

Scanning Probe Microscopy Focus Topic Room 104A - Session SP+SS+TF-WeM

Probing Electronic Properties

Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

8:00am SP+SS+TF-WeM1 Local Probe Investigation of 1D Structures and Interfaces in 2D Materials, *Chenggang Tao*, Virginia Tech **INVITED**

Emerging two-dimensional (2D) materials, such as graphene and atomically thin transition metal dichalcogenides, have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. The interfaces in these 2D materials, including domain boundaries and edges, strongly govern the electronic and magnetic behavior and can potentially host new quantum states. On the other hand, these interfaces are more susceptible to thermal fluctuation and external stimuli that drive mass displacement and generate disorder. In this talk we will present our scanning tunneling microscopy (STM) and spectroscopy (STS) explorations of edges of few layered molybdenum disulfide (MoS_2) nanostructures with unique structural and electronic properties and show how step edges on titanium diselenide (TiSe_2) surfaces change dynamically due to electrical fields. We will also discuss temperature evolution of quasi-1D C_{60} nanostructures on graphene. Through careful control of the subtle balance between the C_{60} surface mobility and the linear periodic potential of rippled graphene, C_{60} molecules can be arranged into a novel 1D C_{60} chain structure, and this chain structure can further transition to a compact hexagonal close packed stripe structure by tuning the annealing temperature.

8:40am SP+SS+TF-WeM3 Investigation of Electronic Structures from Monolayers to Multilayers in Charge Transfer Complex, TTF-TCNQ using Low-temperature Scanning Tunneling Microscopy/Spectroscopy, *Seokmin Jeon, P. Maksymovych*, Oak Ridge National Laboratory

The properties of few-layer molecular films are in general distinct from both bulk and monolayer phases, particularly in the case of metallic substrates, whose high-density electronic structure dominate the monolayer electronic structure and hamper characterization of the intrinsic properties of the molecular layer. This is especially true for charge transfer molecular solids, whose interesting electronic properties derive from a subtle alignment of each individual component's states, balance of dielectric screening, long-range electrostatic interactions, and relative molecular geometry. In contrast to vast effort on bulk phase study of the historic organic charge-transfer complex, TTF-TCNQ, study of its low-dimensional phases has been limited to monolayer phases. We investigated the evolution of the electronic structure of TCNQ and TTF-TCNQ multilayers using STM/STS at 4.3 K.

Thanks to submolecular resolution STM data and DFT calculations we were able to accurately determine the stacking relationship between the overlying layer and the underlying layer at an atomic scale. In such a well-defined layered model structure, we scrutinize the electronic structures of multilayered TCNQ and TTF-TCNQ using STS. Double-periodic charge ordering and Coulomb gap features are observed in the bilayer TTF-TCNQ. The effect of substrate variation (Ag, Au, and HOPG) on multilayer growth and electronic properties are discussed. The STS data from the multiple combinations of adsorbates and substrates allow us to assign states reliably and understand of transition of the surface, molecular, and charge transfer states clearly in the multilayer systems.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:00am SP+SS+TF-WeM4 Investigation of Initial Stages of Oxidation of Ni-Cr and Ni-Cr-Mo Alloys by Scanning Tunneling Microscopy/Spectroscopy (STM/STS), *Gopalakrishnan Ramalingam, P. Reinke*, University of Virginia

Ni-Cr based superalloys are excellent candidates for use in highly corrosive environments due to their exceptional oxidation and corrosion resistance. Our work focuses on unraveling the initial reaction steps of alloy oxidation as a function of composition, moving from the clean Ni-surface to a Ni-base alloy with 33wt% Cr. In the study presented here, we used STM/STS to investigate the initial stages of oxidation reaction in Ni-Cr (0-35wt.% Cr) alloys and the impact of Mo (2-10 wt.%) on the reaction. We developed spectroscopy maps which yield highly coveted information on the spatial distribution of oxide nuclei and the transition from chemisorbed oxygen to oxide. The STS maps capture the evolution of oxide during various stages of

oxidation and provides valuable insight into the reaction as a function of composition of alloy.

Cr is the main alloying addition in Ni-based superalloys and the minimum amount of Cr necessary to form a continuous, passive oxide layer is 6-13 wt.% based on empirical observations. The passivating quality of an oxide layer strongly depends on the initial nucleation of the oxide, the oxide growth during continued oxidation, and eventual coalescence to form a complete oxide layer. However, the effect of Cr content on the initial nucleation and growth behavior of the oxide is not well understood. Similarly, the underlying mechanisms at the atomic scale and the role of electronic structure changes due to Mo addition are not well understood.

In this study, alloy thin films grown on $\text{MgO}(100)$ substrates in an ultrahigh vacuum chamber are oxidized in situ at 300 °C with O_2 exposure up to 130 L. In the initial stages of oxidation (0.5-7 L of O_2), oxide nuclei are initially formed at the step-edges with some nucleation also present on the flat terraces. Subsequent oxygen exposure (>30 L) results in growth of existing oxide islands with additional nucleation of oxide. The amount of oxygen required for complete oxide coverage depends strongly on the Cr content of the alloy: >85% of the surface is covered with oxide in a Ni-14wt.%Cr alloy after 80 L oxidation while the same coverage is achieved in Ni-33wt.%Cr alloy after only 11.5 L. In contrast, we do not observe a complete oxide layer on Ni surface even after 180 L oxidation. Scanning tunneling spectroscopy maps provide spatially resolved electronic structure information and the variation of bandgap of the oxide as a function of oxide thickness and Cr content will be discussed. Preliminary data on the changes in the atomic and electronic structure of the thin film and oxidation behavior due to the addition of Mo will be presented.

9:20am SP+SS+TF-WeM5 Au(111) Characterization, Single Atom Manipulation and Si(100):H Surface Imaging by LT-UHV-4 STM, *Corentin Durand, D. Sordes, C. Joachim*, CNRS, France **INVITED**

Advance in nanotechnology requires the development of new instruments capable of imaging, communicating, manipulating and measuring at the atomic scale. The performances of the new ScientaOmicron LT-UHV 4-STM microscope have been certified by a series of state-of-art STM experiments on an Au(111) surface at 4.2 K [1]. During the STM operation of the 4 STM scanners (independently or in parallel), a ± 2 pm stability of about 2 pm per STM was demonstrated. With this LT-UHV 4-STM stability, single Au atom manipulation experiments were performed on Au(111) by recording the pulling, sliding and pushing manipulation signals. Jump to contact experiments lead to perfectly linear low voltage I-V characteristics on a contacted single Au ad-atom with no need of averaging successive I-V's. Our results show that the 4 scanners of this new instrument working in parallel have performances equivalent to single tip state-of-art LT-UHV-STM. Two tips surface conductance measurements were performed on Au(111) using a lock-in technique in a floating sample mode of operation to capture the Au(111) surface states via two STM tips dI/dV characteristics. The capabilities of this microscope being demonstrated, we now move on to our next project, the realization of atomic devices. The hydrogen passivated Si(100) surface is a good candidate to achieve this goal. Here, I will show our preliminary results regarding the investigation of this surface and its topography. The surface has been prepared by a "wafer-bonding" method [2]. Large scale STM images show that this technique provides large and clean terraces essential to the fabrication of atomic circuits. Atomic resolution imaging enables us to confirm the position of the dimers, these latter ones having a different aspect depending on the polarity of the tunneling junction [3]. Finally, I will introduce the route of our project, the different steps we must achieve in order to build up a device made of few atoms on this surface [2].

[1] J. Yang et al. Eur. Phys. J. Appl. Phys, 73, 10702, 2016

[2] M. Kolmer et al. Appl. Surf. Sci., vol. 288, p. 83, 2014

[3] T. L. Yap et al. Surf. Sci., vol. 632, p. L13, 2015

11:00am SP+SS+TF-WeM10 Heterochiral to Homochiral Transition in Pentahelicene 2D Crystallization Induced by 2nd-layer Nucleation, *Anaïs Mairena*, Universität Zürich, Switzerland

Chirality is ubiquitous in our world (human body, pharmaceuticals, liquid crystals...). Nevertheless, the principles of intermolecular recognition are still poorly understood. Therefore, it is not possible to predict the outcome of crystallization, which is still the most important method to separate chiral molecules into their enantiomers, or to explain why a minority of chiral compounds crystallize into conglomerate. A promising approach towards a better understanding of chiral interactions is the study of self-

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assembly of chiral molecules on single crystal surfaces with STM (sub-molecular resolution).

We studied the 2D self-assembly of racemic-pentahelicene ([5]H, C₂₂H₁₄) on Cu(111) with STM. Adsorption of [5]H leads, already at very low coverages to formation of homochiral pairs, i.e. both molecules have the same handedness.

At coverages close to the saturated monolayer, two distinct long-range ordered structures have been observed. Both structures have the homochiral pairs as building blocks. However, while one structure consists of a conglomerate of homochiral domains, the second structure is racemic, i.e. composed of homochiral pairs with opposite handedness. At monolayer coverage, only the racemic structure prevails. Above monolayer coverage, the dense racemate phase in the monolayer disappears on the expense of a homochiral conglomerate phase with lower density due to 2nd-layer-nucleation. Our results indicate that a long-range chiral communication between 2nd layer islands and other areas on the surface are at work.

These findings are also compared with those obtained for heptahelicene (C₃₀H₁₈) on Cu(111). A surface-mediated selection mechanism, taking different intermolecular interactions into account, will be presented.

11:20am SP+SS+TF-WeM11 Two-stage Chiral Selectivity in the Molecular Self-Assembly of Tryptophan, *Nathan Guisinger*, Argonne National Laboratory; *B. Kiraly*, Northwestern University; *R. Rankin*, Villanova University

Both chirality and molecular assembly are essential and key components to life. In this study we explore the molecular assembly of the amino acid tryptophan (both L- and D- chiralities) on Cu(111). Our investigation utilizes low temperature scanning tunneling microscopy to observe resulting assemblies at the molecular scale. We find that depositing a racemic mixture of both L- and D- tryptophan results in the assembly of basic 6 molecule "Lego" structures that are enantiopure. These enantiopure "Legos" further assemble into 1-dimensional chains one block at a time. These resulting chains are also enantiopure with chiral selectivity occurring at two stages of assembly. Utilizing scanning tunneling spectroscopy we are able to probe the electronic structure of the chiral Legos that give insight into the root of the observed selectivity.

11:40am SP+SS+TF-WeM12 Mask Free Approach to Selective Growth of Transition Metal Dichalcogenides Heterostructures enabled with Scanning Probe based Nanolithography, *R. Dong*, *L. Moore*, *N. Aripova*, *C. Williamson*, *R. Schurz*, Saint Louis University; *L.E. Ocola*, Argonne National Laboratory; *Irma Kuljanishvili*, Saint Louis University

Advances in graphene research ignited interest in other type of two-dimensional (2D) atomic crystals, such as hexagonal boron nitride and layered transition metal dichalcogenides (TMDCs). Among these new types of 2D materials, the applications of TMDCs in logic electronics and optoelectronics are promising because of their sizable bandgaps and natural stability. The techniques which enable heterostructure formation with different TMDCs systems have provided further solution to the design of high performance electronic devices such as those for photovoltaics and optoelectronics. The existing heterostructures fabrication methods, based on mechanical exfoliation and/or wet chemical transferring rely on traditional fabrication methods such as photo- and e-beam lithography.

To realize the selective growth and layered assembly of heterostructures at predefined location, here, we report on application of mask free, scanning probe based direct writing method. With the use of AFM cantilevers and developed water based "inks", we demonstrate arrays of MoS₂ and WS₂ dots and ribbon arrays at predefined locations on variety of substrates. Employing this SPM based patterning method we have also fabricated MoS₂/WS₂ heterostructures of sub-micrometer scales in a controlled fashion. The quality of MoS₂/WS₂ heterostructures was confirmed by Raman spectroscopy, AFM characterization and electrical transport measurements. Our mask free nanolithography approach offers an alternative route for patterning and growth of TMDCs with added benefit of potential reduced contamination of the TMDCs surfaces and interfaces between materials and substrates. It demonstrates a promising unconventional technology for fabrication of high quality TMDCs heterostructures in convenient manner capable of nanoscale precision.

Acknowledgements

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12:00pm SP+SS+TF-WeM13 Non-Destructive Electrical Depth Profiling across Nanometric SiO₂ Layers, *Hagai Cohen*, Weizmann Institute of Science, Israel; *A. Givon*, Tel Aviv University, Israel

The access to sub-nm scale depth information in thin dielectric layers, considering both the compositional and the electrical sub-surface characteristics, is challenging. A remarkable answer may be provided by CREM (chemically resolved electrical measurements), a technique based on x-ray photoelectron spectroscopy (XPS). CREM exploits the chemical contrast within a given structure to gain rich electrical information, or alternatively, apply electrical tests to gain improved structural & compositional analyses. Yet, for compositionally uniform domains, CREM becomes rather insensitive to the fine profiling details. Here, we show that this principal limitation can be overcome and the CREM resolution be improved significantly. Applied to nanometric silica layers, we reveal hidden impurity concentration profiles and further correlate them with the depth-dependent dielectric quality. Based on this leap improvement in resolution and sensitivity, our advanced CREM analysis promises diverse applications in device contact-free electrical studies.

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