

Wednesday Afternoon, October 30, 2013

Surface Science

Room: 202 A - Session SS+AS+NS+SP-WeA

Single Molecules at Surfaces: Structure and Dynamics

Moderator: A.L. Utz, Tufts University

2:00pm **SS+AS+NS+SP-WeA1 Probing the Interface of Organic Coatings on Metals**, H.A. Terry, VUB/TU Delft, Belgium, T. Taheri, TU Delft, the Netherlands, T. Hauffman, VUB, Belgium, O. Ozkanat, J.A. Mol, TU Delft, the Netherlands

During the functional lifetime of coated metals, interfacial bonds at polymer/(oxyhydr)oxide/metal joints have to withstand high mechanical forces and corrosive attack. Therefore, it is crucial to control and understand the bonding mechanism originating at polymer/(oxyhydr)oxide/metal interfaces in order to achieve long-term stability. While the type of bonding contributes to the strength of adhesion, the nature of the interface depends on both functionality present in the organic molecules of the coating and the nature of the oxide film e.g. hydration, hydroxyl content, oxide thickness, surface morphology and chemical composition. Those properties might be extremely sensitive to the small changes in the environmental conditions, such as ageing and humidity.

Studying the bonding properties of the polymeric coating to the metal surface is experimentally difficult, because the interface is hard to be reached by analytical techniques due to the relatively high thickness of the polymer coatings. Consequently, the interfacial bonding can be modeled through adsorption of functional groups -representative interfacial adhesive molecules- on differently pretreated surfaces by means of bonding mechanism (FTIR) and affinity (XPS) studies. Furthermore, the buried interface and delamination mechanisms at this location can be studied by Scanning Kelvin Probe (SKP) measurements.

Recent References

In situ study of buried interfacial bonding mechanisms of carboxylic polymers on Zn surfaces, *Journal of Physical Chemistry C*, Volume: 117, N° in volume: 7, pp: 3374 - 3382, 2013, Taheri p., Flores J., Hannour F., de Wit J., Terry H., Mol J.

Effects of Zinc Surface Acid-Based Properties on Formation Mechanisms and Interfacial Bonding Properties of Zirconium-Based Conversion Layers, *Journal of Physical Chemistry C*, Volume: 116, pp: 8426 - 8436, 2012, Taheri p., Lill K., de Wit J., Mol J., Terry H.

A comparison of the interfacial bonding properties of carboxylic acid functional groups on zinc and iron substrates, *Electrochimica Acta*, Volume: 56, pp: 1904 - 1911, 2011, Taheri p., Wielant J., Hauffman T., Reyes Flores J., Hannour F., de Wit J., Mol J., Terry H.

Role of surface oxide properties on the aluminum/epoxy interfacial bonding, *Journal of Physical Chemistry C*, Volume: 117, N° in volume: 9, pp: 4480 - 4487, 2013, Salgin B., Ozkanat O., Mol J., Terry H., Rohwerder M.

Bonding mechanisms at buried interfaces between carboxylic polymers and treated zinc surfaces, *Journal of Physical Chemistry C*, Volume: 117, N° in volume: 6, pp: 2780 - 2792, 2013, Taheri p., Ghaffari M., Flores J., Hannour F., de Wit J., Mol J., Terry H.

2:20pm **SS+AS+NS+SP-WeA2 Ultra-High Vacuum Tip-Enhanced Raman Spectroscopy with Molecular-Resolution Scanning Tunneling Microscopy**, N. Jiang, J. Klingsporn, E. Pozzi, M.C. Hersam, R.P. Van Duyne, Northwestern University

The study of ultrahigh vacuum (UHV) tip-enhanced Raman spectroscopy (TERS) has been raised to an unprecedented level. By using ex-situ laser focusing and Raman collection optics, optimization of the optical path is achieved without compromising UHV. All sample preparation and tip degassing are performed in-situ, maintaining atomically clean surfaces, greatly enhancing the stability of the tip-sample junction, and ensuring minimal contamination in the field enhancement region beneath the STM tip. At 292K, multiple vibrational modes for copper phthalocyanine (CuPc) adlayers on Ag (111) have been resolved in TER spectra obtained concurrently with molecular resolution UHV Scanning tunneling Microscopy (STM). Then Rhodamine 6G (R6G) molecules were studied as they have larger Raman cross-section. The sample was cooled down to 19 K to decrease the diffusion of R6G on surface at very low coverage. Single R6G molecules and clusters were observed using STM. For the first time, TERS vibrational modes for a few R6G molecules on Ag (111) have been resolved with concurrent molecular resolution STM images at 19 K. In comparison with the TER spectra at 292 K, the sharpening of TERS peaks

and the existence of new peaks at 19 K demonstrates the utility of UHV-TERS towards obtaining site-specific chemical information about adsorbed molecules. This study sets the stage for Raman vibrational fingerprinting and correlated sub-molecular resolution topography of site-specific binding of molecules on solid surfaces.

2:40pm **SS+AS+NS+SP-WeA3 High Resolution STM-IETS Characterization for Single Molecule on Metal Surface**, C. Xu, C. Jiang, Y.N. Zhang, R.Q. Wu, W. Ho, University of California, Irvine

Inelastic electron tunneling spectroscopy (IETS) with the scanning tunneling microscope (STM) has been regarded as the ultimate tool to identify and characterize single molecules adsorbed on solid surfaces with atomic spatial resolution. With the improvement of energy resolution obtained at ~600 mK, STM-IETS is able to resolve the lowest vibrational energies and reveal subtle interactions between the molecule and its environment which were previously not possible at higher temperatures. Here we demonstrate the capability of sub-Kelvin STM on detecting the influence of the tip as well as the anisotropy of the reconstructed Au(110) surface on the low energy hindered vibrational motions of single adsorbed CO molecule.

3:00pm **SS+AS+NS+SP-WeA4 Electronic Structure of H₂Pc on Ultrathin NaCl Films with Various Thickness**, M. Imai, The University of Tokyo, Japan, H. Imada, T.K. Shimizu, RIKEN, Japan, M. Kawai, The University of Tokyo, Japan, Y. Kim, RIKEN, Japan

We have investigated thickness dependence of electronic states of single metal-free Phthalocyanine (H₂Pc) on NaCl insulating films on Au(111), using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Our aim is to understand how the thickness of NaCl films affect the molecular properties using the well-known and widely studied molecule.[1] NaCl films are known to weaken the molecular-metal interaction,[2] but we found the electronic properties of the H₂Pc adsorbed on 2 ML and 3 ML-thick NaCl are indeed different. Isolated H₂Pc molecules are adsorbed on both 2 ML and 3 ML thick NaCl islands, which are grown from Au(111) step edges. Appearances of H₂Pc are similar for both islands, four-lobe or eight-lobe depending on bias voltages. STS spectra acquired at the centers of molecules on both islands show one peak in occupied and one in unoccupied states. By visualizing spatial distribution of density of states at the peak bias, we found that these two peaks corresponded to the highest occupied molecular orbital (HOMO), and degenerated lowest unoccupied molecular orbitals (LUMO and LUMO+1). A difference between 2ML and 3 ML is the peak position of degenerated LUMO and LUMO+1 states and thus HOMO-LUMO gap. Our observation implies that the effect of NaCl is not just to decouple metal electronic states, but it indeed affects the electronic states of adsorbed molecules, which might arise from the metal-insulator interaction such as interfacial dipole.

[1] T. Komeda, H. Isshiki, and J. Liu, *Sci. Tech. Adv. Mater.* **11**, 054602 (2010).

[2] J. Repp, G. Meyer, S. Stojković, A. Gourdon, and C. Joachim, *Phys. Rev. Lett.* **94** (2005).

4:00pm **SS+AS+NS+SP-WeA7 Species-Selective Atomic Resolution Imaging with Scanning Probe Methods**, H. Monig, University of Muenster, Germany, M. Todorovic, Universidad Autónoma de Madrid, Spain, M.Z. Baykara, Bilkent University, Turkey, J. Goetzen, O.E. Dagdeviren, Yale University, T.C. Schwendemann, Southern Connecticut State University, L. Rodrigo, Universidad Autónoma de Madrid, Spain, E.I. Altman, Yale University, R. Perez, Universidad Autónoma de Madrid, Spain, U.D. Schwarz, Yale University

INVTED
Despite the evolution of scanning probe microscopy (SPM) into a powerful set of techniques that image surfaces and map their properties down to the atomic level, significant limitations in both imaging and mapping persist. Currently, typical SPM capabilities qualitatively record only one property at a time and at a fixed distance from the surface. Furthermore, the probing tip's apex is chemically and electronically undefined, complicating data interpretation. To overcome these limitations, we started to integrate significant extensions to existing SPM approaches. First, we extended noncontact atomic force microscopy with atomic resolution to three dimensions by adding the capability to quantify the tip-sample force fields near a surface with picometer and piconewton resolution. Next, we gained electronic information by recording the tunneling current simultaneously with the force interaction. We then moved on to study the influence of tip chemistry and asymmetry on the recorded interactions. Through a combination of experimental work and theoretical analysis, we show how specific atomic species can be selectively imaged in both the force and the current channels depending on the choice of imaging parameters and tip

chemistry. Applications to metal oxides are shown. From this platform, we present our vision of a method capable of characterizing full atomic-scale chemical and electronic properties.

4:40pm SS+AS+NS+SP-WeA9 Surface Morphology of Chemisorbed N on Pt(111). Z. Liang*, University of Illinois at Chicago, H. Yang, Y. Kim, RIKEN, Japan, M. Trenary, University of Illinois at Chicago

The surface morphology of chemisorbed N on a Pt(111) surface has been studied at the atomic level with low temperature scanning tunneling microscopy (LT-STM). At high coverages, two phases, $p(2\times 2)$ -N and $(\sqrt{3}\times\sqrt{3})R30^\circ$ -N, are found to coexist at temperatures between 360 and 400 K. For both phases nitrogen occupies fcc-hollow sites. At temperatures of 400 K and slightly above, only the $p(2\times 2)$ -N phase is present on the surface. At temperatures above 420 K, nitrogen starts to desorb. The $p(2\times 2)$ -N phase shows a honey-comb structure in STM images with three nitrogen and three platinum atoms forming a six-member ring, which can be attributed to the strong nitrogen binding to the underlying Pt atoms. At low coverages, incomplete (2×2) patches of N, but no $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure, are observed on the surface. When N and O are coadsorbed on the surface, they form a mixed (2×2) overlayer of N+O at high coverages. N and O can be clearly distinguished from each other by their appearance in the STM images.

5:00pm SS+AS+NS+SP-WeA10 Relative Stability of Thiols and Selenols SAMs on Ag(111) – Exchange and Desorption Experiments. J.W. Ossowski, J. Rysz, Jagiellonian University, Poland, A. Terfort, Goethe University, Germany, P. Cyganik, Jagiellonian University, Poland

The stability of chemical bonding between molecule and substrate is one of the key factor considering diverse applications of Self-Assembled Monolayers (SAMs). Addressing this issue experimentally or theoretically is difficult considering complex interplay of the molecule-substrate and molecule-molecule interactions in SAMs. So far most of experiments have been performed for thiol based SAMs on Au(111) substrate and far less is known for equally important Ag(111) substrate.

In this presentation we report exchange and desorption experiments probing the effect of S to Se substitution on stability of molecule-substrate interface in SAMs on Ag(111) substrate by using two homologue series of molecules in the form $\text{BPnS/Ag(111)} (\text{CH}_3-(\text{C}_6\text{H}_4)_2-(\text{CH}_2)_n-\text{S}-\text{Ag}, n = 2-6)$ and $\text{BPnSe/Ag(111)} (\text{CH}_3-(\text{C}_6\text{H}_4)_2-(\text{CH}_2)_n-\text{Se}-\text{Ag}, n = 2-6)$.¹ Such experiments were possible since both analogs form similar structures on Ag(111) substrate² and thus observed differences in stability between these two types of SAMs could be related to the molecule-substrate interface stability. Quantitative control of the exchange process was obtained using IRRAS (Infrared Reflection Absorption Spectroscopy). Additionally, ion-induced desorption experiments by means of SIMS (Secondary Ion Mass Spectrometry) were performed. Obtained results will be discussed together with analogical experiments³⁻⁵ performed previously for Au(111) substrate enabling comparison of molecule substrate-interface stability for thiol and selenol based SAMs on Ag(111) and Au(111) substrates.

References

- (1) J. Ossowski, P. J. Rysz, A. Terfort and P. Cyganik *in preparation*.
- (2) T. Weidner, A. Schaporenko, J. Muller, M. Schmid, P. Cyganik, et al. *J. Phys. Chem. C* **2008**, *112*, 12495.
- (3) K. Szelagowska-Kunstman, P. Cyganik, et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400.
- (4) F. Vervaecke, S. Wyczawska, P. Cyganik, et al. *ChemPhysChem(Communication)* **2011**, *12*, 140. (5) S. Wyczawska, P. Cyganik, A. Terfort, P. Lievens, *ChemPhysChem(Communication)* **2011**, *12*, 2554.

5:20pm SS+AS+NS+SP-WeA11 Formation Mechanism of van der Waals Interface between a π -conjugated Molecule and Au(111). J. Jung, RIKEN, Japan, J.-H. Kim, The University of Tokyo, Japan, K. Tahara, Y. Tobe, Osaka University, Japan, M. Kawai, The University of Tokyo, Japan, Y. Kim, RIKEN, Japan

Van der Waals (vdW) force is one of the most abundant interactions in nature, and thus it plays a pivotal role in determining architectures of molecular and biological systems or in constructing interfaces between chemically non-reactive materials. Understanding interfacial electronic and geometric structures at organic-metal contacts formed by the vdW interactions is, in particular, of great importance in order to finely control the functions of organic electronic and photovoltaic devices. Nevertheless, fundamental insights into a formation mechanism of vdW interface have not yet been fully achieved due to the weak adsorption characters. Here, we propose a detailed description on formation mechanisms of interfacial electronic and geometric structures at vdW interface between a π -

conjugated hydrocarbon (π -CHC) molecule and the noblest Au surface, using vdW density functional (vdW-DF) calculations based on atomically-resolved scanning tunneling microscopy (STM) imaging and scanning tunneling spectroscopy (STS) at a cryogenic temperature. Based on the first direct observation of adsorption geometry of an isolated π -CHC molecule on Au(111) and an efficient computational approach, we revealed that the interfacial electronic structures form in a way to maximize the interfacial orbital interaction between a π -CHC molecule and the noble Au surface through processes of *interlocking-dragging-splitting* induced by the local splitting of the Au d state due to electronic coupling with the molecular π -state. Furthermore, the orbital interaction between a π -CHC molecule and the Au surface can play a decisive role in constraining adsorption geometry, i.e., both horizontal orientation and adsorption distance, even in the archetypal vdW adsorption system. Considering that the overlap of the frontier electronic states is important in a charge-carrier path at the organic-metal contact, our observations provide not only deeper insight into the weak adsorption process but also new perspectives to organic electronics using π -CHC molecules on the Au electrodes.

5:40pm SS+AS+NS+SP-WeA12 Scanning Tunneling Microscopy/Spectroscopy Studies of Indolo[2,1-b]quinazolin-6,12-dione (tryptanthrin) and its Analogs Adsorbed at the Solution-HOPG Interface. J. Olson, J.C. Baum, M. Novak, K. Sriraman, Florida Institute of Technology

Tryptanthrins represent a class of compounds of interest for their anti-parasitic properties. Particularly, they have shown in-vitro efficacy versus organisms that cause malaria, leishmania, trypanosomiasis, tuberculosis, and fungal infections. However, little is known of their mode(s) of action at the molecular level. To investigate their geometric and electronic behavior, STM has been used to observe molecular monolayers of these compounds. Sub-molecular resolution has allowed the direct observation of individual lobes of the HOMO and LUMO states. The parent compound forms rows that alternate in contrast (light/dark), which is attributed to adsorption-induced stereoisomerization, with each row comprised of one enantiomer. Also excellent lobe-to-lobe resolution is observed for the LUMO of the parent compound as well as the HOMO of 8-fluorotryptanthrin (which similarly displays adsorption-induced stereoisomerization). Additionally, the authors have undertaken measurements of the tunneling barriers of these molecules, with a quantitative structure-activity relationship (QSAR) correlation as the goal. Sub-molecular quantitative measurements of the tunneling barriers have been accomplished for the parent compound, and show an interesting correlation to its known chemistry. Also, preliminary correlations of biological efficacy and molecular barrier heights have been observed over several analogs. Generally speaking, increased anti-parasitic efficacy corresponds to lower measured barrier heights, which is consistent with a possible tunneling mechanism.

Authors Index

Bold page numbers indicate the presenter

— A —

Altman, E.I.: SS+AS+NS+SP-WeA7, 1

— B —

Baum, J.C.: SS+AS+NS+SP-WeA12, 2

Baykara, M.Z.: SS+AS+NS+SP-WeA7, 1

— C —

Cyganik, P.: SS+AS+NS+SP-WeA10, 2

— D —

Dagdeviren, O.E.: SS+AS+NS+SP-WeA7, 1

— G —

Goetzen, J.: SS+AS+NS+SP-WeA7, 1

— H —

Hauffman, T.: SS+AS+NS+SP-WeA1, 1

Hersam, M.C.: SS+AS+NS+SP-WeA2, 1

Ho, W.: SS+AS+NS+SP-WeA3, 1

— I —

Imada, H.: SS+AS+NS+SP-WeA4, 1

Imai, M.: SS+AS+NS+SP-WeA4, 1

— J —

Jiang, C.: SS+AS+NS+SP-WeA3, 1

Jiang, N.: SS+AS+NS+SP-WeA2, 1

Jung, J.: SS+AS+NS+SP-WeA11, 2

— K —

Kawai, M.: SS+AS+NS+SP-WeA11, 2;
SS+AS+NS+SP-WeA4, 1

Kim, J.-H.: SS+AS+NS+SP-WeA11, 2

Kim, Y.: SS+AS+NS+SP-WeA11, 2;
SS+AS+NS+SP-WeA4, 1; SS+AS+NS+SP-
WeA9, 2

Klingsporn, J.: SS+AS+NS+SP-WeA2, 1

— L —

Liang, Z.: SS+AS+NS+SP-WeA9, 2

— M —

Mol, J.A.: SS+AS+NS+SP-WeA1, 1

Monig, H.: SS+AS+NS+SP-WeA7, 1

— N —

Novak, M.: SS+AS+NS+SP-WeA12, 2

— O —

Olson, J.: SS+AS+NS+SP-WeA12, 2

Ossowski, J.W.: SS+AS+NS+SP-WeA10, 2

Ozkanat, O.: SS+AS+NS+SP-WeA1, 1

— P —

Perez, R.: SS+AS+NS+SP-WeA7, 1

Pozzi, E.: SS+AS+NS+SP-WeA2, 1

— R —

Rodrigo, L.: SS+AS+NS+SP-WeA7, 1

Rysz, J.: SS+AS+NS+SP-WeA10, 2

— S —

Schwarz, U.D.: SS+AS+NS+SP-WeA7, 1

Schwendemann, T.C.: SS+AS+NS+SP-WeA7, 1

Shimizu, T.K.: SS+AS+NS+SP-WeA4, 1

Sriraman, K.: SS+AS+NS+SP-WeA12, 2

— T —

Tahara, K.: SS+AS+NS+SP-WeA11, 2

Taheri, T.: SS+AS+NS+SP-WeA1, 1

Terfort, A.: SS+AS+NS+SP-WeA10, 2

Terryn, H.A.: SS+AS+NS+SP-WeA1, 1

Tobe, Y.: SS+AS+NS+SP-WeA11, 2

Todorovic, M.: SS+AS+NS+SP-WeA7, 1

Trenary, M.: SS+AS+NS+SP-WeA9, 2

— V —

Van Duyn, R.P.: SS+AS+NS+SP-WeA2, 1

— W —

Wu, R.Q.: SS+AS+NS+SP-WeA3, 1

— X —

Xu, C.: SS+AS+NS+SP-WeA3, 1

— Y —

Yang, H.: SS+AS+NS+SP-WeA9, 2

— Z —

Zhang, Y.N.: SS+AS+NS+SP-WeA3, 1