

Thursday Morning, November 7, 2002

Surface Science

Room: C-108 - Session SS-ThM

Electronic Structure and Stimulated Processes

Moderator: R. Bartynski, Rutgers University

8:20am **SS-ThM1 Electronic Structure of Atomic Chains on Vicinal Silicon**, **J.N. Crain***, University of Wisconsin - Madison, **K.N. Altmann**, Synchrotron Radiation Center, **Ch. Bromberger**, Philipps - University, Germany, **A. Kirakosian**, **J.-L. Lin**, **J.L. McChesney**, **F.J. Himpsel**, University of Wisconsin - Madison

Surface states on semiconductors provide a unique opportunity to study low-dimensional electron systems. States at the Fermi level are in the band gap and thus do not couple to the bulk states. Thereby, truly two- and one-dimensional metals can be achieved. An example of a 2D metal is Si(111)- $\sqrt{21} \times \sqrt{21}$ (Ag + Au) which exhibits two distinct Fermi surfaces associated with Ag and Au.¹ By growing chains of gold atoms on Si(111), Si(557), Si(335), and Si(337) we demonstrate the capability of engineering one-dimensional metallic states with varying inter-chain spacings and electron count. In addition, we find a new Si(111)- 5×2 Gadolinium reconstruction akin to a lattice of 1D spin chains. Using a combination of STM and angle resolved photoemission we map the real-space and momentum-space electronic structures for these atomic chains. By locking the atoms to the silicon lattice the Peierls transition is overcome. The resulting metallic bands exhibit novel properties including the formation of two half-filled metallic bands in place of a single semiconducting band and a continuous 1D to 2D transition within a single band.^{2,3,4} The engineering of 1D metals is instrumental in the search for exotic electron behavior like the Luttinger liquid.⁵

¹ J. N. Crain, K. N. Altmann, C. Bromberger, and F. J. Himpsel, Submitted to Phys. Rev. B.

² R. Losio, K. N. Altmann, and F. J. Himpsel, Phys. Rev. Lett. 85, 808 (2000).

³ R. Losio, K. N. Altmann, A. Kirakosian, J.-L. Lin, D. Y. Petrovykh, and F. J. Himpsel, Phys. Rev. Lett. 86, 4632 (2001).

⁴ K. N. Altmann, J. N. Crain, A. Kirakosian, J.-L. Lin, D. Y. Petrovykh, F. J. Himpsel, and R. Losio, Phys. Rev. B 64, 035406 (2001).

⁵ J. Voit, Rep. Prog. Phys. 58, 977 (1995).

8:40am **SS-ThM2 Origin of the Negative Shift Observed in the XPS Spectra of Cu and Ag Cations having d⁰ Electronic Configuration**, **D.A. Kukuruznyak**, **J.G. Moyer**, **A.L. Ankudinov**, **J.J. Rehr**, **F.S. Ohuchi**, University of Washington

We discuss the phenomenon of the negative chemical shift in the XPS spectra, where an oxidized ion appears to be chemically reduced. The effect is illustrated in the Cu¹⁺ cation within a spinel crystal structure and in Ag¹⁺ in silver fluorides, AgF and AgF₂. We have found that the negative chemical shift of the core levels is caused by similar shifts of the ions 3-d and 4-d Valence Bands. We therefore modeled the experimental valence band photoemission spectra by theoretical DOS of the d-levels using an ab initio FEFF8 code. This code is based on a relativistic Greens function real space full multiple scattering formalism and allows accurate determination of the position of the levels with respect to the Fermi energy. We have determined that the negative shift of the d-levels is not caused by a long-range electrostatic interaction (Madelung potential). The amount of the total charge on the Cu¹⁺ cation in the spinel structure was similar to that of copper in Cu₂O, thus charging is not the cause of negative shift either. It was also found that only Cu 4s and 4p electrons participate in the chemical bonding. Completely filled d¹⁰ shells of the copper in spinel structure do not form a band, but were localized, having an atomic-like character. The 3d-level therefore appeared as a false valence band edge in the spectrum. A similar effect was observed for the silver compounds. We claim that the negative chemical shift is not due to charging or splitting effects, but occurs when a completely occupied non-bonding d¹⁰ shell appears on the XPS spectra as a false valence band edge.

9:20am **SS-ThM4 Electronic Band Structure of Sn/Si(111)**, **J. Lobo**, **A. Tejada**, Universidad Autonoma de Madrid, Spain, **A. Mugarza**, Universidad del País Vasco, Spain, **E.G. Michel**, Universidad Autonoma de Madrid, Spain

We report an investigation on the electronic band structure of the Sn/Si(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase using angle-resolved photoemission, in the coverage range between 1/6 and 1/3 ML, both at room and at low temperature, with special emphasis in the analysis of its metallic character and in the evolution of the surface states as a function of temperature and

coverage. The photoemission experiments have been performed at HASYLAB (Hamburg, Germany). This phase has deserved widespread attention since the discovery of a temperature induced phase transition to a low temperature (3x3) phase. Several different models have been put forward to explain the nature of the phase transition, that is observed only in the case of Ge(111): formation of a surface charge density wave, stabilized by correlation effects or defects; dynamical fluctuations, that destroy the (3x3) phase at RT; or existence of a soft phonon. There is no indication of a (3x3) pattern at low temperature for Sn/Si(111), but several features of the (3x3) phase are found in the valence band. We present also an analysis on the influence of the defect density in the surface state behavior and metallic character. The results found for the ideal $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase at 1/3 ML coverage support the dynamical fluctuations model for the phase transition. While a (3x3) phase is not observed in the temperature range accessible, the system exhibits a behavior similar to the one found in Sn/Ge(111) (split surface state band that survives at RT). The existence of a semiconductor to metal transition has been investigated in detail.

9:40am **SS-ThM5 Electron Confinement in Metallic Ultrathin Films**, **Z.Q. Qiu**, University of California at Berkeley **INVITED**

Electron confinement or quantum well (QW) state manifests in metallic thin films as the film thickness is reduced to nanometer scale. Photoemission provides the most direct observation of QW states in k-space. The unique capabilities now available at the Advanced Light Source (ALS) at Berkeley make it possible to image QW states on the atomic scale. The photoemission results from ALS on Cu thin films grown on fcc Co(100) are presented using single- and double-wedge samples. First, we will discuss how the QW states are formed in the Cu film and how to describe it using the phase accumulation model. Second, we will show how the QW states result in the oscillatory interlayer coupling between two ferromagnetic Co layers across a thin Cu layer.

10:20am **SS-ThM7 Dominance of the Final State in Photoemission Mapping of the Fermi Surface of Co Thin Films**, **R.L. Kurtz**, **X. Gao**, Louisiana State University, **A.N. Koveshnikov**, Simon Fraser University, Canada, **R.L. Stockbauer**, Louisiana State University

The Fermi surface of tetragonally-distorted fcc Co grown on Cu(001) has been investigated with angle-resolved photoemission and compared with first-principles calculations. Photoelectron angular distributions were obtained with a display-type ellipsoidal-mirror analyzer at the LSU CAMD synchrotron light source for electrons emitted from E_F using photons in the energy range of 20-80 eV. These angular distributions show distinct patterns that vary with photon energy as different regions of the Brillouin zone are sampled. In order to evaluate the correspondence to Fermi surface contours, we have computed the band structure of tetragonally-distorted Co. We have used WIEN97.9 to perform a spin-polarized gga FLAPW calculation including spin-orbit interactions for a pseudomorphic fcc structure with an in-plane lattice constant that of Cu while the vertical lattice parameter is reduced by 5%. From this, the resulting Fermi surfaces have been extracted and cross-sectional contours were produced corresponding to the various photon energies used in the measurements. We find that there is rather poor agreement between these contours and the structures seen in photoemission. To investigate this further, we have computed the momentum matrix elements using the final states produced in the band calculation. In the case of Co, the resulting angular distributions that we predict are in much better agreement with our data, and even reproduce the photon polarization effects that are observed. These observations suggest that comparison with first principles calculations are extremely important, particularly in the case of flat-band materials such as the d-bands of Co seen here. The slow dispersion of the occupied states, when coupled with the rapid dispersion of the final state, produces angular distributions whose contours are heavily influenced by the final state.

10:40am **SS-ThM8 Spin-Resolved Photoemission of Surface States in H on W(110)**, **E. Rotenberg**, Lawrence Berkeley National Laboratory, **H. Hochstrasser**, **J.G. Tobin**, Lawrence Livermore National Laboratory, **S.D. Kevan**, University of Oregon

Surface states of metals can be split due to the spin-orbit-coupling (SOC) interaction, as first shown experimentally by LaShell et al for Au(111) surface states.¹ Their conjecture was that the surface states could be split by SOC when the bulk inversion symmetry was broken at the vacuum/metal interface. Later we found a similar splitting for W(110) and Mo(110) surfaces and furthermore that this splitting could be enhanced with hydrogen or alkali metal adsorption.² In the present work, the hydrogenated surface electronic states on W(110) have been measured using spin-resolved photoemission. The origin of the splitting is confirmed to be spin-orbit-

* Morton S. Traum Award Finalist

coupling. In confirmation of the conjecture by LaShell et al, we observe 100% polarization of these states in local regions of momentum space. The spins are aligned in the plane of the surface, perpendicular to the electronic momentum relative to the S-bar symmetry point.

¹ S. LaShell, B. A. McDougall, and E. Jensen, Phys. Rev. Lett. 77, 3419 (1996).

² E. Rotenberg, J. W. Chung, S. D. Kevan, Phys. Rev. Lett. 82, 4066 (1999).

11:00am **SS-ThM9 Ultraviolet Laser Interactions with Single Crystal Sodium Nitrate: Wavelength Dependence of Photodesorbed Products, L. Cramer, J.T. Dickinson, Washington State University, W.P. Hess, Pacific Northwest National Laboratory**

Sodium nitrate is a wide bandgap ionic material containing an oxyanion. Single crystals show a strong absorption band in the ultraviolet due to a π to π^* transition in the nitrate. Previous work has suggested that a number of neutral emission products are due to direct excitation of this band. In this study we compare the laser induced ion and neutral atom/molecule emissions from single crystal NaNO_3 at three wavelengths: at the band maximum (193 nm) and two minima on either side of the maximum (248 nm and 157 nm). Surprisingly, little correlation with the π to π^* absorption is observed, including molecular species derived from the nitrate. Our results are better explained by defect mediated processes attributed to anion vacancies. These results are corroborated by simultaneous laser induced photoelectron emission measurements that are very sensitive to low densities of electron trap defects at insulating surfaces.

11:20am **SS-ThM10 Low Dimensional Metallic States in Heavily Irradiated CaF_2 Thin Films on Si(111), A.A. Bostwick, J.A. Adams, A. Klust, University of Washington, E. Rotenberg, Advanced Light Source, M.A. Olmstead, University of Washington**

Calcium fluoride is a wide band gap ionic insulator that undergoes photosimulated desorption of fluorine. It has been previously reported by Karlsson et al.¹ that heavily irradiated thin ($2.5 \text{ \AA}$ –4 triple layers) $\text{CaF}_2/\text{Si}(111)$ films show a sharp metallic defect state associated with an ordered array of surface fluorine vacancies. We find two additional states in thicker, irradiated films (5-10 triple layer), one at higher binding energy and one at lower energy than the surface state. These states also cross the Fermi level dispersing upwards from normal emission. The zone-center energies of these states depend on the thickness of the initial CaF_2 film, hinting that the electrons are confined in the growth direction. The upper state could lie within the band gap of the silicon substrate, but the lower state, which is more than 1.5 eV below the Fermi level at the zone-center, does not. These states are observed after prolonged irradiation, much longer than that necessary to produce the surface state. We postulate that these new states are due to the formation of fluorine vacancy clusters (Ca metal quantum dots) within the CaF_2 . Funded by DOE grant DE-FG03-97ER45646/A0003.

¹ Karlsson et al., Phys. Rev. Lett. 57,1247 (1986).

11:40am **SS-ThM11 Ion Emission from Ultrathin Resists during Exposure to Metastable Atom Beams, Y. Yamauchi, X. Ju, T. Suzuki, M. Kurahashi, National Institute for Materials Science, Japan**

The combination of ultrathin resists and slow metastable atom beams has attracted attention because of its potential for downscaling the semiconductor lithography beyond the diffraction limit, proximity effect, or transmission of conventional exposure radiations, i.e., ultraviolet light, electron beam, and soft x-ray. Slow metastable atoms carrying fairly large excitation energy in their electronic system interact only with topmost atoms at surfaces because the kinetic energies of the atoms are so low that they are reflected above surfaces. These extreme surface sensitivity and damage-free feature to under layers are desirable for an exposure radiation in lithography. Since Berggren et al.¹ had suggested the atom lithography, several groups have reported their success on pattern transfer employing metastable atom beams for ultrathin resists (self-assembled monolayer (SAM) of alkanethiolate,¹ hydrogen passivation on silicon surface² followed by wet chemical etching. As to the fundamental phenomena of resists caused by the irradiation of metastable atoms, however, are not well understood. Recently metastable-atom-stimulated desorption (MSD) was discovered for water and alkali coadsorbed surfaces.³ We have investigated MSD of positive ions from alkanethiolate-SAMs and from hydrogen-passivated Si(111) surfaces. The MSD data show H^+ and CH_4^+ desorption from the alkanethiolate-SAMs and H^+ desorption from the hydrogen-passivated Si(111) surfaces, which provide direct evidence for the dissociation of alkanethiolate-SAMs and of silicon hydrides by metastable helium atom beams at the initial stage of the pattern transfer.

¹ K. K. Berggren, et al., Science 269 (1995) 1255.

² S. B. Hill, et al., Appl. Phys. Lett. 74 (1999) 2239.

³ M. Kurahashi and Y. Yamauchi, Phys. Rev. Lett. 84 (2000) 4725; T. Suzuki, et al., Phys. Rev. Lett. 86 (2001) 3654.

Authors Index

Bold page numbers indicate the presenter

— A —

Adams, J.A.: SS-ThM10, 2
Altmann, K.N.: SS-ThM1, 1
Ankudinov, A.L.: SS-ThM2, 1

— B —

Bostwick, A.A.: SS-ThM10, **2**
Bromberger, Ch.: SS-ThM1, 1

— C —

Crain, J.N.: SS-ThM1, **1**
Cramer, L.: SS-ThM9, **2**

— D —

Dickinson, J.T.: SS-ThM9, 2

— G —

Gao, X.: SS-ThM7, 1

— H —

Hess, W.P.: SS-ThM9, 2
Himpel, F.J.: SS-ThM1, 1

Hochstrasser, M.: SS-ThM8, 1

— J —

Ju, X.: SS-ThM11, 2

— K —

Kevan, S.D.: SS-ThM8, 1
Kirakosian, A.: SS-ThM1, 1
Klust, A.: SS-ThM10, 2
Koveshnikov, A.N.: SS-ThM7, 1
Kukuruznyak, D.A.: SS-ThM2, **1**
Kurahashi, M.: SS-ThM11, 2
Kurtz, R.L.: SS-ThM7, **1**

— L —

Lin, J.-L.: SS-ThM1, 1
Lobo, J.: SS-ThM4, **1**

— M —

McChesney, J.L.: SS-ThM1, 1
Michel, E.G.: SS-ThM4, 1
Moyer, J.G.: SS-ThM2, 1

Mugarza, A.: SS-ThM4, 1

— O —

Ohuchi, F.S.: SS-ThM2, 1
Olmstead, M.A.: SS-ThM10, 2

— Q —

Qiu, Z.Q.: SS-ThM5, **1**

— R —

Rehr, J.J.: SS-ThM2, 1
Rotenberg, E.: SS-ThM10, 2; SS-ThM8, **1**

— S —

Stockbauer, R.L.: SS-ThM7, 1
Suzuki, T.: SS-ThM11, 2

— T —

Tejeda, A.: SS-ThM4, 1
Tobin, J.G.: SS-ThM8, 1

— Y —

Yamauchi, Y.: SS-ThM11, **2**