Tuesday Afternoon, October 26, 1999

Applied Surface Science Division
Room 6A - Session AS-TuA

Modeling in Applied Surface Science

Moderator: C.S. Fadley, Lawrence Berkeley National Laboratory

2:20pm **AS-TuA2 A Microscopic View of Energetic Desorption Events***, **B.J. Garrison**,* Pennsylvania State University **INVITED**

Molecular dynamics computer simulations have been used to model desorption processes of energetic particle bombardment (SIMS, FABMS) as well laser ablation of organic films (MALDI). The results of the simulations are used to compare with experimental data and to provide microscopic insight into the fundamental events. The particle bombardment examples to be discussed include energy and angular distributions of ejected metal atoms and benzene molecules, mechanisms of ejection of organic molecules, and bombardment by cluster projectiles. Topics to be discussed from the laser ablation studies include microscopic mechanisms of ablation, an analytic expression of the velocity distribution of the plume and conditions for desorption of large molecules as in MALDI experiments. Further information can be found at http://galilei.chem.psu.edu/.

3:00pm **AS-TuA4 Theory of Multi-Atom Resonant Photoemission***, **F.J. Garcia de Abajo**, C.S. Fadley, M.A. Van Hove,* Lawrence Berkeley National Laboratory

Multi-atom resonant photoemission (MARPE) takes places when a core electron of a solid can be excited by an incoming photon beam via two different channels: direct photoexcitation and resonant excitation of a nearby atom that decays via inter-atomic interaction giving rise to the emission of the same core electron. This process permits one to detect the presence in the sample of neighboring atoms A and B of different atomic identity by observing the photoemission signal coming from atom A when the photon energy runs across an absorption edge of atom B. MARPE has been recently observed in several materials, including alloys and multilayered surfaces. A theory of this phenomenon is described here showing good agreement with experiment.

3:20pm **AS-TuA5 Oxide-free Phosphate Films on Metals probed by Core and Valence Band X-Ray Photoelectron Spectroscopic Studies in an Anaerobic Cell***, J.A. Rotole, **P.M.A. Sherwood**,* Kansas State University

This paper will show how clean metal surfaces can be reacted via aqueous electrochemical treatment in an anaerobic electrochemical cell to yield a phosphate film that can be directly attached to the metal surface without the presence of any intervening oxide. Such oxide-free films have the potential to serve as a corrosion inhibiting film, and may have other applications such as in the formation of biocompatible surfaces. Previously published work on aluminum and iron will be discussed but the focus of the paper will be new studies on copper. The work illustrates how it is essential to start with an oxide-free metal surface and to perform the treatment in an inert environment in an anaerobic electrochemical cell using aqueous phosphoric acid. It will also be seen that valence band photoemission, interpreted by band structure and other calculations, is a very effective tool for conclusively identifying the surface species present, and in particular distinguishing between oxide and phosphate surface films. This material was based upon work supported by the National Science Foundation under Grant No. CHE-9421068.

3:40pm **AS-TuA6 Spatial Resolution in Scanning Auger Microanalysis of Complex Systems***, **A.L. Linsebigler**,* General Electric Corporate Research and Development Center

Auger electron spectroscopy is one of the primary surface analytical tools in industrial laboratories. The introduction of analytical instrumentation with field emission sources has expanded the capabilities of Auger analysis to include sub-micron phase and particle identification. The spatial resolution of scanning Auger microanalysis is always in question, especially for complex samples such as alloys and multi-component systems. The primary beam size, the primary beam voltage, and the material under investigation are some of the variables which limit the spatial resolution of Auger electron spectroscopy. This study examines the interfacial resolution of metal films with atomic number differences ranging from delta Z = 6 to 65 as a function of primary beam voltage. The interfacial resolution of practical samples such as intermetallic/metal and oxide/metal combinations are also examined. The experimental results will be compared to predictions made by Monte Carlo simulations of electron - solid interactions.

4:00pm **AS-TuA7 Atomic Level Characterization of Metal-Ceramic Interface Energetics and Dynamics via Ab Initio Methods***, **E.A. Carter**, A. Christensen, E. Asche,* University of California, Los Angeles **INVITED**

This talk will be divided into a progress report on ab initio theoretical methods that have been developed to characterize the behavior of interfaces at the atomic level followed by applications of first principles techniques to applied problems. First, w e will discuss a newly developed systematic and accurate theory of adsorption energetics on metals. Second, we will present calculations aimed at understanding the adhesion and ultimate spallation of ceramic coatings on metals. Thermal barrier coatings us ed in high temperature mechanical applications consist of ceramics that are generally spray-coated onto alloy metal surfaces. We will show how one can learn about the interfaces in such materials at the atomic level, via first principles electronic structure techniques. In particular, we will discuss results and insights gleaned from examining surfaces and thin films of ZrO2, Al2O3, their interactions with each other, as well as with Ni surfaces.

4:40pm **AS-TuA9 Surface Science Studies of Model Ziegler-Natta Polymerization Catalysts***, G.A. Somorjai, **S.H. Kim**,* University of California at Berkeley

Model Ziegler-Natta catalysts of titanium chloride, supported on Au and MgCl@sub 2@, have been synthesized using chemical vapor deposition (CVD) methods in a ultra-high vacuum (UHV) chamber and tested for polymerization of ethylene and propylene with triethylaluminum, AlEt@sub 3@, as a co-catalyst in a high-pressure reaction cell. The deposition kinetics, chemical composition, surface sites, and activation of model catalysts are investigated using Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD). TiCl@sub 4@ does not chemisorb on either Au or MgCl@sub 2@ to form a film stable at room temperature in UHV. The titanium chloride films supported on Au (TiCl@sub x@/Au) are produced by electron beam irradiation onto the substrate during the TiCl@sub 4@ exposure. Electrons induce the ionization and dissociation of TiCl@sub 4@, producing active species that can be deposited on Au at both 100K and 300K. The deposition temperature alters the stoichiometry and structure of TiCl@sub x@/Au due to difference in deposition kinetics. The titanium chloride films supported on magnesium chloride (TiCl@sub x@/MgCl@sub 2@/Au) are prepared by reaction of TiCl@sub 4@ with Mg on Au. Two deposition sequences, co-deposition of gas-phase Mg and TiCl@sub 4@ and deposition of TiCl@sub 4@ on a Mg film, are used. Regardless of deposition sequence, the uppermost layers of the TiCl@sub x@/MgCl@sub 2@/Au films are mostly composed of titanium chloride, though the distribution of titanium chloride in the film changes with deposition sequence. For these model catalysts before and after the AlEt@sub 3@ treatment, desorption behaviors of organic molecules are studied to differentiate various adsorption sites on the surface. Identification of active sites for polymerization will be attempted from the comparison of the distribution of surface sites with polymerization activity.

5:00pm **AS-TuA10 Dynamic Monte Carlo Simulations of Catalytic Surface Reactions: CO + NO on Rhodium***, **J.W. Niemantsverdriet**, M.J.P. Hopstaken, J.J. Lukkien, A.P.J. Jansen, P.A.J. Hilbers,* Eindhoven University of Technology, The Netherlands

A Dynamic Monte Carlo simulation procedure which succesfully describes diffusion, adsorbate interactions, island formation and reconstructions, has recently been described.@footnote 1@ We have used this approach to describe adsorption, desorption and dissociation of NO, as well as reactions between CO and NO on Rh(111) and Rh(100). When NO is adsorbed on Rh(111), TPD shows that the saturation increases from 0.68 ML at 150 K to a 0.75 ML at 225 K.@footnote 2@ This is accompagnied by ordering of the adsorbate layer, as evidenced by LEED. These phenomena are accounted for by a delicate interplay between mobility of and lateral interactions between NO molecules. We have also used Monte Carlo techniques to simulate recent experimental results on NO adsorption at elevated temperatures, where NO adsorbs both dissociatively and molecularly. Static SIMS shows that dissociation starts at 250 K and continuously increases up to 350 K. These experimental observations are satisfactorily explained in the model by adding pairwise repulsive interactions between neighbouring adsorbed species, which increases the activation barrier for dissociation. Similar effects play a role in the explosive reaction between CO and NO on fully occupied surfaces. In addition to repulsive interactions, fast diffusion of adsorbed molecules appears to be essential to reproduce explosive behavior in the simulations. The key point is that for a realistic description of repulsion between adsorbates, one has to consider the local environment of an adsorbed atom or molecule. @FootnoteText@ @footnote 1@ R.J. Gelten, A.P.J. Jansen, R.A. van Santen, J.J. Lukkien, J.P.L. Segers, P.A.J. Hilbers, J. Chem. Phys. 108 (1998) 5921. @footnote 2@ R.M. van Hardeveld, M.J.P. Hopstaken, J.J. Lukkien, P.A.J. Hilbers, A.P.J. Jansen, R.A. van Santen, J.W. Niemantsverdriet, Chem. Phys. Lett. 302 (1999) 98.

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