

Tuesday Morning, November 11, 2014

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 313 - Session IS+AS+MC+SS-TuM

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

Moderator: Franklin (Feng) Tao, University of Notre Dame

8:00am **IS+AS+MC+SS-TuM1 The ISS Facility at BESSY II and Beyond: The Application of Near Ambient Pressure X-ray Electron Spectroscopy in the Surface Characterization of Technical Catalysts**, Michael Hävecker, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherung BESSY II, Germany, Ch. Heine, M. Eichelbaum, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, F. Rosowski, BasCat, UniCat-BASF JointLab, Germany, A. Trunschke, R. Schlögl, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

INVITED

The surface of functional materials like catalysts responds to the ambient conditions. Surface sensitive in-situ spectroscopy, i.e. in the presence of a reactive gas allows studying the formation of the gas/solid interface of a catalyst. The ISS facility operated by the FHI at the synchrotron radiation source BESSY II of the HZB is dedicated to this kind of in situ studies [1 - 3]. Online gas analytics allows correlating the electronic surface structure with the catalytic performance. Examples for the dynamic formation of the electronic surface structure by interaction with the ambient gas under equilibrium will be presented focusing on technical catalysts like multi-element mixed oxide powders. The direct catalytic oxidation of alkanes to olefins and oxygenates is becoming increasingly important for the chemical industry due to the up-coming shortage of crude oil resources. Vanadyl pyrophosphate is the industrially used catalyst in the selective oxidation of n-butane to maleic anhydride. We characterized the surface of this catalyst material with NAP-XPS in the mbar pressure range and with NAP-soft XAS in the electron yield mode at pressures up to 1000mbar at various gas mixtures. In addition to the determination of composition and vanadium oxidation state also semiconductor properties like work function changes and Fermi level pinning have been studied [4].

Finally, an outlook on future activities at HZB/BESSY to develop further synchrotron based ambient pressure characterization methodologies will be given. The Energy Materials In-Situ Laboratory Berlin (EMIL) is a research alliance of the HZB and FHI that will include a NAP-high kinetic energy XPS endstation capable to operate at kinetic energy of photoelectrons up to 7000eV that allows studying buried layers and liquid/solid interfaces.

References

Salmeron, M., Schlögl, R., Ambient pressure photoelectron spectroscopy: A new tool for surface science and nanotechnology. Surf. Sci. Rep., 32, 1022 (2008).

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Heine, Ch. et al., Work function, band bending, and microwave conductivity studies... J. Phys. Chem. C, 117, 26988 (2013).

8:40am **IS+AS+MC+SS-TuM3 Recent Trends and Instrument Development in Ambient Pressure Photoelectron Spectroscopy**, Henrik Bergersen, J. Åhlund, VG Scienta AB, Sweden

The field of Ambient Pressure Photoelectron Spectroscopy (APPEs) has gone through rapid development in recent years. Although the field was pioneered in the 1970's, most instrument as well as application development has happened in the last decade. In this contribution we will discuss some recent trends in APPEs and present state-of-the-art work within the different applications areas.

Experiments done under normal surface science conditions (Ultra High Vacuum) are of limited use in some applications, e.g. catalysis, due to the pressure gap problem. This motivates the study of systems at ambient pressures. While the presence of a gas atmosphere surrounding the sample enables new types of studies, it also poses instrumentation difficulties. The most notable of these is signal decrease due to inelastic scattering of the photoelectrons in the surrounding gas. We will show state-of-the-art solutions to limit this scattering together with recent results.

Photoelectron spectroscopy went through a revolution in the 1990's, with the development of parallel angular detection using 2D detectors, a

development that VG Scienta is proud to have contributed to. The possibility of simultaneous recording of Angular Resolved PES (ARPES) spectra enables not only band structure measurements, but also x-ray photoelectron diffraction (XPD), depth profiling and standing wave spectroscopy. Recent examples within APPEs will be given.

The use of 2D detectors to record parallel spatially resolved spectra is a related technique. Here we will show experimental results as well as very recent instrument development to obtain world leading spatial resolution at ambient conditions.

The combination of APPEs and Hard X-ray Photoelectron Spectroscopy (HAXPES) has recently become an established technique. We will show results of the use of this combination to decrease inelastic scattering of the photoelectrons as well as to tailor the probing depth of advanced systems.

In APPEs, more than in UHV PES, instrument usability and sample handling is a key to successful measurements. VG Scienta has developed several complete system offerings to maximize productivity in the lab. These will be discussed on a conceptual level, as well as in some detail.

9:00am **IS+AS+MC+SS-TuM4 In Situ Studies of Exceptionally Active Catalyst of Earth Abundant Elements for Complete Combustion of Methane at a Relatively Low Temperature**, F. Tao, J. Shan, L.T. Nguyen, S. Zhang, Weixin Huang, University of Notre Dame

It is critical to develop a catalyst made of earth-abundant elements highly active for a complete combustion of CH₄ at a relatively low temperature for catalytically transforming CH₄ to electrical energy in power plant. The currently available catalysts with high activity consist of precious metal nanoparticles supported on rare earth oxides. Their high cost limits the application of these catalysts at industrial scale. Here we report a new catalyst, early transition metal oxide-based mixed oxide only consisting of earth-abundant elements which can completely combust CH₄ at 350°C at a gas hourly space velocity of 240,000 ml 0.5% CH₄ on 1 gram in one hour. This comparable or even higher catalytic activity results from the integration of Ni cations and surface lattice oxygen atoms at the atomic scale. With such an integration, the carbon atom dissociated from CH₄ can bond with its neighboring surface oxygen atoms to form an intermediate of CO₂ and then desorb.

In-situ studies of catalyst surface using AP-XPS and monitoring of products formed from isotope-labeled catalysts show that (1) molecules O₂ dissociates on surface oxygen vacancies, (2) half of the dissociated oxygen atoms stay in oxygen vacancies, (3) the other half of dissociated oxygen atoms directly bond with hydrogen atoms dissociated from CH₄ to form OH and then H₂O molecules, (4) CH₄ progressively dissociates on Ni cations to form CH_n (n=3, 2, 1, 0), (5) carbon atoms bind to two surface lattice oxygen atoms nearby to form a carboxylate species, O-C-O intermediate, and then desorb. The mixed cations and surface lattice oxygen atoms in this mixed oxide at atomic level makes the formation of an -O-C-O- intermediate at a mild temperature since a spillover of dissociated species is not necessary.

9:20am **IS+AS+MC+SS-TuM5 Ambient Pressure XPS Studies of Fuel Cell and Electrolysis Catalysis**, Hirohito Ogasawara, SLAC National Accelerator Laboratory

INVITED

Fuel cell and electrochemical reactions were studied by ambient pressure X-ray photoemission spectroscopy at Stanford Synchrotron Radiation Lightsource (SSRL) [1]. We will present our recent studies: platinum catalyst under different operating conditions of oxygen reduction fuel cell reaction, iridium oxide catalyst during the oxygen evolution reaction and molybdenum sulfides catalyst during the hydrogen evolution reaction. Surface changes under these electrochemical reactions, which are keys to understanding activity and durability will be shown [2,3].

[1] Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry, CatalysisToday 205 (2013) 101.

[2] Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode, Nature Communications 4 (2014) 2817

[3] In situ observation of surface species on iridium oxide nanoparticles during the oxygen evolution reaction, submitted

11:00am **IS+AS+MC+SS-TuM10 Environmental Cells with 2D Electron Transparent Windows for Ambient Pressure Photoelectron Imaging and Spectroscopy**, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

We have designed and characterized electron transparent windows for environmental cells dedicated for ambient pressure XPS spectroscopy and electron microscopy of liquid and gaseous samples. These windows made of single or multi-layered graphene have thicknesses comparable to the effective attenuation length of 200-1000 eV electrons what allow to conduct

interfacial spectroscopy of fully hydrated samples without differential pumping setup. In addition, these membranes are thermally and chemically stable, gas impermeable and mechanically robust. Based on this unique combination of properties and on recent developments in graphene fabrication and transfer protocols we demonstrate the capability to perform in situ XPS and electron microscopy studies of the electrochemical processes taking place at liquid electrolyte-solid interface.

11:20am **IS+AS+MC+SS-TuM11 The Effect of Interfacial Ethanol on Ionic Distributions in Aqueous Solution**, *Marijke Van Spyk, K.A. Perrine, M.J. Makowski*, University of California Irvine, *H. Bluhm*, Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California Irvine

In this study, liquid microjet X-ray photoelectron spectroscopy (LJ-XPS), carried out at beam line 11.0.2 of the ALS synchrotron at LBNL, was used to probe the interfacial behavior of aqueous magnesium or sodium chloride solutions with the addition of organics including ethanol under one torr of water vapor. Our results address fundamental issues of solvation at the surface and in the bulk of ternary solutions. For these studies, aqueous ethanol solutions were generated, and salt was added to produce an ionic solution. The ternary solution is pumped continuously through a temperature-controlled quartz capillary to produce a micron-sized laminar jet within 0.5 mm of the PES analyzer aperture. Synchrotron radiation ionizes the solution, and ejected photoelectrons are detected using differentially pumped electron optics. Tunable photon energy, together with the inelastic scattering attenuation of photoelectrons in solution, provide a variable probe depth. Here, photoelectrons with low kinetic energies (200 eV) are detected from the surface of solution, and those with high kinetic energies (600 eV) are detected from deeper into solution, where chemistry is consistent with bulk solution. The high kinetic energy photoelectrons have sufficiently large inelastic mean free paths so that a percentage are attenuated by inelastic scattering.

Carbon (C1s), oxygen (O1s), sodium (Na2s), magnesium (Mg2s), and chloride (Cl2p) photoelectron spectra were collected at two photoelectron kinetic energies to investigate the relative concentration of species at the surface and in the bulk for various ethanol concentrations. The C1s spectra were deconvolved into two gas phase and two solution phase peaks corresponding to the carbon groups in ethanol. Surface adsorption was evident for aqueous ethanol without ions, and was diminished in the presence of ions. The relative ionic propensities at the surface change with ethanol concentration. In particular, the solvation of magnesium was impacted by dehydration. Understanding the interfacial solute distribution of these ternary solutions is important for predicting reactivity at aqueous surfaces.

11:40am **IS+AS+MC+SS-TuM12 Studying Zeolites and Clays with the Tools of Surface Science from UHV to Near-Ambient Pressures**, *Jorge Boscoboinik*, Brookhaven National Laboratory **INVITED**

While Surface Science provided useful insights into a variety of materials of interest for catalysis, its contribution to the understanding of zeolites and clays has been limited. This was mainly due to the lack of suitable well-defined surfaces that successfully mimic the properties of these important materials while allowing its analysis using the vast toolkit of surface science. This talk will describe an aluminosilicate ultra-thin (~ 0.5 nm) film that was recently synthesized, which provides a good model system for zeolites and clays. It consists of a bilayer structure, as shown in the figure, and it counts with bridging hydroxyl groups. The latter are the active sites in zeolite catalysts, of great importance for energy transformations such as the cracking of crude oil and the methanol to gasoline conversion. This model system allows then to study the interaction of molecules involved in these catalytic processes and potentially contribute to the understanding of these chemical transformations. I will provide first a description of the system itself as characterized in ultra-high vacuum (UHV) conditions and then move on to analyze the interaction of these aluminosilicate films with different molecules of interest from UHV to near-ambient pressures.

References

- [1] J.A. Boscoboinik, X. Yu, B. Yang, F.D. Fischer, R. Wlodarczyk, M. Sierka, S. Shaikhutdinov, J. Sauer, H.-J. Freund, *Angew. Chem. Int. Ed.* 51 (2012) 24, 6005-6008. *Angew. Chem.* 124 (2012) 6107-6111.
- [2] J.A. Boscoboinik, X. Yu, B. Yang, S. Shaikhutdinov, H.-J. Freund. *Micropor. Mesopor. Mater.* (2013) 165, 158-162.
- [3] J.A. Boscoboinik, X. Yu, E. Emmez, B. Yang, S. Shaikhutdinov, F. Fischer, J. Sauer, H.-J. Freund. *J. Phys. Chem. C* (2013) 117, 13547-13556.

Tuesday Afternoon, November 11, 2014

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 313 - Session IS+AS+MC+SS-TuA

Environmental Electron Microscopies

Moderator: Jorge Boscoboinik, Brookhaven National Laboratory

2:20pm **IS+AS+MC+SS-TuA1 Nanocrystal Shape Evolution during Growth, Haimei Zheng,** Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

An understanding of nanocrystal shape control mechanisms during growth is critical for the design of novel functional materials with surface-enhanced properties. However, the atomic level shape evolution of nanocrystals during growth is mostly unknown due to the lack of direct observation. We use liquid cells under transmission electron microscope (TEM) to study the growth of Pt or Pt-alloy nanoparticles in situ, where growth either by nanoparticle attachment or by monomer attachment has been observed. First, I will present Pt-Fe nanorods formation by shape-directed nanoparticle attachment under the electron beam. Winding polycrystalline nanoparticle chains are achieved at the early stage then they are straightened to yield single-crystal nanorods. Tracking their growth trajectories allows us to distinguish the force fields exerted by single nanoparticles and nanoparticle chains. Second, I will show the observation of platinum nanocube growth and the facet development. By in situ imaging with high spatial and temporal resolution, we have identified unique growth mechanisms that cannot be predicted by Wulff construction or other existing growth theorems. We found layer-by-layer growth of the {100} and {111} facets while the {110} facets show steps. We also found that the growth rates of these facets are similar until the {100} facets stop growth. Hence, the distance from {100} facets to the crystal center is fixed throughout the subsequent growth. The {110} facets are eliminated when two adjacent {100} facets meet. Lastly, the growth of {111} facets fills the corners to complete a nanocube. Our calculation suggests oleylamine ligand mobility on the facet is responsible for the arresting of {100} growing facets. References:

1. Liao et al. "Facet Development during Platinum Nanocube Growth" Science in review.
2. H. G. Liao, L. Cui, S. Whitlam, H. Zheng, "Real time imaging Pt3Fe nanorod growth in solution." Science 336, 1011 (2012).
3. We used TEM facility at National Center for Electron Microscopy of Lawrence Berkeley National Laboratory (LBNL), which is supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering of the U.S. Department of Energy under Contract #DE-AC02-05CH11231. H.Z. thanks the support of DOE Office of Science Early Career Research Program.

3:00pm **IS+AS+MC+SS-TuA3 Microfluidic Cell for In Situ Scanning Electron Microscopy of Hydrated Dynamic Systems, Christopher Brown, A. Yulaev, A. Kolmakov,** National Institute of Standards and Technology (NIST)

The ability to conduct nanoscale imaging of fluid hydrated dynamic systems is a long sought goal within the scientific community. While improvement of commercial instrumentation and environmental cells has enabled in situ imaging of fluid hydrated systems using transmission electron microscopy (TEM) at the nanoscale, additional opportunities exist in implementing in situ techniques within scanning electron microscopy (SEM) instruments equipped with fluidic cells. Factors that motivate this work include: ubiquity and reduced cost of SEM instrumentation compared to TEM, drastically reduced restrictions on the sample size, and greater flexibility of systems and detectors designed for the SEM compared to TEM.

In this communication we report on development of the microfluidic environmental cell designed for in situ studies of fully hydrated dynamic objects. We describe strategies and experimental results that enable improved in situ imaging using the SEM, including development of electron transparent graphene windowed devices that increase signal-to-noise ratio of images of fluid hydrated objects. Limiting factors of in situ imaging of hydrated samples within the SEM are discussed including radiolysis and decreased electron beam penetration into liquid cells compared to higher acceleration voltage electron microscopy modalities.

3:20pm **IS+AS+MC+SS-TuA4 Liquid Jet -X-ray Photoelectron Spectroscopy and MD Simulations indicate that Li Cations in Aqueous Solutions Exhibit High Surface Propensity, Kathryn Perrine, M.H.C. Van Spyk, M.J. Makowski, A.C. Stern, K. Parry, D.J. Tobias,** University of California Irvine, *A. Shavorskiy, H. Bluhm,* Lawrence Berkeley National Laboratory, *B. Winter,* Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherung BESSY II, Germany, *J.C. Hemminger,* University of California Irvine

Ions impact chemistry at the aqueous liquid/vapor interface in environmental chemistry, electrochemistry and biomolecular chemistry. Ions are characterized as structure makers or breakers for protein mixtures, and the trend is known as the Hofmeister series.¹ The Born electrostatic model of ions at interfaces has shown that ions should be repelled from the liquid/vapor interface due to a decrease in free energy when solvation by water occurs.² Molecular dynamic (MD) simulations and recent experimental studies have shown that anions tend to adsorb to the liquid interface in an inverse Hofmeister trend.^{3,4} Our synchrotron based XPS studies carried out over the last five years have provided experimental evidence that most cations follow classical ionic solution behavior and are repelled from the liquid/vapor interface, whereas some anions exhibit significant propensity for the surface. In this talk we present our recent experiments on Li salt solutions. Our experiments indicate that unlike larger cations, Li⁺ is not repelled from the interface and has a significant surface propensity.

Liquid jet-X-ray photoelectron spectroscopy (LJ-XPS) is used to explore the relative ion concentrations at different depths in aqueous salt solutions. Low photoelectron kinetic energies are used to probe the surface of solutions yielding relative ionic concentrations that are present at the liquid/vapor interface. Higher photoelectron kinetic energies probe deeper into the bulk of aqueous solutions. The relative ionic concentrations of solutions prepared from lithium halide salts are compared to potassium halide solutions at different depths. MD simulations support our studies and suggest that Li⁺ cations have interfacial propensity due to factors such as the tight water solvation shell on the Li⁺ ions. Density profiles reveal anion and Li⁺ ion adsorption to the liquid/vapor interface. In addition, we also compare various concentrations of KI and LiI aqueous solutions to determine ion adsorption at the aqueous interface.

1. K. D. Collins and M. W. Washabaugh, *Quarterly Reviews of Biophysics*, 1985, **18**, 323-422.
2. M. Born, *Zeitschrift Fur Physik*, 1920, **1**, 45-48.
3. P. Jungwirth and D. J. Tobias, *Journal of Physical Chemistry B*, 2002, **106**, 6361-6373.
4. D. J. Tobias, A. C. Stern, M. D. Baer, Y. Levin and C. J. Mundy, *Annual Review of Physical Chemistry*, Vol 64, 2013, **64**, 339-359.

4:20pm **IS+AS+MC+SS-TuA7 Complementary Microscopy and Spectroscopy Investigations of the Initial Oxidation Stages of Binary Alloy Thin Films, Judith Yang,** University of Pittsburgh **INVITED**

The transient stages of oxidation – from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide – represent a scientifically challenging and technologically important terra incognita. These issues can only be understood through detailed study of the relevant microscopic processes at the appropriate length scale in situ. We are studying the dynamics of the initial and transient oxidation stages of a metal and alloys with complementary in situ methods - ultra-high vacuum (UHV) transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). We have previously demonstrated that the formation of epitaxial Cu₂O islands during the transient oxidation of Cu and Cu-Au thin films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. We are presently investigating the early stages of oxidation of binary alloys where both elements compete to oxidize. Specifically, we are studying Cu-Ni and Ni-Cr single crystal thin films as a function of relative concentration, oxygen partial pressures and temperatures. For Cu-Ni oxidation, the addition of Ni causes the formation Cu₂O and/or NiO where the oxide type(s) and the relative orientation with the film depend on the Ni concentration, oxygen partial pressure and temperature. For Ni-Cr model alloys containing 4, 8 and 16 at.% Cr and isothermally oxidized at 600°C and 10⁻⁷ to 10⁻³ torr O₂ pressure, our XPS experiments reveal that after 2 min of oxidation only Cr₂O₃ forms on the surface of all three alloys. However, with further exposure (i.e., 30 min or 2 h), a competitive growth between Cr₂O₃ and NiO under all the tested conditions is clear. These XPS data are remarkable results, since prior studies reported in the literature suggest that NiO + internal Cr₂O₃ or NiO/NiCr₂O₄/Cr₂O₃+ internal Cr₂O₃ should form at

least for the lower Cr content (4 and 8%) alloys. These experiments will be complemented with electron microscopy of scale cross sections to better understand the competitive nucleation and growth processes as a function of the oxygen partial pressure.

5:00pm **IS+AS+MC+SS-TuA9 Direct Observation of Structure Controlled Carbon Growth by Environmental TEM**, *J. Kling, T.W. Hansen, Jakob Wagner*, Technical University of Denmark **INVITED**

In order to meet the increasing demand of faster and more flexible electronics and optical devices and at the same time decrease the use of the critical metals, carbon based devices are in fast development. Furthermore, the rich resource of carbon element limits the need for recycling and the material supports the friendly environment approach.

Layered carbon structures spanning from graphene to few layered graphite are used for extremely compact devices with outstanding performance [1,2]. A relative cheap and easy way to produce layered carbon structures on the large scale is via chemical vapor deposition (CVD) growth on catalysts like copper and nickel. However, the exact growth mechanism is still under debate and is most likely dependent on precursor pressure and growth temperature.

Here, we have used environmental transmission electron microscopy (ETEM) to follow the growth of layered structures directly at the atomic level and thereby coupling growth rate and quality of the material on the local scale to the growth parameters. Acetylene and methane are exposed to the catalyst (Ni or Cu) in situ in the microscope at pressures ranging from 0.1Pa 100Pa at temperatures ranging from 500-700C. Following the subsequent appearance of carbon layers allows for determination of instant growth rates under controlled conditions.

Single walled carbon nanotube (SWCNT) based electronics is another way of addressing the environment friendly approach of faster and better electronics. In order to exploit the potential of SWCNTs in the electronic industry fully, selective growth of either conducting or semiconducting tubes is of high importance. Growing the tubes in situ in the ETEM under relevant growth conditions gives fundamental insight in the parameters controlling the chirality and thereby the electronic properties of the SWCNTs.

References:

[1] K. S. Novoselov, S. V. Morozov, T. M. G. Mohinddin, L. a. Ponomarenko, D. C. Elias, R. Yang, I. I. Barbolina, P. Blake, T. J. Booth, D. Jiang, J. Giesbers, E. W. Hill, and a. K. Geim, *Phys. Status Solidi* **244**, 4106 (2007).

[2] F. Schwierz, *Proc. IEEE* **101**, 1567 (2013).

5:40pm **IS+AS+MC+SS-TuA11 In Situ Energy Loss Spectroscopy, A Novel Approach to the Characterization of Surfaces during MBE Growth**, *Philippe Staib*, Staib Instruments, Inc.

A new energy analyzer for Auger Electron Spectroscopy (AES), the Auger Probe, is able to operate in growth vacuum chambers to measure *in-situ during growth* the composition of the surface [1,2,3]. The primary beam is provided by the RHEED electron gun at a very grazing incidence angle (2 to 3 degrees). The analyzer is also used in EELS mode to measure Characteristic Energy Losses (CEL). The use of a grazing incidence angle strongly enhances the strength of the energy losses peaks, which become more prominent than the elastic line

EELS data from the Auger Probe are presented showing the evolution of the CEL distributions during oxidation (ZnO), during thermal de-oxidation of GaSb, and during growth of binary and ternary materials (GaAsSb). Surprisingly, even during deposition of homoepitaxial layer, the CEL distributions show a marked dependence upon the flux of material to the sample which can reflect the formation of phys- rather than chemisorbed layers and the smoothness of the surface [4].

The CEL spectra cannot be interpreted simply, due to the strong overlapping of multiple excitations of single energy losses. A model is presented that takes into account the probability distribution for multiple losses, and allows extraction of the elementary energy loss lines from the distribution. Using this model, accurate energy loss values can be measured and an effective electron density can be calculated. The intensity of the extracted energy losses versus the intensity of the elastic peak is a measure of the ratio d/l between the electron path length d and mean inelastic free path l of the specific loss. The inelastic mean free path for each loss line can be deducted using d values from monte-carlo simulation of the electron trajectories and the intensity ratio of the loss peak vs. elastic peak.

Special thanks to S. Svensson and W. Sarney of ARL for their collaboration during measurements used in this work.

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6:00pm **IS+AS+MC+SS-TuA12 Selective Staining for Enhanced Spectroscopic Identification of Domains in Immiscible Polymer Blends by Micro-Raman Spectroscopy**, *Nicholas Heller, C.R. Clayton*, SUNY Stony Brook, *S.L. Giles, J.H. Wynne*, Naval Research Laboratory, *M.J. Wytiaz, M.E. Walker*, Sherwin-Williams Company

Blends of incompatible polymers combined with fillers and pigments were used to produce unique low reflectance thermoset coatings. Understanding the origins of low reflectance from the coatings was approached through microscopy, thermal analysis and spectroscopic analysis of both pigmented and control clear coatings. Polymeric phase separation was confirmed by the presence of two distinct glass transition temperatures. Microscopy revealed random surface features for the pigmented coatings. Therefore, the pigments and fillers were removed to observe the polymer-polymer interactions within the blend under curing conditions. Identification of the polymeric domains was obtained using Raman spectroscopy mapping of cross-section samples embedded within a polyester resin. Cross-section samples of coatings were utilized to isolate encapsulated polymer domains from the continuous polymer network to minimize spectral averaging from both domains. Raman analysis of the blends was compared to cured films generated using the individual resins. The embedding process produced a marker peak in one phase and in one individual resin. The marker peak was found to be from styrene monomer and was found to selectively bind to one component of the polymer blend, based on polar and hydrogen bonding characteristics..

Wednesday Morning, November 12, 2014

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 313 - Session IS+AS+MC+SS-WeM

In-Situ X-ray Absorption and Raman Spectroscopy

Moderator: Hirohito Ogasawara, SLAC National

Accelerator Laboratory

8:00am **IS+AS+MC+SS-WeM1 In Situ Studies on the Behavior of Metal/Oxide Catalysts during the Water-gas Shift Reaction**, *Jose Rodriguez, D. Stacchiola, S. Senanayake, J. Hanson*, Brookhaven National Laboratory **INVITED**

In this talk, it will be shown how a series of *in-situ* techniques [X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)] can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxide catalysts used for the production of hydrogen through the water-gas shift reaction (WGS , $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$). Under reaction conditions most WGS catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the synthesis process. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO₂, TiO₂, CeO_x/TiO₂ and Fe₂O₃ essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal and oxide phases. IR and AP-XPS have been used to study the reaction mechanism for the WGS on the metal/oxide catalysts. Data of IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for the water-gas shift on Cu-, Au- and Pt-based catalysts. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO₃, HCO₃) or carboxyl (HOCO) species should be considered. In the last two decades, there have been tremendous advances in our ability to study catalytic materials under reaction conditions and we are moving towards the major goal of fully understanding how the active sites for the production of hydrogen through the WGS actually work.

8:40am **IS+AS+MC+SS-WeM3 Tuning Catalytic Performance of Bimetallic Nanoparticle Catalysts through a Single or Sequential Post-Synthesis Reaction in a Gas Phase**, *F. Tao, J. Shan, S. Zhang, L.T. Nguyen*, University of Notre Dame, *A. Frenkel*, Yeshiva University, *J. Greeley*, Purdue University, *Shibi Zeng*, University of Notre Dame

Besides a sophisticated synthesis of bimetallic nanocatalysts in a colloidal solution, a post-synthesis reaction in a gaseous phase is a complementary method to tailor the surface structure and composition of a bimetallic nanocatalyst to tune its catalytic performance. Here we illustrate the capability of creating a new catalyst surface exhibiting a lower activation barrier through segregation of a bimetallic catalyst in a post-synthesis reaction in a reactive gaseous environment. *In-situ* surface chemistry of bimetallic nanocatalysts were analyzed with AP-XPS. Coordination environment of Pt and Cu atoms under different reaction conditions was tracked with *in-situ* EXAFS. The surface restructuring was simulated with DFT calculation from thermodynamic point of view. The composition and geometric structure of the newly formed surface of the bimetallic nanocatalysts strongly depend on the reactant gas used in the post-synthesis reaction. A further sequential reaction in a different gas after the initial post-synthesis reaction in a gas forms a different catalyst surface. A post-synthesis reaction of a Pt-Cu regular nanocube (Pt-Cu RNC) in hydrogen forms a near surface alloy (NSA) which exhibits an activation barrier of 39 kJ/mol for CO oxidation, much lower than pure Pt nanocubes. These studies demonstrate a method of tuning catalytic performances and generate another catalytic phase through a post-synthesis reaction in a gas phase.

9:00am **IS+AS+MC+SS-WeM4 In Situ Characterization of Metal-Based Ionic Liquids using X-ray Spectroscopy**, *Robert Meulenberg*, University of Maine, *C. Apblett, H. Pratt, T. Anderson*, Sandia National Laboratories

Energy storage for vehicles is advancing rapidly, and one of the possible contenders for a battery that can quickly be recharged is a redox flow battery, which uses liquids that are pumped into the battery to be charged or discharged, and then removed to storage containers. This makes the chemistry roughly analogous to liquid fuels employment, where the charged chemistry is pumped into the battery, discharged, and then pumped into a

waste container, similar to fuel pumped into an engine, ignited, and then expelled through the tailpipe. Unlike internal combustion engines, however, the discharged product is retained on the vehicle, and can be subsequently either recharged on the vehicle, or pumped off the vehicle to be recharged at a filling station, while replacing with freshly charged material.

To date, however, the concentrations of most redox flow battery chemistries have been low, below the 1-2M concentration level. Recently, a new type of ionic liquid (IL) redox flow chemistry has been developed that raises this to 5-6M, and improves the energy density of the system. However, little is known about the structure of the molecule in the charged and discharged states. The current understanding of the structure of the IL, primarily the Fe IL, comes from primarily from FTIR, Raman, and TGA/DSC data, as traditional methods such as NMR to probe surface chemistry are limited due to the paramagnetic Fe center. It is believed the coordination of the ligand to the metal center occurs primarily through the alcohol groups. Cyclic voltammetry of the FeIL exhibits behavior associated with Fe(III)/Fe(II) reduction/oxidation, with some evidence that the ligands are coordinating to adjacent Fe atoms, resulting in antiferromagnetic coupling between the metal centers. A complete, fundamental understanding of the local coordination and ligand environment is not known and is the primary goal of our research. To further understand this structure, we have constructed a new electrochemical cell to be used for *in situ* transmission Fe K-edge x-ray absorption fine structure (XAFS) spectroscopy. We conduct our measurements at various states of charge, and the structure of the molecule in these various states is determined using this from analyzing both the XANES and EXAFS. Effects of electrochemical cell potential on local structure of the FeIL will be discussed.

9:20am **IS+AS+MC+SS-WeM5 Monitoring Catalysts during Catalytic Reactions with In Situ Raman Spectroscopy**, *Israel Wachs*, Lehigh University **INVITED**

The surfaces of heterogeneous catalysts in reactive environments are dynamic and require *in situ* characterization studies under reaction conditions to fully understand their fundamental structure-activity relationships. This presentation will focus on the application of Raman spectroscopy to determine the nature of the catalytic active sites in different reaction environments. Emphasis will be placed on investigating heterogeneous supported metal oxide catalysts containing multiple catalytic active sites and determining the roles of each of the sites. Some of the examples to be presented will be the metathesis of H₂C=CHCH₃ to H₂C=CH₂ and H₃C-CH=CHCH₃ by supported ReO_x/Al₂O₃ catalysts, polymerization of H₂C=CH₂ by supported CrO_x/SiO₂ and methane conversion to aromatic liquids by supported MoO_x/ZSM-5 catalysts.

11:00am **IS+AS+MC+SS-WeM10 Photoelectron Spectroscopy on Ice, Mineral Oxides and Aqueous Solutions of Atmospheric Relevance**, *Markus Ammann*, Paul Scherrer Institut, Switzerland **INVITED**

Aerosol particles and ice are key in atmospheric chemistry as many chemical and physical processes occurring on and within them are relevant for air pollution and climate. The fundamental understanding of these processes increasingly relies on a molecular level description of structures and mechanisms. This requires tools to access condensed phase – air interfaces with structural and chemical selectivity. Recent advances in pushing the pressure limits of ultrahigh-vacuum surface science methods such as photoelectron spectroscopy have allowed the investigation of environmentally relevant surfaces under nearly ambient conditions and have thereby significantly contributed to the advancement of our understanding of interfaces in the atmosphere. In this overview, recent results on the interaction of acidic gases with ice surfaces, of chemical and photochemical processes on mineral oxides, and of the structure of aqueous solution surfaces will be presented. These examples also demonstrate the instrumental requirements for such *in situ* experiments, and our recent developments of sample environments to facilitate experiments with environmental substrates will be presented.

11:40am **IS+AS+MC+SS-WeM12 In Situ Analysis of Materials Under Mechanical Stress: A Novel Instrument for Simultaneous Nanoindentation and Raman Spectroscopy**, *Chris Michaels, Y.B. Gerbig, R.F. Cook*, NIST

Instrumented indentation or “nanoindentation” is a method that is widely used in the study of the mechanical deformation of materials on small length scales (~ micrometer). Raman spectroscopy is a technique that provides insight into the molecular or crystallographic level processes involved in the mechanical deformation of materials, such as strain build-up, phase transformations and variations in crystallinity. Typically these approaches have been used separately wherein the spectroscopic analysis of the material might take place prior to and after the end of a mechanical

transformation. Of course, there is significant interest in *in situ* analyses of materials during mechanical transformation as such an approach promises a richer understanding of the underlying physics than is likely possible with analysis limited to pre- and post-transformation. For example, the ability to follow the path of phase transformations rather than just the endpoints is certainly desirable. Consequently, significant effort has been directed toward the coupling of indentation instruments with various *in situ* analysis capabilities.

This talk describes the design and operation of a nanoindentation instrument that is coupled with a laser scanning Raman microscope to conduct *in situ* spectroscopic analyses of mechanically deformed regions of optically transparent materials under contact loading. The force transducer of the device allows adjustment of crucial experimental parameters, such as indentation loads and loading rates. An incorporated displacement sensor allows for collection of force-displacement curves comparable to conventional nanoindentation instruments. The device is mounted on the sample stage of an inverted optical microscope that is configured for Raman microscopy, allowing optical access to the mechanically deformed regions of transparent samples. The capabilities of this novel instrument will be demonstrated by *in situ* studies of the indentation-induced phase transformations in an epitaxial silicon-on-sapphire (SoS) thin film, in both a microspectroscopy and a laser scanning Raman imaging configuration.

Wednesday Afternoon, November 12, 2014

In-Situ Spectroscopy and Microscopy Focus Topic Room: 313 - Session IS+2D+MC+NS+SP+SS-WeA

In-Situ Scanning Microscopy

Moderator: Markus Ammann, Paul Scherrer Institut

2:20pm IS+2D+MC+NS+SP+SS-WeA1 *In Situ* Studies of Model Fuel Cells, **Zhi Liu**, Lawrence Berkeley National Laboratory **INVITED**

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields. Multiple new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will give an overview of science projects at ALS BL9.3.2 in heterogeneous catalysis and electro-chemistry using these new systems. Furthermore, I will present results of our in-situ study on the electrolyte/electrode interface of a working model electrochemical cell at ALS BL9.3.1. We believe the successful development of soft and hard X-ray APXPS endstations will provide energy research community a powerful in-situ tool to directly study the electrolyte/electrode interface of many important electrochemical devices.

3:00pm IS+2D+MC+NS+SP+SS-WeA3 **Probing of Nanoscale Objects in Reactive Liquids through Membranes using Near-Field Microwave Microscopy**, **Alexander Tselev**, Oak Ridge National Laboratory, A. Komakov, National Institute of Standards and Technology (NIST)

Many functional objects (and interfaces) have to be studied in situ when the object is immersed in liquid environment. In addition, for energy, chemical, (bio-) medical and other applications, there is a need to study the encapsulated objects, which otherwise can be chemically reactive or toxic. These samples are often mesoscopically small or exist in minuscule quantities. Recently, we have developed a process for preparation of liquid-filled cells sealed with ultrathin membranes. Such cells can be implemented for in-situ studies using, for example, electron or soft x-ray microscopy due to a high transparency of these membranes to electron beams. However, in many cases electron microscopy is an invasive technique due to various electron beam induced parasitic effects (e.g. radiolysis or beam induced deposition). To overcome these impediments, we demonstrate the scanning microwave impedance microscopy (sMIM) to image different nanoscale objects immersed in the liquid environment through 30 nm SiN membranes. In the sMIM, microwaves of a frequency of 3 GHz are sent through a coaxial cable connected to a shielded cantilever probe fully compatible with an AMF microscope. The sharp probe tip provides "focusing effect" for the electric component of the microwave. For imaging, the tip is brought into gentle mechanical contact with a membrane. Amplitude and phase of microwaves reflected from the probe are monitored. Since the wave reflection is dependent on the tip-sample system impedance, reflected waves carry information about sample local properties. The effective distance into the sample depth, where the tip-induced field enhancement takes place, is approximately equal to the tip apex radius. Since the membrane thickness is smaller compared to the tip radius of a typical probe (about 50 nm for a fresh tip), the tip-sample impedance is dependent on the dielectric properties of the material beneath membrane, and therefore, it is possible to "see" through the membrane. We demonstrate imaging of different combinations of model liquids and nanoparticles: water and water-based solutions ($\epsilon \sim 80$), organic solvents ($\epsilon \sim 10-25$), and oils ($\epsilon \sim 2-3$) containing Ni metal, polystyrene ($\epsilon \sim 2.5$) and PbO ($\epsilon \sim 25$) particles. This technique can be further implemented for a broad range of objects in confined liquids, and can be used to monitor interfacial electrochemical reactions. Imaging with sMIM was performed at CNMS, which is sponsored at ORNL by the SUFD, BES, US DOE.

4:20pm IS+2D+MC+NS+SP+SS-WeA7 **Caught in the Act! Live Observations of Catalysts Using High-Pressure Scanning Probe Microscopy**, **Irene Groot**, Huygens-Kamerlingh Onnes Laboratory, Leiden University, Netherlands **INVITED**

Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra) high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction

mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra) high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts *in situ* under industrially relevant conditions.

This talk focuses on the development of scanning probe microscopy for *operando* observations of active model catalysts. In our group, we have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. As a proof of principle, results for the fruit fly of surface science, *i.e.* CO oxidation, will be shown. But additionally, results for more complex reactions such as NO reduction, Fischer-Tropsch synthesis, desulphurization, and production of chlorine will be discussed.

5:00pm IS+2D+MC+NS+SP+SS-WeA9 **X-ray Photoelectron Spectroscopy Studies of H₂O Dissociation on Pre-oxidized Al (111) and Cu (111) Single Crystal Surface**, **Qianqian Liu**, SUNY, Binghamton University, X. Tong, Brookhaven National Laboratory, G.W. Zhou, SUNY, Binghamton University

Dissociation of H₂O molecules on ultrathin oxide overlayers formed on metal surfaces plays a critical role in many catalytic reactions. However, the effects of chemical states and thickness of oxide overlayers on the microscopic process of H₂O dissociation are still poorly understood. In this work, X-ray photoelectron spectroscopy (XPS) is employed to study H₂O dissociation on oxidized Al (111) and Cu (111) surfaces with controlled chemical states and thicknesses of the oxide films. For Al (111), the experiment was performed under two water vapor pressures (10⁻⁶ Torr and 5 Torr) on aluminum oxide films with the thicknesses varying from 2.47 Å to 5.14 Å; for Cu (111), the experiment was performed by varying the water vapor pressure from 10⁻⁷ Torr to 10⁻⁵ Torr and temperature from 100°C to 450°C on the oxide film with a constant thickness. Al (2p), Cu (2p), Cu (LMM) and O (1s) spectra were monitored by XPS after each oxygen exposure followed by subsequent H₂O exposure. Upon exposing the oxide to water vapor, the O (1s) peak shifts to a higher energy and becomes broader. A detailed analysis of the spectra indicates that H₂O molecules dissociate into OH groups for both oxidized Al and Cu surfaces. However, the subsequent reaction of OH groups with the oxide films on Cu (111) and Al (111) surfaces are dramatically different. On the oxidized Al(111) surface, OH is further incorporated into the aluminum oxide that results in the thickening of the oxide film, whereas on the oxidized Cu (111) surface, OH works as a reducing agent to remove oxygen from the oxide film that results in the thinning of the Cu oxide film. The microscopic processes underlying the differences in H₂O dissociation on oxidized Al (111) and Cu (111) will be described in detail.

5:20pm IS+2D+MC+NS+SP+SS-WeA10 **Operando APXPS of the Liquid-Solid Interface: Au Oxidation**, **Ethan Crumlin**, S.A. Axnanda, P.N.R. Ross, Z.L. Liu, Lawrence Berkeley National Laboratory

Interfaces play an important role for many reaction processes and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to lithium ion batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. Previous capabilities of ambient pressure X-ray Photoelectron Spectroscopy (APXPS) have primarily only been able to observe the gas-solid and gas-liquid interfaces. However, recent enhancements now enable new APXPS systems to work at pressures larger than 20 Torr, and utilize 'Tender' X-rays (2.5 – 7 keV). These features provide new capabilities and opportunities for probing the liquid-solid and solid-solid interfaces. Using synchrotron X-rays at Lawrence Berkeley National Laboratory, the Advanced Light Source and our 'Tender' X-ray APXPS endstation that is outfitted with various *in situ/operando* features such as electrical leads to apply electrical potentials and operates at

pressures >20 Torr, to observe the liquid-solid interface of a gold foil electrode that has been immersed and partially removed from a liquid electrolyte. This talk will provide details on how we used this technique to probe liquid-solid interface and in real-time observe the oxidation of the gold foil electrode under varying applied potentials and different electrolyte solutions.

5:40pm **IS+2D+MC+NS+SP+SS-WeA11 Water on ZnO(10-10) Investigated by Ambient Pressure X-ray Photoelectron Spectroscopy.**
Chris Goodwin, University of Delaware, *A. Boscovich*, Brookhaven National Lab, *C. Arble*, *J.T. Newberg*, University of Delaware

The extent to which ZnO hydroxylates under ambient conditions can significantly influence catalytic properties. Thus, it is critical to understand the composition of different ZnO terminations as a function of relative humidity (RH) in order to elucidate the true interfacial surface terminations. In this talk we present results of ambient pressure XPS (APXPS) for water exposures to a ZnO(10-10) single crystal. It will be shown that ZnO(10-10) extensively hydroxylates at the interface, and both molecular and dissociative water increase as the RH increases. These results are consistent with simulations in the literature that highlight the efficacy for ZnO(10-10) to dissociate water.

Thursday Evening Poster Sessions

In-Situ Spectroscopy and Microscopy Focus Topic

Room: Hall D - Session IS-ThP

In-Situ Spectroscopy and Microscopy Poster Session

IS-ThP1 In Situ Synchrotron Radiation Photoemission Spectroscopy Study of Property Variation of Ta₂O₅ Film during the Atomic Layer Deposition. *SeungYoub Lee*, Sungkyunkwan University, Republic of Korea, *C. Jeon*, Korea Basic Science Institute, Republic of Korea, *Y. Kim*, Sungkyunkwan University, Republic of Korea, *J. Lee*, Korea Basic Science Institute, Republic of Korea, *C.-Y. Park*, Sungkyunkwan University, Republic of Korea

Atomic layer deposition (ALD) can be regarded as a special variation of the chemical vapor deposition method for reducing film thickness. ALD is based on sequential self-limiting reactions from the gas phase to produce thin films and over-layers in the nanometer scale with perfect conformality and process controllability. These characteristics make ALD an important film deposition technique for nanoelectronics. Tantalum pentoxide (Ta₂O₅) has a number of applications in optics and electronics due to its superior properties, such as thermal and chemical stability, high refractive index (>2.0), low absorption in near-UV to IR regions, and high-k. In particular, the dielectric constant of amorphous Ta₂O₅ is typically close to 25. Accordingly, Ta₂O₅ has been extensively studied in various electronics such as metal oxide semiconductor field-effect transistors (FET), organic FET, dynamic random access memories (RAM), resistance RAM, etc.

In this experiment, the variations of chemical and interfacial state during the growth of Ta₂O₅ films on the Si substrate by ALD was investigated using *in-situ* synchrotron radiation photoemission spectroscopy. A newly synthesized liquid precursor Ta(N^tBu)(dmamp)₂Me was used as the metal precursor, with Ar as a purging gas and H₂O as the oxidant source. The core-level spectra of Si 2p, Ta 4f, and O 1s revealed that Ta suboxide and Si dioxide were formed at the initial stages of Ta₂O₅ growth. However, the Ta suboxide states almost disappeared as the ALD cycles progressed. Consequently, the Ta⁵⁺ state, which corresponds with the stoichiometric Ta₂O₅, only appeared after 4.0 cycles. Additionally, tantalum silicide was not detected at the interfacial states between Ta₂O₅ and Si. The measured valence band offset value between Ta₂O₅ and the Si substrate was 3.08 eV after 2.5 cycles.

IS-ThP2 Application of LEEM, PEEM and STM/ncAFM Techniques to Graphene on Metal Surfaces. *A. Thissen*, *Violeta Simic-Milosevic*, SPECS Surface Nano Analysis GmbH, Germany

Abstract Summary: We present recently obtained results in graphene-based systems as measured with LEEM / PEEM and STM / NC-AFM techniques. We highlight the latest state-of-the-art developments in these two techniques and show how these techniques are applied in the latest graphene research as well in other experimental systems.

Introduction: Eighty years ago, Ernst Brueche developed the first photoemission electron microscope (PEEM) in the AEG laboratories in Berlin. Today, the state-of-the-art Low Energy Electron Microscope (LEEM) is produced just a few kilometers away from Brueche's former laboratory carrying forward this groundbreaking developments into the SPECS FE-LEEM P90. This instrument - based on the sophisticated electron-optical design by Ruud Tromp - combines user friendly operation with highest stability and ultimate resolution measurements. Graphene monolayer step edges on Si-sublimated SiC measured using the aberration corrector show a spatial resolution of 1.6 nm, closely approaching theoretical limits.

One of the advantages of SPECS systems is their interconnectability, in this case, by combining the LEEM / PEEM with a SPECS SPM Aarhus 150 with KolibriSensor. The SPM is an ideal system for investigating lattice mismatched surfaces, with a focus in the present talk of SPM measurements on the graphene/Ir(111) system. Microscopy experiments were performed in constant current / constant frequency shift (CC/CFS) and constant height (CH) modes, exploiting a combination of the STM and NC-AFM capabilities of the system. We found that in STM imaging the electronic contribution is prevailing compared to the topographic one and the inversion of the contrast can be assigned to the particular features in the electronic structure of graphene on Ir(111). Contrast changes observed in constant height AFM measurements are analyzed on the basis of the energy, force, and frequency shift curves, obtained in DFT calculations, reflecting the interaction of the W-tip with the surface and are attributed to the difference in the height and the different interaction strength for high-symmetry sites within the moiré unit cell of graphene on Ir(111). The presented findings are of general importance for the understanding of the

properties of the lattice-mismatched graphene/metal systems especially with regard to possible applications as templates for molecules or clusters.

IS-ThP3 Quantum Cascade Laser Cavity Ring Down Spectroscopy: New Method for the Characterization and Detection of Aerosols. *E.M. Durke*, *Angela Buonaugurio*, Excet, Inc./Edgewood Chemical Biological Center, *J.M. Edmonds*, Edgewood Chemical Biological Center

Aerosolized chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) are potential threats for the warfighter, resulting in the need for aerosol identification and detection for further developments in protection and mitigation. One of the most reliable techniques for the identification of trace gas species is absorption spectroscopy. Cavity ring down spectroscopy (CRDS) is a highly sensitive and selective absorption method with the ability to detect trace levels of chemical species. Its advantage is based on the extremely long effective path length, providing precise detection of the rate of decay of light from a high finesse optical cavity to directly measure the absorption of the trace gas. The mid-wave (MWIR) and long-wave (LWIR) infrared regions are of particular interest due to the characteristic rovibrational absorption bands exhibited in these regions for identification of a species. Quantum cascade lasers (QCLs) have the capability of emitting both infrared wavelength regions, of 3-8 μm and 8-15 μm, respectively. During the first year of this multi year effort, we have developed a new method for the characterization of aerosols by combining the highly powerful spectroscopic method of cavity ring down spectroscopy and the ability to detect in the IR fingerprint region using quantum cascade lasers for identification. This novel technique results in *in-situ* investigations of chemical aerosols. The development of this method and preliminary data on accepted test vapors and simulants, leading up to aerosols of chemical warfare agents, are presented.

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