

Tuesday Afternoon, November 14, 2006

Surface Science

Room 2002 - Session SS1-TuA

Surface Structure and Morphology

Moderator: S. Chiang, University of California, Davis

2:00pm **SS1-TuA1 Interfacial Strains in Nanocrystals Revealed by Coherent X-ray Diffraction**, *I.K. Robinson*, University College and Diamond Light Source, UK

INVITED

Nanocrystals are fundamentally different from the bulk because strain can build up more easily inside the lattice. Interface from a nanometre-sized crystal to an adjacent material can lead to pattern formation, which can be very dramatic. X-ray diffraction is a generally useful way to measure structure at the atomic level. Recent development of methods exploiting the very high coherence of the latest sources have allowed direct imaging of crystal shapes at lower-than-atomic resolution. We have developed a new method to retrieve 3D complex density functions that reveal these strains. We will report new results in which interfacial strains between lead nanocrystals and SiO₂ substrates have been observed. "Partial Coherence Effects on the Imaging of Small Crystals using Coherent X-ray Diffraction", I. A. Vartanyants and I. K. Robinson, *Journal of Physics Condensed Matter* 13 10593-611 (2001). "Three-dimensional Imaging of Microstructure in Gold Nanocrystals", G. J. Williams, M. A. Pfeifer, I. A. Vartanyants and I. K. Robinson, *Physical Review Letters* 90 175501-1 (2003). "Three Dimensional X-ray Diffraction Microscopy", Ian Robinson and Jianwei Miao, *Materials Science Bulletin* 29 177-181 (2004). "Coherent X-ray Diffraction from Quantum Dots", I. A. Vartanyants, I. K. Robinson, J. Onken, M. A. Pfeifer, G. J. Williams, F. Pfeiffer, T. H. Metzger, Z. Zhong and G. Bauer, *Physical Review B* 71 245302 (2005).

2:40pm **SS1-TuA3 Binding Distances of Pi-conjugated Molecules on Cu(111) Studied by X-ray Standing Waves**, *A. Gerlach, F. Schreiber, S. Sellner*, Universität Tübingen, Germany; *N. Koch*, Humboldt University, Germany; *T.-L. Lee, J. Zegenhagen*, ESRF, France

Although the binding distances are very fundamental parameters, it is remarkable how little is known about these for most organic semiconductors on metal contacts. We study the adsorption of different aromatic molecules such as phthalocyanines, perylene derivatives, and oligoacenes on Cu(111) using the X-ray standing wave (XSW) technique. Element specific structural information of high precision is derived from the analysis of XSW yield measurements. Using the C(1s), N(1s), and F(1s) photoelectron signals we show that the molecules adsorb in a lying-down configuration, but with different distances relative to the metal substrate. The binding distances between the aromatic ring structure and the metal substrate are generally found to be larger than covalent bond lengths. Furthermore, we discuss more subtle effects as e.g. deformations of the adsorbed molecules that are related to the charge distribution at the interface, which can be discussed in terms of rehybridization. Finally, we discuss recent attempts to determine the bending of aromatic ring structures based on chemical shift in the XPS signal. A. Gerlach et al, *Phys. Rev. B* 71 (2005) 205425.

3:00pm **SS1-TuA4 Surface Segregation in a Polycrystalline Palladium-Copper Alloy**, *J.B. Miller, P. Ye*, Carnegie Mellon University; *C. Matranga*, U.S. Dept. of Energy; *A.J. Gellman*, Carnegie Mellon University

The surface composition of an alloy is rarely the same as its bulk. The differences are reflected in a number of important surface properties, including corrosion rates and catalytic activity. This work addresses the phenomenon of surface segregation in a polycrystalline palladium-copper alloy. Palladium-copper is of significant practical interest because of its potential as a hydrogen separation membrane for corrosive environments, like those found in coal gasification process streams. We combine X-ray Photoelectron Spectroscopy (XPS) and Low Energy Ion Scattering (LEIS) techniques to understand how the compositions of the surface region (SR, ~ top 3-4 atomic layers) and top layer (TL) of a bulk 70:30 (atomic) Pd:Cu alloy vary with thermal treatment and adsorption of hydrogen sulfide. On the clean surface, copper enrichment, both in the SR relative to the bulk and in the TL relative to the SR, occurs at all temperatures above 600K. Adsorption of sulfur as hydrogen sulfide results in a palladium-only TL, illustrating how the presence of an adatom can significantly affect segregation patterns. We consider our results from the perspective of

thermodynamic theory, and demonstrate that consideration of the heat of mixing is important for a complete description of this system.

3:20pm **SS1-TuA5 Sub-monolayer Sn/Cu(001) and Sn/Si/Cu(001) Structures**, *J. Lallo, L.V. Goncharova, B.J. Hinch, S. Rangan, R.A. Bartynski*, Rutgers University; *D. Strongin*, Temple University

Studies of Sn metal films on copper have been undertaken, as part of a wider program in understanding the thermal stability of Sn, and Sn with Si, films on copper surfaces. This STM investigation is motivated by the promoter effects of Sn in dichloro-dimethyl-silane production from Si/Cu catalysts. Four periodic superstructures, with sub-monolayer tin films grown at room temperature, have been seen with LEED. Comparatively recently, helium atom scattering (HAS) studies have also identified a superlattice phase at room temperature. While one STM identified phase has been previously reported in this presentation we will show images of each of the known phases, and of surfaces supporting co-existing phases. Auger Electron Spectroscopy (AES) is used to establish relative Sn coverages, and to correlate the STM images with previously reported LEED and He diffraction data. We propose atomic structures for each of the stable room temperature Sn/Cu(001) phases. We also report on the thermal stability of these phases. At least one additional phase is produced only on annealing to 450K. Finally we present data on an ordered ternary Sn/Si/Cu(001) phase, and discuss the thermal stability of this phase also. L. Goncharova, Ph.D. Thesis, May 2003, Chemistry; Rutgers, The State University of New Jersey. A.A. Cafolla, E. McLoughlin, *Surface Science* 544 (2003) 121-133.

3:40pm **SS1-TuA6 Epitaxial Growth of Gd Silicide Nanostructures on Si(001)**, *G. Ye, M.A. Crimp*, Michigan State University; *J. Nogami*, University of Toronto, Canada

Self-assembled gadolinium disilicide nanostructures grown on Si(001) substrates have been studied by scanning tunneling microscopy, transmission electron microscopy and atomic force microscopy. The nanostructures can be divided into two classes: highly elongated nanowires with hexagonal crystal structure and compact, rectangular islands with orthorhombic (or tetragonal) crystal structure. The different polymorphs of GdSi₂ have slightly different lattice parameters, and the nanostructure morphology is correlated with the magnitude and the direction of the silicide lattice mismatch with respect to the substrate. Different crystal structures can coexist within a single nanostructure, and the microscopy suggests that this is a result of phase transformation rather than coalescence. Possible mechanisms for this transformation are discussed. These results will be compared with similar data from Dy, Tb, and Sc silicide nanostructures to further reinforce the relationship between nanostructure morphology and crystal structure in these systems.

4:00pm **SS1-TuA7 Impact of Intrinsic Vacancy Ordering on Nanoscale Morphology and Structure: (Group-III)Al_xSe_y on Si(111)**, *C.Y. Lu, T.C. Lovejoy, M.A. Olmstead, F.S. Ohuchi*, University of Washington

Group III-Selenide semiconductors, where III=Al, Ga and In, are both structurally and chemically compatible with silicon, and have potential applications for spintronics and phase change memory devices. They crystallize a variety of bulk structures that incorporate intrinsic vacancies, including layered, defected zinc-blende, and defected wurtzite. Heteroepitaxy allows control of nanostructure morphology by inducing different arrangements of intrinsic vacancies. We report here an in-situ study using scanning tunneling microscopy and photoelectron spectroscopy to elucidate the role of intrinsic vacancies when Group III-Se films are grown on Si(111). Growth of Al_xSe_y starts with a stable AlSe bilayer, followed by growth of Al₂Se₃, which forms triangle islands with edges aligned to directions of Si(111), consistent with wurtzite Al₂Se₃ (helical vacancy structure). Ga_xSe_y also starts with a stable interface bilayer (GaSe), but subsequent growth is layered Ga₂Se₃, with intrinsic vacancies in planes between the layers. For In_xSe_y, a stable InSe bilayer is not formed. Rather, it keeps the 7x7 substrate registry intact, eventually wetting the surface to form a flat morphology with ~10 nm hexagonal domains separated by misfit dislocations, consistent with crystalline In₂Se₃. This is despite the +4% lattice mismatch that might be expected to lead to 3-D island formation.

Tuesday Afternoon, November 14, 2006

4:20pm **SS1-TuA8 Anisotropy in the Continuum Step Model: From Step Stiffness to Step-Edge Mobility***, *T.J. Stasevich, C. Tao, E.D. Williams, T.L. Einstein*, University of Maryland

The evolution of vicinal surfaces can be efficiently simulated using the continuum step model.¹ An important model parameter is the step stiffness, which quantifies how easily a step fluctuates and responds to driving forces. Due to the underlying crystal structure of vicinal surfaces, the stiffness can depend sensitively on step orientation, especially at temperatures low compared to the surface roughening transition (for noble metals, room temperature is considered low). Analytically accounting for this anisotropy within a lattice-gas framework is challenging, making direct comparisons with experiment or implementation in simulations time-consuming and computationally demanding. In this talk, we discuss simple, low-temperature approximations for the stiffness anisotropy on both {001} and {111} surfaces.² These approximations only fail for steps aligned close to the high-symmetry direction, where an exact, explicit solution can fortunately be obtained. We exploit this by combining our simple formulas with small-angle expansions of the high-symmetry solutions, producing explicit, analytic approximations for the full anisotropy of step stiffness, accurate at nearly all experimentally relevant temperatures. We have recently implemented our formulas into finite-element simulations of the continuum step model. To make contact with experiment, we simulate the relaxation of a Ag(111) step initially pinned by surface impurities. By STM scanning, one pinning point was removed, and the step was thereafter observed to relax to a more favorable configuration. Matching our simulation to the experiment allows us to extract information about the adatom step-edge mobility,³ a parameter traditionally difficult to isolate. ⁴ *Work supported by NSF-MRSEC at UMD.¹ Jeong and Williams, Surf. Sci. Rep. 34, 171 (1999).² Stasevich et al., PRB 70, 245404 (2004) and PRB 71, 245414 (2005).³ Tao et al., PRB 73, 125436 (2006).

4:40pm **SS1-TuA9 Argon Beam Mediated Modification of Nanotube-Based Structures using Classical Molecular Dynamics**, *S.K. Pregler, S.B. Sinnott*, University of Florida

Argon deposition on polymer and nanostructured carbon substrates can induce localized surface chemical modifications that include cross-linking and chemical functionalization. Here, we examine argon deposition at 80 eV on graphite sheets, multi-walled carbon nanotubes, and polymer-carbon nanotube composites at experimentally relevant fluences. The approach is classical molecular dynamics simulations using the reactive empirical bond-order (REBO) potential to determine the interactions for short-ranged interactions and the Lennard-Jones potential to determine the forces for long-ranged interactions in the multi-walled carbon nanotube and nanotube-polymer composite systems. The graphite system is modeled with the adaptive intermolecular REBO (AIREBO) potential. Several types of defects are predicted to occur in the graphite system, and they show good agreement with experimental findings. In the case of the multi-walled carbon nanotube system, the influence of deposition on the mechanical properties of the nanotube (sword-in-sheath failure) is shown to be considerable. Lastly, the argon beam is predicted to cause substantial changes to the interfaces in the nanotube-polymer composite systems. This work is supported by the National Science Foundation (CHE-0200838).

Author Index

Bold page numbers indicate presenter

— B —

Bartynski, R.A.: SS1-TuA5, **1**

— C —

Crimp, M.A.: SS1-TuA6, **1**

— E —

Einstein, T.L.: SS1-TuA8, **2**

— G —

Gellman, A.J.: SS1-TuA4, **1**

Gerlach, A.: SS1-TuA3, **1**

Goncharova, L.V.: SS1-TuA5, **1**

— H —

Hinch, B.J.: SS1-TuA5, **1**

— K —

Koch, N.: SS1-TuA3, **1**

— L —

Lallo, J.: SS1-TuA5, **1**

Lee, T.-L.: SS1-TuA3, **1**

Lovejoy, T.C.: SS1-TuA7, **1**

LU, C.Y.: SS1-TuA7, **1**

— M —

Matranga, C.: SS1-TuA4, **1**

Miller, J.B.: SS1-TuA4, **1**

— N —

Nogami, J.: SS1-TuA6, **1**

— O —

Ohuchi, F.S.: SS1-TuA7, **1**

Olmstead, M.A.: SS1-TuA7, **1**

— P —

Pregler, S.K.: SS1-TuA9, **2**

— R —

Rangan, S.: SS1-TuA5, **1**

Robinson, I.K.: SS1-TuA1, **1**

— S —

Schreiber, F.: SS1-TuA3, **1**

Sellner, S.: SS1-TuA3, **1**

Sinnott, S.B.: SS1-TuA9, **2**

Stasevich, T.J.: SS1-TuA8, **2**

Strongin, D.: SS1-TuA5, **1**

— T —

Tao, C.: SS1-TuA8, **2**

— W —

Williams, E.D.: SS1-TuA8, **2**

— Y —

Ye, G.: SS1-TuA6, **1**

Ye, P.: SS1-TuA4, **1**

— Z —

Zegenhagen, J.: SS1-TuA3, **1**