

# Tuesday Afternoon, November 5, 2002

## Surface Science

Room: C-108 - Session SS1-TuA

## Ultrafast Phenomena & Dynamics at Surfaces

**Moderator:** B.D. Kay, Pacific Northwest National Laboratory

2:00pm **SS1-TuA1 Electron Dynamics at Surfaces, T. Fauster, University of Erlangen, Germany** **INVITED**

Two-photon photoelectron spectroscopy permits the study of the time evolution of electronic states at surfaces with femtosecond resolution. Image-potential states at metal surfaces provide examples for various fundamental processes in electron dynamics: exponential decay, dephasing, quantum beats and interband scattering. At semiconductor surfaces the relevant time scales can be of the order of picoseconds. For dangling bond states on Si(100) intraband and interband scattering lead to a delayed build-up and slow decay of the electron population.

2:40pm **SS1-TuA3 Observation of Isotope Effect in Femtosecond Laser-Induced Desorption of O<sub>2</sub>/Pd(111), D.P. Quinn, T.F. Heinz, Columbia University**

A significantly higher yield for femtosecond laser-induced desorption is observed for <sup>16</sup>O<sub>2</sub> than for <sup>18</sup>O<sub>2</sub> in the saturated co-adsorbed <sup>16</sup>O<sub>2</sub> + <sup>18</sup>O<sub>2</sub>/Pd(111) system. Similar isotope effects<sup>1</sup> have been reported for conventional photochemistry and electron-stimulated desorption. Such isotope effects have also been used to examine reaction mechanisms for femtosecond laser-induced surface processes.<sup>2,3</sup> In the present case, investigations of the O<sub>2</sub>/Pd(111) system have demonstrated that the desorption process is mediated by the substrate electronic excitations induced by the femtosecond laser pulses. The observation of a significant isotope effect is compatible with such an electronic mechanism, but implies that the adsorbed molecules are out of equilibrium with the electronic degree of freedom of the substrate during the desorption process. We consider this phenomenon in the context of both DIMET<sup>4</sup> and electronic friction models of the adsorbate-substrate coupling.

<sup>1</sup> T.E. Madey et al., J. Chem. Phys. 52, 5215 (1970).

<sup>2</sup> R.J. Finley et al., Chem. Phys. Lett. 274, 499 (1997).

<sup>3</sup> M. Bonn et al., Science 285, 1042 (1999).

<sup>4</sup> J.A. Misewich et al., Phys. Rev. Lett. 68, 3737 (1992).

3:00pm **SS1-TuA4 Time Resolved Femtosecond Laser Desorption from Ionic Crystals, W.P. Hess, A.G. Joly, K.M. Beck, Pacific Northwest National Laboratory, J.T. Dickinson, Washington State University**

We have used femtosecond laser pulse pairs to measure the positive ion yield, from wide band-gap single crystals, as a function of time-delay between pulses. The two-pulse technique allows direct observation of solid state and surface dynamics on a femtosecond timescale. We find the ion yield, from 265 nm irradiated MgO, KBr, and LiF, depends critically on the time delay between pulses. For example, the Mg<sup>+</sup> desorption yield displays three distinct features; a coherence peak, followed by rise, and decay features. In contrast, the yield of K<sup>+</sup> and Li<sup>+</sup> from KBr and LiF display only the coherence peak and picosecond decay features. The observed thresholds suggest, that although the ion desorption mechanism is dominated by defect photoabsorption, significant electron-hole pair production may contribute to the desorption mechanism following femtosecond excitation. The picosecond lifetimes correspond well with known electron-hole lifetimes in each material. We hypothesize that fs laser desorption may be related to the creation of electron hole pairs. By determining the ultrafast time-dependence we hope to reveal details of the ion desorption mechanism.

3:20pm **SS1-TuA5 On the Detection of Chemically-Induced Hot Electrons in Surface Processes: from X-ray Edges to Schottky Barriers, J.W. Gadzuk, National Institute of Standards and Technology**

The potential involvement of electron-hole pair excitations in atomic/molecular processes such as sticking/adsorption/dissociation at metal surfaces has long been debated, particularly by those previously involved with similar issues in electron spectroscopies of localized core levels in solids. Of special relevance here are the fundamental studies of Müller-Hartmann et al.<sup>1</sup> on the dynamic response of Fermi systems to transient localized perturbations as subsequently applied to problems in non-adiabatic surface dynamics.<sup>2</sup> Recent experiments have detected hot electrons produced when various gases were adsorbed on a thin metal film that formed a Schottky barrier with an n-type Si substrate upon which the

film was deposited.<sup>3</sup> Drawing on analogies with electron-hole pair shakeup in spectroscopic processes which lead to the x-ray edge singularity, a theoretical model for the electronically non-adiabatic effects is presented here that accounts for the observed initial hot electron production, roughly 10<sup>-3</sup>-10<sup>-2</sup> electrons per incident strongly-interacting adsorbate such as O, H, and NO<sub>2</sub> on Ag. Since the fundamental physical content of the x-ray edge model is the Fermi-level phase shift associated with the localized perturbation and the rate at which it is switched on, straightforward connections with friction-based models<sup>4</sup> are easily established in an intuitively satisfying way.

<sup>1</sup> E. Müller-Hartmann, T. V. Ramakrishnan, and G. Toulouse, Phys.Rev.B 3,1102(1971).

<sup>2</sup> J. W. Gadzuk and H. Metiu, Phys.Rev.B 22,2603(1980); *ibid.* 24,1866(1981).

<sup>3</sup> B. Gergen, H. Nienhaus, W. H. Weinberg, and E. W. McFarland, Science 294,2521(2001); H. Nienhaus, Surface Sci. Repts. 45,1(2002).

<sup>4</sup> K. Schönhammer and O. Gunnarsson, Phys. Rev.B 27,5113(1983).

3:40pm **SS1-TuA6 Kinetics and Dynamics of CO Oxidation on Oxygen Precovered Gold Nanoclusters Supported on Titania, C.B. Mullins, T.S. Kim, J. Stiehl, C.T. Reeves, R.J. Meyer, University of Texas at Austin** **INVITED**

Studies of the kinetics and dynamics of carbon monoxide oxidation have been carried out on a titania single crystal surface with a (110) orientation and decorated with gold nanoclusters. The investigations employed molecular beam surface scattering techniques as well as thermal desorption mass spectrometry and Auger electron spectroscopy. An rf-powered plasma jet source was used to create a beam of atomic oxygen which was used to populate the surface with oxygen adatoms. After the surface was prepared a molecular beam of carbon monoxide was directed at the surface in order to study oxidation of CO as a function of oxygen coverage and surface temperature. There is a maximum in the reactivity as a function of oxygen coverage and surface temperature. Competing processes, such as adsorption and desorption, will be discussed as well as the effect of adsorbed oxygen upon the surface reactivity of the gold nanoclusters.

4:20pm **SS1-TuA8 O<sub>2</sub> and NO Island Formation on Al(111), J.Z. Sexton, A.C. Kummel, University of California, San Diego**

The oxidation of aluminium is a fundamentally important process that is not well understood. Scanning tunneling microscopy was employed to study the mechanisms for the oxidation of Al(111) with thermal O<sub>2</sub> and NO at medium to high oxygen coverage regime (20-50% ML). The STM-UHV studies provided the following observations: 1) Oxygen islands on the Al(111) surface, prepared with thermal oxygen, are elongated and non-compact. 2) Al(111) step edges change shape upon O<sub>2</sub> chemisorption to relieve strain from oxide islands. 3) Islands produced with thermal nitric oxide (NO) produce round, compact islands in contrast to the non-compact, elongated islands formed with thermal oxygen. 4) Above a critical oxygen coverage (30-40% ML), Al-atom protrusions appear within oxygen islands. These protrusions increase with increasing coverage and indicate the onset of the phase transition from isolated chemisorbed oxygen islands to an ionic Al<sub>2</sub>O<sub>3</sub> amorphous layer. 5) Pre-existing oxygen features can locally enhance the sticking coefficient. This local enhancement of oxygen adsorption on the Al(111) surface is likely due to a perturbation in the local electronic structure surrounding an oxygen feature. The enhanced O<sub>2</sub> chemisorption results from lattice strain coupled to a work-function change in the proximity of pre-existing oxygen islands. The lattice strain at high oxygen coverages eventually yields the phase transition to amorphous Al<sub>2</sub>O<sub>3</sub>.

5:00pm **SS1-TuA10 Adsorption Dynamics and Desorption Kinetics of Argon and Methane on MgO(100), Z. Dohnálek, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory**

The adsorption dynamics and desorption kinetics of Ar and CH<sub>4</sub> on MgO(100) are studied using a combination of molecular beam scattering and temperature programmed desorption (TPD). Both Ar and CH<sub>4</sub> exhibit an initial trapping probability that decreases dramatically with increasing kinetic energy and is independent of incident angle indicating adsorption is a barrier-less process obeying total energy scaling. The trapping probability for both adsorbates increases roughly linearly with the increasing coverage in the first layer. Such behavior can be described by a simple model involving constant but different trapping probabilities on clean and adsorbate covered MgO(100) with fast intra-layer diffusion leading to preferential filling of the bare MgO(100). Analogous behavior is observed for trapping on the second and third layers and indicates layer-by-layer growth of the adsorbate overlayer with layer dependent trapping probabilities. Analysis of the TPD spectra yields desorption energies of 8.5 and 13 kJ/mole for Ar and CH<sub>4</sub>, respectively in agreement with previous measurements and theoretical calculations. The total energy scaling

observed for the initial trapping of Ar and CH<sub>4</sub> on MgO(100) is in sharp contrast with the normal energy scaling previously observed for these species on Pt(111). These differences indicate that the adsorbate-substrate interaction is laterally smooth on Pt(111) and highly-corrugated on MgO(100). Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

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