

## Surface Science Division

### Room 319 - Session SS+AS-ThM

#### Memorial Session in Honor of Patricia Thiel II

**Moderators:** James Evans, Ames Laboratory, Cynthia Jenks, Oak Ridge National Laboratory

#### 8:20am SS+AS-ThM-2 Navigating Complex Interfaces: In Memory of Patricia A. Thiel, Cynthia Jenks, Oak Ridge National Laboratory INVITED

At a time when simple systems in surface science were the norm, Professor Thiel would choose two paths for her research group. Part of the group focused on the seemingly simplistic and part of the group focused on the seemingly complex. A key to her success was not shying away from complexity or diving deep into the detailed mechanisms of what at first appeared simple, yet turned out to be anything but simple. Additionally, she garnered success by bringing together experts from different disciplines and backgrounds to tackle her research focus areas. Among the areas the group focused on from 1992 through 2008, when I worked with her, was on understanding the deposition of Ag on Ag and also on understanding the vast unknown of quasicrystalline surfaces with their all of their complexity. This talk will highlight some of the research during that time and how that work inspired a move toward understanding more complex interfaces in the field of surface science.

#### 8:40am SS+AS-ThM-3 Atomic Scale Investigation of Friction Properties of Quasicrystals and Beyond, Jeong Young Park, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea INVITED

Quasicrystals that have rotational symmetry but no translational periodicity has been one of the key topics that Pat Thiel has explored and pioneered. Complex metallic alloys, including quasicrystals and approximants often have peculiar mechanical and tribological properties associated with the unique structure. For example, quasicrystals exhibit high hardness, low friction, and good wear resistance, prompting applications as anti-stick and low friction coatings. In this talk, I highlight the research efforts on nanomechanical and tribological properties of quasicrystal and approximant surfaces using atomic force microscopy. It was found that the friction response on twofold surfaces of the clean Al-Ni-Co decagonal quasicrystal where atoms are arranged periodically along the tenfold axis, and aperiodically in the perpendicular direction was anisotropic at different length scales (macroscale and nanoscale). The result indicates that there is an intrinsic relationship between the aperiodic atomic structure of quasicrystals and their low friction. On the oxidized surface and in the elastic regime, friction is dominated by the bulk properties of the metal beneath the oxide and is not sensitive to whether the metal is quasiperiodic or periodic. I discuss the role of the surface oxide and the length scale of mechanical contact in determining nanomechanical and tribological properties.

In the second part of my talk, I will highlight the recent investigation on the frictional behavior of intercalated water between the hydrophilic surfaces and more hydrophobic two-dimensional atomic layers. The water layers confined between the hydrophilic substrate and hydrophobic layers exhibit the bilayer structure that was proposed by Pat Thiel. We found that the water intercalated between 2-dimensional (2D) materials (e.g., graphene and MoS<sub>2</sub>) and the hydrophilic substrate increases the friction force between the AFM tip and 2D flakes deposited. Moreover, the friction on both graphene and MoS<sub>2</sub> increased as the number of stacking water layers increased. This study provides that the intrinsic vibration modes of the water molecules play a key role in the coupling of the 2D materials modes to the phonon bath of the substrate. Finally, I will address the relationship between nanoscale friction on ultrananocrystalline diamond surface and the surrounding environment of water by using ambient pressure-atomic force microscopy. This result elucidates the role of vapor-phase water in the tribological properties of carbon-based materials.

#### 9:20am SS+AS-ThM-5 Quantification of Structure-Property Relationships at Interfaces, Susan Sinnott, Pennsylvania State University INVITED

Many-body, dynamic charge, physics-based potentials are used in classical molecular dynamics (MD) simulations to investigate the chemistry associated with heterogeneous systems. In particular, the interaction of graphene with titanium metal and titanium-carbide-derived-carbon (Ti-CDC) systems are investigated. The resulting Ti-CDC structures are then examined for the adsorption of acid gases. These findings illustrate the usefulness of classical MD simulations in designing new material systems.

#### 9:40am SS+AS-ThM-6 Metal Nodes in Bimetallic Metal-Organic Frameworks as Isolated Sites for Gas-Phase Catalytic Hydrogenation, Donna Chen, University of South Carolina INVITED

The Cu<sub>x</sub>Rh<sub>3-x</sub>(BTC)<sub>2</sub> catalyst (abbreviated CuRhBTC, BTC<sup>3-</sup> = benzene tricarboxylate) provides excellent dispersion of active metal sites coupled with well-defined, robust structures for propylene hydrogenation reactions. This material therefore serves as a unique prototype for understanding gas-phase catalytic activity in metal organic frameworks (MOFs). The active sites for hydrogenation are identified as Rh<sup>2+</sup>, while role of Cu<sup>2+</sup> is primarily to provide stability for the MOF structure. In situ XRD studies show that the crystalline MOF structure is retained during hydrogenation. The appearance of the O-H stretch for COOH at ~3690 cm<sup>-1</sup> in the diffuse reflectance infrared Fourier transform spectra is characteristic of defects consisting of missing Rh-O bonds. These experimental results are consistent with the reaction mechanism proposed by density functional theory, in which H<sub>2</sub> is dissociated at a Rh<sup>2+</sup> site with a missing Rh-O bond, while protonation of the de-coordinated carboxylate linker stabilizes the active sites and promotes H<sub>2</sub> dissociation.

#### 11:00am SS+AS-ThM-10 Quasicrystals in Two Dimensions: From Metals To Molecules And Oxides, Vincent Fournée, Institut Jean Lamour - CNRS-Université de Lorraine, France INVITED

Quasiperiodic structures exhibit long-range order like normal crystals but they lack translational symmetry. Quasicrystals were first discovered as a new class of intermetallic compounds, now comprising hundreds of members in binary and ternary systems. They usually adopt either the icosahedral or the decagonal point group symmetry. The discovery of quasicrystals has led to a paradigm shift in crystallography and has attracted a large interest in the material science community, motivated by unexpected physical properties that could be linked to quasiperiodicity. This remarkable class of materials has also challenged our understanding of metal surfaces. An atomic scale description of their surfaces is especially important, as it forms the basis for understanding and predicting phenomena such as gas adsorption, metal epitaxy, and friction. Pat Thiel and her group played a major role in the surface science of quasicrystals.

Pat Thiel also pioneered studies of nucleation and growth of metal thin films on quasicrystalline surfaces, demonstrating that local pseudomorphic growth can occur due to preferred adsorption of the metal ad-species at specific sites of the surface quasilattice. The idea was that the complex potential energy surface of quasicrystalline surfaces could serve as a template to grow new 2D quasicrystalline systems.

Here, we will review the different results obtained along this direction, from local pseudomorphic growth of Al starfish islands on the 5-fold surface of the icosahedral *i*-Al-Cu-Fe quasicrystal [1] to pseudomorphic single layer high islands in the case of Ag/5f-Al-Pd-Mn [2] and up to the formation of complete 2D quasiperiodic metal layers (Pb, Bi or Sn) templated on various quasicrystalline surfaces [3]. Self-organized molecular films with long-range quasiperiodic order could also be grown by using the complex potential energy landscape of quasicrystalline surfaces as templates. The long-range order arises from a specific subset of quasilattice sites acting as preferred adsorption sites for the molecules, thus enforcing a quasiperiodic structure in the film [4]. Finally we will show some recent examples of 2D quasicrystalline oxide layers obtained by reduction of ABO<sub>3</sub> perovskite thin films grown on Pt(111) [5,6].

[1] T.A. Cai *et al.*, Surface Science, 526 (2003) 115-120.

[2] B. Unal *et al.*, Phys. Rev. Lett., 102 (2009) 196103.

[3] J. Ledieu *et al.*, PRB Rapid Comm., 77 (2008) 073409.

[5] V. Fournée *et al.*, ACS Nano, 8 (2014) 3646–3653.

[6] S. Förster *et al.*, Nature, 502 (2013) 215–218.

[7] C. Ruano M. *et al.*, Phyc. Chem. Chem. Phys., 24 (2022) 7253.

#### 11:40am SS+AS-ThM-12 Unusual Flat and Extended Morphology of Intercalated Cu Under MoS<sub>2</sub>, Dapeng Jing, Y. Han, J. Evans, M. Kolmer, Z. Fei, M. Tringides, Ames Laboratory USDOE INVITED

There has been intensive research on ultra-thin metal films and surface structures for use as transparent conductor layers in optical and thermal applications. In this study, we present a novel approach to fabricate such metal structures of Cu encapsulated near the surface of a layered material, MoS<sub>2</sub>. We use scanning electron microscopy, atomic force microscopy and x-ray photoelectron spectroscopy to characterize this Cu-MoS<sub>2</sub> system formed via physical vapor deposition of Cu in ultrahigh vacuum at 1000 K. Necessary conditions for encapsulation are preexisting ion-induced defects in the MoS<sub>2</sub> substrate and elevated deposition temperature of 1000 K.

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Under such conditions, Cu grows both on the MoS<sub>2</sub> surface as faceted clusters and beneath the MoS<sub>2</sub> surface as encapsulated structures. The encapsulated Cu starts underneath a surface cluster and grow laterally in size maintaining a thickness of under 10 nm. The Cu structure growth behavior deviates significantly from the Cu intercalation in graphite system where Cu predominantly grows as intercalated islands with much smaller lateral size. Density functional theory calculations reveal the driving force for Cu mass transport from surface clusters to encapsulated structures.

## 12:00pm **SS+AS-ThM-13 Helium Ion Microscopy for Surface Modification and Characterization, Alex Belianinov**, Sandia National Laboratory **INVITED**

There is a growing need to expand the experimental arsenal with tools to visualize and modify materials at a breadth of scales, from atomic to visible with a naked eye. The helium ion microscope (HIM) offers a large dynamic range, and quickly gained popularity since its debut in 2006. Its unique gas field ion source (GFIS) is ideal for high-resolution imaging, milling, localized damage, direct-write, and additional analytical techniques like secondary ion mass spectrometry as well as ion beam induced current imaging.

This presentation aims at providing an overview of the status of HIM technology for imaging, analysis, and nanofabrication. Specifically, the instrument design, ion-matter interaction, imaging, localized material modification, and material characterization will be discussed. Contrast will be drawn between the HIM and other focused ion beam tools in this class that rely on liquid metal alloy ion sources. Current challenges and research opportunities for ion beam tools will be highlighted. A plethora of supporting examples of working with 2D, cleanroom-relevant, soft, polymeric, and biological materials will be shown.

This presentation is dedicated to my mentor and advisor Prof. Patricia A. Thiel. She lives on through the memories of all of us that were lucky enough to spend time with her.

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