

## Surface Science Division

Room: 25 - Session SS+AS+MI-MoM

### Organic/Inorganic Surfaces and Interfaces

Moderators: Liney Arnadottir, Oregon State University,

Bruce Koel, Princeton University

8:20am **SS+AS+MI-MoM1 The Use of EC-STM to Study the Nanoscale Structure and Behavior of Atomically Thin Ag Films on Au Surfaces.** J.A. Phillips, H.R. Morgan, L.E. Jackson, G. LeBlanc, Erin Iski, University of Tulsa **INVITED**

The formation of an atomically thin Ag monolayer on a Au(111) surface has been shown to significantly alter the properties of the underlying substrate (1). A further exploration into the chemical mechanisms by which these thin films are deposited reveals two different sources of Ag during the formation of the monolayer. Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are used to probe the *in-situ* interfaces of these systems. EC-STM is a unique technique in that in addition to providing a local probe of the atomic surface structure, EC-STM also functions as a 3-electrode cell in which redox chemistry can be performed to understand the chemical reactivity of the surface. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. In addition to the ability to perform two kinds of Ag Underpotential Deposition (UPD) on Au(111) using a single solvent system (AgCl), this investigation also includes the examination of the effect of different halides on the thermal stability of the as-formed Ag monolayers. While it has been previously demonstrated that deposition from a AgCl system affords oxidative and thermal stability up to 1,000 K (1), the role of the identity of the halide has yet to be explored, specifically comparing depositions from both AgBr and AgI solutions. Preliminary investigations indicate that a monolayer formed from the AgBr system remains on the surface after the 1,000 K thermal treatment, while the same is not true for the AgI system. The origin of these differences will be examined in detail with EC-STM, CVs, and Density Functional Theory (DFT). Studies of this nature are critical to understanding the fundamental mechanisms behind thin film growth using UPD and the exact role of halides in the observed thermal stabilization. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during deposition could lead to exciting new directions for thin film technologies.

(1) Iski *et al.* *Electrochimica Acta* (2011), 56, 1652-1661.

9:00am **SS+AS+MI-MoM3 Decomposition and Self-Assembly of Coronene on Pt(111).** Chen Wang, University of California Irvine, K. Thurmer, N. Bartelt, Sandia National Laboratories

Composed of seven benzene rings that form a larger, hexagonal structure, coronene is a molecule often referred to as "the smallest flake of graphene". As such, this molecule provides insight into the nature and dominance of edge effects in graphene-based systems and devices. Furthermore, as a polynuclear aromatic hydrocarbon, coronene serves as a common chemical precursor and building block in soot formation, a process that is still largely mysterious in its earliest stages. This work presents the study of coronene assembly on Pt(111) at the nanoscale by using scanning tunneling microscopy and density functional theory calculations. Both experimental and theoretical methods focus on understanding the intramolecular interactions between neighboring molecules of coronene and with the underlying metal substrate by characterizing the molecular assembly at the monolayer and bilayer. At the monolayer, the platinum surface is highly interactive with the coronene, resulting in fragmentation of the molecule on and a high binding energy to the platinum surface. At the bilayer, platinum interference is screened, and several coronene-based structures are observed. In situ annealing allows for the observation of molecular clustering as the surface dewets. The coronene molecules first form chains, then clumps, and finally large clusters which bear notable resemblance to incipient soot. These findings are promising contributions to soot research and further general understanding of graphene at its smallest scale.

9:20am **SS+AS+MI-MoM4 Understanding of Single-layer ZnS Supported on Au(111).** Xingyi Deng, D.C. Sorescu, J. Lee, National Energy Technology Laboratory

We investigate the structure and energetics of ZnS single-layer supported on Au(111) using a combination of experimental and theoretical approaches. Single-layer of ZnS, consisting of one atomic layer of ZnS(111) plane, has been grown on Au(111) via sulfurization of metallic Zn in H<sub>2</sub>S at T = 550 K. ZnS single-layer on Au(111) forms a ZnS-(3 × 3)/Au(111)-(4 × 4)

coincidence structure based on the LEED measurement. High resolution STM images reveal hexagonal unit cells of 6.7 × 6.7 Å<sup>2</sup> and 11.6 × 11.6 Å<sup>2</sup>, corresponding to √3 and 3 times the unit cell of the ideal zincblende ZnS-(1 × 1), respectively, depending on the tunneling conditions. A significantly reconstructed non-planar structure of ZnS single-layer is suggested based on density functional theory (DFT) calculations. Specifically, 2/3 of the S anions are found to be located nearly in the plane of the Zn cations and the rest 1/3 of the S anions protruding above the Zn plane. These results are discussed and compared with other related systems, such as ultrathin ZnO supported on Au(111), in order to advance our understanding of materials in the ultrathin regime.

9:40am **SS+AS+MI-MoM5 X-ray Microscopy and Spectroscopy Insights of Metal-Organics Contacts.** Der-Hsin Wei, K.T. Lu, T.H. Chuang, C.I. Lu, Y.J. Hsu, National Synchrotron Radiation Research Center, Taiwan, Republic of China

#### Abstract

After the giant magnetoresistance (GMR) was demonstrated in Co/Alq<sub>3</sub>/LSMO trilayers [1], the rise of organic spintronics was no longer a question of if, but when. Latter it was even suggested that the interfaces are the most critical players toward the success of organic spintronics [2]. Unfortunately, despite much effort, vertical organic spin valve (OSV) could not establish a meaningful GMR at room temperature unless a thin insulator film is inserted between the ferromagnetic electrode and organic spacer [3-5]. Calls for spectroscopic studies were thus made to improve or even scrutinize the existing understandings [6]. In this report, I describe a jointed X-ray microscopy and spectroscopy investigations on multiple ferromagnet-organic hybrid structures including Co/pentacene, Fe/C<sub>60</sub>, Co/C<sub>60</sub>, and Ni/C<sub>60</sub>. Our study indicates that the ferromagnetic (FM) 3d transition metals land on organic semiconductor (OSC) films suffer an apparent magnetization retardation. Further investigation reveals that there is more than a reactive interface behind the scenes. Finally, the connection between our findings and reported transport measurements is addressed.

#### Acknowledgments

Financial supports from Minister of Science and Technology (MoST) and National Synchrotron Radiation Research Center at Taiwan are greatly acknowledged.

#### References

- [1] - Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, *Nature* **427**, 821 (2004).
- [2] - P. P. Ruden, *Nat. Mater.* **10**, 8 (2011).
- [3] - T. S. Santos, J. S. Lee, P. Migdal, I. C. Lekshmi, B. Satpati, and J. S. Moodera, *Phys. Rev. Lett.* **98**, 016601 (2007)
- [4] - M. Gobbi, F. Golmar, R. Llopis, F. Casanova, F.èlix, and L. E. Hueso, *Adv. Mater.* **23**, 1609 (2011).
- [5] - X. Zhang, S. Mizukami, T. Kubota, Q. Ma, M. Oogane, H. Naganuma, Y. Ando, and T. Miyazaki, *Nat. Comm.* **4**, 1392 (2013).
- [6] - C. Boehme, J. M. Lupton, *Nat. Nano.* **8**, 612 (2013).

10:00am **SS+AS+MI-MoM6 Anchoring of Carboxylic and Phosphonic Acids on Atomically Defined Oxide Surfaces: The Role of Protons, Hydroxyl Groups and Water.** M. Schwarz, T. Xu, S. Mohr, C. Schuschke, Joerg Libuda, University Erlangen-Nuernberg, Germany

Organic-oxide interfaces are at the heart of various emerging technologies, ranging from organic electronics to solar energy conversion. Their functionality arises from complex organic layers which are normally anchored to the oxide surface via specific linker groups. Typically, the anchoring groups release protons, thus forming surface hydroxyl groups. The role of these protons, the surface hydroxyl groups, and the interfacial water is one the most essential but, simultaneously, also one of the most poorly understood aspects in organic film formation.

We studied the interaction of water, carboxylic acids, and organic phosphonic acids with different cobalt oxide surfaces, namely Co<sub>3</sub>O<sub>4</sub>(111), CoO(111) and CoO(100), prepared in form of thin well-ordered films on Ir(100). The interaction of water with these surfaces is strongly structure-dependent and ranges from weak molecular adsorption on CoO(100) to the formation very strongly bound OH groups on Co<sub>3</sub>O<sub>4</sub>(111). Similarly, pronounced structure dependencies are observed upon anchoring of benzoic acid. Time-resolved and temperature-programmed vibrational spectroscopies with deuterated carboxylic acids indicate the formation of well-defined mixed adsorbate layers consisting of bridging benzoates and OD groups formed in the anchoring reaction. For phthalic acid, which may bind via one or via two linker groups, the adsorption geometry is controlled by the arrangement of the surface Co<sup>2+</sup> ions. Organophosphonic acids, on the other hand, show a complex temperature-dependent anchoring behavior, which originates from

the multiple adsorption geometries which these molecules can adopt. Finally, we investigated the anchoring behavior of larger organic species, such as carboxylated porphyrin derivatives, for which differently oriented phases can be observed by time-resolved in-situ spectroscopy during organic film growth in UHV. Intriguingly, the same reactions can also be monitored by in-situ vibrational spectroscopy at the solid/liquid interface on the same oxide surfaces prepared in UHV. We present first spectroscopic data, in which we directly compare these anchoring reactions in UHV and at the solid/liquid interface.

[1] K. Werner, S. Mohr, M. Schwarz, T. Xu, M. Amende, T. Döpfer, A. Görling, J. Libuda, *Journal of Physical Chemistry Letters* 7, 555 (2016)

[2] T. Xu, M. Schwarz, K. Werner, S. Mohr, M. Amende, J. Libuda, *Chemistry - A European Journal* 15, 5384 (2016)

[3] T. Xu, M. Schwarz, K. Werner, S. Mohr, M. Amende, J. Libuda, *Physical Chemistry Chemical Physics* 18, 10419 (2016)

10:40am **SS+AS+MI-MoM8 Thiolate versus Selenolate: Structure, Binding Strength, Thermal Stability, and Charge Transfer Properties**, J. Ossowski, Jagiellonian University, Poland, T. Wächter, Universität Heidelberg, Germany, T. Żaba, Jagiellonian University, Poland, L. Silies, M. Kind, Universität Frankfurt, Germany, A. Noworolska, Jagiellonian University, Poland, F. Blobner, Technische Universität München, Germany, D. Gnatek, J. Rysz, Jagiellonian University, Poland, M. Bolte, Universität Frankfurt, Germany, P. Feulner, Technische Universität München, Germany, A. Terfort, Universität Frankfurt, Germany, M. Zharnikov, Universität Heidelberg, Germany, Piotr Cyganik, Jagiellonian University, Poland

Selenolate is considered as an alternative to thiolate to serve as a headgroup mediating the formation of self-assembled monolayers (SAMs) on coinage metal substrates. There are however ongoing vivid discussions regarding the advantages and disadvantages of these anchor groups, regarding, in particular, the energetics of the headgroup-substrate interface, thermal stability and their efficiency in terms of charge transport/transfer. Here we introduce a well-defined model system of 6-cyanonaphthalene-2-thiolate and -selenolate SAMs on Au(111) to resolve these controversies. The exact structural arrangements in both types of SAMs are somewhat different, suggesting a better SAM building ability in the case of selenolates [1]. At the same time, both types of SAMs have similar packing densities and molecular orientations [1]. This permitted reliable competitive exchange and ion beam induced desorption experiments which provided an unequivocal evidence for a stronger bonding of selenolates to the substrate as compared to the thiolates [1]. The thermal analysis reveals higher stability of thiolates as compared to selenolates due to the higher stability of the S-C bond as compared to the Se-C which results from stronger bonding of selenolates with the Au(111) substrate [2]. Regardless of these differences, the dynamic charge transfer properties of the thiolate and selenolate based adsorbates were found to be identical as determined by the core-hole-clock approach, which is explained by a redistribution of electron density along the molecular framework, compensating the difference in the substrate-headgroup bond strength [1].

#### References

[1] Ossowski, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; Terfort\*, A.; Cyganik\*, P.; Zharnikov\*, M., *ACS Nano, Thiolate versus Selenolate: Structure, Stability and Charge Transfer Properties*, 9, 4508-4526 (2015).

[2] Ossowski J. *et al* paper in preparation.

11:00am **SS+AS+MI-MoM9 Preserving Material Morphology by Gas-Phase Functionalization: Surface Modification of ZnO with Propiolic Acid**, F. Gao, University of Delaware, S. Aminane, Université Pierre et Marie Curie, France, S. Bai, Andrew Teplyakov, University of Delaware

Chemical functionalization of ZnO surface is commonly performed using reactions of carboxylic acids with the surface of this material. However, liquid phase reactions of carboxylic acids with ZnO often cause changes in surface morphology. Etching has been widely acknowledged as a potential problem in this functionalization process. This work will use gas-phase propiolic acid dosed in vacuum to modify ZnO nano-powder while preserving its morphology and leaving the alkyne group available for subsequent chemical modification via the azide-alkyne cycloaddition “click” reaction with benzyl azide. The formation of the surface carboxylate following gas-phase exposure of propiolic acid is shown to be a highly selective process confirmed by solid-state nuclear magnetic resonance spectroscopy, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy. Electron microscopy is used to confirm that the morphology of the material is not affected during this modification and to compare with the liquid phase processing. It is also found that ZnO surface is stabilized by propiolic acid, as following this initial modification, further secondary postmodification based on either gas-phase exposure or liquid phase reactions were tested and confirmed to not affect the morphology of ZnO material. Based on this functionalization approach, delicate

nanostructures, nanorods, or nanopowders and even ZnO-based devices can be chemically modified for further functionalization for applications where preserving surface morphology during chemical modification is especially important.

11:20am **SS+AS+MI-MoM10 Enhanced Long-range Magnetic Order by the Organic-Ferromagnetic Hybrid Interface**, Yao-Jane Hsu, M.W. Lin, National Synchrotron Radiation Research Center, Taiwan, Republic of China, P.H. Chen, National Tsing-Hua University, Taiwan, Republic of China, Y.L. Lai, National Synchrotron Radiation Research Center, Taiwan, Republic of China, T.N. Lam, National Chiao-Tung University, Taiwan, Republic of China, D.H. Wei, H.J. Lin, Y.Y. Chin, National Synchrotron Radiation Research Center, Taiwan, Republic of China, J.H. Wang, National Taiwan Normal University, Taiwan, Republic of China

The interplay between ferromagnetic and organic layers critically affects the efficiency of spin filtering in the organic/molecular spintronics. The hybridized properties at organic-ferromagnetic heterostructure is hence important. We investigated the spin interface in terms of the electronic structure and magnetic coupling of tetrafluorotetracyanoquinodimethane (F4-TCNQ) on nickel (Cu(100)/Ni) surface. The experimental results display magnetic hardening upon F4-TCNQ adsorbed on Ni surface. This enhanced magnetic ordering after molecular tailoring was studied by the surface-sensitive and element specific X-ray Magnetic Circular Dichroism (XMCD). The XMCD reveals that the orbital and spin moment of Ni is significantly increased on the in-plane, while that keep almost unaltered at out-of-plane. Through the strong superexchange coupling at in-plane surface, the nonmagnetic F4-TCNQ is spin polarized. Additionally, we found the enhanced magnetic ordering expressed larger domain sizes and less domain boundary from the measurements of surface magnetic anisotropy performed by magneto-optical Kerr effect (MOKE) and the magnetic domains inspected by photoelectron-emission microscope (PEEM). It suggests that the enhanced long-range magnetic order of organic-ferromagnetic interface is an effective spin filtering for constructing high efficient organic spintronics.

11:40am **SS+AS+MI-MoM11 Interaction of Coronene with Mo-C<sub>60</sub> Nanospheres: The Effects of Substrate Curvature on Molecular Adsorption**, Nathaniel W. Kabat, E. Monazami, P. Reinke, University of Virginia

Surface curvature has been observed to effect molecular adsorption, but little systematic work has been done in the regime where substrate corrugation is the same magnitude as molecule size. Here we present a scanning tunneling microscopy/spectroscopy (STM/STS) study of the interaction between molybdenum-fullerene nanospheres and coronene molecules. The nanospheres template is formed by a solid-state reaction between Mo thin films and a fullerene layer which is triggered by an annealing step. The reaction between the fullerenes and molybdenum breaks the symmetry of a fullerene layer but retains a dense molecular packing of visibly distorted fullerene-like structures. The electronic structure and bandgap of the nanospheres can be adapted by annealing and is driven by substitutional metal atom incorporation in the C<sub>60</sub>. The interaction of coronene molecules with a gold surface serves as a model system representing the limiting case of a flat metallic surface and indicates that the molecular height varies with annealing temperatures while still exhibiting long range order. We will present coronene adsorption on nanospheres from wide bandgaps (2 eV) to fully metallic surfaces and discuss the adsorption geometries of coronene. We do not observe long range order of coronene molecules on the nanospheres surface, indicating that the localized nanosphere curvature has a strong influence on the absorption geometry. These results provide the beginning steps of understanding the ways in which nanosphere-molecule interaction can be controlled by the localized surface curvature. We acknowledge the support from the National Science Foundation award CHE-1507986 by the Division of Chemistry (Macromolecular, Supramolecular and Nanochemistry).

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