Monday Morning, November 2, 1998

Surface Science Division Room 308 - Session SS1-MoM

Issues in Surface Electronic Structure

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am SS1-MoM1 The Physical Origin of Surface Relaxation@footnote 1@, T. Zhang, University of Tennessee, Knoxville; J.-H. Cho, Oak Ridge National Laboratory; E.W. Plummer, University of Tennessee, Knoxville; Z. Zhang, Oak Ridge National Laboratory

The subtantial difference in the valence charge distributions between sp and df metals can be so large that for hcp (0001) surfaces, the first interlayer spacing of berillium will expand while that of zirconium will contract. This difference in relaxation can be traced to a difference in the direction of the traditional Smoluchowsky charge smoothing at the two surfaces. The failure of the Finnis-Heine (FH) picture in explaining material dependence of surface relaxation lies in its neglect of this critical difference in valence charge distributions. This work is supported by Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract number DE-AC05-960R22464 @FootnoteText@ @footnote 1@ Tianjiao Zhang, Jun-Hyung Cho, E.Ward Plummer, Zhenyu Zhang, submitted to Physical Review Letters @footnote 2@ R. Smoluchowsky, Physical Review,60,661(1941) @footnote 3@ M W Finnis and Volker Heine, J. Phys. F: Metal Phys., 4, L37(1974)

8:40am SS1-MoM2 Unoccupied States vs Coverage in Alkali Metals on Mo(110) by Auger Decay, NEXAFS, and Bandmapping, *E. Rotenberg, C.M. Lee,* Lawrence Berkeley National Laboratory; *S.D. Kevan,* University of Oregon

In recent years, the nature of the chemical bonding between alkali metals (AMs) and metal substrates has been intensely debated. For many alkalis on metals, the workfunction rapidly falls with coverage, reaching a minimum at about 1/2 monolayer before recovering somewhat up to saturation. The key issue is whether this work function change directly reflects a strong change in the charge distribution around the AM, as proposed by Langmuir and Gurney (LG) over 60 years ago, or whether the charge distribution somewhere else (in the substrate or in the space between adsorbate and substrate) dominates the workfunction change. Using localized, core-hole processes at the AM (near edge xray absorption fine-structure spectroscopy (NEXAFS) and Auger decay) we can now infer the alkali s-level occupation as a function of coverage, and correlate this with other measurements such as bandmapping and workfunction measurements. Measurements were performed for Li or K on Mo(110). At low coverages (below about ~0.1 ML) we find no occupied states at the AM atoms. At somewhat higher coverages, we observe a reoccupation of the AM valence orbital. This reoccupation, however, appears largely complete before the workfunction minimum occurs. Therefore, we conclude that there is a significant change in AM valence occupation with coverage, roughly following the LG model (donation of charge from AM to the substrate at low coverage, followed by backdonation at higher coverages). However, the workfunction change cannot be explained only by our measurements of the AM valence occupation, but instead has additional contributions from redistribution within the substrate.

9:00am SS1-MoM3 Auger Photoelectron Coincidence Spectroscopy of Ag and the Ag/Cu(100) Surface Alloy, *D.A. Arena*, *R.A. Bartynski*, Rutgers, The State University of New Jersey; *Q. Qian*, New Jersey Institute of Technology; *S.L. Hulbert*, Brookhaven National Laboratory

The question of atomic versus band-like contributions to the core-valencevalence (CVV) Auger line shape in Ag remains a controversy. Theoretical predictions are ambiguous as the correlation energy, U, is comparable to the 4d valence band width, W. Using Auger-photoelectron coincidence spectroscopy (APECS), we measured the line shape of the Ag M@sub 4,5@VV and N@sub 2,3@VV Auger transitions from single crystal Ag. In addition to a dominant atomic-like component, both spectra show a significant contribution from band-like decays. However, the N@sub 2,3@VV spectrum cannot be accounted for within the Cini-Sawatzky theory, suggesting that dynamical effects of the very rapid 4p core hole decay influences the lineshape. Furthermore, the N@sub 2,3@VV transition exhibits a much larger low energy tail that may be of the same origin. We have also measured the Ag CVV Auger spectra for 0.1ML Ag/Cu(100) to investigate the electronic structure of this prototypical surface alloy. In contrast to theoretical predictions, the Auger lineshape suggests that the Ag d-band shifts towards the Fermi level.

9:20am SS1-MoM4 Photoelectron Spectroscopy Studies of Adhesion, Alloying and Segregation in the Platinum - Tungsten Bimetallic System, *J.J. Kolodziej, T.E. Madey,* Rutgers University; *J.W. Keister, J.E. Rowe,* North Carolina State University

High resolution soft X-ray photoelectron spectroscopy (SXPS) using synchrotron radiation, and Auger electron spectroscopy, are used to study Pt films on W (211). It is found that the films grow in layer-by-layer mode at 300 K. As a function of Pt film thickness four different Pt 4f@sub7/2@ photoemission peaks are observed, corresponding to a single monolayer of Pt/W, a Pt interface layer, Pt surface atoms and Pt bulk atoms. A single monolayer of Pt is stable up to the onset of desorption. In contrast, when multilayer Pt films are annealed above 600 K, substrate W atoms diffuse in the Pt overlayer to form an alloy. Evidence for a dilute alloy, in which the W 4f@sub7/2@ signal from the W impurity in a Pt host is found to have a binding energy 1 eV higher than bulk W, is observed up to 900K. The evolution of the bimetallic Pt - W sample as a function of Pt coverage and annealing temperature is diagnosed by analysis of intensities and angular dependencies of the W 4f@sub7/2@ and Pt 4f@sub7/2@ features. In all cases a single monolayer of Pt "skin" covers the alloy film. The data provide detailed information on energetics of adhesion, segregation and alloving in an early d - late d transition metal system.

9:40am SS1-MoM5 Electronic Structure of Sn/Ge(111) along the @sr@3 x @sr@3 to 3x3 Phase Transition, J. Avila, LURE and CSIC, France; A. Mascaraque, Universidad Autonoma Madrid, Spain; G. LeLay, CRMC2-CNRS, France; E.G. Michel, Universidad Autonoma Madrid, Spain; M.C. Asensio, LURE and CSIC, France

The @sr@3 x @sr@3-Sn/Ge(111) structure undergoes a phase transition to a 3x3 phase at low temperature,@footnote 1@@footnote 2@ which has been interpreted as a charge-density-wave@footnote 1@ where electron localization gives rise to strong correlation effects.@footnote 2@ We report an angle-resolved photoemission investigation on the band structure and the Fermi vector of this interface along the phase transition. The electronic bands at room temperature exhibit a prominent surface state originated from Sn p@sub z@ orbitals, dispersing 0.3 eV with minima at K points. The Fermi vector obtained from these data is close to 0.3 Å@super -@@super 1@, much smaller that the calculated value.@footnote 1@ The surface state band splits at low temperature in two dispersing bands with strong 3x3 periodicity, at variance with previous data.@footnote 2@ The observation of these two bands correlates with the appearance of two components in the shallow Sn core levels. These data together with several other evidences support that the phase transition is of the order-disorder type. The mechanism driving the phase transition will be discussed in view of different theoretical models. @FootnoteText@ @footnote 1@J.M. Carpinelli et al, Phys.Rev.Lett. 79, 2859 (1997). @footnote 2@A. Goldoni and S. Modesti, Phys.Rev. Lett. 79, 3266 (1997).

10:00am SS1-MoM6 Surface Electronic Structure of Wurtzite GaN(0001)1x1 Studied with Angle-Resolved Photoemission, Y.-C. Chao, C.B. Stagarescu, J. Downes, K.E. Smith, Boston University; D. Hanser, M. Bremser, North Carolina State University; R.F. Davis, North Carolina State University, US

The surface electronic structure of the n-type, Si-doped, wurtzite GaN(0001)1x1 surface has been studied in detail with angle-resolved photoemission. The GaN film was grown on a AIN buffer layer on a 6H-SiC(0001) Si-face, on-axis substrate using a low-pressure metalorganic vapor phase epitaxy technique. A very sharp 1x1 LEED pattern was observed from the surface after the cleaning by repeated cycles of sputtering with nitrogen ions and annealing in ultra-high vacuum. The photoemission spectra reveal a previous unidentified highly dispersive surface-state band. The dispersion of this surface state has been determined along the [@GAMMA@KM] azimuthal direction of the 1x1 surface Brillouin zone. At @GAMMA@ point, the surface state is located at ~2 eV below the valence band maximum. For small emssion angles, this surface state rapidly disperses towards the VBM by ~1 eV. As the emssion angle is increased, the state starts to disperse downward and moves into the projected bulk band gap close to the K point. The identification of this state as originating from a surface band is confirmed by exposure of the surface to activated hydrogen. The intensity of emission from the surface state decreases dramatically following H exposure. This work was supported in part by the National Science Foundation under grant umber DMR-95-04948.

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10:20am **SS1-MoM7 Fermi Surface and Metallization of the Ag/Si(111)7x7 Interface**, *J. Avila*, LURE, Centre Universitaire Paris Sud and ICMM, France; *M. DeSeta*, III Universita di Roma, Italy; *M.C. Asensio*, LURE, Centre Universitaire Paris Sud and ICMM, France

The determination of the metallization onset of metal/semiconductor interfaces is an important goal for diverse applications as well as for its fundamental interest. In this field, the early stage of nucleation and growth plays an essential role in determining the final morphology and electronic structure of the interfaces. In this work, we address this particular issue for the epitaxial growth of silver overlayers on Si(111)7x7 surfaces studied by LEED, Photoelectron Diffraction and High Energy Resolution Angular Resolved Photoemission. The films were prepared by Ag deposition at room temperature and the silicon substrates were chemically treated previously to be introduced to the ultra high vacuum system. The evolution of the valence band as a function of the silver coverage, at particular high symmetry points of the reciprocal space, has put clearly in evidence the onset of the metallization of this interface. The presence of Si features even at 4 silver monolayers is consistent with the existence of Ag islands since the first layers. The Fermi Surface of the Ag/Si(111)7x7 interface, measured in situ, shows the coexistence of two domains of Ag(111) rotated 60° each others. In addition, the valence bands recorded along the @GAMMA@K, @GAMMA@M and @GAMMA@M' azimuths are in excellent agreement with band theoretical calculations.

10:40am SS1-MoM8 Analysis of High-Index Si(001) Surfaces by Reflectance-Difference Spectroscopy, *L. Mantese*, University of Texas, Austin; *Q. Xue*, Tohoku University, Japan; *D.E. Aspnes*, North Carolina State University

High-index Si surfaces are of interest as potential substrates for electronic device applications. The growth properties of these surfaces are expected to be superior to those of the commonly used (001) and (111) orientations. It is believed that higher concentrations of surface steps may lead to higher nucleation densities. In addition, these surfaces provide new opportunities for meeting the requirements demanded by increasingly complex structures. Here, we consider the surface-induced optical anisotropies (SIOA) of three high-index Si surfaces: (113), (114) and (115) representing offcut angles of 25.2, 19.5, and 15.8 degrees from (001) toward [110], respectively. The SIOA of these surfaces were measured first in their airoxidized conditions, second as-cleaned by heating, and third following Ge deposition. In some instances previous results on lower index Si(001) surfaces offcut 6 and 10 degrees toward [110] are available for comparison. The air-oxidized surfaces show sharp derivative-type structures near the critical point energies of bulk Si, consistent the lower index Si(001) surfaces. We have previously interpreted these structures in terms of photon-induced localization of the excited electronic states, which results from final-state correlation effects ordinarily discarded in conventional descriptions of optical absorption in solids. Spectra of clean reconstructed surfaces show a broad feature near 3 eV and a small step-related structure near the (E@sub 0@',E@sub 1@) transition of bulk Si. Atomic H exposure decreases the amplitude of the broad 3 eV feature suggesting it to be a dangling-bond-related state. In contrast, H exposure of Ge-deposited Si surfaces sharpens and enhances features below 3 eV while structures near the critical point energies of bulk Si remain. The optical response of Si(114) is consistent with its STM analysis, which indicates that this is the highestindex surface to demonstrate a terrace-plus-step morphology.

11:00am SS1-MoM9 HRPES Study of Acetylene Adsorption and Reaction with Si(100)-2x1 Surface, S.H. Xu, Y. Yang, H. Cruguel, Montana State University; E. Rotenberg, Lawrence Berkeley National Laboratory; G.J. Lapeyre, Montana State University; J.T. Yates Jr., University of Pittsburgh The adsorption and reaction of acetylene with Si(100)-2x1 surface has been studied using high resolution photoemission measurement the Si 2p, C 1s and valence band(VB)spectra as a function of acetylene coverage and post annealings at several temperatures. After the clean Si(100) surface is exposed to 0.5 ML acetylene, the surface state in valence bands is totally gone. Meanwhile, there is only one interface component in the Si 2p core line. These results indicate that the asymmetry of Si dimers is gone after acetylene adsorption, which is in excellent agreement with the tetra-@sigma@ model proposed by our previous photoelectron holographic results.@super [1]@ Significant changes in the electronic structure(Si 2p, C 1s and VB) are found after subsequent annealing of a saturation overlayer. Annealing at lower temperatures can induce a bit of acetylene desorption but most of the molecules decompose to C@sub 2@H@sub x@ (x=1, 0) and H species. After annealing at above 650 °C, there develops a surface state in valence bands and a Si 2p surface core-level component indicating some restoration of a Si(100)-2x1 structure. The C 1s line shows a single

component indicating that a SiC compound forms on the Si surface. Both of the reacted components of the Si 2p and C 1s lines show that the SiC species form cluster-like feature. At the same time, the surface core-level components indicate that the clean surface Si dimers reappear on the silicon surface. This work is supported by NSF. The ALS of LBNL is supported by the DOE. [1]. G. J. Lapeyre et al., to be published.

11:20am SS1-MoM10 The Electronic Structure of Nanosized Mg Clusters on MgO Surfaces: Characterization with MIES, J. Günster, J. Stultz, S. Krischok, Texas A&M University; P. Stracke, V. Kempter, Technische Universitat Clausthal, Germany; D.W. Goodman, Texas A&M University

MgO films (2nm thick) were grown on Mo and W substrates with "in situ" investigation by MIES and UPS(HeI). Apart from the valence band emission no additional spectral features could be detected with electron spectroscopies. The oxide surface was exposed to Mg atoms (substrate temperature between 100 K and RT). An additional peak, not seen in UPS, located within the bandgap developed in MIES, located about 2.3eV above the top of the valence band with ca. 1.5eV FWHM at the lowest exposures. Both the energetic position and the peak width depended (weakly) on the exposure time. This additional emission could be detected in MIES until its intensity fell below a level of 10 ppm of that from the valence band. We attribute this additional emission to the formation of small, non-metallic Mg clusters. For small exposures these are 2D clusters.@footnote 1@ It is remarkable that the energetic position of the cluster emission closely matches that expected for the ionization of surface Fs+ / Fscenters.@footnote 2@ Indeed, the existence of Mg-induced F-type centers an MgO has recently been detected by both ESR@footnote 3@ EELS.@footnote 4@ Therefore, we suggest that in the initial phase of Mg exposure F-type point defects are produced when the Mg adsorbs close to extended defects, such as steps, corners etc. These point defects may play an important role as nucleation sites for the cluster formation. @FootnoteText@ @footnote 1@C.T. Campbell: Surf. Sci. Rep. 27 (1997) 1 @footnote 2@L.N. Kantorovich, J.M. Holender, M.J. Gillan: Surf. Sci. 343 (1995) 221 @footnote 3@E. Giamello, A. Ferrero, S. Coluccia, A. Zecchina: J. Phys. Chem. 95 (1991) 9385 @footnote 4@K.-M. Schr@um o@der, D. Peterka, H. Pfn@um u@r: DPG Fr@um o@hjahrstagung Regensburg, and to be published in Surf. Sci.

11:40am SS1-MoM11 Scattered and Recoiled Ion Fractions From Cd- and S-Terminated CdS(0001) Surfaces, L. Houssiau, M. Liu, J.W. Rabalais, University of Houston; J. Wolfgang, P. Nordlander, Rice University

Scattered and recoiled ion fractions from CdS(0001) and CdS(000-1) surfaces have been determined by means of time-of-flight scattering and recoiling (TOF-SARS) spectrometry. An acceleration tube placed between the sample and the CEM detector enabled separation of the ions and neutrals. By applying a positive (negative) high voltage on the tube, the negative (positive) ions are accelerated, giving rise to neutral and ion peaks in the TOF spectra. On the Cd-terminated surface, 4 keV Ne@super +@ ions scattered at an incident angle @alpha@ = 11° through a scattering angle @theta@ = 50° exhibit a pronounced angular dependence, i.e. the lowest ion fractions (Ne@super +@/Ne@super 0@) are observed along the close packed atomic rows and . On the S-terminated surface however, the same experiment exhibits the opposite angular dependence, i.e. the highest ion fractions (Ne@super +@/Ne@super 0@) being now observed along the close packed rows. 4 keV Kr@super +@ ions were also used to study the S recoiled ion fractions. On the Cd-terminated surface, the lowest S@super -@ ion fractions are found along both the and rows. On the Sterminated surface, the lowest S@super -@ ion fractions are found along the rows, but the highest ion fractions are found along the rows. The final charge state of the ejected atoms is determined by electron tunneling between the surface and the atom as it leaves the surface. This process has been modeled using ab initio calculations of the potentials in the CdS surfaces. In conclusion, it is found that the ion fractions and their angular dependence are extremely sensitive to the nature of the surface terminating layer. This is important in determining the microscopic reactive sites on surfaces.

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