Surface Science
Room 305 - Session SS-MoA

Surface Electronic, Magnetic, and Optical Properties

Moderators: Prof. Abner de Siervo, University of Campinas (UNICAMP), **Alexander Sinitskii**, University of Nebraska-Lincoln

1:30pm **SS-MoA-1 Graphene Nanoarchitectonics: Exploring Dimensionality Effects from 0 to 1.X**, ***Aitor Mugarza***, Catalan Institute of Nanoscience and Nanotecnology - ICN2, Spain **INVITED**

Nanostructuring Graphene Confers Multiple Functionalities to This Material, Making It Attractive to Very Diverse Applications in Electronics, Molecular Sensing and Filtering. For Instance, Semiconducting Gaps Can Be Induced by Reducing Its Dimensions to the Nanometer Scale. At This Scale, Edges Play a Crucial Role in Determining the Physico-Chemical Properties of the Nanomaterial, with the Emergence of Magnetism Localized at Zigzag Edges, or the Capability to Add Functional Groups Being Representative Examples. on the Other Hand, Introducing Pores of Similar Sizes Turns Impermeable Graphene Into the Most Efficient Molecular Sieve Membrane. For Both the Material and Void Components, the Interesting Scale for Applications Is Below 3-5 Nm, a Regime Where Bottom-Up Synthesis Can Be Particularly Efficient.

Here I Report Different Surface-Assisted Methods to Grow *0d* Graphene Quantum Dots with Magnetic Zigzag Edges (1-4), *1d* Nanoribbons Where the Electronic Properties Are Tuned by Controlled Edge Functionalization (5,6), and Nanoporous Graphene Sheets That Combine 1nm Size Ribbons and Pores (7). The Highly Anisotropic Structure of These Weakly Coupled Ribbon Arrays and the Modular Strategy Employed for Their Synthesis Allow Us to Control Their *1.X* Dimensionality by Molecular Bridge Engineering (8), or Even the Realization of 1nm Wide Lateral Heterostructure Superlattices Where Novel Excitonic States Are Predicted (9).

the Novel Electronic States of the Synthesized Nanoarchitectures Are Correlated with the Particular Atomic Structures by Using Scanning Tunnelling Microscopy. Their Potential Application in Devices Is Illustrated by Gate Modulated Transport Measurements in Nanoporous Graphene Sheets.

References:

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2:00pm **SS-MoA-3 Spatially Probing the Topologically Protected Surface State of Bi_2Se_3 to Local Impurities and Defects**, ***Nathan Guisinger***, Argonne National Lab

Low-dimensional materials functioning at the nanoscale are a critical component for a variety of current and future technologies. The exploration of novel quantum materials and architectures to advance quantum information science (QIS) is at the forefront of condensed matter research. There has been tremendous interest in alternative strategies that utilize topologically protected states. Because these states are robust to their local environment, topological QIS offers advantages towards longer coherence time and a more fault tolerant platforms. This talk will discuss our recent atomic-scale study of the well-known topological insulator Bi_2Se_3 that has been doped n-type with magnetic Fe atoms. Specifically, the impact of sub-surface impurities, Se vacancies, and adatoms on the two-dimensional topologically protected surface state. An ultrahigh vacuum low-temperature scanning tunneling microscope was used to perform this study with applied magnetic field up to 9T. Both topographic imaging and spectroscopy were utilized for spatial characterization. This research was performed at the Center for Nanoscale Materials (CNM) at Argonne National Laboratory, which is one of the five Department of Energy Nanoscale Research Centers.

2:15pm **SS-MoA-4 Spectro-Microscopic Characterization of Surface Magnetization in Bulk Fe_3GeTe_2**, *Trevor A. Tyson,* New Jersey Institute of Technology*; Abdullah Al-Mahboob,* ***Jerzy T. Sadowski***, Brookhaven National Laboratory

The spatial variation of the magnetic structure in Fe_3GeTe_2 has previously been investigated using scanning tunneling microscopy, magnetic force microscopy, X-ray magnetic circular dichroism (XMCD), scanning electron microscopy with polarization analysis, and Lorentz transmission electron microscopy. Here, we employ the XMCD imaging mode of X-ray photoemission electron microscopy (XMCD-XPEEM) to investigate the magnetic domain structure of Fe_3GeTe_2 in zero applied magnetic field. The observed domain configuration follows the expected pattern for thick crystals with strong uniaxial magnetic anisotropy.

To further probe the magnetic texture, we use low-energy electron microscopy (LEEM) with a tilted incident electron beam to image magnetic domain walls. Unlike spin-polarized LEEM, this method does not require specialized sample preparation or a spin-polarized electron source. Instead, magnetic contrast is generated by tilting the incident electron beam relative to the sample surface normal, or equivalently by tilting the sample itself. We demonstrate how the resulting contrast can be analyzed to determine the domain-wall type and to extract critical exponents associated with the surface magnetic behavior.

Acknowledgement: This work is supported by NSF Grant No. DMR-1809931. This research used resources of the Center for Functional Nanomaterials and the National Synchrotron Light Source II, which are U.S. Department of Energy (DOE) Office of Science facilities at Brookhaven National Laboratory, under Contract No. DE-SC0012704.

2:30pm **SS-MoA-5 Surface Electronic Structure of $Sr_3Ir_2O_7$ (001) Thin Films**, ***Peace Adegbite***, *M. Zaid Zaz, Yuanyuan Zhang, Arjun Subedi,* University of Nebraska-Lincoln, USA*; Alpha T N'Diaye,* Lawrence Berkeley National Laboratory*; Kenya Shimada,* Research Institute for Synchrotron Radiation Science, Hiroshima University, Japan*; Takashi Komesu, Xia Hong, Peter Dowben,* University of Nebraska-Lincoln, USA

$Sr_3Ir_2O_7$ is a narrow band-gap Mott insulator and member of the Ruddlesden-Popper strontium iridates. It is a layered material with competing energy scales for strong spin-orbit coupling and Coulombic interactions. The competing energies for band width (W), correlation (U) and spin-orbit coupling affects the surface characteristics in interesting ways. In this study, we investigated the surface electronic behavior and band structure of $Sr_3Ir_2O_7$ (001) thin films, using a variety of surface-sensitive spectroscopy techniques.

Angle-resolved photoemission spectroscopy (ARPES) revealed the presence of a finite density of states at the Fermi level that is localized to the surface, indicating a metallic surface coexisting with an insulating bulk. This surface-localized metallicity is further supported by transport measurements, as the electrical conductivity of $Sr_3Ir_2O_7$ thin films increases with decreasing film thickness. X-ray photoemission spectroscopy shows no measurable band bending with increasing Au overlayer thickness on the $Sr_3Ir_2O_7$ thin film, consistent with the measured linear I-V character and indicating the absence of a Schottky barrier at the Au/$Sr_3Ir_2O_7$ interface. From the valence band dispersion in ARPES, we estimated a light effective hole mass of 0.11 m_0 along the Γ-M direction of the surface Brillouin zone. To obtain a comprehensive view of the electronic structure, the unoccupied band structure was mapped using angle-resolved inverse photoemission spectroscopy and the orbital symmetry of the unoccupied bands at the Sr L-edge was assigned through angle-resolved X-ray absorption spectroscopy.

Furthermore, low energy electron diffraction reveals an anomalous temperature dependence of the surface scattering intensity that contradicts the conventional Debye-Waller behavior. We attribute this behavior to the damping of the normal mode vibrations via thermally activated carriers with increasing temperature.

2:45pm **SS-MoA-6 Revealing the Band Structure of High Entropy Oxides with Angle Resolved Photoemission**, ***Elena Salagre***, *Elliot Fuller,* Sandia National Laboratories

Recent years have seen interest rise for materials that can be tuned beyond traditional means. Compositionally complex oxides (CCOs), also identified as High Entropy Oxides (HEOs), are a unique approach to tailor properties by introducing multiple cations (typically 4+) to a lattice site. Despite such disorder, CCOs often maintain high crystal quality and homogeneity due to entropy stabilization effects. High entropy oxides have been explored as catalyst and as materials for microelectronics, applications in which their surface band structure becomes critical. However, few works have captured

the electronic structure of these oxides. Here we reveal how electronic properties emerge due to the competing effects of compositional complexity, disorder and strong correlations. We present a combination of electronic transport and Angle Resolved Photoemission (ARPES) on ABO_3 high entropy oxides both in terms of the A-site and B-site cation substitutions. For the A site substitution by La, Sm, Nd, Gd, Y adds compositional complexity as a fraction substitution (La_{1-x}[Sm, Nd, Gd, Y]$_{x/4}BO_3$) while Sr can be used as a traditional hole dopant to tune the electronic behavior. For B site, a mixture of the transition metals Cr, Mn, Fe, Co, Ni is used to add complexity while tuning *U*, *W*, *Δ* and spin degrees of freedom. Our results present clear evidence that a unified and coherent band structure is maintained in CCOs, even when the valence band is formed by 5 transition metal oxide *d*-levels. Additionally, we explore using compositional complexity in a strongly correlated double exchange metal (LSMO), where it can be used as a tool to systematically explore how new phases emerge, including a crossover regime between correlation and disorder induced behaviors. With these new measurements of the band structure of these CCOs, a better understanding of observed transport and magnetic properties can be achieved.

3:00pm **SS-MoA-7 Unveiling the Surface Electronic and Morphological Properties of the Centrosymmetric Nano-Skyrmion Host $EuAl_4$**, ***Jarred Grant***, *David King, Nikiphoros Vlastos, Yuri Dahnovsky, Jinke Tang, TeYu Chien,* University of Wyoming

Centrally symmetric (centrosymmetric) magnets capable of hosting skyrmions have attracted intense interest because they lack the Dzyaloshinskii-Moriya interaction (DMI). In these materials, inversion symmetry is preserved, requiring alternative mechanisms beyond DMI for skyrmion formation and stabilization. Proposals include symmetry-breaking effects such as charge density waves (CDW). The interplay among possible DMI, Ruderman-Kittel-Kasuya-Yosida (RKKY), and four-spin interactions in these systems creates a rich platform for diverse magnetic textures and phases. Centrosymmetric $EuAl_4$ is a particularly promising example, owing to its exceptionally small reported skyrmion size (~3 nm). Direct visualization of these nanoscale skyrmions is highly desirable. Spin-polarized scanning tunneling microscopy (SP-STM) is ideally suited for this length scale; however, key surface properties of cleaved $EuAl_4$, including the cleavage plane, surface morphology, local electronic structure, and termination—remain largely unexplored. In this talk, I will present STM, LEED, and DFT results detailing the cleavage plane, atomic-scale surface morphology, and corresponding dI/dV spectra of cleaved $EuAl_4$(001) single crystals.

*This work was supported by: DMR- 2414748

3:15pm **SS-MoA-8 Engineering Electronic States in High-Entropy Materials: From Disorder-Induced Pseudo Gaps to Gap Tuning in Transition Metal Dichalcogenides**, ***TeYu Chien***, University of Wyoming

High-entropy materials provide a unique platform to engineer novel electronic states through extreme chemical disorder. This talk presents scanning tunneling microscopy and spectroscopy (STM/STS) investigations into local electronic structures across two distinct high-entropy systems.

First, we examine the impact of atomic-scale chemical disorder in high-entropy alloys (HEAs). Local d*I*/d*V* spectra reveal the emergence of a disorder-induced pseudo gap at the Fermi level, directly reflecting modifications to the local density of states driven by electron-electron interactions caused by random potentials seen by electron wave function in random elemental distribution environment.

Second, we demonstrate electronic tuning in high-entropy transition metal dichalcogenides (HE-TMDs). By controlling metal compositions, we show a systematic evolution of the tunneling spectrum from low entropy to medium entropy HE-TMDs. Specifically, the characteristic V-shaped d*I*/d*V* spectrum transitions into a distinct U-shaped gap structure. These findings highlight the potential of entropy-stabilized configurations to precisely tailor quantum phases and electronic behaviors at the nanometer scale.

3:30pm **SS-MoA-9 Revealing Cu-Mn Electronic Structure Interaction in Activated CuMn/Al_2O_3 Catalyst by Decoupling of Overlapping XPS Spectra**, ***Yong Yang***, Shanghaitech University, China; *Rongjia Du,* ShanghaiTech University, China; *Evgeny I. Vovk,* ShanghaiTech University, China, Russian Federation

Mn promoted Cu based catalysts demonstrate high efficiency and stability in various chemical processes including methanol synthesis. Investigation of active centers in bimetallic Cu-Mn catalysts meets certain problems: Mn oxidation state cannot be directly determined because of strong overlapping of Mn and Cu photoelectron and Auger spectra. In this study, a new approach of convoluted background subtraction was proposed to separate the net Mn photoelectron spectra from overlapping Cu signal. The structure of CuAl and CuMnAl catalysts was investigated by XPS, XRD and EXAFS. XPS data were obtained after *in situ* activation and passivation treatments. After dedicated data analysis, the XPS results indicated the interaction and charge transfter between the Cu and Mn species on the CuMnAl catalyst. This study insighted how Mn promoter can effectively tune the electronic states of Cu catalyst; while it also provided a methodology example of separating low intensity Mn photoelectron spectra from overlapped complex background signals that can be aplyed to Mn-Cu or similar multicomponent systems.

4:00pm **SS-MoA-11 Understanding of STS Maps of Strongly Correlated Molecules on Surfaces: Can We Image Molecular Orbitals?**, ***Pavel Jelinek***, Institute of Physics of the Czech Academy of Sciences, Czechia **INVITED**

Traditionally, scanning tunneling spectroscopy (STS) of individual molecules is interpreted within the formalism of one-electron molecular orbitals [1]. Although this theoretical approach gives satisfactory agreement with experiment in some cases [2], it is in direct contradiction with the basic principle of quantum mechanics, which excludes direct observation of the wave function [3].

Moreover, recent progress in on-surface synthesis has enabled the preparation of strongly correlated polyradical molecules [1], which are not available by traditional solution-phase synthetic approaches. It is not surprising that interpreting STS maps of such polyradical molecules based on standard one-electron STM theory often fails. In this talk, we will discuss a many-body theoretical framework that enables us to simulate STS maps of strongly correlated molecules accurately [3]. Namely, we will introduce the concept of Dyson orbitals [4] to interpret ionic resonances in STS maps and natural transition orbitals [5] describing spin excitations in STS maps. Finally, we will discuss Kondo orbitals [6] to understand the origin of the spatial Kondo signal in high-spin molecules on metal surfaces.

References

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4:30pm **SS-MoA-13 Nanoscale Characterization of Metal-Supported Ultrathin Films Using Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy**, ***Nan Jiang***, University of Illinois - Chicago

Metal-supported ultrathin films exhibit unique structural and vibrational properties governed by reduced dimensionality and strong interfacial coupling. Probing these properties at the nanoscale requires techniques that combine high spatial resolution with chemical specificity under well-controlled surface conditions. Here, we utilize ultrahigh vacuum (UHV) tip-enhanced Raman spectroscopy (TERS) to investigate model two-dimensional systems with sub-nanometer resolution.

Our measurements focus on ultrathin films grown on metallic substrates, such as two-dimensional materials and metal oxides. Borophene, a polymorphic two-dimensional boron phase, presents substrate-dependent lattice configurations and anisotropic vibrational responses. UHV-TERS enables identification of distinct vibrational modes associated with different borophene polymorphs and reveals nanoscale structural heterogeneity. In parallel, ultrathin iron oxide films serve as model oxide systems with thickness- and phase-dependent properties. TERS measurements resolve localized phonon modes and provide insight into spatial variations in oxidation state and coordination at the metal–oxide interface.

The UHV environment ensures clean surfaces and reproducible tip–sample junctions, allowing direct correlation between spectroscopic signatures and atomic-scale structure. These results demonstrate the capability of UHV-TERS to probe structure–property relationships in supported ultrathin films with unprecedented spatial resolution. This approach provides a pathway for nanoscale characterization of complex oxide and low-dimensional materials relevant to catalysis and surface science.

4:45pm **SS-MoA-14 Precision Force-Volume HR-AFM Reveals Single-Molecule Reactive Sites and Reactivity Landscapes Quantitatively***, **Percy Zahl**,* Brookhaven National Laboratory*; Xinzhe Wang,* Yale University*; Jara Trujillo-Mulero, Emiliano Ventura-Macias,* Universidad Autonoma de Madrid, Spain*; Yunus Dogan, Bugrahan Guner,* Yale University*; Rubén Pérez,,* Universidad Autonoma de Madrid, Spain*; Eric I. Altman, Udo D. Schwarz,* Yale University

Studying molecular interactions at surfaces is crucial for advancing catalytic technologies and addressing numerous challenges in materials science. While three-dimensional atomic force microscopy (3D-AFM), introduced in 2009 [1], enables measurements of tip–sample interactions with sub-angstrom spatial resolution and piconewton force precision, quantitative site-specific information on molecule–molecule interactions has thus far remained inaccessible. This limitation arises because the recovered total tip–sample force contains substantial contributions from the substrate (denoted F_1 and F_2 (see below) as well as from the back part of the tip (F_4), which typically dominate the measured interaction and obscure details in the force (F_3) of interest.

Here, we demonstrate a novel post-processing correction framework that removes these unwanted F_1, F_2, and F_4 contributions. Using the interaction between cobalt phthalocyanine (CoPc)—a prototypical CO_2 reduction catalyst deposited on Ag(111)—and a CO molecule attached to the tip apex, we isolate the CoPc–CO interaction force F_3. This approach reveals site-specific reactivity landscapes and their modulation through $–NH_2$ substitution. Our advance transforms 3D-AFM into a chemically specific and quantitative tool for probing interaction forces between complex molecules, achieving an accuracy previously accessible only through theoretical modeling.

[1] B. J. Alberset al.,Nature Nanotechnology 4, 307 (2009)

[2] Xinzhe Wanget al.,ACS Nano18, 4495 (2024)

Forces assuming a CO terminated metal tip:
F_1: substrate — tip [background]
F_2: background, CO — substrate [background]
F_3: molecule — CO [the one of interest]
F_4: metal apex of tip — molecule [the main enemy]

5:00pm **SS-MoA-15 Statistical Adsorption Mapping and 3D-AFM Characterization of Cobalt Phthalocyanine (CoPc) on Au(111)***, **Bugrahan Guner**, Yunus E. Dogan,* Yale University*; Percy Zahl,* Brookhaven National Laboratory*; Xinzhe Wang,* Oak Ridge National Laboratory, USA*; Eric I. Altman, Udo D. Schwarz,* Yale University

Molecule-substrate interactions play a critical role in molecular adsorption because local atomic registry, reconstructions, and related surface strain can influence where molecules adsorb, how they orient, and how strongly they interact with the surface. Au(111) is one of the most widely used model substrates for such studies, as it is chemically stable, atomically well-defined, and exhibits the characteristic herringbone reconstruction, which creates distinct fcc, hcp, domain-wall, and elbow/kink regions. Cobalt phthalocyanine (CoPc) is also a widely studied model molecule due to its relevance in substrate-supported molecular catalysis [1].

To examine how the reconstructed Au(111) surface guides CoPc adsorption, we employ low-temperature scanning tunneling microscopy to first identify the positions and orientations of individual adsorbed CoPc molecules, followed by a statistical analysis where molecules are assigned to specific reconstruction regions while considering their distance to the nearest elbow. This allows adsorption near elbows/kinks, along herringbone/domain-wall regions, and within fcc/hcp domains to be compared systematically.

This analysis is then connected to three-dimensional atomic force microscopy (3D-AFM) measurements, where frequency-shift data collected at different tip-sample distances are used to reconstruct local interaction forces between the sample and a tip functionalized by attaching a CO molecular to its apex [2-3], which yields complementary force-sensitive information on molecule-substrate coupling and chemically relevant interactions. Together, these approaches connect surface reconstruction, molecular organization, and local interaction forces, providing a framework for understanding how structured metal substrates influence molecular catalyst behavior.

References

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5:15pm **SS-MoA-16 Energy-Resolved Low-Energy Electron Microscopy as a Quantitative Metrology for EUV Photoresist Films***, **Peter Sun**, Chang-Yong Nam, Jerzy Sadowski,* Brookhaven National Laboratory

Extreme ultraviolet (EUV) lithography drives photoresists toward thinner films, smaller features, and tighter line-edge roughness (LER), placing new demands on the characterization of resist behavior. Resist chemistry is governed by low-energy secondary electrons (<20 eV) generated from 13.5 nm photons, but transient surface charging shifts the effective landing energy throughout exposure, leaving film response at these energies unresolved by existing metrology.

We address this gap with charging-compensated low-energy electron microscopy and diffraction (LEEM/LEED) as a quantitative metrology platform for next-generation EUV resist films. Using 25 nm PMMA as a model system irradiated at 5–20 eV, we monitor the diffuse diffraction response and resolve the landing energy and surface potential. A conductance-based charging model extracts the total electron yield and dissipation parameters, enabling a dynamic electron-energy ramping scheme that locks the landing energy and turns LEEM/LEED into a controllable, energy-resolved metrology for resist films.

The energy-resolved method enables studies of resist-degradation performance and efficiency, including stochastic energy diffusion correlated with LER, and supports next-generation EUV and beyond-EUV resist development.

This research is supported by the U.S. Department of Energy Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research used resources (XPEEM/LEEM end station of the ESM beamline) of the Center for Functional Nanomaterials and the National Synchrotron Light Source II, which are the U.S. Department of Energy (DOE) Office of Science facilities at Brookhaven National Laboratory, under Contract No. DE-SC0012704.

5:30pm **SS-MoA-17 DFT Insights into Electronic Modulation of Cobalt Sites for N_2O Decomposition on Ni-Doped Spinel Oxides***, Hyung Chul Ham, **Chi Hun Lee**,* Inha university, Republic of Korea*; Su Keun Kuk, Jong-Min Lee, Hyuk Jae Kwon,* Samsung Advanced Institute of Technology, Republic of Korea

Nitrous oxide decomposition on transition-metal oxide surfaces is controlled by the adsorption and conversion of N_2O-derived intermediates, as well as by the ability of the surface to release oxygen. In this study, we use density functional theory calculations to investigate the surface reaction mechanism of N_2O decomposition on Co_3O_4(110) and $NiCo_2O_4$(110) spinel surfaces, which serve as representative models for oxidized shells formed on Co–Ni co-exsolved nanoparticles. Particular attention is given to how Ni incorporation modifies the surface reaction energetics and the electronic structure of Co-centered active sites.

Our calculations show that N_2O activation occurs near surface octahedral Co sites on both Co_3O_4(110) and $NiCo_2O_4$(110). The reaction proceeds through a bent trans-$N_2O_2^{2-}$ intermediate, consistent with experimentally observed hyponitrite-like surface species. Compared with Co_3O_4(110), $NiCo_2O_4$(110) stabilizes adsorbed N_2O more strongly and lowers the energetic penalty for forming the trans-$N_2O_2^{2-}$ intermediate. Transition-state calculations further show that Ni incorporation reduces the activation barrier for hyponitrite decomposition into N_2 and surface oxygen species. In addition, the subsequent O_2 formation step becomes more favorable on $NiCo_2O_4$(110), which can be attributed to weaker binding of surface oxygen species.

Electronic-structure analyses reveal that the improved reaction energetics originate from Ni-induced restructuring of Co-centered active sites. Ni incorporation modifies metal–oxygen covalency and stabilizes hybridized metal 3d–N 2p states involved in N_2O adsorption, as supported by projected density of states and crystal orbital Hamilton population analyses. In addition, surface octahedral Co sites exhibit a surface-induced spin-state change, suggesting that the spin-polarized electronic structure of these sites contributes to N_2O activation and intermediate conversion.

These results indicate that Ni-modified Co_3O_4 spinel surfaces enhance N_2O decomposition by simultaneously promoting N_2O adsorption, hyponitrite intermediate decomposition, and oxygen release. More broadly, this work highlights how surface composition and electronic structure, including spin-

state effects, can be tuned to design non-noble-metal oxide catalysts for greenhouse-gas decomposition.

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