Surface Science
Room 200 - Session SS1-WeA
Surface Structure and Morphology Modification

Moderator: P.F. Lyman, University of Wisconsin-Milwaukee

2:00pm **SS1-WeA1 Structure and Reactivity of Nanoscale Faceted Surfaces***, **T.E. Madey**, I. Ermanoski, H. Wang, W. Chen, A.S.Y. Chan, E. Loginova, N.M. Jisrawi,* Rutgers University*; W. Swiech,* University of Illinois at Urbana-Champaign **INVITED**

Many planar metal surfaces that are rough on the atomic scale, such as fcc Ir(210), hcp Re(12_31), NiAl(111) and bcc W(111), are morphologically unstable when covered by monolayer films of oxygen, or of certain metals: they become "nanotextured" when heated to elevated temperatures. Faceting occurs when an initially planar surface converts to a "hill and valley" structure, exposing new crystal faces of nanometer scale dimensions. Faceting is driven by surface thermodynamics (anisotropy of surface free energy), but controlled by kinetics (diffusion, nucleation). We report here on the relations between structure, reactivity and electronic properties of nanoscale faceted surfaces. Measurements include STM, LEED, TPD, low energy electron microscopy (LEEM) and soft x-ray photoemission (SXPS) using synchrotron radiation. For example, annealing oxygen-covered Re(12_31) gives a sequence of faceted surfaces ranging from from long sawtooth ridges, to complex structures exposing up to 5 different facets. Surface reactivity of O-covered Re is sensitive to facet structure. Oxygen-faceted NiAl(111) is covered by an alumina "skin". Annealing O-covered Ir(210) generates nanoscale pyramids with {311} and (110) facet orientations; average pyramid sizes 5 to 15 nm are controlled by annealing T. Oxygen can be completely removed at low T (by exposing to H@sub2@, to form H@sub2@O) thus creating a clean, faceted surface that is stable to 600K. Faceted Ir is a template for studies of energy-related surface reactions whose rates are sensitive to atomic structure and/or nanoscale (facet) size effects, including decomposition of H@sub2@, C@sub2@H@sub2@ and NH@sub3@. We will discuss structural and electronic properties of the surfaces, nucleation and growth of facets, implications for catalysis, and potential of faceted substrates as nanotemplates for nanoscale cluster growth. Experimental results are compared to theory. @FootnoteText@ @footnote 1@ supported by DOE - BES.

2:40pm **SS1-WeA3 Atomistic Reasons for the Oxygen Induced Step Bunching on Rh(553)***, J. Gustafson, A. Resta, A. Mikkelsen, R. Westerstrom,* ***J.N. Andersen****, J. Weissenrieder, E. Lundgren,* Lund University, Sweden*; F. Mittendorfer, G. Kresse,* Universität Wien, Austria*; X. Torelles,* Institut de Ciencia de Materials de Barcelona (C.S.I.C), Spain*; S. Ferrer,* ERSF, France*; N. Kasper,* Max-Planck Institut f@um u@r Metalforschung, Germany*; M. Schmid, P. Varga,* Technische Universität Wien, Austria

One of the most fundamental gas-surface interactions is that between oxygen and metal surfaces. Many studies on low index single crystal surfaces have led to an atomic scale understanding of the possible dissociation pathways for the oxygen molecule and the adsorption sites of O-atoms and molecules on such flat surfaces. Oxygen interaction with vicinal surfaces - which due to their high step density better model small metal particles typically used in catalysis - has received much less attention. Similarly only few studies have been performed under conditions - higher temperatures and/or higher oxygen pressures - where strong rearrangements of the substrate surface may occur. Accordingly an atomic level understanding of the oxygen-surface interaction under conditions - material, pressure, and temperature - typical for instance for catalysis is still in its infancy. Here we present an extensive study, using a multi-method approach, of the initial oxidation of Rh(553), a surface vicinal to (111) with a large density of steps. Our results show that the surface undergoes step bunching when exposed to oxygen, forming lower index facets. At a pressure of about 10-6 mbar and a temperature of 400Â°C this leads to (331) facets with 1D-oxide chains along the steps, co-existing with (111) facets. Increasing the pressure and temperature further results in (111) facets only, covered by a O-Rh-O surface oxide as found on Rh(111).@footnote 1@ @FootnoteText@@footnote 1@ J. Gustafson et al., Phys. Rev. Lett. 92 (2004) 126102.

3:00pm **SS1-WeA4 Atomic-Scale Visualization of Surface Alloys: Sb/Au(110)***, **S.S. Parihar**, V.L. Shneerson, R. Fung, H.T. Johnson-Steigelman, E.D. Lu, D.K. Saldin, P.F. Lyman,* University of Wisconsin-Milwaukee

Surface x-ray diffraction (SXRD) allows quantitative, high-resolution determinations of surface structure via @chi@@super 2@ refinement of a model structure to the observed data. However, the most difficult step in this process is often generating model structures to refine. While this is often possible based, e.g., on chemical intuition, a model-independent method of generating accurate starting structures is sorely needed. We have developed an iterative algorithm to supply the phases, normally not accessible to experiment, from data that are oversampled (relative to the Nyquist frequency of the normal dimensions of the selvedge) along the crystal truncation rods. The algorithm alternately satisfies known constraints of these oversampled data in real and reciprocal space, and incorporates knowledge of the bulk structure, to progressively determine the surface structure factor phases. An inverse Fourier transform then constructs an "image" of the atomic contents of a unit cell of the selvedge.@footnote 1@ We have discovered a rich sequence of Sb-induced reconstructions on Au(110). A c(2x2) appears at 0.5 ML, changing continuously to a (@sr 3@x@sr 3@)R54.7° structure at higher Sb coverages; finally, a p(5x6) structure emerges for several ML Sb deposition. We have applied our novel SXRD algorithm to these surfaces to directly visualize the Sb and Au atomic locations, and thereby solve these structures. This breakthrough affords an automated, model-independent method of determining unknown structures of the outermost few atomic layers of a crystal surface. @FootnoteText@ @footnote 1@ P.F. Lyman, V.L. Shneerson, R. Fung, R.J. Harder, E. D. Lu, S.S. Parihar, and D.K. Saldin, Phys. Rev. B 71, 081402(R) (2005).

3:20pm **SS1-WeA5 Adatom-Pair Chain Structures: Metastable Precursors to Island Formation on the Ge-Si(100) 2xN Alloyed Surface***, **K.J. Solis**, L.R. Williams,* University of New Mexico*; B.S. Swartzentruber,* Sandia National Laboratories*; S.M. Han,* University of New Mexico

We have identified that adatom pairs are the main transport adspecies on the 2xN SiGe wetting layer, using polarity-dependent scanning tunneling microscopy. These adatom pairs form chevron-like, conjugated chains on the SiGe alloy surface, ranging in length from 1 to approximately 10 units of adatom pairs. The adatom-pair chains exhibit kinked and straight segments. We measure a kink-to-straight ratio of 2:1, surpassing the 1:1 ratio predicted from random chain configurations. Substrate-mediated-strain interactions are likely to render the kinked segments energetically favorable. These adatom-pair chains convert to compact islands at elevated temperatures, suggesting that they are the main precursor to island formation on the SiGe wetting layer. We use a pattern-recognition algorithm to distinguish adatom pairs from compact islands in dual-polarity images, and measure the conversion rate from 90 to 150 °C to extract the activation barrier. The authors acknowledge support from NSF CAREER (DMR-0094145) and ARO (W911NF-05-1-0012). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:40pm **SS1-WeA6 Growth and Subsequent Decomposition Kinetics of Very Thin Oxide on Si(001) Surface Studied by Real-Time RHEED Combined with AES***, **S. Ogawa**, Y. Takakuwa,* IMRAM, Tohoku University, Japan

In order to clarify the rate-limiting reaction of layer-by-layer oxidation on Si surfaces, the growth and subsequent decomposition kinetics of very thin oxide on the Si(001)2X1 surfaces were investigated by a real-time monitoring method of Reflection High Energy Electron Diffraction combined with Auger Electron Spectroscopy (RHEED-AES) to measure the oxide coverage and surface structure/morphology simultaneously. The 1@super st@ oxide layer was grown by two oxidation manners of Langmuir-type adsorption at 500°C and two-dimensional (2D) oxide island growth at 690°C under 2X10@super -6@ Torr of O@sub 2@ pressure. No progress of 2@super nd@ oxide layer growth was observed after completion of 2D oxide island growth, although the 2@super nd@ oxide layer can grow gradually following the Langmuir-type adsorption. It is difficult to interpret the observed difference in the 2@super nd@ oxide layer growth kinetics, because the observed tendency is contrary to thermal activation from 500°C to 690°C. Furthermore, thermal decomposition of the oxide grown at 690°C is more difficult than that grown at 500°C. Thus the rate of 2@super nd@ oxide layer growth is closely concerned with that of decomposition. The reason for the correlation is quantitatively discussed with the time of void nucleation measured as a function of oxidation time after completion of 1@super st@ oxide layer growth.

4:00pm **SS1-WeA7 Surface Morphologies produced by Oxygen Etching of Stable and Unstable Si Surfaces*, A.A. Baski,* *M.L. Willis, J.W. Dickinson, J.L. Skrobiszewski,* Virginia Commonwealth University

We have used scanning tunneling microscopy (STM) and atomic force microscopy (AFM) to study the morphologies produced on Si surfaces by oxygen etching. When Si surfaces are heated to between 700 and 850°C and exposed to O@sub 2@, the simultaneous processes of etching and oxide nucleation can significantly modify the surface structure. As etching removes surface atoms, oxide-induced pinning sites can modify the step structure and lower-energy facet planes can be exposed. In these experiments, a range of O@sub 2@ exposures (50 to 400 L) have been explored for surface orientations that include: (001), (111), (113), (5 5 12), and (112). All of these orientations except Si(112) form stable, clean surface reconstructions. At lower exposures and temperatures, oxygen etching on all of the surface orientations leads to step retraction and the appearance of islands on terraces and at step edges. These islands are presumably due to oxide-induced pinning sites that remain as the surrounding area is etched. The high-index (113) and (5 5 12) surfaces show significantly less terrace etching and enhanced island nucleation along step edges. At higher exposures and temperatures, fewer kinetic limitations are present and the resulting morphologies reflect the stability of surface planes. The (001), (111), and (113) surfaces remain relatively flat with monolayer islands that reflect the surface symmetry. In contrast, the less thermodynamically stable (5 5 12) surface is etched to expose linear sawtooth structures composed of (111) and (113) planes. Similarly, the unstable (112) surface shows dramatic restructuring with the formation of sawtooths composed of (111), (113), (225), and/or (337) planes. Short (112) segments are also sometimes observed, indicating that adsorbed oxygen may stabilize this otherwise unstable orientation. Further studies are in progress to examine exposures above 1000 L where a steady-state morphology should exist.

4:20pm **SS1-WeA8 Cyclic Transformation of 1-D Structures during Homoepitaxy of Si(5 5 12)-2x1*, H. Kim*,** *Y. Cho, J.M. Seo,* Chonbuk National University, Korea

In the homoepitaxy of Si(5 5 12)-2x1 at a finite temperature, 500 C, it has been found by STM that Si overlayer grows in the layer-by-layer fashion and there are three distinct stages, such as dimer-filling, faceting, and valley-filling stages, for recovering Si[5 5 12]-2x1. In each transformed stage, the number of dangling bonds as well as 1-D symmetry with three kinds of reconstructed features, such as honeycomb(H) chain, tetramer(T) row, and dimer-facing-adatoms(D/A) row, are always preserved on the reconstructed surface under a quasi-equilibrium state with deposited Si atoms. The simple rule observed in this 1-D structural transformation is as follows: A honeycomb(H) chain is broken into a tetramer(T) row by the compressive stress, a T row is split to a dimer-facing-adatoms(D/A) row by the tensile stress, and a D/A row is transformed to a H chain by two adsorbed-dimers. Only in the last transformation, the center of 1-D feature shifts in the direction of [-6-6 5] by 3.04 A. It takes only 28 atoms per unit cell to recover the identical, planar and reconstructed Si(5 5 12)-2x1. The reason why such an amount of Si atoms for recovering the original surface is much smaller than that of surface atoms involving in the reconstruction of Si(5 5 12) is in the fact that the exact growth-direction is not along [5 5 12] but along [-1-1 2]. One-cycle of homoepitaxy is completed when seven (111) double-step edges of a unit-cell of Si(5 5 12)-2x1 are filled with two dimers respectively, and results in the effective height increment of 1.36 A and horizontal shift of 3.04 A toward [-6-6 5].

4:40pm **SS1-WeA9 Intrinsic Vacancy-Induced Nanostructure of Al@sub 2@Se@sub 3@: Another New Silicon Compatible Chalcogenide Based Semiconductor*, C.Y. Lu*,** *J.A. Adams, D.A. Schmidt, X. Li, Q. Yu, M.A. Olmstead, F.S. Ohuchi,* University of Washington

Adding new functionalities, such as magnetism and spintronics, to existing silicon-based technology requires combining different crystalline materials with silicon through heteroepitaxy. One intriguing class of materials that is both structurally and chemically compatible with silicon is the Group-III-Selenide semiconductors, such as Ga@sub x@Se@sub y@ and Al@sub x@Se@sub y@. These materials have intrinsic vacancies that influence the film morphology and resultant crystalline structure during the heteroepitaxial growth, and may also be used to host dissimilar atoms, such as magnetic transition metals, to add unique functionalities. We report here in-situ scanning tunneling microscopy and photoelectron spectroscopy of aluminum-selenide (Al@sub x@Se@sub y@) heteroepitaxy on Si(111)-7x7 and As-terminated Si(100). Unlike Ga@sub x@Se@sub y@, which crystallizes into either a layered GaSe or defected zinc-blende Ga@sub 2@Se@sub 3@, Al@sub x@Se@sub y@ exhibits only one bulk structure: defected wurtize. We find heteroepitaxy of Al@sub x@Se@sub y@ on Si(111) results in hexagonal Al@sub 2@Se@sub 3@, likely wurtzite, but defected zinc-blende Al@sub 2@Se@sub 3@ is initially formed on As-terminated Si(100). The morphology of Al@sub 2@Se@sub 3@/Si(111) consists of triangular nanodots with single orientation, in contrast to the mixed orientation of layered GaSe on Si(111). For Al@sub 2@Se@sub 3@/Si(100):As, we observe oriented nanowire structures at low coverage, similar to low coverage Ga@sub 2@Se@sub 3@/As:Si(100)nanowires;@footnote 1@ hexagonal crystalline islands nucleate after 2-3 bilayers. In these first 2-3 layers, the spiral vacancy arrangement unique to the wurtize structure is altered to a linear array by the symmetry of Si(100)substrate. We propose that different symmetry and bonding of the substrate surfaces induces different configurations of vacancies, resulting in the distinct surface nanostructures. @FootnoteText@ @footnote 1@T. Ohta et al., Phys. Rev. Lett. 94, 116102 (2005).

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