

Surface Science

Room 122 - Session SS3-WeA

Electronic Structure I

Moderator: S.D. Kevan, University of Oregon

2:00pm **SS3-WeA1 Medard W. Welch Award Lecture: Intertwined Charge Density Wave and Defect-Ordering Phase Transitions in a 2-D System**@footnote 1@, **E.W. Plummer**, The University of Tennessee and Oak Ridge National Laboratory, US; **A.V. Melechko**, The University of Tennessee and Oak Ridge National Laboratory

INVITED

The study of macroscopic properties of phase transitions in low-dimensional systems provides an understanding of the fundamental aspects of systems of interacting particles. Phase transitions are strongly affected by defects, especially in systems with lower dimensionality. In quasi-1D or -2D systems that exhibit a CDW transition, a small proportion of microscopic disorder can control the global properties because of the collective nature of the phenomena. It has been speculated that the interaction of mobile defects with CDW leads to alignment of defects with the CDW, or the formation of Defect Density Waves.@footnote 2@ In this dynamic picture, the distribution of defects is neither random nor static, instead defects align their positions to optimize the energy of the pinned CDW. Here, we will discuss a complex symmetry lowering ($\sqrt{3}\times\sqrt{3}$) to (3x3) phase transition in Sn/Ge(111) and similar systems that can be decomposed into two intertwined phase transitions: a second order CDW transition and a first order disorder-order transition in the defect distribution. We present two phenomenological models that describe these transitions and their interrelation.@footnote 3@ These models allow us to understand the formation of the domains and domain walls seen in STM at low temperatures, defect-induced waves above the CDW transition temperature, and ordering of the defects caused by the CDW-mediated defect-defect interactions.@footnote 4@ The models predict a shift in the CDW transition temperature with impurity density and a dependence of the (3x3) lattice structure on the specific defect alignment. @FootnoteText@ @footnote 1@ Supported by NSF DMR 980130. ORNL is supported by the U.S. DOE through contract DE-AC5-92OR22725 with UT-Battelle, LLC.@footnote 2@ H. Mutka, in *Advances in the crystallographic and microstructural analysis of charge density wave modulated crystals*, edited by F. W. Boswell and J. C. Bennet, Kluwer Academic Publishers, Dordrecht, 1999.@footnote 3@ A. V. Melechko, M. Simkin, N. F. Samatova, J. Braun, and E. W. Plummer, submitted for publication.@footnote 4@ A. V. Melechko, J. Braun, H. H. Weitering, and E. W. Plummer, *Phys. Rev. Letters*, **83**, 999 (1999). H. H. Weitering, A. Melesko, J. M. Carpinelli, and E. W. Plummer, *Science*, **285**, 2107-2110 (1999).

2:40pm **SS3-WeA3 Lifetimes of Surface States at Si(001) Surfaces**, **M. Weinelt**, **M. Kutschera**, **C. Kentsch**, **Ch. Orth**, **Th. Fauster**, Universität Erlangen-Nürnberg, Germany

With ultrafast two-photon photoemission spectroscopy the temporal evolution of an excited electronic system can be studied on the femtosecond time scale. A pump pulse excites electrons to distinct intermediate states while a second time-delayed pulse probes the evolving population dynamics. This allows to determine lifetimes of conduction bands and unoccupied dangling-bond states on semiconductor surfaces directly in the time domain. Using time-resolved two-photon photoemission we have studied the $c(4 \times 2)$ and (2×1) reconstructions of the Si(100) surface. Several bulk and surface transitions involving unoccupied intermediate states below the vacuum energy are identified. In particular, the surface band gap at the center of the surface Brillouin zone, i.e., the gap between occupied and unoccupied dangling-bond states is determined to 0.96 ± 0.05 eV. The unoccupied dangling-bond state shows a rich dynamic ranging from fs to more than 100 ps. Population and decay are dominated by electron-phonon scattering which couples bulk and surface states. The decay rate is strongly influenced by surface defects in the band gap.

3:20pm **SS3-WeA5 Electronic Structure of Complex Manganite Spinel Studied by XPS, XANES, EXAFS and Nanoprobe EELS**, **D.A. KuKuruznyak**, **B.W. Reed**, **J.G. Moyer**, **M.C. Gregg**, **S.-W. Han**, **E.A. Stern**, **M. Sarikaya**, **F.S. Ohuchi**, University of Washington

Ni-Co-Cu-Mn-O spinels, owing to their strong temperature influence on resistivity, are technologically important oxide materials for thermistor applications, among which $\text{Ni}_{x\text{sub}}\text{O}_{0.48}\text{Co}_{x\text{sub}}\text{O}_{0.24}\text{Cu}_{x\text{sub}}\text{Mn}_{x\text{sub}}\text{O}_{2.28-x}\text{O}_{4\text{sub}}$ ($x = 0.6$, and 1.2) are the compositions of

specific industrial interests. In this study, we synthesized nanocrystalline thin films and powders using low temperature metallorganic decomposition technique, rather than conventional solid state sintering. The materials were subsequently annealed at temperatures between 500 and 800°C, and it was found that annealing temperature was a decisive factor in controlling transport properties. Electronic structure of the bulk and surface was investigated by combinations of XPS, XANES, and nanoprobe EELS. The analysis revealed that the annealing caused change of the oxidation state from $\text{Cu}^{\text{super } 1+}$ to $\text{Cu}^{\text{super } 2+}$, which was accompanied by reduction of manganese cations from $\text{Mn}^{\text{super } 4+}$ to $\text{Mn}^{\text{super } 3+}$. EXAFS analysis showed that both the $\text{Cu}^{\text{super } 1+}$ and $\text{Cu}^{\text{super } 2+}$ ions occupied the tetrahedral lattice sites, whereas both the $\text{Mn}^{\text{super } 4+}$ and $\text{Mn}^{\text{super } 3+}$ were in the octahedral sites in the spinel structure. During the course of annealing, an unusually large negative binding energy shift in both Cu 2p and Cu 3d levels for the $\text{Cu}^{\text{super } 1+}$ state was observed. This negative shift appears to be unique to this system, and was attributed to the change in the Fermi surface topology due to strong 3d-4p hybridization which occurs in the tetrahedral coordination because of the completely filled 3d^{super 10} orbital of $\text{Cu}^{\text{super } 1+}$ ion.

3:40pm **SS3-WeA6 Quantum Well Behavior without Confining Barrier Observed via the Dynamically Screened Photon Field**, **S.R. Barman**, Inter-University Consortium for DAE Facilities; **P. Haberle**, Universidad Tecnica Federico Santa Maria; **K. Horn**, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; **J. Maytorena**, Universidad Nacional Autonoma de Mexico; **A. Liebsch**, Forschungszentrum Julich, Germany

Quantum well states are a striking manifestation of elementary quantum mechanics. An electron confined in a one-dimensional potential well, formed by the vacuum on one side and a band gap in the substrate on the other, may occupy discrete energy levels whose quantum number specifies the number of half-wavelengths spanning the well. Angle resolved photoemission spectra from Na adlayers on Al(111) reveal features which behave as quantum well resonances, even though the substrate does not provide a barrier for electron confinement. These features are observed in a narrow photon energy range where overlayer collective excitations cause resonant enhancement of the photoemission intensity. The quantum well behavior is shown to be due to surface resonances of the Na/Al system. These are observable since the screened photon field is dynamically enhanced and spatially confined to the overlayer. The special role of the photon field distinguishes the present system from ordinary quantum wells. The quantum well-like spectral features are associated with virtual states induced by the large negative potential step between overlayer and substrate. To observe these resonances it is crucial to suppress emission from substrate bands in the same energy region. This is achieved by tuning the photon energy to the collective modes of the overlayer. The local electric field is then enhanced and confined to the overlayer so that the Na resonances can be observed in a wide range of coverages. Thus, while in usual quantum well systems the photon field plays no special role, here it serves as a novel mechanism ensuring the confinement of the excitation region.

4:00pm **SS3-WeA7 Molecular Resonant Quantum Wells at Organic-Metal Interfaces**, **G. Dutton**, **X.-Y. Zhu**, University of Minnesota

Quantum-well like molecular resonances have been observed in electron transfer at a model molecule/metal interface: $\text{C6F6}/\text{Cu}(111)$. Two photoemission measurement reveals a transient molecular anionic resonance located at 3 eV above the Fermi level. This molecular resonance is dispersed parallel to the surface, i.e. resonant quantum well behavior. Both the energetic position and the dispersion of this molecular resonance depend intimately on the interfacial electronic structure and the strength of molecule-surface interaction. With increasing coverage of pre-adsorbed atomic hydrogen which weakens molecule-surface interaction, the position of molecular resonance in C6F6 increases while the effective electron mass decreases. We conclude that the resonant molecular quantum well is confined to the interface and is a result of both molecule-molecule and molecule-surface interaction.

4:20pm **SS3-WeA8 Dynamics of Photo Excited Carrier Trapping and Recombination at Si(111) Interfaces Probed By Time-Resolved Second Harmonic Generation**, **D. Bodlaki**, **E. Borguet**, University of Pittsburgh

Carrier trapping and recombination is the primary fate of conduction band electrons. Interfaces are known to play an important role in these processes. However, probing the interface is challenging as the interface represents but a small fraction of the total number of atoms in a macroscopic sample. Distinguishing between photoprocesses due to

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surface states and those from excitation of states in the bulk, resulting from crystal impurities or defects, is difficult especially if one is monitoring a bulk property such as photocurrent. Second Harmonic Generation (SHG) is known to be a versatile in-situ, real time probe of buried interfaces. In this study SHG was used to probe carrier relaxation at various Si interfaces and to assess the passivating nature of the surface. Carriers were created by optical excitation via an interband transition induced by an 800 nm, 4 psec pump pulse. Subsequently, the nonlinear optical response of the interface was probed by SHG of 800 nm light. The SHG dynamics depend strongly on the surface chemistry. Native oxide covered surfaces exhibit an initial increase in SHG response followed by a linear decay on a nanosecond timescale. Surface modification changes the dynamics. RCA cleaned, oxide covered samples also show an initial increase in SHG response, but the subsequent decay appears slower. H terminated surfaces show distinctively different behavior: initially the SHG signal decreases then recovers faster than the oxide covered silicon. The different dynamics probably reflect the degree of interface passivation. Defect sites deplete the conduction band carrier population by trapping or recombination.

4:40pm **SS3-WeA9 Surface Femtochemistry: Observing and Controlling Adsorbate Motion on Metal Surfaces on Femtosecond Time Scale, H. Petek**, University of Pittsburgh **INVITED**

Electronic and nuclear dynamics of alkali atoms adsorbed on noble metal surfaces are investigated in real time by the interferometric time-resolved two-photon photoemission technique. Photoinduced charge transfer with a <20 fs laser pulse turns on repulsive Coulomb force between alkali atoms and the substrate, thereby initiating desorption from the surface. The resulting nuclear wave packet motion is detected through changes in the surface electronic structure. In the extreme case of Cs/Cu(111), the alkali atom desorptive motion can be observed for up to 200 fs, which according to a Newton's law model corresponds to stretching of the Cu-Cs bond by ~ 0.3 Å. Furthermore, the coherent polarization created by the charge-transfer excitation persists for up to 60 fs. Demonstration of quantum control, whereby it is possible to generate displaced ground and excited state wave packets, is accomplished by interference between the pump and probe excited polarization in the sample. However, the photodesorption process is frustrated by the wave packet spreading and decay through recoil-induced phonon generation, reverse charge transfer, and electron inelastic scattering, which induce the phase and energy relaxation. Prospects of controlling the electronic and nuclear motion of atoms and molecules at surfaces will be discussed. @FootnoteText@ @footnote 1@S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. Lett. 82, 1931 (1999). @footnote 2@H. Petek, H. Nagano, M. J. Weida, and S. Ogawa, Science 288, 1402 (2000). @footnote 3@H. Petek, M. J. Weida, H. Nagano, and S. Ogawa, J. Phys. Chem. A 104, 10234 (2000). @footnote 4@H. Petek, H. Nagano, M. J. Weida, and S. Ogawa, J. Phys. Chem. (Feature Article; in press). .

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