

Surface Science

Room 2004 - Session SS2-TuA

Water-Surface Interactions on Metals

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

2:40pm SS2-TuA3 Wetting on Metal Surfaces at Ambient Conditions: A Photoemission Spectroscopy Study, S. Yamamoto, K. Andersson, Stanford Synchrotron Radiation Laboratory; **H. Bluhm, G. Ketteler, D.E. Starr,** Lawrence Berkeley National Laboratory; **T. Schiros,** Stanford Synchrotron Radiation Laboratory; **M. Salmeron,** Lawrence Berkeley National Laboratory; **H. Ogasawara, A. Nilsson,** Stanford Synchrotron Radiation Laboratory

The wetting phenomena at surfaces play a crucial role in chemical, biological and environmental processes, such as heterogeneous catalysis, corrosion and the global cycling of chemical elements. The structure and property of water on surfaces in equilibrium with its vapor at ambient conditions, however, remains poorly understood. Here we have investigated the adsorption of water on Cu(110) and Cu(111) at ambient conditions ($T = 0 \sim 200$ °C, relative humidity < 25 %), using in-situ X-ray photoemission spectroscopy. Cu(110) and (111) surfaces exhibit a remarkable difference in the wettability and water chemistry. On Cu(110), the OH and H₂O mixed layer is observed at relative humidities below 0.1 % (wetting). In contrast, on Cu(111), neither hydroxyl species nor molecular water are present even at a relative humidity of 25 % (non-wetting). This difference originates from the activation barrier for water dissociation on two Cu surfaces ((111) > (110)). Once the hydroxyl groups are formed on the surface, they act as anchoring sites for water molecules. This is because the hydrogen bond between OH and H₂O is stronger than that between two water molecules. We will also show that the wettability of surfaces can be controlled by preadsorbed oxygens, which change the dissociation barrier of water.

3:00pm SS2-TuA4 Water Clusters Growth on Pd(111) and Ru(0001) Studied by STM, M. Tatarkhanov, E. Fomin, University of California at Berkeley; **D.F. Ogletree, M. Salmeron,** Lawrence Berkeley National Laboratory

Water clusters formation on clean Pd(111) and Ru(0001) surfaces has been studied using home-built variable temperature ultra-high vacuum scanning tunneling microscopy. Clusters with honeycomb internal structure were formed after low coverage and low temperature adsorption. Increasing the coverage of water at low temperature doesn't create complete monolayer on both Pd(111) and Ru(0001), water forms very dense clusters and then starts to form second layer. This double layer exists only below 140K temperatures, after which it transforms into elongated clusters with bright perimeter for increased temperatures.

3:20pm SS2-TuA5 Effect of Oxygen on the Structure and Dissociation of Water on Ru(0001), A. Mugarza, Lawrence Berkeley National Laboratory and Institut de Ciència de Materials de Barcelona, Spain, US; **T.K. Shimizu¹,** Lawrence Berkeley National Laboratory; **J. Cerda,** Instituto de Ciencia de Materiales de Madrid CSIC, Spain; **D.F. Ogletree, M. Salmeron,** Lawrence Berkeley National Laboratory

The adsorption and dissociation of water on Ru(0001) with 0.03 ML of pre-adsorbed O has been studied as a function of temperature by scanning tunneling microscopy. Below 140 K and at very low coverage (0.004 ML) water form complexes with O as well as dimer and trimer aggregates. At higher coverage (0.012ML) in this temperature range larger clusters with visible internal structure are observed. After annealing to 140 K, extended chain (worm-like) structures with enhanced contrast at the periphery are observed. By comparing the experimental images with theoretical calculations these structures have been attributed to mixtures of H₂O and OH. The presence of O lowers the onset temperature for partial dissociation of water and affects the shape and internal structure of the clusters. In addition, atomic O reacts with the H on the surface to form OH. As the annealing temperature is raised to 220 K the worm-like structures disappear while, the concentration of H and OH increase, giving rise gradually to the formation of 2x2 O islands. These observations will be discussed and compared to the structures found on clean Ru(0001).

3:40pm SS2-TuA6 The True Ground State of Water Adlayers on Ru(0001), F. Traeger, D. Langenberg, C. Wöll, Ruhr-Universität Bochum, Germany

Recently the structure of water adlayers adsorbed on Ru(0001) has given rise to a pronounced controversy.¹⁻⁵ One reason for the ongoing debate are experimental problems arising from the fact that H₂O adlayers on this surface exhibit a very low threshold for electron beam damage. Here we present the first results on the structure of water (D₂O) adlayers on Ru obtained with a method where electron beam damage (either through primary or secondary electrons) can be strictly excluded. Results from He-atom scattering (HAS) reveal that the true ground-state of water on this surface exhibits a high-order commensurate structure. The HAS diffraction patterns are not consistent with any of the previous structural models proposed for this adsorbate system, either on the basis of experimental results or theoretical investigations. Test experiments revealed that the water adsorbate is indeed very sensitive to electrons, even short exposure times in front of the LEED instrument led to the formation of the well-known (R3xR3)R30° structure.¹ HAS measurements also demonstrate that electron irradiation results in both, electron induced desorption and electron-induced dissociation. We have developed an optimized preparation procedure for high-quality water adlayers, which is somewhat different from the previously proposed procedure. Structural models for the true ground state of water on the Ru(0001)-surface will be presented in the talk.¹ ¹ G. Held and D. Menzel, Surf. Sci. 316, 92, (1994).² P. J. Feibelman, Science 295, 99, (2002).³ C. Clay, S. Haq and A. Hodgson, Chem. Phys. Lett. 388, 89, (2004).⁴ K. Andersson et al., Phys. Rev. Lett. 93, 196101-1, (2004).⁵ J. Weissenrieder et al., Phys. Rev. Lett. 93, 196102-1, (2004).

4:00pm SS2-TuA7 Wetting and Multilayer Growth on Metal Surfaces, A. Hodgson, G. Zimbitas, M. Gallagher, S. Haq, G.R. Darling, The University of Liverpool, UK

We describe the wetting behaviour of water ice films on Ru(0001) and Pt(111) and how this is modified by OH co-adsorption. Both metals will form an intact water monolayer, but with different structures and wetting behaviour. Water forms a labile wetting layer on Pt(111), with hexagonal @sr@37 and @sr@39 ice structures at increasing coverage. Multilayer adsorption forms clusters whose size and registry to the @sr@39 layer depends on thickness and preparation conditions, thick ice films forming an oriented incommensurate crystalline ice, stabilised by reconstruction of the interface layer. OH co-adsorption pins the wetting layer into registry with Pt, forming an ordered (OH+H₂O) phase which can not restructure in response to multilayer adsorption. Although this layer has a similar OH_x skeleton to ice Ih, water does not form a stable 2D wetting layer and the surface is hydrophobic. On Ru(0001) the strong water-metal interaction pins the first monolayer into a structure that is unfavourable for hydrogen-bonding to a multilayer ice film. This layer does not wet, even for thick films, instead thick 3D multilayer ice clusters form which minimise their contact to the water monolayer. No ordered multilayer ice structure is formed, indicating that the tightly bound wetting layer does not reconstruct to accommodate the incommensurate ice Ih(0001) film to the metal surface. The factors influencing multilayer adsorption are examined using DFT calculations to compare adsorption on top of different water and (OH+H₂O) structures. We argue that wetting is determined by the ability of the first layer to restructure to optimise the bonding between a bulk ice layer and the metal surface.

4:20pm SS2-TuA8 Adsorption and Desorption Kinetics on a Porous Solid: N₂ on Amorphous Solid Water, T. Zubkov, Pacific Northwest National Laboratory; **T.R. Engstrom,** University of Texas at Austin; **R.S. Smith, B.D. Kay,** Pacific Northwest National Laboratory

Desorption of a weakly bound adsorbate from a porous solid was studied for the case of molecular nitrogen on amorphous solid water (ASW). Porous ASW films of different thickness were grown on Pt(111) by ballistic deposition. N₂ adsorption and desorption kinetics were monitored mass-spectrometrically. Temperature programmed desorption spectra show that with the increasing film thickness, the N₂ desorption peak systematically shifts to higher temperatures. The results are explained and quantitatively reproduced by a simple model, which assumes that the N₂ transport within the film is faster than the depletion rate to vacuum. The local coverage at the pore mouth determines the desorption rate. For thick ASW films (>1 μm), the assumption of the fast equilibration within the film is shown to be no longer valid due to diffusion limitations. The mechanisms of the adsorbate transport are discussed.*

¹ Morton S. Traum Award Finalist

Tuesday Afternoon, November 14, 2006

@FootnoteText@ *Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

Author Index

Bold page numbers indicate presenter

— A —

Andersson, K.: SS2-TuA3, **1**

— B —

Bluhm, H.: SS2-TuA3, **1**

— C —

Cerda, J.: SS2-TuA5, **1**

— D —

Darling, G.R.: SS2-TuA7, **1**

— E —

Engstrom, T.R.: SS2-TuA8, **1**

— F —

Fomin, E.: SS2-TuA4, **1**

— G —

Gallagher, M.: SS2-TuA7, **1**

— H —

Haq, S.: SS2-TuA7, **1**

Hodgson, A.: SS2-TuA7, **1**

— K —

Kay, B.D.: SS2-TuA8, **1**

Ketteler, G.: SS2-TuA3, **1**

— L —

Langenberg, D.: SS2-TuA6, **1**

— M —

Mugarza, A.: SS2-TuA5, **1**

— N —

Nilsson, A.: SS2-TuA3, **1**

— O —

Ogasawara, H.: SS2-TuA3, **1**

Ogletree, D.F.: SS2-TuA4, **1**; SS2-TuA5, **1**

— S —

Salmeron, M.: SS2-TuA3, **1**; SS2-TuA4, **1**; SS2-TuA5, **1**

Schiros, T.: SS2-TuA3, **1**

Shimizu, T.K.: SS2-TuA5, **1**

Smith, R.S.: SS2-TuA8, **1**

Starr, D.E.: SS2-TuA3, **1**

— T —

Tatarkhanov, M.: SS2-TuA4, **1**

Traeger, F.: SS2-TuA6, **1**

— W —

Wöll, C.: SS2-TuA6, **1**

— Y —

Yamamoto, S.: SS2-TuA3, **1**

— Z —

Zimbitas, G.: SS2-TuA7, **1**

Zubkov, T.: SS2-TuA8, **1**