

Surface Science

Room 327 - Session SS2-WeM

Surface and Interface Structure: Metals

Moderator: R.J. Hamers, University of Wisconsin-Madison

8:20am SS2-WeM1 Dislocation Mediated Interactions in Self-assembly: The S-induced Triangular Hole-array in Ag/Ru(0001), K. Thurner, N.C. Bartelt, R.Q. Hwang, Sandia National Laboratories

By depositing S onto a monolayer of Ag/Ru(0001) we are able to create very regular arrays of 2D-vacancy islands. Real-time STM measurements reveal the mechanisms of such adsorbate induced restructuring: Starting from a herringbone pattern of the clean Ag-film, the S transforms the film by a sequence of dislocation reactions that individually decrease the Ag density. Eventually all threading dislocations are eliminated and the film assumes a Moire-like structure, in which on-top Ag-atoms are replaced by holes filled with S. These holes form a strikingly regular triangular lattice with a nearest neighbor spacing of 5nm. The conventional assumption is that such pattern formation is caused by substrate-mediated long-range elastic interaction. To test this assumption, we have used STM to measure the thermal vibrations of the hole array as a function of temperature. Surprisingly, we find we can account for these observations without invoking substrate relaxations: By comparing the measured vibration amplitudes to 2D Frenkel-Kontorova simulations we find that the hole-array is stabilized by a pattern of partial dislocations connecting the holes. First principles electronic structure calculations of the 2D FK model parameters for Ag/Ru quantitatively reproduce the hole-hole interaction strength extracted from our measurements. @FootnoteText@ @footnote 1@K. Pohl et al. Nature 397 (1999) 238.

8:40am SS2-WeM2 Molecule-Metal Surface Interactions Evidenced Quantum Mechanically via Tip-induced CS₂ Interaction with Friedel Oscillations on Au{111}, E.C.H. Sykes, P. Han, P.S. Weiss, The Pennsylvania State University

Sub-monolayer coverages of CS₂ adsorbed on Au{111} at 4 K were studied using scanning tunneling microscopy. The molecule forms well ordered islands on the terraces and molecular chains at the bottoms of the steps. The adsorption of the CS₂ molecule at specific surface sites is explained in terms of the substrate electron density. Strong tip/molecule interactions are shown to be prevalent in this system at negative tip biases and yield images showing reversed corrugation. At low positive tip bias, the tip again perturbs the molecules, but in this regime the tip/molecule interaction is comparable to the molecule/surface interaction and higher residence times at certain surface sites are observed. This effect is explained fully in terms of the CS₂ molecule having increased interactions with the areas of high electron density on the peaks of standing waves arising from electrons close to the Fermi energy. The importance of this result is discussed in terms of the fundamental surface physics of adsorbate/metal bonding.

9:00am SS2-WeM3 Interactions Mediated by Surface States: Lines and Ordered Overlayers@footnote 1@, P. Hyltdgaard, Chalmers University of Technology and Göteborg University, Sweden; T.L. Einstein, University of Maryland, College Park

Since surface states on (111) noble metals are free-electron like, their propagators can be evaluated analytically. @footnote 2@ Since they are well-screened, one can use simple tight-binding formalism @footnote 3@ to study their effects. @footnote 4@ Applications to metallic surface states on semiconductors may also be fruitful. The needed phase shifts can be extracted from experiment. @footnote 2,4@ Hence, we can now make quantitative predictions of indirect interactions--at least the asymptotically dominant contribution from surface states. @footnote 2,4@ Here, we discuss the interactions of linear defects, relating them to the interactions of (n x 1) ordered overlayers and to the constituent pair and trio interactions. We discuss implications for step-step interactions (on vicinal surfaces), for extracting pair interactions from first-principles calculations of ordered overlayers or from experiments, and for atoms approaching large clusters. @FootnoteText@ @footnote 1@PH supported by ATOMICS, financed by the Swedish Foundation for Strategic research; TLE supported by NSF Grants EEC-0085604 and MRSEC DMR 00-80008. @footnote 2@ J. Repp et al., Phys. Rev. Lett. 85 (2000) 2981; P. Hyltdgaard and M. Persson, J. Phys.: Condens. Matt. 12 (2000) L13. @footnote 3@ T.L. Einstein, in Handbook of Surface Science, vol. 1, ed. W.N. Unertl (Elsevier, Amsterdam, 1996), chap. 11. @footnote 4@ P. Hyltdgaard and T.L. Einstein,

9:20am SS2-WeM4 Structural Evolution of an Atomically Rough Surface: Faceting and Alloying of Re(12-31), A.S.Y. Chan, H. Wang, W. Chen, Rutgers University; J.E. Rowe, United States Army Research Office; T.E. Madey, Rutgers University

The thermal stability of ultrathin metal and oxide films on an atomically rough Re(12-31) surface has been studied using Low Energy Electron Diffraction (LEED) and High Resolution Soft X-ray Photoelectron Spectroscopy (HRSXPS) using synchrotron radiation. Re(12-31) is a morphologically unstable surface with 6 surface layers of atoms exposed. This highly corrugated surface exhibits a surface shift in the Re4f core levels of 0.17 eV towards higher binding energy, relative to the bulk peak. Adsorption of oxygen at room temperature leads to a disordered chemisorbed oxygen overlayer with a rich distribution of chemical binding states, while the surface retains a planar morphology. However, when the O-precovered surface is annealed to temperatures above 700 K, drastic restructuring of the surface occurs to form nanosized facets with a ridged "hill-and-valley" morphology. The facet planes are identified as (01-10) and (11-21) based on kinematic simulations of LEED patterns, and are consistent with Field Emission Microscopy results of our collaborators. By controlling the coverage of oxygen, different oxygen coordination sites on the Re facet planes can be selectively populated and identified by distinct chemical shifts (up to 0.73 eV) to higher binding energies in the Re4f core levels. In contrast, the Re substrate does not facet when precovered with a Pt or Pd overlayer and annealed. Ultrathin Pt films form a dilute alloy with the Re substrate at temperatures as low as 300 K; this surface alloy becomes increasingly Re-rich as the film is annealed.

9:40am SS2-WeM5 Multilayer Thermal Expansion at Surfaces from Surface Core Level Shifts, A. Baraldi, Sincrotrone Trieste S.C.p.A. and Università di Trieste, Italy; S. Lizzit, Sincrotrone Trieste S.C.p.A., Italy; K. Pohl, University of New Hampshire; Ph. Hofmann, University of Aarhus, Denmark; S. de Gironcoli, Scuola Internazionale Superiore di Studi Avanzati (SISSA), Italy

Understanding the thermal properties of nanostructures is of great importance when it comes to making reliable predictions on their stability. By decreasing the size of nanoparticles the thermal behavior of the surface is going to dominate their properties. A basic manifestation of these anharmonic effects is thermal structural expansion. However, some open surfaces are violating our common sense by exhibiting significant negative thermal contraction while some close-packed surfaces show anomalously large thermal expansion. A theoretical understanding of the anharmonic effects at surfaces does not exist and state-of-the-art LDA calculations show large disagreements with experimental results. An especially puzzling case is the thermal expansion of Be(0001). A recent LEED investigation measured an anomalously large thermal surface expansion between 110 K and 700 K, 6 times larger than the bulk. This observation seems inconsistent with measurements reporting no anharmonicity in the out-of-plane surface phonon modes and with a subsequent LDA study within the quasiharmonic approach resulting in no significant thermal expansion. We will present a novel, independent, approach to determine the thermal expansion of Be(0001). We measured the binding energy of the surface state and the values of the surface core level shifts as a function of temperature and compared them to calculated DFT values for different geometries. Our results reveal that, in the temperature range from 300 to 700 K the 1st-to-2nd, 2nd-to-3rd and 3rd-to-4th interlayer coefficient of thermal expansion are 88 ± 15 , -10 ± 15 and $-6 \pm 20 \times 10^{-6} \text{ K}^{-1}$, respectively, to be compared with a bulk value of $12 \times 10^{-6} \text{ K}^{-1}$. Our results confirm the anomalously large thermal expansion of the surface and establish Be(0001) as a firm experimental standard for advances in our theoretical understanding of the thermal behavior of surfaces.

10:00am SS2-WeM6 The Electronic and Geometrical Structures of Ultrathin Bimetallic Films of Pd and Cu on Ru(0001), J. Onsgaard, L. Bech, Aalborg University, Denmark; Z. Li, University of Aarhus, Denmark; T.H. Andersen, University of Southern Denmark; S.V. Hoffmann, University of Aarhus, Denmark

Alloying conditions, low-dimensional effects and catalytical properties of ultrathin bimetallic films of Pd and Cu have been studied. Codeposition of the two metals on a relative inert substrate, Ru(0001), with overlayer thicknesses in the range 1 ML to 4 ML, were carried out. Deposition temperatures were either room temperature or 550 K and the thin films were characterized as a function of temperature. The information is based

Wednesday Morning, November 5, 2003

upon photoelectron spectroscopy based upon use of synchrotron radiation with high resolution core level studies of Pd 3d, Ru 3d, Cu 2p and valence band measurements. LEED was used to follow the order of the overlayers. Cu and Pd are distributed in one layer with temperature dependent mixing when the total coverage is one monolayer. The valence bands of the surface alloys are characterized by the Cu 3d band separated from the Pd 4d band at a temperature of 550 K. Heating causes hybridization of the Cu 3d and Pd 4d bands with formation of a new band between the individual metal bands. Surface alloying takes place at 660 K and above this temperature the structures of the overlayers are independent of the order of deposition. Cu 2p core-level binding energy shifts show two linear relationships with the composition of the film in 2- and 3 dimensions. An effect which is attributed to the different coordination numbers between Pd and Cu in 2- and 3 dimensions.

10:20am **SS2-WeM7 A Novel Local Free Energy Minimum on the Cu(001)-Surface**, *H. Wormeester*, *M. Ovsyanko*, *G. Stoian*, *B. Poelsema*, University of Twente, The Netherlands

Glancing incidence Ar⁺ ion bombardment of the Cu(001) surface leads to the formation of two atom layer deep nanogrooves parallel to the incident ion beam. High resolution LEED patterns show that sputtering along [110] and [100] leads to an intergroove distance that depends on temperature, ionfluence and -energy. Surprisingly, prolonged sputtering along [100] leads at various temperatures (175 to 235 K) to a persistent feature located at 1.0% BZ of the Brillouin Zone (BZ). Annealing at temperatures between 250 and 290 K of nanogrooves prepared after a much shorter sputter time leads to an increase of their separation distance. Here too, the appearance of this persistent feature at 1.0% BZ is observed. These various preparation routes are indicative of a thermodynamic origin of this 1.0% feature, i.e. a local free energy minimum. Mild annealing above 400K transfers the surface to the global free energy minimum: It suffices to remove both the nanogroove structure and the feature at 1.0% BZ. The occurrence of the 1.0% BZ feature is attributed to the relieve of tensile strain, generally present at (001) fcc metal surfaces, leading to a contraction of the in-plane lattice constant of the (001) surface along the [010] azimuth. The energy balance between gain by stress relieve and cost due to lattice mismatch will be discussed. The presence of the nanogrooves along a azimuth turns out to be essential for the relieve of this strain.

10:40am **SS2-WeM8 Low Energy Electron Microscopy of the Quantum Electronic Structure and Stability of Ag Films on Fe(100)**, *K.L. Man*, Hong Kong University of Science and Technology; *Z.Q. Qiu*, University of California at Berkeley; *M.S. Altman*, Hong Kong University of Science and Technology, Hong Kong

Laterally resolved measurements of the reflected electron intensity from Ag films on the Fe(100) surface have been made with low energy electron microscopy (LEEM). Intensity peaks are observed at very low energy that are associated with quantum well resonances in the Ag film above the vacuum level. The dispersion of the quantum well peaks with increasing film thickness is well accounted for by the phase accumulation model, which has been used widely to explain the occupied quantum well states that are observed with photoemission in this and other systems. The signature quantum well peaks that are observed in electron reflectivity are then used in combination with real-space LEEM measurements to monitor film stability during annealing. We find that uniform three monolayer (ML) thick films decompose directly into spatially separated two and five ML thick film regions, whereas uniform four ML thick films decompose initially into three and five ML thick regions and eventually into two and five ML thick regions. The greater stability of two and five ML thick films has been attributed to band structure features near the zone center, which are the source of long period magnetic oscillatory coupling through Ag films. The relative stability of three and four ML thick films may be evidence that band structure features related to the neck of the Fermi surface, which give rise to the short period oscillatory coupling, also play a role in film quantum electronic stability.

Author Index

Bold page numbers indicate presenter

— A —

Altman, M.S.: SS2-WeM8, **2**
Andersen, T.H.: SS2-WeM6, **1**

— B —

Baraldi, A.: SS2-WeM5, **1**
Bartelt, N.C.: SS2-WeM1, **1**
Bech, L.: SS2-WeM6, **1**

— C —

Chan, A.S.Y.: SS2-WeM4, **1**
Chen, W.: SS2-WeM4, **1**

— D —

de Gironcoli, S.: SS2-WeM5, **1**

— E —

Einstein, T.L.: SS2-WeM3, **1**

— H —

Han, P.: SS2-WeM2, **1**

Hoffmann, S.V.: SS2-WeM6, **1**

Hofmann, Ph.: SS2-WeM5, **1**

Hwang, R.Q.: SS2-WeM1, **1**

Hylgaard, P.: SS2-WeM3, **1**

— L —

Li, Z.: SS2-WeM6, **1**

Lizzit, S.: SS2-WeM5, **1**

— M —

Madey, T.E.: SS2-WeM4, **1**

Man, K.L.: SS2-WeM8, **2**

— O —

Onsgaard, J.: SS2-WeM6, **1**

Ovsyanko, M.: SS2-WeM7, **2**

— P —

Poelsema, B.: SS2-WeM7, **2**

Pohl, K.: SS2-WeM5, **1**

— Q —

Qiu, Z.Q.: SS2-WeM8, **2**

— R —

Rowe, J.E.: SS2-WeM4, **1**

— S —

Stoian, G.: SS2-WeM7, **2**

Sykes, E.C.H.: SS2-WeM2, **1**

— T —

Thurmer, K.: SS2-WeM1, **1**

— W —

Wang, H.: SS2-WeM4, **1**

Weiss, P.S.: SS2-WeM2, **1**

Wormeester, H.: SS2-WeM7, **2**