# Tuesday Morning, October 16, 2007

## Surface Science

## Room: 611 - Session SS2-TuM

## Surface Structure and Growth on Metals

**Moderator:** T. Risse, Fritz-Haber-Institut der MPG, Germany

8:00am **SS2-TuM1 Crystalline Structure of Sn/Cu(100) Across a Surface Phase Transition**, ***J. Martínez-Blanco***, *V. Joco,* Universidad Autónoma de Madrid, Spain, *C. Quirós,* Universidad de Oviedo, Spain, *P. Segovia, E.G. Michel*, Universidad Autónoma de Madrid, Spain

The crystalline structure of 0.5 monolayer of Sn atoms adsorbed on Cu{100} has been studied by surface X-ray diffraction (SXRD) measurements. This surface undergoes a temperature-induced phase transition at 360 K from a single domain ($\sqrt{2}$ x $\sqrt{2}$)R45° phase at high temperature to a two rotated domains ($3\sqrt{2}$ x $\sqrt{2}$)R45° phase at low temperature. In a previous work[1] this phase transition was identified as being due to the stabilization of a charge density wave (CDW), with gapping of nested regions of the high temperature Fermi surface in excellent agreement with the CDW periodicity. We performed temperature-dependent SXRD measurements in order to obtain information on the atomic displacements across the phase transition and to understand the nature of the two phases observed. A full data set including in-plane reflections, superstructure rods and crystal truncation rods was measured for each phase. The optimization method employed for fitting the experimental data for both the high and low temperature phases is a type of genetic algorithm called Differential Evolution,[2] used in this work for the first time to extract crystallographic information from SXRD data. For the low temperature phase, we compare the model obtained with a previous surface structure model.[3] Our results confirm the removing of every third row of copper in the alloyed top layer and a concomitant pairing of Sn atoms as the origin of the triple periodicity. However, we obtain slightly different values for the atomic displacements in deeper layers. For the high temperature phase, the overall dependence of the measured structure factors with the perpendicular momentum transfer is similar to the values extracted from the low temperature phase, suggesting a disordered nature for the high temperature phase. We propose a detailed model for this phase and for the nature of the thermal induced disorder. We discuss possible mechanisms to keep the local structure across the phase transition and the nature of the high temperature disordered phase.

[1]J. Martínez-Blanco et al., Physical Review B, 72 (2005), 041401(R)
[2]M. Wormington et al., Phil. Trans. Roy. Soc. London Sers A, 357 (1999), 2827-2848
[3]K. Pussi et al., Surface Science, 549 (2004), 24-30.

8:20am **SS2-TuM2 Self-assembled MnN Superstructure on Cu(001) Surface**, *X. Liu, B. Lu, T. Iimori,* ***K. Nakatsuji***, *F. Komori*, University of Tokyo, Japan

Recently, self-assembled nanostructures have attracted tremendous interest. Among them, the ones with regular spatial array, uniform and well-defined geometric and structural characters, are especially desirable. However, it is still difficult to prepare such high-quality nanostructures. In the present paper, we describe the fabrication of self-assembled manganese nitride nano-islands on the Cu(001) surface and propose a new mechanism of the nano-self-assembling.[1] Each island shows a square shape and has a well-defined size of 3 nm x 3 nm. They are regularly arranged with a periodicity of (3.5 ± 0.1) nm and form a two-dimensional square superstructure. The depth of the trench between the islands is the same as the step height of the surface or the height of the island on the superstructure. The nano-islands adopt a NaCl-like structure which is oriented in the same way as the fcc Cu(001) substrate. They are reproducibly prepared in three steps in ultrahigh vacuum by mono-atomic layer of Mn deposition, atomic nitrogen exposure to the saturation and gradual annealing up to 630 K. The stoichiometry of the manganese nitride islands has been studied by in-situ X-ray photoelectron spectroscopy. It is determined that the formula of the manganese nitride is MnN. This stoichiometry is the same as that of the bulk MnN crystal, which has a face-centered tetragonal structure (distorted NaCl structure) with a lattice constant lager than that of Cu(001).[2] Thus, the nanostructure formation is attributed to strain-relief at the interface. However, different from the conventional stress-domain dominated self-assembly, the shape, size, and periodicity of the MnN islands do not change even when they coexist with the clean Cu(001) surface. This indicates that the self-assembling is driven not by the long-range strain relief, but by a short-range mechanism.

[1]X. Liu, B. Lu, T. Iimori, K. Nakatsuji and F. Komori, Phys. Rev. Lett. 98, 066103 (2007).
[2]K. Suzuki, T. Keneko, H. Yoshida, Y. Obi, H. Fujimori, and H. Morita, J. Alloys Comp. 306, 66 (2000).

8:40am **SS2-TuM3 Surface Morphology and Step Fluctuations on Ag Nanowires**, ***C.G. Tao****, *W.G. Cullen, E.D. Williams,* The University of Maryland, College Park, *S.E. Hunyadi, C.J. Murphy*, The University of South Carolina

Semiconducting and metallic nanowires have been the subject of intense research efforts for their potential applications in nanoscale electrical circuits and chemical sensors. For all the applications, and especially for sensors, the morphological and thermodynamic nature of the nanowire surfaces, including the presence of defects like steps and twin boundaries, play a crucial role in the functional response. Even though there have been many demonstrations of nanowire applications, extremely few studies directly address the issues of cleanliness and structural morphology of the surfaces of nanowires at the atomic scale. Here we will present the surface morphology and thermodynamic properties of Ag nanowires, characterized by scanning tunneling microscopy (STM) at room temperature. The Ag nanowires were prepared via a seedless, surfactantless wet chemical synthesis process and suspended in water. They then are redispersed into methanol by centrifugation, and are deposited onto atomically clean Ag thin films in ultra-high vacuum via a solution deposition method. By gently annealing the samples, methanol on the substrate and the surfaces of Ag nanowires is removed. The STM topography images reveal the facets of the penta-tetrahedrally twinned crystals which constitute the Ag nanowires, and sawtooth features of the boundaries of neighboring twinned crystals. On the facets, frizzy monatomic steps and rectangular shapes monolayer islands are clearly observed. Using a dynamic STM scan method, we obtain quantitative properties of step fluctuations, which are governed by periphery diffusion. Combing previous density functional theory (DFT) calculations and dynamics studies on low-index faces of Ag, we propose that the side facets are Ag(100) surfaces. Related studies about the time evolution of the twin boundaries and how the surface defects are associated with the electrical current flowing through the nanowires will also be discussed. --Supported by the NSF MRSEC (DMR 05) at the University of Maryland.

9:00am **SS2-TuM4 Capture-Zone Scaling and Universal Fluctuation Phenomena**, ***T.L. Einstein***, University of Maryland, *A. Pimpinelli*, Univ. of Maryland & U. Blaise Pascal--Clermont 2, France

As one approaches the nanoscale, fluctuations play an ever more important role in the physics of systems. Universal aspects of fluctuations are thus an especially timely topic. The Wigner distribution from random matrix theory has successfully described a vast array of physical phenomena, from energy spacings between nuclear levels to conductance fluctuations in wires, as well correlations of stock prices, spaces between parked cars, and times between successive unscheduled buses. It is easy to use, having the simple, one-parameter form a $s^{\beta}$ exp $(-bs^2)$ [with a and b being constants assuring normalization and unit mean, and s the fluctuating variable divided by its mean]. Here we apply this approach to the long-standing problem of island-size distributions during growth. We consider the distribution of the areas of Voronoi polygons (proximity cells) around nucleation centers, i.e. the capture zones (CZ). Generalizations of the Wigner distribution (to allow more than the 3 values of β based on symmetry) account well for data generated in kinematic Monte Carlo studies by several groups, much as it did for terrace-width distributions (TWD) on vicinal surfaces. For CZ distributions we find $\beta = i + 1$, where i is the size of the critical nucleus. (In spatial dimension $d = 1$, $\beta = 2(i + 1)$.) We demonstrate excellent fits of numerical data for both $d = 1$ and $d = 2$. To clarify the underlying physics, we present a phenomenological derivation by constructing a Langevin equation similar to that used in accounting for the equilibration of TWDs; we discuss the competing forces that lead to the WD. Our expression also describes well experimental data for pentacene adsorption and for CZ distribution of growing quantum dots. We compare this analysis with others using less-well-motivated Gamma distributions or more complicated expressions.

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***** Morton S. Traum Award Finalist

9:20am **SS2-TuM5 Sulfur Adsorption on Ag(111): Self-Organization of Metal-Sulphur Complexes below 300K**, ***M. Shen***, Iowa State University, *D.-J. Liu, C.J. Jenks, J.W. Evans, P.A. Thiel*, Ames Laboratory - USDOE, Iowa State University

We have investigated the interaction of sulfur with Ag(111). Sulfur was deposited using an electrochemical evaporator, which generated gas-phase sulfur in the form of $S_2$. Sulfur coverage was measured with Auger electron spectroscopy.[1] Images from scanning tunneling microscopy (STM) showed different structures at temperatures between 135 and 300 K. Deposition at 135 K led to the formation of two-dimensional (2D) islands. After heating to 200 K, the surface exhibited a quasi-1D "dot-row" structure, in which each dot was about 0.7 nm in diameter. The dots were aligned in rows that were separated by distances ranging from about 1.6 to 5 nm. Cooling back to 135 K did not restore the initial 2D island structure, indicating that the 2D islands may consist of $S_2$ that dissociates irreversibly in the heating step. At 300 K, no ordered structures were visible, suggesting that the adsorbate becomes very mobile. The STM observations at 300 K and 200 K could be produced reversibly, pointing to a reversible phase transition below room temperature. Development of the dot-row structure at high S coverage was accompanied by pitting on the terraces, indicating participation of Ag. DFT calculations show that $Ag_3S_3$ is a candidate for the dots. This complex is analogous to a metal-sulfur complex that has been proposed to exist on Cu(111).[2]

[1] K. Schwaha, N.D. Spencer, R.M. Lambert, Surf. Sci., 81, 273 (1979).

[2] P.J. Feibelman, Phys. Rev. Lett., 85, 606 (2000).

9:40am **SS2-TuM6 Structure of the Al(100)-c(2x2)Ti Surface***, ***M. Kopczyk***, *W. Priyantha, H. Chen,* Montana State University, *D. Tonn,* Balwin-Wallace Collage, *R.J. Smith,* Montana State University, *D.S. Choi,* Kangwon National University, Korea, *G. Bozzolo*, Ohio Aerospace Institute

The atomic structure of sub-monolayer amounts of Ti deposited on the Al(100) surface at room temperature has been studied using low-energy electron diffraction (LEED) and low-energy ion-scattering spectroscopy (LEIS/ ISS). The Ti coverage was determined using Rutherford backscattering spectroscopy. From the symmetry of the observed c(2x2) LEED images we infer a structure which places the Ti atoms in every other Al unit cell. Analysis of the LEIS spectra, including both azimuth- and polar-angle scans, corroborates this hypothesis. This conclusion is relevant to recent studies of Ti as a catalyst in Na alinates presently being studied for their use in hydrogen storage applications important in fuel cell research.

*This work was supported by the National Science Foundation, NSF Grant DMR 0516603.

10:40am **SS2-TuM9 Hard Superconductivity in Soft Quantum Films**, ***H.H. Weitering***, University of Tennessee **INVITED**

Superconductivity is inevitably suppressed in reduced dimensionality. Questions of how thin superconducting wires or films can be before they lose their superconducting properties have important technological ramifications and go to the heart of understanding coherence and robustness of the superconducting state in quantum-confined geometries. In this talk, I will show how quantum confinement of itinerant electrons in a soft metal, Pb, can be exploited to stabilize superconductors with lateral dimensions of the order of a few millimeters and vertical dimensions of only a few atomic layers. These extremely thin superconductors show no indication of defect- or fluctuation-driven suppression of superconductivity and sustain enormous supercurrents of up to 10% of the theoretical depairing current density. Their magnetic hardness implies a superconducting critical state with strong vortex pinning that is attributed to quantum trapping of vortices. Our study paints a conceptually appealing, elegant picture of a model nanoscale superconductor with calculable critical state properties and surprisingly strong phase coherence. Finally, I will show how the quantum growth and superconductive properties of the films can be tailored by Fermi surface engineering, and I will discuss the possibility of multi-gap superconductivity in quantum-confined thin films. This work was done in collaboration with M.M. Ozer, J.R. Thompson, Yu Jia, and Z.Y. Zhang.

11:20am **SS2-TuM11 Initial Bilayer-by-Bilayer Growth of Ag Islands on NiAl(110): DFT Analysis of underlying Quantum Size Effects**, ***Y. Han***, *D.-J. Liu, B. Unal, F. Qin, C.J. Jenks, J.W. Evans, P.A. Thiel*, Iowa State University

Growth of Ag on NiAl(110) is distinguished by an almost perfect match of the lateral unit cell of the substrate to that of Ag(110). Thus, Ag/NiAl(110) provides an ideal system in which to study morphological evolution during heteroepitaxy in the absence of lateral mismatch strain. Our STM studies reveal the nucleation and growth of large rectangular Ag islands for deposition of submonolayer amounts of Ag between 130K and 300K. Subsequent deposition produces smooth growth with large rectangular islands forming on top of coalesced clusters of such lower layer islands. However, the step height for the first layer islands is ~0.33 nm, and only slightly lower at ~0.29 nm for the next two layers. These values far exceed the step height of ~0.15 nm for Ag islands on Ag(110). Thus, we propose that islands have a predominantly bilayer Ag(110) structure for the first three (bi-) layers. This claim is supported by DFT calculations which reveal step heights for this structure in close agreement with experiment, and also indicate that the driving force for this bilayer growth is the presence of a quantum size effect perpendicular to the surface plane for electrons confined in the Ag film. Specifically, there is a strong oscillation of period 2 monolayers (ML) in the surface energy, and also in the binding energy of single Ag atoms on top of flat Ag films, favoring film heights equal to an even number of monolayers. For thicker films, step heights decrease so film structure must deviate from the perfect Ag(110) bilayer structure (a feature also reflected in a weak height modulation across the tops of Ag islands).

11:40am **SS2-TuM12 Role of Surface Structure on Thin Film Nucleation on Quasicrystal Surfaces**, ***B. Unal****, Ames Lab., Iowa State Univ., *V. Fournee,* CNRS-UMR7584, France, *K.J. Schnitzenbaumer, C. Ghosh,* Iowa State Univ., *C.J. Jenks,* Ames Lab., Iowa State Univ., *A.R. Ross,* Iowa State Univ., *T.A. Lograsso,* Ames Lab., Iowa State Univ., *J.W. Evans,* Iowa State Univ., *P.A. Thiel*, Ames Lab., Iowa State Univ.

Quasicrystals are non-periodic but well-ordered solids. Their unusual atomic structures foster peculiar surface properties such as low friction and enhanced oxidation resistance. Using scanning tunneling microscope (STM) we have investigated clean surfaces of icosahedral (i) Al-Pd-Mn quasicrystals. By analyzing bulk structural models of i-Al-Pd-Mn quasicrystals, we suggest a relationship between the terminating layers and the clusters that form the basic building blocks of quasicrystals. Using STM, we have also investigated the nucleation and growth of Ag islands on the fivefold surface of an i-Al-Pd-Mn quasicrystal. The temperature dependence of island density suggests that trap sites control nucleation of Ag islands. We identify these trap sites as the cut clusters in the aforementioned structure analysis. Furthermore, we have developed a mean field rate equation model to explain this behavior. Our model suggests that the binding energy between Ag atoms at traps are significantly higher than that of Ag at regular terrace sites and the size of critical clusters is larger than one. This model will allow (qualitative) manipulation of experimental parameters to tailor island characteristic on quasicrystal surfaces.

12:00pm **SS2-TuM13 A Photoelectron Diffraction Study of $Cu_3Mn(100)$**, ***J. King-Lacroix***, *N. Loh, D.-H. Yu, A.P.J. Stampfl,* Australian Nuclear Sci. and Tech. Org., *H. Ruppender, H. Over,* Justus-Liebig-Univ. Gießen, Germany, *E. Huwald, J.D. Riley,* La Trobe Univ., Australia, *A. Smith,* Monash Univ., Australia, *L.-J. Fan, Y.-W. Yang*, National Synchrotron Radiation Res. Ctr., Taiwan

In the Angstrom to nanoscale regime where electronic localisation blurs to itinerant behaviour, magnetic phenomena become highly dependent on dimensionality and local environment. Magnetic exchange between two different magnetic phases is one such phenomenon that is affected when dimensions are reduced to the nanoscale. We are specifically interested in studying the exchange properties at the interface of an antiferromagnetic or ferromagnetic material and a spin glass surface. Our first task however is to fully understand a spin-glass surface by mapping out the surface and bulk band structure as well as determine the surface crystalline structure. We have chosen the CuMn system because it represents a model spin-glass whose transition temperature is easily attainable. The bulk phase-diagram for the CuMn system displays a face-centered-cubic phase at room temperature for atomic percent concentrations of Mn from 0 to ~25% and the spin-glass transition temperature for CuMn in this percentage region increases linearly to ~110K at 25%at. Mn. We present here synchrotron-based azimuthal-scanned photoelectron diffraction measurements using the Cu and Mn 3p-orbitals from a $Cu_3Mn(100)$ surface and compare them to simulation and to corresponding data sets for Cu(100). The number of Mn-atoms in the upper-most layer is lower than expected from a truncated bulk surface suggesting surface segregation or oscillatory behaviour. Details of surface reconstruction and near-surface relaxation will be presented.

***** Morton S. Traum Award Finalist

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