

Wednesday Morning, October 21, 2015

Surface Science

Room: 113 - Session SS+AS+NS-WeM

Metals, Alloys & Oxides: Reactivity and Catalysis

Moderator: John Russell, Jr., Naval Research Laboratory

8:00am **SS+AS+NS-WeM1 Surface Chemistry of Single-Layer MoS₂**, *Koichi Yamaguchi, E. Li, L. Bartels*, University of California - Riverside
Molybdenum disulfide (MoS₂) is a semiconducting transition metal dichalcogenide (TMD) that forms a stable monolayer 2D crystal structure similar to graphene. It is the key material for industrial hydrodesulfurization (alloyed with cobalt) and has shown promise in electrocatalytic water splitting. We present a study of MoS₂'s ability to bind small reactants and its stability when exposed to them at elevated temperature. We utilize a combination of thermally programmed desorption measurements and in-situ PL imaging. The latter permits us to study the film activity over a wide pressure range (high-vacuum to ambient).

8:20am **SS+AS+NS-WeM2 On the Adsorption Behavior of a Porphyrin on Different Cu Surfaces: A Comparative Scanning Tunneling Microscopy Study**, *Liang Zhang*, Universität Erlangen-Nürnberg, Germany, *M. Lepper*, Universität Erlangen-Nürnberg, Germany, *M. Stark, S. Ditze, H.-P. Steinrück, H. Marbach*, Universität Erlangen-Nürnberg, Germany

Self-assembly of functional molecular building blocks on well-defined surfaces is a promising approach for the bottom-up fabrication of two-dimensional nanostructures with outstanding properties. In this respect, porphyrins are particularly attractive because of their distinct chemical and physical properties.^{1,2}

In this presentation, we investigate and compare the adsorption behaviour of 2H-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) on different substrates, i.e., Cu(111),^{3,5} Cu(110) and Cu(110)-(2X1)O, under ultra-high vacuum conditions by scanning tunneling microscopy (STM). At room temperature, supramolecular arrangements of 2HTTBPP are observed on Cu(111) and Cu(110)-(2X1)O, while on Cu(110) individual 2HTTBPP molecules are observed in a disorder layer. Interestingly, the intramolecular conformations of the molecules are quite different on the investigated substrates, as determined by STM.⁴ The corresponding findings are interpreted by accounting for specific molecule-molecule and molecule-substrate interactions. In addition, the so-called self-metalation of 2HTTBPP with Cu atoms will be reported and discussed.^{4,5}

References:

1. Auwärter, *et al.*, Nat. Chem., 2015, 7, 105.
2. Gottfried, Surf. Sci. Rep., 2015, doi:10.1016/j.surfrep.2015.04.001.
3. Ditze *et al.*, J. Am. Chem. Soc., 2014, 136, 1609.
4. Stark *et al.*, Chem. Commun., 2014, 50, 10225.
5. Marbach *et al.*, Chem. Commun., 2014, 50, 9034.

8:40am **SS+AS+NS-WeM3 Redox-Active On-Surface Assembly of Metal-Organic Chains with Single-Site Transition Metals**, *Steven Tait*, Indiana University
INVITED

Programming the specific chemistry of single-site transition metal centers at surfaces by organic ligand design is a promising route to improve selectivity in surface catalysis. The chemical behavior of the surface and redox chemistry happening at the surface need to be further developed and understood. These studies benefit from interdisciplinary research into the programming of the growth, reactivity, and functionality of nano-scale systems in general and metal-organic complexes as surface catalysts in particular. Our group has recently demonstrated the formation of structurally ordered and chemically uniform single-site centers at surfaces by on-surface redox chemistry of metallic precursors including platinum, chromium, iron, and vanadium with organic ligands on a gold surface (*J. Am. Chem. Soc.* 2014, **136**, 9862-9865; *J. Chem. Phys.* 2015, **142**, 101913; and newly submitted work). The on-surface redox process relies on straightforward vapor deposition protocols and takes advantage of the catalytic role of the surface to show promise as an approach for the growth of inorganic complexes at surfaces. The ability to tune the reactivity and catalysis of these systems is a central question in this field. We report new results here that probe the extent of oxidation state control in these systems using tailored tetrazine-based ligands and vanadium metal; vanadium is an excellent candidate for probing access to a variety of oxidation states. The oxidizing power of the tetrazine species is tuned by peripheral functional groups to access two and three electron oxidation processes, as determined

by X-ray photoelectron spectroscopy (XPS). Platinum(II) centers have also been formed with these ligands. In each of these cases, the metal-ligand complexes take the form of nearly identical one-dimensional polymeric chains, resolved by molecular-resolution scanning tunneling microscopy (STM). These structures provide highly uniform quasi-square-planar coordination sites for the metal, which contributes to the well-defined chemical state of the metal. This strategy is also applied to earth-abundant metals such as iron and chromium using commonly available phenanthroline ligands and is allowing us to develop understanding of how to control and program single-site metal centers on surfaces for next-generation catalysis.

9:20am **SS+AS+NS-WeM5 Ultra-thin Bi(110) Films on Si(111) $\sqrt{3}\times\sqrt{3}$ -B Substrates**, *I. Kokubo, Y. Yoshiike, K. Shishikura, K. Nakatsuji, Hiroyuki Hirayama*, Tokyo Institute of Technology, Japan

Bismuth (Bi) takes the rhombohedral (A7) crystalline structure in bulk. However, it also takes the black phosphorous (BP) structure in ultrathin films. Theoretically, a few bilayer thick Bi(110) films with the BP structure were predicted to be a nontrivial two-dimensional topological insulator by removing the buckling at the surfaces [1]. In the meantime, ultrathin Bi(110) films with the A7 structure was suggested to realize the Dirac electron system at the surfaces [2]. From these viewpoints, the growth, structure, and electronic states of the Bi(110) ultra-thin films are of great interest. In this study, we investigated the details of the atomic arrangements and electronic states at the Bi(110) islands on the Si(111) $\sqrt{3}\times\sqrt{3}$ -B substrate experimentally using scanning tunneling microscope (STM) [3] and angle-resolved photoelectron spectroscopy (ARPES) in a synchrotron radiation facility.

In the study, we found that atomically flat, long, narrow Bi(110) islands grew along specific orientations on the Si(111) $\sqrt{3}\times\sqrt{3}$ -B substrate. The orientations belonged to one of the two sets of three-fold rotational axes, which differed by 26° each other. The preference of the specific orientations were reasonably attributed to the commensuration of the diagonal of the rectangular Bi(110) lattice to the $\sqrt{3}\times\sqrt{3}$ substrate unit cell. The islands grew as to make their edges parallel to the short side of the Bi(110) rectangular unit cell. The combination of the Bi domains of different orientations caused various types of boundaries on the wide terraces of the Bi(110) islands. In particular, the domains along $\pm 87^\circ$ from the {1-10} direction were found to be connected perfectly on the atomic scale at the straight boundary by inserting a local switching of the bond direction to the zigzag chains of the in-plane bonds. On the Si(111) $\sqrt{3}\times\sqrt{3}$ -B substrate, both the odd layer thick A7 and even layer thick BP Bi(110) islands appeared. The dispersive surface bands and their Fermi surface mapping with characteristic electron and hole pockets were observed in ARPES spectra. Details will be reported in the presentation.

[1] Y. Lu, W. Xu, M. Zeng, G. Yao, L. Shen, M. Yang, Z. Luo, F. Pan, K. Wu, T. Das, P. He, J. Jiang, J. Martin, Y. P. Feng, H. Lin, X. Wang, Nano Lett. 15, 80 (2015).

[2] G. Bian, X. Wang, T. Miller, T. -C. Chiang, P. J. Kowalczyk, O. Mahapatra, S. A. Brown, Phys. Rev. B 90, 195409 (2014).

[3] I. Kokubo, Y. Yoshiike, K. Nakatsuji, H. Hirayama, Phys. Rev. B 91, 075429 (2015).

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9:40am **SS+AS+NS-WeM6 STM Study of Growth Processes for Ir/Ge(111)**, *M.S. van Zijll, B.H. Stenger, C.H. Mullet, E.S. Huffman, D. Lovinger, W.F. Mann, Shirley Chiang*, University of California, Davis

Using scanning tunneling microscopy (STM), we have characterized the surface of clean Ge(111) dosed with 0.66 to 2.0 monolayers (ML) of Ir and then annealed to temperatures between 550 K and 800 K. We observed a broad range of surface formations, including Ir adatom clusters and various stages of island formation. Islands with winding, wormy shapes formed around 580K. As the annealing temperature increased above 650K, round islands formed. In addition, a new type of growth is observed in which the Ir gathers along the antiphase domain boundaries between competing surface domains of the Ge surface reconstruction; this gives the appearance of the Ir forming pathways interconnecting different Ir islands. The low energy electron diffraction (LEED) pattern for this surface shows domains with $(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction and becomes sharper as the temperature is increased. In the STM images, the Ge top layer reconstruction, the Ir adatom clusters, the pathways, and the Ir round islands all have $\sqrt{3}$ -spacing between features. X-ray photoemission spectroscopy (XPS) was used to determine that the IR coverage was ~ 2.0 monolayers when low energy electron microscopy (LEEM) images showed completion of 1 overlayer of Ir grown on Ge(111) at 600C. We present a model consistent with our XPS and LEEM data that suggests that each Ir adatom cluster observed in STM

images corresponds to three Ir adatoms. To model the surface-adsorption processes for the Ir/Ge(111) system, we used simple Monte Carlo simulations with pair-wise surface potentials and random walks of atoms to imitate surface diffusion. Particular parameter choices yielded growth along pathways between domain boundaries of the substrate, in agreement with the experimental data.

11:00am **SS+AS+NS-WeM10 Gas Sensor Resistance Changes for Ar/O₂ and H₂O Plasma Modified SnO₂ Nanomaterials**, *Erin Stuckert, C.J. Miller, E.R. Fisher*, Colorado State University

Although steps have been made to decrease toxic gas emissions globally, these emissions persistently cause detrimental health effects worldwide. Current household gas sensors are limited in their abilities to detect sensitively and selectively at or below relevant toxicity levels for many gases. Tin(IV) oxide (SnO₂) nanomaterials are well-equipped to address some of these limitations as a result of dual valency (Sn²⁺ and Sn⁴⁺) and high surface area, thus creating diverse surface chemistry. These properties are advantageous for gas sensing devices because SnO₂ functions as a sensor via gas-surface interactions, facilitated by adsorbed oxygen species. By measuring changes in resistance upon gas exposure, sensitivity and selectivity are observed. To increase sensitivity through maximizing gas surface interactions, chemical vapor deposition-grown SnO₂ nanowires and commercial nanoparticles were treated with an Ar/O₂ and H₂O_(v) plasma resulting in increased oxygen adsorption. Surface and bulk characterization throughout the plasma treatment process demonstrate an increase in adsorbed oxygen content over a 30 - 150 W applied power range regardless of plasma precursor, in addition to showing that tin reduction occurs upon H₂O_(v) plasma treatment. Gas sensing performance was initially explored by exposing SnO₂ sensors to air at temperatures of 25-300° C to determine base resistance of the materials in an ambient atmosphere. The data show changes in resistance that are dependent upon nanomaterial architecture, plasma treatment conditions, and sensor temperature. Base resistance changes for specific plasma and sensor conditions will be discussed as well as sensor responses and selectivity upon exposure to toxic gases including benzene and carbon monoxide. By combining materials characterization with gas sensor responses, we can optimize sensor sensitivity and selectivity by tuning plasma modification conditions with aims for targeted gas sensing applications.

11:20am **SS+AS+NS-WeM11 Enhanced Adsorption of CO₂ at Steps of Planar ZnO(0001) Grown on Au(111)**, *Xingyi Deng, D. Sorescu, J. Lee*, National Energy Technology Laboratory

In this work, we study the energetics of CO₂ adsorbed on the bi- and tri-layer ZnO(0001) grown on Au(111) using temperature programmed desorption (TPD) and calculations based on density functional theory (DFT). Both bi- and tri-layer ZnO(0001) on Au(111) adopt a planar, graphite-like structure via an inter-layer relaxation to minimize the surface dipole arising from alternating Zn²⁺ and O²⁻ layers. CO₂ is adsorbed weakly on these planar ZnO(0001) surfaces, desorbing between 125-130 K in TPD. Two other desorption peaks were also observed in TPD at ~ 150 and 280-320 K and are attributed to the CO₂ adsorption at the steps between the bi- and tri-layer ZnO(0001) surfaces. This enhanced adsorption of CO₂ at the steps is supported by DFT calculations: the computed energetics of CO₂ adsorbed on surfaces and at steps is indeed consistent with that estimated from the TPD experiments via the Redhead method. Implications of our fundamental results for ZnO based catalysts will be discussed.

11:40am **SS+AS+NS-WeM12 Characterization of Band Gap and Lattice Constant of Ultrathin ZnO Layers on Au(111)**, *Junseok Lee, D. Sorescu, X. Deng*, National Energy Technology Laboratory

Ultrathin layers of ZnO grown on the Au(111) substrate have been characterized using low-temperature scanning tunneling microscopy (STM). Under reactive deposition condition, the ZnO layers have been found to grow by forming islands. Detailed analysis of electronic structure have been conducted using scanning tunneling spectroscopy (STS) and the density functional theory (DFT) calculations. The band gap of ultrathin layers of ZnO is found to be larger compared to the bulk ZnO wurtzite structure. The density functional theory calculations provides understanding of the increased band gaps of thin ZnO layers. The lattice constants of ultrathin ZnO layers on Au(111) are also found to be larger than that of the bulk lattice constant, which could be explained by the formation of graphitic-like ZnO layers.

12:00pm **SS+AS+NS-WeM13 Submonolayer Water Adsorption on Stepped and Planar Pt Surfaces**, *Rachael Farber*, Loyola University Chicago, *M.J. Kolb*, Leiden Institute of Chemistry, *J. Derouin*, Loyola University Chicago, *M.T.M. Koper*, *L.B.F. Juurlink*, Leiden Institute of Chemistry, *D.R. Killelea*, Loyola University Chicago

The adsorption of water onto metal surfaces yields a host of intricate adsorbate structures at

coverages less than a single layer. Complex adsorption structures arise due to the delicate balance

of hydrogen bonding between water molecules as well as attractive forces between water molecules

and the metal surface. Therefore, the complexity of the system provides an excellent opportunity to

refine models of water-water and water-surface interactions. Water molecules are largely confined

to a single plane and, as a result, the geometry of aligned water molecules gives rise to frustrated

hydrogen bonding. At low coverages of water on metal surfaces, these frustrated intermolecular

interactions result in the formation of structures other than the classic hexagons of bulk water. We

will report the results of a combined theory-experiment study of water adsorption on planar Pt(111)

and stepped Pt(553). Experimentally, temperature programmed desorption (TPD) and ultra-high

vacuum scanning tunneling microscopy (UHV-STM) were used to quantify water coverage and to

image the resultant surface structures. On Pt(111), 5, 6, and 7-membered rings were found to form

across the Pt surface, in agreement with previously reported experimental results and electronic

structure calculations. On Pt(553), however, tetragonal structures that have not been previously

observed were found to form across monatomic steps. These observations confirm DFT

calculations for submonolayer water coverage on Pt(553) and provide fine details as to how water-

water and water-surface interactions are balanced on active metal surfaces.

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