# Tuesday Morning, November 5, 2002

## Surface Science
## Room: C-110 - Session SS2-TuM

## Diffusion & Growth on Metal Surfaces
**Moderator:** M. Salmeron, Lawrence Berkeley National Laboratory

8:20am **SS2-TuM1 Long Jumps in the Surface Diffusion of Large Molecules**, *M. Schunack,* ***T.R. Linderoth****, F. Rosei, E. Laegsgaard, I. Stensgaard, F. Besenbacher*, University of Aarhus, Denmark

While the surface mobility of atomic adsorbates has been studied extensively, similar investigations of large organic molecules are very scarce. Here, we report a detailed variable-temperature Scanning Tunneling Microscopy investigation of the one-dimensional diffusion of two largish molecules, decacyclene (DC) and hexa-tert-butyl-decacyclene (HtBDC), on a Cu(110) surface. The molecular diffusion was studied by acquiring series of STM-images at substrate temperatures of 172-200 K and 218-251 K for HtBDC/DC, respectively. Surprisingly, we find that long jumps, i.e. adsorbate transitions spanning multiple lattice sites, play a dominating role for the diffusion of DC and HtBDC. The root mean-squared (RMS) jump lengths are as large as 3.9 and 6.8 Cu lattice spacings, respectively. The presence of long jumps is revealed by a new and simple method of analysis, which we have tested quantitatively by kinetic Monte Carlo simulations. The dominating role played by long jumps is in strong contrast to previously investigated adsorbate systems where diffusion typically occurs by jumps between nearest neighbor sites. Our results furthermore demonstrate the possibility of tailoring molecular diffusion properties: DC and HtBDC both have the same aromatic plane, which interacts strongly with the surface. In the case of HtBDC, however, the plane is raised away from the surface by spacer groups, resulting in an approximately four orders of magnitude higher diffusion constant compared to DC. The higher diffusivity results both from the larger RMS jump length and from a reduction of the activation barrier for diffusion from 0.73 to 0.59 eV.

8:40am **SS2-TuM2 Observation of the Motion of Individual Lead-oxide Molecules on Reconstructed Au(111) Using Scanning Tunneling Microscopy**, *M.C. Robinson,* ***A.J. Slavin***, Trent University, Canada

Ultra-thin metal oxides are of great technological importance, so it is necessary to understand how these films grow, beginning at the molecular level. In this study we have used scanning tunneling microscopy (STM) to observe the room-temperature diffusion of lead-oxide molecules, most probably PbO, on the reconstructed Au(111) surface at coverages below 0.06 monolayers (ML). To our knowledge, this is the first direct observation of the diffusion of metal-oxide molecules. The existence of mobile molecules suggests that, at least in some cases, oxide layer formation may be driven by the same processes governing metal-on-metal growth. If the motion is not tip-induced, then an upper limit for the molecule diffusion energy is 0.7 eV, based on the motion of the molecules between successive STM images. Atomic resolution is lost above 0.06 ML, probably because the Au reconstruction is lifted allowing a large increase in the rate of adatom diffusion.

9:00am **SS2-TuM3 Initial Stages of Transition-Metal-Assisted Carbon Nanotube Growth: A First-principles Study***, ***Z. Zhang***, Oak Ridge National Laboratory, *Q. Zhang,* The University of Texas at Arlington, *J.C. Wells,* Oak Ridge National Laboratory, *X. Gong*, Fudan University, China **INVITED**

The initial stages of catalytic growth of single-wall carbon nanotubes (SWNT) on transition metal clusters and surfaces are investigated using the first-principles molecular dynamics method. Selected nickel surfaces and magic-sized nickel clusters have been used as a paradigm for this type of catalyst. The method is based on density-functional theory using the local-density approximation with gradient corrections (GGA). The computation scheme is based on the expansion of valance electrons in a plane wave basis. The ultra soft pseudopotentials for nickel (Ni) and carbon (C) are employed to describe their interaction with ionic cores. The energetics involved in the elemental processes of SWNT growth, such as adsorption, diffusion, and nucleation of carbon atoms on the elemental facets of Ni magic clusters as well as on the different Ni surfaces, is investigated and compared, with the objective of identifying the precise role of catalytic clusters. We also investigate the energeticc involved in the possibility of a concerted motion in the atom supply and growth of a baby nanotube on a given surface.

* Research sponsored by the Material Sciences and Engineering Division Program of the Department of Energy (DOE) Office of Science and by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the US DOE under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC, and the National Science Foundation (NSF).

9:40am **SS2-TuM5 Water Diffusion and Clustering on Pd(111)**, ***T. Mitsui***, Lawrence Berkeley National Laboratory, *M.K. Rose, E. Fomin,* University of California, *F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory

The adsorption, diffusion and the formation of clusters of water molecules on Pd(111) has been studied by scanning tunneling microscopy. Water adsorbs in the form of isolated molecules at 40 K. With the help of STM movies of the molecular random walk and of atom-tracking techniques we studied the process of diffusion and cluster formation. When two water molecules meet they form a dimer, then a trimer and so on. The mobility of dimers and trimers was found to be nearly three orders of magnitude larger than that of single molecules. Pentamers and larger clusters are immobile at 40 K, although changes in their conformation were observed. Hexamers with a cyclic configuration are particularly stable. They grow with further coverage forming a commensurate hexagonal honeycomb with $(\sqrt{3}x\sqrt{3})$R30° structure relative to the Pd(111) substrate.

10:00am **SS2-TuM6 A New Mechanism of Mo Growth on Au (111) by Chemical Vapor Deposition from a Mo(CO)$_6$ Precursor**, ***Z. Song****, T. Cai, Z. Chang, G. Liu, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

Chemical vapor deposition (CVD) of metal carbonyls has been attractive for decades in both making supported metal catalysts and fabricating electronic devices. In most of the previous morphology studies of metal deposition on Au (111), the physical vapor deposition (PVD) method was used to prepare the samples. So far, it is not clear what to expect for the growth of metals from CVD of metal carbonyls. In this study, a Mo submonolayer has been grown by CVD of Mo(CO)$_6$ on a reconstructed Au (111) at a substrate temperature of 500 K and studied by STM. The Mo(CO)$_6$ molecules decompose on the Au(111) surface at elevated temperatures and form Mo nano-scale clusters. The Mo clusters grow on both upper and lower steps and at elbows of the Au (111) herringbone structure at low coverages. New clusters are formed with increasing Mo coverage and found preferentially within the fcc troughs and randomly at elbows. In contrast to the Mo-PVD, where Mo clusters form well-ordered arrays by decorating all elbows of Au template, the Mo-CVD clusters aggregate without coalescing and develop ramified islands of clusters. An auto-catalyzed carbonyl decomposition is proposed to explain a facile formation of Mo clusters before they anchor on the surface. The Mo growth at upper steps can be attributed to the presence of CO, that modifies locally the surface potential of Mo. This research was carried out at BNL under Contract No. DE-AC02-98CH10086 with the U.S. DOE (Division of Chemical Sciences).

10:20am **SS2-TuM7 Vacancy-Mediated and Exchange Diffusion in the Pb/Cu(111) Surface Alloy**, ***B.S. Swartzentruber****, M.L. Anderson, M.J. D'Amato, P.J. Feibelman*, Sandia National Laboratories

To understand the formation and stability of surface alloy systems, it is important to know the fundamental atomic-intermixing and mass-transport processes. Using STM measurements and first-principles DFT calculations we have explored them for the formation and evolution of the Pb/Cu(111) surface alloy. When Pb atoms are deposited on Cu(111), they place exchange with surface Cu atoms forming a 2-d surface alloy phase. At low coverage, thermodynamics favors a random distribution of Pb atoms in the surface layer. However, upon deposition, the Pb atoms take the easy path, forming metastable stripes of high Pb concentration embedded near steps. Over time, equilibrium is reached through the much slower decay of this initially non-uniform concentration profile. We measure the kinetics of mass transport, using STM, by following the motion of individual embedded Pb atoms and also the time evolution of the concentration profile. By analyzing the statistics of the local motion we find the most likely process to be one in which diffusion of the embedded Pb atoms occurs via exchange with thermal surface vacancies. There is also a minority process - occurring much less often - wherein an embedded Pb atom exchanges with a thermal Cu adatom and travels over long distance before re-embedding into the surface layer. Although this minority process rarely occurs, the long length scale over which it transports Pb atoms makes it a crucial ingredient of the overall mass transport process as measured in the decay of the concentration profile. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

10:40am **SS2-TuM8 Ultrathin Transition Metal Films on W Surfaces - Conditions for Surface Alloy Formation**, *J. Block*, *E. Schroder*, Chalmers University of Technology and Gothenburg University, Sweden, *J.J. Kolodziej*, Rutgers, The State University of New Jersey, *J.W. Keister*, *J.E. Rowe*, North Carolina State University, ***T.E. Madey***, Rutgers, The State University of New Jersey

We report theory and experiment for the formation of alloy layers in the growth of transition metal films on W surfaces. When W(111) is covered by monolayer films of certain metals (Pt, Pd, Ir, Rh, Au), followed by annealing to T>750 K, the surface becomes covered with three-sided pyramids of nanometer-scale dimensions, having {211} planes as facet sides. High resolution soft x-ray photoelectron spectroscopy using synchrotron radiation is employed to study metal films (Pt, Pd, Ir, Rh) on W(111) and W(211). Surface core level shifts of $4f_{7/2}$ photoemission peaks indicate that single physical monolayers of these metals are stable against thermal rearrangement. In contrast, when multilayer films of Pd, Pt, Ir, Rh are annealed above 700-1000 K, tungsten atoms diffuse into the overlayer to form alloy films. We also characterize ultrathin Pd and Pt films on W(211) by first-principles density-functional theory (DFT) methods. Both to confirm the formation of alloy from theory and to help characterize the alloy, we present studies of Pd and Pt films with included W atoms. The DFT methods allow us to suggest the energetically preferred structures. We studied both pseudomorphically-grown alloy films and alloy films with the atomic positions locally optimized by minimizing the Hellmann-Feynman forces. The DFT calculations are consistent with the experimental observations.

11:00am **SS2-TuM9 Metastable Pb Microcrystals on Ru(0001) Formed by Oxygen Segregation***, ***D.B. Dougherty***, *K. Thuermer*, *J. Reutt-Robey*, *E.D. Williams*, University of Maryland

Microcrystals formed after dewetting a continuous Pb film grown on Ru(0001) have provided a convenient model system for understanding a variety of surface mass transport issues.[1,2] In particular, the relaxation of crystallites toward thermodynamic equilibrium has been studied in detail. Here we report the formation of an unusual metastable crystallite shape and its STM tip induced rapid decay. Combined AES and STM investigations show that this new behavior is the result of minute amounts of oxygen that segregates from the substrate into the Pb. AES is used to observe the segregation of oxygen from the Pb/Ru interface to the surface of the continuous Pb film upon post-deposition annealing. This effect, when combined with the absence of any other detectable contamination explains the presence of nearly spherical crystallites on a surface for which the overwhelming majority have long since decayed to a steady, facetted shape. The decay of the unusual crystallites is induced by repeated scanning of an STM tip, suggesting the removal of a low-mobility oxygen species. This interpretation is consistent with previous observations of the effect of oxygen on single crystal Pb(111) surfaces[3] and our Auger analysis. The highly nonequilibrium tip-induced decay is compared with the previously studied decay of Pb microcrystals. * Work supported by UMD-NSF-MRSEC.

[1] K. Thuermer et al., Step Dynamics in 3D Crystal Shape Relaxation. Phys. Rev. Lett 87 186102 (2001)

[2] A. Emundts et al., Experimental Absolute Step and Kink Formation Energies on Pb(111) Vicinal Surfaces. Surf. Sci. 496 L35-42 (2002)

[3] L. Kuipers et al., Jump to Contact and Neck Formation Between Pb Surfaces and a STM tip. Surf. Sci. 340 231-244 (1995).

11:20am **SS2-TuM10 Selforganized Nanostructures at Vicinal Surfaces**, *N. Nöel*, *T. Maroutian*, *L. Douillard*, ***H.-J. Ernst***, CEA Saclay, France

The use of intrinsic instabilities in epitaxial growth is currently actively explored as a promising pathway for lateral nanostructuring of surfaces as a cost-effective alternative to lithography based schemes. The origin of these instabilities is traced back to the presence of an excess energy barrier for adatom diffusion over descending steps, the Ehrlich-Schwoebel barrier. Upon growth of Cu on vicinal Cu templates a step-meandering instability develops, resulting in an in-plane patterning of the surfaces at the nanometer scale with a temperature- and flux-dependent characteristic wavelength.[1] The step width increases with time (coverage) according to a power law with exponent 1/3. This experimental finding is at variance with currently existing theories.[2]

[1] T. Maroutian et al., Phys. Rev. Lett. 83, 4353, (1999); idem, Phys. Rev. B 64, 165401 (2001)

[2] M. Rusanen et al., Phys. Rev. B 65, 41404 (2002).

11:40am **SS2-TuM11 Azimuth Dependent Nanogroove Creation by Grazing $Ar^+$ Bombardment on Cu(001)**, ***H. Wormeester***, *M.M. Ovsyanko*, *A.A. Mewe*, *G. Stoian*, *B. Poelsema*, University of Twente, The Netherlands

Grazing incidence 800 eV $Ar^+$ sputtering on a Cu(001) surface leads to the formation of nanogrooves in which only 3 layers are involved.[1] We found with high resolution LEED (SPA LEED) that the distance between the nanogrooves L depends on the azimuthal orientation of the incident ions, with a larger distance L for incidence along <100> than <110>. Extrapolation to zero time shows that initially no azimuthal dependence of L is noticable. The time dependent behaviour, however, shows a much larger separation speed for [100] oriented nanogrooves. The creation and azimuth dependent development of these nanogrooves will be discussed.

[1] Phys. Rev. Lett. 86, 4608 (2001).

# Authors Index

## Bold page numbers indicate the presenter