on metal-supported graphene can in some circumstances form a periodic array and have potential applications in fields such as catalysis and nano-electronics. To understand their formation mechanism, we studied the adsorption and diffusion of monomers, dimers, and trimers of Rh and Au on graphene/Ru(0001) using Density Functional Theory (DFT). These two metal species exhibit distinct behaviors in cluster formation on graphene/Ru(0001). We determined the global minimum structure of Au_8 cluster on graphene/Ru(0001) using genetic algorithm. Our results on adsorption and diffusion of small metal clusters M_n (n=1, 2, 3) and Au_8 have given us insights into the nucleation process of metal clusters on graphene moiré and aid us on building a general model to describe the cluster growth mechanism on graphene moiré, which will provide guidance on designing supported sintering-resistant nanoclusters.

11:40am SS+AS+NS-MoM11 Nucleation of Copper Islands on Graphite, ***D. Appy***, *H. Lei, C.Z. Wang, D. Shao, E. Kwolek, P.A. Thiel*, Ames Laboratory, Iowa State University

Graphite, and surface processes on graphite, serves as a valuable benchmark for carbon-based materials such as graphene. We have studied copper on graphite, using STM in UHV, to determine the characteristic features of nucleation and growth of metal islands in this system. We have varied the parameters of deposition temperature, Cu coverage, and Cu flux. In the pre-coalescence regime of coverage, we find that Cu decorates step edges and also forms three-dimensional islands on the terraces. The areal density of the islands is 10^{-4} to 10^{-3} nm^{-2}, after growth at temperatures of 180 to 300 K, over a range of Cu flux and Cu coverage. This relatively-invariant density indicates that nucleation is heterogeneous. After annealing above room temperature (but well below the onset of desorption at about 900 K), both the density of Cu islands and the total volume of Cu are much lower. DFT is used to understand the processes and energetics in this system.

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