

Wednesday Morning, November 11, 2009

Surface Science

Room: M - Session SS1-WeM

Water/Surface Interactions & Environmental Chemistry I

Moderator: D.R. Strongin, Temple University

8:00am **SS1-WeM1 Scanning Probe Microscopy of Interfacial Water Confined Between Silica Surfaces**, *B.I. Kim, J.R. Bonander, E.J. Kim, T. Tran*, Boise State University

Scanning probe microscope (SPM) techniques are employed to study the structure and mechanical properties of water confined between two silica surfaces. Water molecules adjacent to other materials, such as in the vicinity of biological cell membranes, rearrange to form "interfacial water." The interfacial water behaves differently from bulk water to a substantial degree in its structure and mechanical properties. Probing the structure of interfacial water and its mechanical properties is crucial from understanding of the biomolecular functions to the micro-machine development. Even with such importance, however, the interfacial water is difficult to observe with ordinary analytic techniques because of its delicate nature near the surface. The SPM's excellent distance and force control capability allows for investigating the interfacial water near the sample surface. A cantilever based optical interfacial force microscope (COIFM), a newly developed SPM technique at Boise State University, was used to probe the ordered structure of the interfacial water in the direction perpendicular to the surface. A Non-Contact (NC) AFM was used to image the arrangement of the interfacial water in the direction parallel to the surface. The COIFM and NC-AFM measurements were performed on silica surfaces, the most abundant substance on the earth's crust, for various relative humidity. The COIFM data show periodic features as the tip approaches the surface, showing single water-layer ordering effect of the interfacial water. In each layered region, the force decreases nonlinearly as the gap decreases. The NC-AFM images show that some water bundles lay down and some stand up, supporting the COIFM data. The humidity dependent data shows how the structure of water evolves as the thickness of the water film changes from droplets to monolayers to multilayers on the silica surface. The origin of the observed structure of the interfacial water is discussed with a simple two-dimensional self-assembly theory.

8:20am **SS1-WeM2 Theory of Tip-Sample Interaction Force for AFM in Water**, *M. Tsukada*, Tohoku University, Japan

Noncontact AFM(ncAFM) in aqueous condition is an important method for imaging soft biological nano materials as protein. We are attempting theoretical simulation for the atomic force microscopy(AFM) in water[1,2]. So far we found various remarkable features of tip-surface interaction force mediated by water molecules[2]. They are obtained either by the molecular dynamics (MD) calculation or by the 3D-RISM (Reference Interacting Site Model) calculation.

As an example of the numerical simulation by MD method, AFM images and 3D force map of mica surface in water were calculated and compared with the experiments by Yamada's Group. The oscillatory layer structures of water exist around the interface tracing the nano-scale shapes of the sample. The phase and the amplitude of the force oscillation felt by the tip are remarkably changed depending on the lateral tip position, resulting a complicated network structure of the 3D force map. The number of the water layers in the narrow gap between the tip and sample decreased abruptly and finally disappears when the tip approaches to the surface.

The 3D-RISM method was applied to clarify the local charge separation effect on the interaction force in water. The distribution of water molecules around the atomically charged portion on the substrate is significantly disturbed, and this effect is observed in the 3D-force map from much far region as compared with that in vacuum. We discuss how drastically different the water mediated tip-sample force compared with that in vacuum, and how they influence on the images.

[1]M. Tsukada, N. Watanabe, *Jpn.J.Appl.Phys.*, vol.48 No.3 2009

[2] Tsukada, Tagami, *Phys. Rev. B* submitted.

8:40am **SS1-WeM3 Isolated Single Water Molecules on Ultrathin MgO Film Studied by Scanning Tunneling Microscope**, *H.-J. Shin, J. Jung, K. Motobayashi*, RIKEN and University of Tokyo, Japan, *Y. Kim*, RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

The interaction of water molecules with solid surfaces has been a subject of considerable interests, due to its importance in the fields from atmospheric and environmental phenomena to biology, catalysis and electrochemistry [1-2]. Among various kinds of surfaces, a lot of theoretical and experimental studies have been performed regarding water on MgO(100), however, to date, there has been no direct observation of water molecules on MgO by scanning tunneling microscope (STM) as compared with those on metal surface. Here, we will present the direct observation and manipulation of single water molecules on ultrathin MgO(100) films using low-temperature scanning tunneling microscope (LT-STM). Our results rationalize the previous theoretical predictions of isolated water molecules on MgO including the optimum adsorption sites and non-dissociative adsorption of water. Moreover, we were able to dissociate a water molecule by exciting the vibrational mode of water, which is unattainable on metal surfaces. The enhanced residual time of tunneling electrons in molecules on the insulating film is responsible for this unique pathway toward dissociation of water.

[1] P. A. Thiel and T. E. Madey *Surf. Sci. Rep.* **7**, 211 (1987).

[2] M. A. Henderson, *Surf. Sci. Rep.* **46**, 5 (2002).

9:00am **SS1-WeM4 In Situ XPS Study of H₂O and CO₂ Adsorption on MgO(100) Films under Ambient Conditions**, *J. Newberg, D. Starr, E. Mysak*, Lawrence Berkeley National Lab, *S. Yamamoto, S. Kaya*, Stanford Synchrotron Radiation Lab, *T. Kendelewicz*, Stanford University, *S. Porsgaard, M. Salmeron*, Lawrence Berkeley National Lab, *G. Brown, Jr.*, Stanford University, *A. Nilsson*, Stanford Synchrotron Radiation Lab, *H. Bluhm*, Lawrence Berkeley National Lab

Under ambient relative humidity (RH) conditions thin film water coats metals, insulators, semiconductors and ice surfaces [1]. The water-oxide interface plays an important role in chemical, biological and industrial systems [2]. Water on MgO(100) is one of the most widely studied systems, both theoretically and experimentally, due to the simple rock salt cubic structure of MgO. Carbon dioxide is an important greenhouse gas, and the carbonation of MgO in mineral deposits has been suggested as a potential medium for carbon dioxide sequestration [3]. Here we present results from the investigation of the interaction of water and carbon dioxide with MgO(100)/Ag(100) films using the ambient pressure photoemission spectroscopy (APPEs) setup at beamline 11.0.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory [4]. With APPEs we can quantitatively probe on a molecular level the chemical changes of the MgO(100) surface using XPS and NEXAFS while in equilibrium with water and/or carbon dioxide gases. Using 0.5 Torr isobars, we have characterized the uptake of water on MgO surfaces up to 20% RH. At roughly 0.1% RH, the MgO surface is fully hydroxylated with a ML of OH and sub-ML molecular water. At 20% RH there is roughly 1 ML of molecular water interacting with a fully hydroxylated MgO surface. Preliminary results for carbon dioxide reactivity with MgO to form carbonate showed dependency on whether the MgO surface was dry (oxide terminated) or wet (hydroxyl/water terminated). Thus, the presence of thin film water influences carbon sequestration. Ongoing studies are addressing the influences of changing RH on MgO carbonation.

References

[1] G.E Ewing 2006 Chem Rev. 106 1511.

[2] G.E. Brown et al. 1999 Chem. Rev. 99 77.

[3] T. Koljonen et al. 2004 Energy 29 1521.

[4] H. Bluhm et al. 2007 MRS Bulletin 34 1022.

9:20am **SS1-WeM5 Oxide and Carbonate Surfaces in Dynamic Equilibrium with Water Vapor**, *V. Grassian*, University of Iowa
INVITED

Adsorbed water plays an important role in a wide range of surface phenomena. In this talk, the focus is on water interactions with oxide and carbonate surfaces in dynamic equilibrium with water vapor under ambient conditions of temperature and relative humidity. The coverage and nature of the adsorbed water layer as a function of relative humidity are investigated. Both experiment and theory show that the adsorbed water layer is inhomogeneous and the surface is not uniformly covered even at high relative humidity. The impact of the nature of the adsorbed water layer on the surface chemistry of

carbonate and oxide surfaces under ambient conditions will be discussed.

10:40am **SS1-WeM9 The Composition of the Liquid/Vapor Interface of Aqueous Nitrate and Nitric Acid Solutions**, *T.L. Lewis*, Univ. of California, Irvine, *M.A. Brown*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *K. Callahan*, Univ. of California, Irvine, *M. Faubel*, Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, *D. Tobias*, Univ. of California, Irvine, *B. Winter*, Hemholtz-Zentrum Berlin für Materialien und Energie, Germany, *J.C. Hemminger*, Univ. of California, Irvine

Nitrate anions become incorporated into sea salt aerosols through the uptake of gas-phase nitric acid in atmospheric aging processes. It has been suggested that photochemical decomposition of nitrate ions in the near surface region of such aerosols leads to OH radical production and subsequent halogen oxidation. However, the concentration of nitrate ions at the surface of aqueous solutions has been a controversial topic in the literature. We obtain a depth profile of the interfacial composition of nitrate anions in aqueous solution in the presence of alkali halide salts. All experiments were performed with XPS on a liquid micro jet and were acquired using tunable synchrotron radiation from the U41-PGM undulator beamline of the BESSY facility in Berlin, where we can vary the photoelectron kinetic energy to obtain depth dependent composition information. Our previous work shows that while nitrate and nitrite anions have a finite concentration at the interface, both prefer bulk solvation. Current results indicate that co-dissolved alkali halide salts in a sodium nitrate solution push the nitrate anion further into the bulk and away from the liquid-vapor interface. A greater effect is seen with increasing concentration of alkali halide as well as increasing size and polarizability of the halide anion. Comparison will be made with MD simulations of the corresponding solutions. In studies of nitric acid, another key component in the atmospheric chemistry of sea salt aerosols, tunable XPS elucidates the depth dependence of undissociated nitric acid. Results show that a higher concentration of undissociated nitric acid is present in the surface region relative to the bulk. Additionally, the relative concentration of undissociated nitric acid increases with increasing nitric acid concentration. These results have significant implications for the chemistry and photochemistry of sea salt aerosols.

11:00am **SS1-WeM10 Investigation of Hydroxyl Dimer Rows Formed by Thermal Dissociation of Water on Cu(110) Surface**, *B.Y. Choi*, *Y. Shi*, *M. Salmeron*, Lawrence Berkeley National Laboratory

Water dissociation on the surface is the first step in many reactions and wetting processes. A fundamental understanding of this process is necessary and applies to various fields, such as corrosion, catalysis, electrochemistry and hydrogen generation. Thermally dissociated water molecules on an oxygen precovered Cu(110) surface are investigated using scanning tunneling microscopy (STM) at low temperature. Chain structures of elongated molecules are obtained by dosing water on an oxygen precovered Cu(110) at 77K followed by annealing to ~180K. Density functional theory calculations reveal that the elongated molecular shapes are made of two hydrogen bonded OH molecules which form a dimer by tilting one OH to the other¹. The weak interaction between dimers gives rise to the changes in shape of the cluster. We propose that this structural variation is the result of molecular fluctuations and from the interaction with atomic hydrogen produced by water dissociation. Switching between the different dimer shapes can be accomplished by exciting the OH-stretch mode with tunneling electrons.

¹T. Kumagai et al. Phys. Rev. B 79, 035423 (2009)

11:20am **SS1-WeM11 Key Processes of Ice-Multilayer Evolution during Growth and Annealing Studied with STM**, *K. Thürmer*, *S. Nie*, *N.C. Bartelt*, Sandia National Laboratories

Although extensive research has been aimed at the structure of ice films [1], important details of the morphology evolution, especially for films in the nm-thickness range, have remained elusive. Our capability to image up to 30 molecular layers of ice with STM [2], enables us to track the film evolution during growth and annealing. In particular, we investigate the role of new-layer nucleation and surface self-diffusion.

As reported before by others, we observe that water deposited onto Pt(111) below 120K forms amorphous films, whereas metastable cubic ice appears between 120K and ~150K. At 140K and a mean film thickness of ~1nm the film consists of 2-3 nm high crystallites, embedded in a one bilayer high wetting layer. Analyzing the annealing behavior of these crystallites we find [3] that the rate at which new layers nucleate, and not surface diffusion, determines how fast individual crystallites equilibrate. The resistance to nucleate new layers even during deposition has a surprising effect on thicker films: The deposited water attaches preferentially to growth spirals

around screw dislocations, promoting the formation of metastable cubic ice [2].

Finally, we report the first measurements of surface self-diffusion on ice. Using uniform 5-nm-thick ice films (grown at 145K) as templates, we deposited a fraction of a monolayer of water at 115K to create metastable arrays of 2D-islands. By quantifying the Ostwald ripening of these arrays upon annealing between 115 and 135 K, we extract temperature-dependent diffusion rates and determine the activation energy for surface self-diffusion to be (0.4±0.1) eV [4].

[1] A. Verdaguer, G. M. Sacha, H. Bluhm, and M. Salmeron, Chem. Rev. **106**, 1478 (2006).

[2] K. Thürmer and N. C. Bartelt, Phys. Rev. B **77**, 195425 (2008).

[3] K. Thürmer and N. C. Bartelt, Phys. Rev. Lett. **100**, 186101 (2008).

[4] S. Nie, N. C. Bartelt, and K. Thürmer, Phys. Rev. Lett. **102**, 136101 (2009).

11:40am **SS1-WeM12 Structure of Ultra Thin Water Films on Ruthenium**, *S. Maier*, *I. Stass*, Lawrence Berkeley National Laboratory, *J.I. Cerda*, Instituto de Ciencia de Materiales de Madrid, Spain, *P.J. Feibelman*, Sandia National Laboratories, *M. Salmeron*, Lawrence Berkeley National Laboratory

The structure and chemistry of water at surfaces and interfaces is an unresolved and fundamental topic in many areas of science and technology such as catalysis, electrochemistry and environmental sciences. We use low temperature scanning tunneling microscopy in combination with DFT calculations to study the structure and reactions of ultra thin water films on Ru(0001) at the molecular scale.

We present new results on the formation of mixed water-hydroxyl structures following partial dissociation, observed above 130K. We found that the hydrogen produced during partial dissociation can be trapped in the interior of the hexagonal unit cell of the water hydroxyl structures and outside of the hexagons which is thermodynamically more stable. In addition, we studied the structure of water beyond the first layer and discovered that the hexagonal network of the second layer is surprisingly rotated 30° with respect to the first on Ru(0001) as well as on Pd(111). This rotation leads to a bonding structure between the water layers that significantly deviates from the conventional ice-like water model on hexagonal metals. We propose models for this novel structure of the first two water layers based on DFT calculations. Beyond the second water layer, a transition to the growth of compact ice clusters was found.

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