

Wednesday Morning, December 14, 2016

Nanomaterials

Room Hau - Session NM-WeM

Nanocharacterization

Moderator: Kristina Tschulik, Ruhr-Univ. Bochum, Germany

8:00am **NM-WeM1 Nanoscopic Analysis of Semiconductor Heterointerfaces by Kelvin Probe Force Microscopy**, *F. Yamada, T. Kobayashi, K. Takabayashi, K. Shimomura, Y. Zhang, Itaru Kamiya*, Toyota Technological Institute, Japan

The electronic structure of heterointerfaces is known to determine the performance of semiconductor devices. This led to the series rigorous studies on interfaces, *i.e.*, Fermi level pinning or Schottky barrier formation, for decades. However, such studies were not easy and hence the results not conclusive, due to factors such as the reproducibility in preparing identical interfaces or limitation in the availability of tools that could characterize the interfaces on an atomic scale. Kelvin probe force microscopy (KFM) is an atomic force microscopy-based technique that provides us with the opportunity to tackle such problems by mapping the surface potential and topograph on nanometer scale simultaneously. Here, we report the application of KFM for the study of 1) InAs quantum dots (QDs) grown on GaAs(001) and 2) Si heterojunction (SHJ) solar cell structure.

We previously reported that the I-V characteristics of the InAs QD on GaAs(001) vary as a function of QD size, and that the interface may be ohmic-like when the QD diameter is about 100 nm while it exhibited Schottky diode-like behavior when the diameter is about 20 nm [1]. The phenomenon was naively interpreted in terms of a balance between Fermi level pinning in the conduction band of the InAs eventually overcoming that at mid gap for GaAs surrounding the InAs QD as its size is enlarged. Here, we performed KFM on QDs whose diameters are around 20-30 nm. We observe that a ring-like dip of surface potential is formed at the peripheral of the QDs (Fig.1) in agreement with previous work [2]. We converted the surface potential map into band alignment by using the known electron affinity of the bulk materials, as a function of depth from the surface. We find that the Fermi level of the dip region lies in the conduction band suggesting the presence of a source of electric contact, while the Fermi level in the wetting layer and the majority of the QD lies in the band gap (Fig.2).

We also performed KFM measurements on the cleaved interfaces of SHJ solar cell and related structures. The SHJ structure we employed is ITO/*p*-aSi/*i*-aSi/*n*-cSi(001). We observe that while the workfunction, and thus the band alignment, of *i*-aSi/*n*-cSi(001) interface is abrupt, *p*-aSi/*i*-aSi is not, and also that ITO/*p*-aSi interface may be blurred as a result of interdiffusion (Fig.3). This is in strong contrast from the reference sample Ag/Si(001) from which we observe a nearly ideal Schottky-like band alignment.

We will discuss the possible mechanisms and implication of these results.

[1] I. Tanaka, I. Kamiya, H. Sakaki, *et al.*, Appl. Phys. Lett. **74**, 844 (1999).

[2] S. Ono and T. Takahashi, Jpn. J. Appl. Phys. **44**, 6213 (2005).

8:20am **NM-WeM2 Defect Mediated Material Properties of 2-D Transition Metal Dichalcogenides studied by using Parallel Ultra High Resolution AFM and STS Mapping**, *A. Weber-Bargioni, Sebastian Wickenburg*, Lawrence Berkeley National Laboratory, USA

In this presentation we show how individual atomic defects and linear mirror twin boundaries in 2- D MoSe₂, identified with super resolution atomic force microscopy, alter the electronic wave function, imaged via Scanning Tunneling Spectroscopic mapping, leading along mirror twin boundaries to charge density waves and solitons.

Hierarchically ordered defects or adsorbents in two dimensional transition metal dichalcogenides modify the local electronic states in terms of energy and geometry of the electronic wave functions at length scales of individual wave functions, inducing novel functionality. Due to their 2-D nature, 2-D TMDs are an excellent model system to directly access, visualize and determine the effects of defect mediated electronic wave function tuning using high resolution AFM and differential conductance mapping.

We focused on studying various defect classes in 2-D MoSe₂. We identified individual Se vacancies – on both, the SPM facing and the substrate facing surface. Both result in particular electronic wave function related to states localized at the atomic defect [1]. These defect states form atomically sharp type 1 hetero junctions with the surrounding pristine MoSe₂, and form an excellent test bed to study catalytic activity with atomic precision.

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We also identified hierarchically ordered defects in form of Mirror Twin Boundaries (MTB) in MoSe₂, which form truly 1-D metal channels embedded in the surrounding semiconductor. At low temperatures these 1-D metallic states open a band gap at the Fermi level of 100meV. The new band gap frontier states exhibit a spatial modulation along the channels with a periodicity of three times the lattice constant. Density Functional Theory calculation confirm that the observed charge modulation is a result of the formation of a charge density wave [2]. Charging up the charge density wave we observe the creation of solitons – a self-reinforcing wave - and are able to measure its' energetic dispersion [3].

These results demonstrate how defects can not only modify the local electronic wave function, but directly alter the material properties and opens up a large playground to study the effects of linear defects, hierarchically ordered defects or adsorbents.

1 Maps of Electronic Wave functions associated with various atomic defects in MoSe₂, S. Barja, S. Wickenburg, A.Weber-Bargioni et al. *submitted*

2 Charge density wave order in 1D mirror twin boundaries of single-layer MoSe₂, S. Barja, S. Wickenburg, A.Weber-Bargioni et al. *accepted in nature physics*

3 Formation of Charge Density Wave Solitons in Mirror Twin Boundaries embedded in MoSe₂, S.

Wickenburg, S. Barja, A.Weber-Bargioni et al. *submitted*

8:40am **NM-WeM3 Solution Phase Synthesis, Electron Microscopy Characterization and Catalytic and Medical Applications of Nanoparticles**, *Richard Tilley*, University of New South Wales, Australia **INVITED**

Liquid phase synthesis is a powerful method for the formation of uniform sized nanoparticles and nanoparticles with a faceted morphology. General strategies for the formation of nanoparticles and through chemical synthesis will be outlined. The results presented will include the formation of catalytic metals such as gold core palladium shell nanoparticles, below and branched nanostructures of gold, palladium and ruthenium. The growth mechanism of how the particles form will also be presented along with HRTEM observations. Biomedical and catalytic applications will be discussed.

9:20am **NM-WeM5 Atomic Species Identification at the (101) Anatase Surface by Simultaneous Scanning Tunneling and Atomic Force Microscopy**, *O. Stetsovych*, NIMS, Japan; *M. Todorović*, Universidad Autonoma de Madrid, Spain; *T.K. Shimuzu*, NIMS, Japan; *R. Perez*, Universidad Autonoma de Madrid, Spain; *Oscar Custance*, NIMS, Japan

Titanium dioxide (TiO₂) is an important material in a number of energy-related applications such as photocatalytic water splitting, and the conversion of solar energy to electricity. Most of these applications rely on nano-crystalline TiO₂ samples that consist principally of two polymorphs: anatase and rutile. In some commercial TiO₂ samples, anatase nanocrystals account for up to 75% of the product, and anatase is generally regarded as having a higher surface reactivity than rutile.

Despite the pivotal role of anatase as reactive component in TiO₂ samples used as the active phase in commercial catalysts, there is still a relatively scarce amount of experimental studies on anatase surfaces in comparison with rutile. More research is required to better understand the surface properties that define anatase as such a good photocatalyst. In particular, the real space characterization of anatase substrates at the atomic scale is

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essential to elucidate the basic principles that govern the photocatalytic and photovoltaic applications of this TiO₂ polymorph.

In this contribution, we combine atomic force microscopy (AFM) and scanning tunneling microscopy (STM), supported by first-principles calculations, for the simultaneous imaging and unambiguous identification of atomic species at the (101) anatase surface [1]. By using single water molecules as atomic markers, we demonstrate that AFM images the topmost oxygen atoms of the surface, while the main contribution to the STM signal comes from the titanium atoms at the third atomic layer. We show that the STM signal is sensitive to sub-surface defects, and that simultaneous AFM-STM allows the acquisition of STM images with atomic resolution within the surface band gap, where standard STM imaging is challenging.

Based on key distinguishing features extracted from experiments and first principles calculations, we identify candidates for the most common surface defects of the (101) anatase surface and characterize the surface local chemical reactivity with the AFM probe at atomic scale.

The findings reported here provide the foundation for future work on anatase, and pave the way for the study of more complex anatase systems related to water splitting and organic photovoltaics, including the adsorption geometries and binding sites of photoactive molecules as well as metal dopants to enhance hydrogen production.

[1] O. Stetsovych et al. Nature Communications 6, 7265 (2015)

9:40am **NM-WeM6 Electrochemically-generated Nanomaterials Studied by In situ Flow Spectro-electrochemical Scanning Transmission X-Ray Microscopy**, Adam Hitchcock, V. Prabu, McMaster University, Canada; S.M. Rosendahl, Canadian Light Source, Canada; M. Reynolds, H. Hosseinkhannazer, Norcada Inc, Canada

We are using soft X-ray scanning transmission X-ray microscopy (STXM) [1] to investigate Cu thin film and dendritic electrochemical growth on a Au surface under variable pH conditions. Electrochemical reduction of Cu(II) under acid conditions is commonly used to deposit copper for integrated circuit interconnects, and in many other technologically important applications of thin films and nanoscale Cu metal. Improved understanding of the fundamental steps of the reaction and how to control undesirable phenomena such as dendritic growth is needed to further optimize this process. The reduction of Cu(II) to Cu(0) proceeds via a Cu(I) intermediate, which can be detected under weakly acidic to neutral conditions. We have developed a novel device for *in situ* STXM studies of electrochemical reactions which can operate under flow or static conditions [2]. The ability to change electrolyte during an experiment is being used to better understand the role of Cu(I) species in the deposition process. Spectromicroscopy at the Cu 2p and O 1s edges is used to analyze initial and final states, follow the process *in situ*, and search for intermediate species. The apparatus and techniques for spectro-electrochemical-microscopy will be described and results will be presented from deposition & stripping of copper from CuCl₂(aq) and CuSO₄(aq) electrolytic solutions as a function of pH.

STXM performed using BL10ID1 at CLS and BL 5.3.2.2 at ALS. Research supported by NSERC and the Catalyst Research for Polymer Electrolyte Fuel Cells (CarPE-FC) network.

References

[1] A.P. Hitchcock, *Soft X-ray Imaging and Spectromicroscopy in Handbook on Nanoscopy*, eds.

G. Van Tendeloo, D. Van Dyck and S. J. Pennycook 2012. (Wiley)

[2] A.P. Hitchcock, Z. Qin, S.M. Rosendahl, V. Lee, M. Reynolds and H. Hosseinkhannazer, *Electro-deposition of Cu studied with in situ electrochemical scanning transmission x-ray microscopy* Am. Inst. Phys. Conf Series **1696** (2016) 02003 (1-5)

10:20am **NM-WeM8 Structural and Chemical Study of the Stability of Pt-based Fuel Cell Electrocatalysts via 3D Electron Tomography**, Karren More, D.A. Cullen, B.T. Sneed, Oak Ridge National Laboratory, USA

Polymer electrolyte membrane (PEM) fuel cell performance and materials degradation, particularly associated with the cathode catalyst layer (CCL), can be directly attributed to the structure and chemistry of individual material components, as well as their uniformity/homogeneity within a

CCL. The individual material constituents used to form the CCL within the membrane electrode assemblies (MEAs), e.g., the electrocatalyst (Pt or Pt-alloys), catalyst support (C-based), and ionomer films (proton conductor), and especially the critical interfaces that are formed between these various constituents, are critically important in controlling fuel cell performance. Understanding the specific microstructural characteristics of the individual materials within the CCL, and how the materials interact during fuel cell operation/aging, is important for identifying materials optimization parameters that can significantly enhance performance and durability.

Research efforts at Oak Ridge National Laboratory are focused on the high-resolution microstructural and microchemical characterization of MEAs fabricated using different Pt-based electrocatalysts and catalyst loadings, carbon-based support materials, and ionomer solutions, as well as the same MEAs subjected to accelerated stress tests (ASTs) designed to degrade specific MEA components and assess durability. High-resolution analytical microscopy methods are used to study the distribution and chemistry of materials and interfaces within CCLs, which are combined with high-resolution imaging and 3D electron tomography techniques to provide unprecedented insight into the structure and interfaces (ionomer/support, ionomer/catalyst, catalyst/support, ionomer/pore) in "real" MEAs before and after aging. This presentation will focus on understanding materials distributions within the CCL as a function of processing variables, e.g., initial ionomer and/or ink chemistry, electrocatalyst (type, loading, and dispersion), and the type of carbon support used. The stability of the ionomer films, electrocatalyst, and support structures in CCLs after ASTs will be evaluated.

Research sponsored by (1) the Fuel Cell Technologies Office, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy and (2) Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

10:40am **NM-WeM9 Challenges in Synthesis and Characterization of Non-precious Transition Metal Carbide/Nitride Catalysts**, S. Gage, M. Davidson, C. Ngo, C.A. Cadigan, Colorado School of Mines, USA; D. Esposito, Max-Planck Institute for Colloids and Interfaces; Brian Trewyn, R. Richards, S. Pylypenko, Colorado School of Mines, USA

Metal carbides/nitrides have demonstrated unique properties for various catalytic reactions and are attractive as earth-abundant alternatives to precious group metals (PGM). However, synthesis of nanoscale transition metal carbides and nitrides has proven difficult, and obtaining structures with high surface areas and controlled morphologies have been elusive. Additional challenges arise from the complex nature of these nanomaterials and there is limited characterization available in the literature. Through unique synthetic approaches, we have created a wide array of unsupported and supported nickel-based nanomaterials, and utilized bulk and surface characterization techniques to identify synthesis-composition-property relationships.

11:00am **NM-WeM10 Stacking of AlOOH Nano-Rods and Plates: The Effect of Surface Termination Chemistry on the Preferential Interacting Crystal Zones in Solution**, Michele Conroy, J. Soltis, S. Chatterjee, E. Buck, Pacific Northwest National Laboratory, USA

Aluminum oxyhydroxide (boehmite) nanoparticles are used for a wide variety of applications including catalysis and adsorption. It has been shown that boehmite nanoparticles with 010 plane as the largest exposed surface area have increased catalysis and adsorption rate, due to the relatively high OH density of this plane. Additionally synthesizing these nanoparticles in a hierarchical structures instead as mono-dispersed, has been reported to increase the reactivity even further. In this study we utilize cryo-transmission electron microscopy (TEM) and in-situ liquid TEM to achieve fundamental insights into the mechanisms of nanoparticle aggregation and reactivity. Although there is a lot of theoretical debate around the preferential interacting zones of AlOOH crystalline nanoparticles in solution, there has been no experimental confirmation to date. Our initial results show that the particles aggregate along a preferred crystal orientation (the main flat (010)), irrespective of pH and solution content, forming large stacked agglomerates and decreasing the exposed surface area.

Aluminum oxide nanoparticles formed by the dehydration of boehmite are also widely used in industrial catalysis including petrochemical, chemical, and automotive due to their stability at high temperatures. Although the shape of the nanoparticle during the thermal treatment of boehmite

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remains the same the terminating planes of course change with the removal of water. This enabled us to study any change in the aggregation due to the terminating chemistry without the shape of the nanoparticle itself being a possible variable.

11:20am **NM-WeM11 Nanoscale Chemical Imaging with Photo-induced Force Microscopy**, *Sung Park*, Molecular Vista, USA

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology with sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various polymer systems. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

11:40am **NM-WeM12 CNC Modification for the Development of Active Food Packaging**, *Monique Lacroix*, INRS-Institut Armand-Frappier, Canada

Irradiation treatment of CNC was performed at doses of 5-20 kGy followed by reaction with a redox group of ascorbic acid (AA) and hydrogen peroxide in order to promote the formation of radicals on the macromolecule to enhanced the interaction of CNC with gallic acid. Our results have demonstrated that both of these pre-treatments induce the formation of carboxylic acid groups on CNC surface by conductometric titration. Derivates of carboxylic acid are known as food stabilizers and preservers due to their antiradical and antimicrobial effects. Since gallic acid has carboxylic acid groups, it was found that its interaction with pre-treated CNC with gamma-irradiation in the presence of redox group (CNC-g-GA) can impart to native CNC antiradical properties. A solution of 20% of CNC-g-GA was then added to a 1% (w/w) gellan in order to produced antiradical gellan-based film packaging. A significant improvement of the tensile strength (TS), the tensile modulus (TM) and the elongation at break (EB) and the water resistance was observed when CNC-g-GA was added to the film packaging formulation ($p \leq 0.05$). These results bring to a new application of antiradical film packaging or coatings which could be applied for food industry to preserve fruit and vegetables during storage.

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