### Friday Morning, November 6, 1998

### Surface Science Division Room 308 - Session SS1-FrM

### Surface Structure and Strain

Moderator: R.Q. Hwang, Sandia National Laboratories

8:20am SS1-FrM1 Ultrathin Metal Films on W(111) and W(211): Nanoscale Faceting, Structure, Electronic Properties, and Reactivity@footnote 1@, T.E. Madey, Rutgers, The State University of New Jersey INVITED The W(111) surface is morphologically unstable when covered by monolayer films of certain metals (including Pt, Pd, Rh, Au), and develops nanoscale 3-sided pyramidal facets with mainly [112] faces upon annealing. In the present work, we focus on the structure, electronic properties and reactivity of planar and faceted W(111) and W(211) covered by ultrathin films of metals (0 - 8 ML, mainly Pt, Pd, Rh) and non-metals (S, O). The measurements include UHV-STM, soft XPS (SXPS) using synchrotron radiation, Auger spectroscopy, LEED, and thermal desorption spectroscopy. The observed formation of 3-sided pyramids with both [110] and [112] facets, as induced by 1 ML of overlayer metal, is predicted also by recent first-principles calculations of surface energetics. The faceting is caused by an increased anisotropy in surface free energy that occurs for the filmcovered surfaces. The adsorption of S induces a different reconstruction with nanoscale texturing of the surface. At coverages above 1 ML, SXPS data indicate that interfacial alloys are formed upon annealing films of Pt and Pd, but not Au. These findings are discussed in terms of structural and electronic properties of bimetallic systems. The relevance to the surface chemistry of a structure-sensitive reaction (acetylene cyclization to benzene over Pd/W) is also discussed. @FootnoteText@ @footnote 1@Supported in part by US DOE, Office of Basic Energy Sciences @footnote 2@Collaborators include C.-H. Nien, J.J. Kolodziej, K. Pelhos, I. Abdelrehim, H.-S. Tao, R. Barnes (Rutgers); J. Keister, J.E. Rowe (NC State); J. Eng, J.G. Chen (EXXON); C-T. Chan (HKUST)

#### 9:00am **SS1-FrM3 Determination of Thin Film Interface Structure by the Quantum Size Effect in Electron Reflectivity**, *M.S. Altman*, *W.F. Chung*, Hong Kong University of Science and Technology, Hong Kong; *H.C. Poon*, *S.Y. Tong*, University of Hong Kong, Hong Kong

It has long been recognized that it is very difficult to obtain detailed structural information of buried interfaces. The quantum size effect (QSE) in electron reflectivity offers some interesting insight into this and other structural features of thin films. The QSE has been understood qualitatively in the past to be an interference phenomenon between the electron waves which are reflected from the surface of a thin film and from the interface between film and substrate. The prominent QSE interference peaks which occur at very low energies are sensitive indicators of film thickness. We have examined the QSE in electron reflectivity from Ag films on the W(110) surface using the low energy electron microscope (LEEM) as an electron interferometer. This approach allows the reflected intensity from regions of different film thickness to be distinguished with atomic precision. Fundamental disagreement was found between the unique experimental data provided by LEEM and the predictions of the simple free electron model which has been invoked in the past to explain the QSE. A quantum mechanical Kronig-Penney model is presented as the first step towards a better understanding of the QSE. An analysis of the QSE peak positions by dynamical theory, aided by R-factors, also provides an accurate determination of the Ag-W interface spacing as a function of the Ag film thickness.

#### 9:20am **SS1-FrM4 Interaction of Dislocations on Strained Metal Films**, *J. de la Figuera*, *K. Pohl, A.K. Schmid, N.C. Bartelt, R.Q. Hwang,* Sandia National Laboratories

Misfit dislocations appear in thin film growth to relieve the mismatch between substrate and film. A general family of dislocation networks has been found on substrates with triangular symmetry such as Pt(111), Ru(0001) and Au(111). A common uncertainty in understanding the observed surface structures is the stacking sequence followed by each adlayer, information that is relatively simple to extract for single layer films but requires more detailed information in multilayer films. Another recurrent question is the role played by the substrate in the network structure and periodicity, as some networks are attributed to ``long range elastic effects'' on one hand,@footnote 1@ but in other cases can be explained disregarding those effects.@footnote 2@ Cu on Ru(0001) presents a variety of different networks as a function of film thickness,@footnote 3@ and can be considered a testbed for the study of

misfit dislocations on a triangular substrate. But even in this case, most of the studies have not dealt in detail with the stacking sequence in the first few layers (other than by assuming that the dislocations observed are present at the interface between the substrate and the Ru film). We will discuss how one can use STM to unambiguously determine the stacking sequences in films thicker than one monolayer. We then proceed to determine the range of dislocation interactions. On the basis of these measurements it is possible to compare the model of long ranged dislocation interactions due to Ru substrate relaxations versus local exponentially decaying interactions between dislocations due to 2-D distortions within the Cu film. @FootnoteText@ @footnote 1@S. Narasimhan and D. Vanderbilt, Phys. Rev. Lett. 69, 1564 (1992). @footnote 2@J. C. Hamilton and S. M. Foiles, Phys. Rev. Lett. 75, 882 (1995). @footnote 3@C. Günther et al, Phys. Rev. Lett. 74, 754 (1995).

## 9:40am SS1-FrM5 Low Energy Electron Microscope Measurements of Oxygen-Induced Strain Relief on Si(001), J.B. Hannon, B.S. Swartzentruber, G.L. Kellogg, Sandia National Laboratories

Real-time observations of step configurations on Si(001) with the low energy electron microscope (LEEM) show a continuous and irreversible change in the populations of the (1x2) and (2x1) domains (i.e., the ratio of adjacent terrace widths) upon exposure to oxygen at elevated temperatures. In the initial configuration, populations of the two domains differ significantly due to an external strain field. Exposure of the surface to ~10@super-8@ Torr oxygen at temperatures between 750-850 C causes the domains to become approximately equal in area. Based on previous LEED and STM measurements,@footnote 1,2@ we conclude that the progression towards equal domain populations results from the removal of the external strain. During equilibration, the potential in which the step moves is determined from the step velocity. The measured exponential time dependence of the equilibration rate is consistent with step motion in the presence of the step-interaction potential proposed by Alerhand et al.@footnote 3@ This agreement implies that strain relief takes place on a time scale of a few seconds. We propose that the mechanism of strain relief is an oxygen-induced change in the shear threshold of Si due to dissolution of oxygen into the bulk. The ability to modify the elastic properties of materials with common adsorbates such as oxygen is important in heteroepitaxy where strain is known to play a key role in defining the properties of the epitaxial film. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000. @FootnoteText@ @footnote 1@F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. 61, 2469 (1988). @footnote 2@B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, JVST A8, 210 (1990). @footnote 3@O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. 61, 1973 (1988).

### 10:00am SS1-FrM6 The Strain Effect on Ge-covered Si(001) Surface, F.-K. Men, C.-R. Hsu, National Chung Cheng University, Republic of China

By loading the free end of a cantilevered bar, we have studied the effect of strain on the Ge-covered Si(001) surface. On this surface, strain produces a reversible change in the relative population of the 2xn and nx2 domains. This change is driven by the relaxation of the energy associated with a longrange strain field extending into the bulk due to the anisotropy of the intrinsic stress tensor of the two reconstructed domains. The dependence of the surface stress anisotropy, defined as the difference of the components of the surface stress tensor parallel and perpendicular to the dimer bond, on the Ge overlayer thickness has been studied. By varying the separation between two neighboring dimer vacancy lines (DVL's) we have investigated the DVL-DVL interaction. Based on a linear-dipole-force model for the step-step interaction and the theory of long-range elastic relaxation of orientationally inequivalent domains, we have estimated the DVL formation energy and the DVL-DVL interaction strength. We have also studied the change in the relative population of the two orthogonal domains as a function of time at different temperatures. Results on the kinetics of the step migration will be presented.

10:20am **SS1-FrM7 Spontaneous Domain Formation on Ge(001)**, *H.J.W. Zandvliet*, University of Twente, The Netherlands; *B.S. Swartzentruber*, Sandia National Laboratories; *E. Zoethout, G. Rosenfeld, B. Poelsema*, University of Twente, The Netherlands

Scanning tunneling microscopy measurements of Ge(001) reveal the presence of an ordered domain pattern consisting of c(4x2) and (2x1) domains arranged in stripes with a width of several dimer row spacings, oriented along the dimer rows. We suggest that the existence of a soft domain wall between the domains combined with a difference in the stress

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component along the dimer bond for the (2x1) and c(4x2) domains, respectively, can produce such an ordered domain phase. We have observed fluctuations of the domain walls indicating that the system is in thermal equilibrium. A simple model based on strain relaxation explains the observed size of the domain pattern.

#### 10:40am SS1-FrM8 New Results for Analytical Approximants of Terrace-Width Distributions on Vicinal Surfaces, and Some Consequences@footnote 1@, T.L. Einstein, O. Pierre-Louis, University of Maryland, College Park; B. Joós, University of Ottawa, Canada

Quantitative measurement of the equilibrium terrace width distribution P(L) of vicinal surfaces has proved a powerful and convenient way to investigate the interactions between steps. Most analyses have relied on simple analytic results based on the Gruber-Mullins approximation; one "active" step wandering between two fixed straight steps separated by twice the average step spacing . For non-interacting, free-fermion (FF)-like steps, P(L) corresponds to the ground-state density of a confined fermion, going like sin@super 2@(@pi@L/2), while for significant repulsions decaying as A/L@super 2@, this density is a Gaussian.@footnote 2@ For both cases, P(L) vs. L/ can be written as a "universal function." Rather complicated analytic expressions can be written for FF@footnote 3@ and for a special value of A. For FF, H. Ibach concocted a simple but excellent approximation for P(L) involving a power law and a gaussian decay.@footnote 4@ This expression turns out to be the celebrated "Wigner surmise" for the distribution of energies in gaussian unitary ensembles, long known to correspond to free fermions. Based on this recognition and results from random-matrix theory, we present a general universal expression that has just one fitting parameter, the power, from which A can be easily estimated. We provide calibrations at the values of A for which exact solutions exist. We use these results to clarify recent controversies@footnote 5@ about how to extract A from P(L). We also discuss what can be learned from the third moment of P(L) and from the covariance of adjacent terrace widths. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@N. C. Bartelt, T. L. Einstein, and E. D. Williams, Surface Sci. 240, L591 (1990). @footnote 3@B. Joós, T. L. Einstein, and N. C. Bartelt, Phys. Rev. B 43, 8143 (1991). @footnote 4@H. Ibach, private communcation; M. Giesen, Surface Sci. 370, 55 (1997). @footnote 5@L. Masson, L. Barbier, J. Cousty, and B. Salanon, Surface Sci. 317, L1115 (1994); L. Barbier, L. Masson, J. Cousty, and B. Salanon, Surface Sci. 345, 197 (1996); T. Ihle, C. Misbah, and O. Pierre-Louis, Phys. Rev. B 58, xxx (1998).

# 11:00am SS1-FrM9 Enantiospecific Adsorption of Chiral Hydrocarbons on Naturally Chiral Pt and Cu Surfaces, *T.D. Power*, *D.S. Sholl*, Carnegie Mellon University

Many stepped metal surfaces exhibit chiral step structures which can, in principle, affect the properties of adsorbed chiral molecules@footnote 1@. These highly characterizable systems may be useful for isolating the fundamental mechanisms of enantiospecific reactions in chirally active heterogeneous catalysts. We have used Monte Carlo simulations to examine the energetic and entropic contributions to the free energy of adsorption of several chiral hydrocarbons adsorbed on naturally chiral Pt and Cu surfaces. By simulating both enantiomeric forms of the adsorbates, we are able to directly probe the enantiospecific nature of the adsorbate/surface interactions. These simulations have allowed us to explore the roles of adsorbate size and surface step spacing. Our results indicate that many examples of enantiospecific adsorption exist in which the energy shifts between enantiomers should be readily detectable using standard experimental tools such as Temperature Programmed Desorption. @FootnoteText@ @footnote 1@ C. F. McFadden, P. S. Cremer, and A. J. Gellman, Langmuir, 12 (1996) 2483.

### 11:20am **SS1-FrM10 Xe Adsorption Sites on Metal Surfaces**, *M. Caragiu*, *Th. Seyller, R.D. Diehl*, Pennsylvania State University; *P. Kaukasoina, M. Lindroos*, Tampere University of Technology, Finland

Based on an adsorbate-substrate potential which consists of the attractive van der Waals interaction and a repulsive interaction due to wave function overlap, the equilibrium site for physisorbed noble gases would be expected to be a high-coordination site. The presumption which arose from this expectation, that physisorbed atoms prefer high-coordination sites, has been a great hindrance to the development of physisorption potentials since it has delayed experiments to measure the adsorption geometries of physisorbed atoms. Several years ago, a top-site geometry was proposed for Xe/Pt(111) based on He-atom diffraction intensities from an incommensurate phase, although this assignment was disputed by a later SPLEED study. Nevertheless, a density-functional theory cluster calculation

suggested that a preference for top sites in this case may arise from the hybridization of the Xe 5p electrons with the Pt 6d states. Recently it has been shown that Xe on Ru(0001) adsorbs in the top-site geometry in the (@sr@3x@sr@3)R30° phase. If hybridization with substrate d-states is the origin for top-site adsorption, then Xe would not be expected to occupy the top sites on Cu surfaces where the d-states are several eV below the Fermi energy. We present the findings of LEED I(E) studies of Cu(111)-(@sr@3x@sr@3)R30° and Pt(111)-(@sr@3x@sr@3)R30° which were carried out to test this hypothesis and to resolve the disagreement on the adsorption site for Xe on Pt(111). These LEED studies indicate that Xe occupies the top site in both cases. Since it is unlikely that Xe atoms hybridize appreciably with the deep d-levels in Cu(111), we propose a new model for Xe adsorption on metal surfaces in which the hybridization occurs between the occupied part of the excited Xe 6s resonance (which extends below the substrate Fermi energy) and the unoccupied substrate orbitals near the Fermi level.

11:40am **SS1-FrM11 A NIXSW Study of the InP(001)-(4x2) and InP(001)-(1x1)-Cl Surfaces**, A.A. Davis, C.J. Fisher, **R.G. Jones**, University of Nottingham, United Kingdom; G. Scragg, J. Ludeke, D.P. Woodruff, University of Warwick, United Kingdom; B.C.C. Cowie, Daresbury Laboratory, United Kingdom

The Normal Incidence X-ray Standing Wave (NIXSW) technique has been used to study the reconstructed, indium terminated InP(001)-(4x2) surface and the InP(001)-(1x1)-Cl chemisorbed surface, using the (002), (20-2) and (113) Bragg reflections. Auger electrons and photoelectrons from the In, P and Cl were used to monitor the X-ray absorption profiles. The reconstructed, indium terminated surface was found to contain In dimers orientated in the direction of the four times periodicity, which is in contrary to earlier studies, but in agreement with the findings of Sung et al.@footnote 1@ The chemisorbed chlorine surface had chlorine bonded to the top layer In atoms with the In-Cl bond probably extending along the [110] substrate direction. The inadvisability of using low energy Auger peaks, and the effects of non-dipole photoemission in XSW determinations, are also discussed. @FootnoteText@ @footnote 1@M. M. Sung et al; Surface Sci. 322(1995)116

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