Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA+AS+LS+LX+MN+SE+SS-TuM

Novel Developments and Applications of Interfacial Analysis

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

8:00am **CA+AS+LS+LX+MN+SE+SS-TuM-1 Hypervelocity Nanoprojectile Impacts on Graphene, Graphene-Solid/Liquid Interphases: From Mechanisms of Interaction/Ejection to Practical Applications**, *Dmitriy Verkhoturov*, Texas A&M University; *S. Lee,* Mayo Clinic*; M. Eller,* California State University Northridge*; M. Gołuński, S. Hrabar,* Jagiellonian University, Poland*; S. Verkhoturov,* Texas A&M University*; Z. Postawa,* Jagiellonian University, Poland*; A. Kolmakov,* National Institute for Science and Technology (NIST)*; A. Revzin,* Mayo Clinic*; E. Schweikert,* Texas A&M University **INVITED**

Presented here are the experiment and theory on processes accompanying the impacts of C_{60} and Au_{400} projectiles (~1 keV/atom) on graphene/matter interphases. A variety of targets were used: a) free standing graphene, b) molecules and extracellular vesicles (EVs) deposited on free standing graphene, c) interphases graphene-solids/liquids, d) EVs deposited on functionalized monocrystals.

Two custom-built Cluster ToF secondary ion mass spectrometry (SIMS) devices with similar parameters were used. The experiments were run in the event-by-event bombardment/detection mode where the regime of bombardment is super-static[1]. The analyzed surfaces were bombarded at the rate of ~1000 impacts/sec with $1-6\times10^6$ impacts collected on a surface area of 50-500 μm in diameter. This regime allows acquisition of individual mass spectra for each impact, thus allowing the comparison of experimental data with MD simulations at the level of single projectile impacts. The method allows detection of ejecta in reflection (3D case) and transmission (2D case) directions.

The mechanisms of ejection from 2D and 3D materials (including graphene-solid/liquid interphase) are different. For example, in the case of C_{60} impacts on a molecular layer deposited on graphene (2D case) the mechanism of ejection is described with the "trampoline" model[2]. For the 3D case of graphene-solid/liquid interphase, graphene suppresses the ejection of molecules. The compression of matter in the excitation volume around the impact is not sufficient to destroy the graphene[3].

Our method allows to test individual nano-objects. A biological example is EVs. There were anchored on functionalized Si and graphene substrates, with the EVs labeled with antibodies carrying lanthanide tags (Ab@Ln) for normal hepatic and liver cancer markers. Up to four Ab@Ln tags could be detected simultaneously, enabling analysis of population heterogeneity with single EV resolution and to distinguish between normal and cancer EVs based on surface marker expression. Using co-localization of cancer biomarkers, it is possible to find small subpopulation of EVs originating from cancerous cells potentially allowing for early cancer detection. The sensitivity of the method can be increased several folds via transmission configuration where ejecta are emitted and detected in the forward direction. In this case nano-objects, such as EVs, are anchored on graphene oxide, a 2D material.

[1]S.V. Verkhoturov et al. J. Chem. Phys. 150 (2019)

[2]R.D. Rickman et al. Phys. Rev. Lett. 92, 047601 (2004)

[3] D.S. Verkhoturov et al. Biointerphases 11, 02A324 (2016)

8:40am **CA+AS+LS+LX+MN+SE+SS-TuM-3 Applying *in Situ* Bias During TOF-SIMS Analysis to Investigate Ion Migration in Perovskite Devices**, *Steven Harvey,* National Renewable Energy Laboratory; *I. Gould,* University of Colorado, Boulder*; D. Morales, M. McGehee,* University of Colorado Boulder*; A. Palmstrom,* National Renewable Energy Laboratory

Metal Halide Perovskite Photovoltaics have the potential to be a game-changing technology in photovoltaics, with low cost solution processing inherent to the technology and a rapid progress in device efficiency and stability. Understanding ion migration in these materials has lead to improvements in both efficiency and reliability, and further understanding of these phenomena is of great importance.

Time of flight secondary ion mass spectrometry is well suited to provide unique insight for this class of materials, as it can reveal the distribution of both the organic and inorganic components of a device stack (both through the depth as well as laterally with 2-D and 3-D imaging). We will briefly cover our past work on technique development for this class of materials, before presenting new work where an *in situ* electrical bias was placed on a perovskite device while under investigation with TOF-SIMS. This was completed with simple commercial off the shelf components in an ION-TOF TOF-SIMS V instrument and could be easily implemented on other instruments. A device stack of glass / ITO / Me-4PACz / DMA0.1FA0.6Cs0.3Pb(I0.8Br0.2)3 / LiF (1 nm) / C60 (30 nm) / SnOx (15 nm)/Au (20 nm) was used for this study. An electrical bias was applied between the top gold contact and the bottom ITO contact during TOF-SIMS measurements. By applying a +0.75V and -0.75V forward and reverse bias to the device, a driving force for negatively charged halide ions is created to migrate towards the back or front of the device, respectively. The *in-situ* data shows the halide ion migration towards the back ITO contact after the forward bias is applied. The negative bias was then applied and the halide ions migrate back towards the front of the device and return to the original unbiased state. In both cases the formamidinium and lead traces do not show similar migration, showing only the charged species in the device are affected by the bias. The results show a framework that can be used for further study. Potential complications with the analysis of this type of data will be discussed.

9:00am **CA+AS+LS+LX+MN+SE+SS-TuM-4 Oxidation of a Single Fe Nanoparticle at the Nanoscale and Real-Time by Operando Atom Probe**, *Sten V. Lambeets,* Pacific Northwest National Laboratory; *N. Cardwell, I. Onyango,* Washington State University; *T. Visart de Bocarmé,* Université libre de Bruxelles, Belgium*; J. McEwen,* Washington State University*; D. Perea,* Pacific Northwest National Laboratory

Physics governing surface chemical reactions and interfaces involved in heterogeneous catalysts fundamentally depends on the synergistic interactions between reactive gases and specific surface structures. Surface science techniques are continuously evolving to help bridge knowledge gaps between fundamental research and real-world applications. In the past decade, an increasing number of analytical techniques successfully achieved their evolution towards an in situ and operando version of themselves, and recently such approaches are being developed for atom probe microscopy (APM) techniques. In this work, we will present the recent advances in the conversion of Atom Probe Tomography (APT) to study surface dynamics of O_2/Fe using two different APM techniques and modifications: Field Ion Microscopy (FIM), and Operando Atom Probe (OAP).

APM techniques are capable of imaging the apex of sharp needles with nanometric lateral resolution, which can be seen as model nanoparticles. FIM is used to image such needles with atomic resolution and to identify the crystal orientation along with the local surface reaction dynamics during oxygen interaction with Fe. The resulting FIM image corresponds to a stereographical projection of the apex and allows the identification of the crystal orientations with atomic resolution. Regular APT, from which the OAP derives, relies on the thermally assisted field evaporation of positively charged ions from a needle shaped specimen. In regular use, the APT is performed in an Ultra High Vacuum ($<10^{-11}$ mbar) while the sample is cooled at 50K. The OAP modification consists of performing the atom probe analysis in the presence of reactive gas at 300 K.

Once the FIM characterization is complete the sample is maintained at 300K before starting APT analysis and introducing 1.1×10^{-7}mbar of pure O_2. As soon as the O_2 is introduced, we can measure the surface formation of Fe oxides by monitoring the local concentration of Fe_2O^{n+} ion species extracted from the surface over time. We can track the local concentration over the different surface regions in real time. We observe the progressive surface oxidation starting from open facets structures, such as Fe{222} and Fe{112}, towards the central Fe(011) and the Fe{024} which show significantly higher resistance toward oxidation. The combination of the different concentrations allows us to reconstruct the full movie of the surface oxidation in real-time. However, since the measurements are

performed in the presence of very strong electric fields (>10 V/nm), it is necessary to discuss the potential influences of it on the system as well.

9:20am CA+AS+LS+LX+MN+SE+SS-TuM-5 Reporting Interfaces: Unconventional Excitation of Interfaces Enables Exquisite Gas Sensing Toward Our Sustainable Future, *Radislav Potyrailo*, GE Research **INVITED**
As our society is developing solutions for more sustainable types of energy, the need for reliable, yet affordable tools for monitoring of emissions of greenhouse and other gases in urban and industrial environments is a substantial undertaking for two main reasons. First, to achieve a desired accuracy, existing gas monitoring solutions in complex backgrounds utilize traditional analytical instruments. While their mathematical design principles provide needed independent response outputs, their hardware design principles do not allow cost-effective ubiquitous implementations. Second, all gas sensors based on interface-driven interactions between gases of interest and sensing materials are single-output devices. By their original design principles from early last century, these sensors operate well only when levels of interfering gases are low. Once levels of interfering gases increase, existing sensors lose their accuracy because of competing interactions between the sensor interface and numerous interfering gases versus a gas of interest.

In this talk, we will present gas sensors that we built following mathematics of traditional analytical instruments but with our own different types of independent variables for detection of multiple gases with enhanced accuracy and stability. These sensors are multivariable gas sensors where independent response outputs are provided by our unconventional methodologies of excitation of interfaces between a sensing material and different ambient gases. We will show that our approach results in a reliable differentiation of one or more analyte gases in complex backgrounds of interfering gases with an individual multivariable gas sensor. This exquisite (i.e., accurate and reliable) gas sensing provides an affordable technical solution for monitoring of emissions of greenhouse and other gases in urban and industrial environments. Such technical solution is mathematically not feasible using conventional single-output sensor designs. We will also show that such multivariable gas sensors have the ability for self-correction for sensor drift. Our approach for the multi-gas detection and drift self-correction should allow implementations of gas sensors in diverse applications that cannot afford weekly, monthly, or quarterly periodic maintenance, typical of traditional analytical instruments.

11:00am CA+AS+LS+LX+MN+SE+SS-TuM-10 A "Simple" Approach to Combine Electrochemistry and Operando Near Ambient Pressure XPS Studies, *F. Mirabella, Paul Dietrich, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany **INVITED**
Electrochemical water splitting is an environmentally friendly technology to store renewable energy in the form of chemical fuels. Among the Earth-abundant, first-row transition metal-based catalysts, Ni and Fe oxides have shown promising performances as effective and low-cost catalysts of the oxygen evolution reaction (OER) in alkaline media. Notably, their structure evolves under oxygen evolution operating conditions with respect to the as-prepared catalysts but these changes and consequently the active sites have not been identified yet due to the difficulties associated with surface analysis measurement under working conditions (*operando*).

In this presentation, we will demonstrate the enormous potential of laboratory NAP-XPS for investigations of solid-liquid interfaces in electrochemical systems at elevated pressures (≤ 25 mbar), also illustrating the ease of use of this specific setup. We will show a versatile three-electrodes electrochemical setup that allows for operando studies of solid-electrolyte interfaces, i.e., of nickel oxide foils as cathode for OER in alkaline environment as a simple laboratory NAP XPS experiment.

11:40am CA+AS+LS+LX+MN+SE+SS-TuM-12 Recent Developments in Probing Buried Interfaces Using Standing-Wave Photoelectron Spectroscopy, *Slavomir Nemsak,* Lawrence Berkeley Lab
Standing-wave photoelectron spectroscopy of multi-layer structures proved to be a very powerful technique for probing solid/solid, but also solid/liquid and solid/gas interfaces. Its superior depth selectivity and non-destructive nature were crucial to answer key questions in problems spread over several scientific fields, such as emergent phenomena at complex oxide interfaces [1], artificial multiferroics [2], adsorption mechanisms in liquids [3], corrosion [4], and electrocatalysis [5].These achievements were only possible thanks to innovative approaches both in experiments and analyses, including development of X-ray optical simulations package [6] and its coupling with the black-box optimizer [7]. In this talk I will introduce novel tools and approaches for standing-wave experiments and I will highlight some of the recent applications [8,9,10].

[1] S. Nemsak et al., *Physical Review B* **93** (24), 245103 (2016).

[2] H. P. Martins et al., *arXiv preprint arXiv:2012.07993.*

[3] S. Nemsak et al., *Nature Communications* **5**, 5441 (2014).

[4] O. Karslioglu et al., *Faraday Discussions* **180**, 35 (2015).

[5] C. Baeumer et al., *Nature Materials* **20**, 674 (2021).

[6] S.-H. Yang et al., *Journal of Applied Physics* **113**, 073513 (2013).

[7] O. Karslioglu et al., *Journal of Electron Spectroscopy and Related Phenomena* **230**, 10 (2019).

[8] M Scardamaglia, et al., *Journal of Electron Spectroscopy and Related Phenomena* **262**, 147281 (2023).

[9] G. Conti et al., *Journal of Micro/Nanopatterning, Materials, and Metrology* **20**, 034603 (2021).

[10] H.P. Martins et al., *Journal of Physics D: Applied Physics* **56**, 464002 (2021).

12:00pm CA+AS+LS+LX+MN+SE+SS-TuM-13 The Influence of Surface Structure and Electrostatics on Measuring Unoccupied Electronic States via Low Energy Inverse Photoemission Spectroscopy (LEIPS), *James Johns,* Physical Electronics USA
A material's energetic distribution of electronic states near the fermi level is a key physical property for determining how it behaves in electronic, chemical, and optical applications.Photoemission has long been the gold standard for measuring the occupied electronic states below the Fermi level and is one of the most common surface science techniques worldwide.Inverse photoemission (IPES), the related process whereby an electron is absorbed at the surface and a photon is emitted, is similarly a very powerful tool for measuring the unoccupied electronic states. Unfortunately, the intrinsically lower rate for IPES and technical hurdles related to relevant photodetectors has historically necessitated the use of electron sources with sufficient energy to damage all but the most chemically robust surfaces.

The availability of narrow bandpass optical filters at UV photon energies between 3.5 and 6 eV over the past decade have enabled the development and commercialization of Low Energy Inverse Photoemission Spectroscopy (LEIPS)[1,2].Efficient detection of low energy UV photons (lower than traditional IPES at 9-10 eV) enables the use of low energy electrons (below 5 eV) which avoid damaging sensitive materials including organics.This key innovation has revitalized interest in IPES because the technique can now be applied to molecular materials and interfaces relevant to wide range of applications *e.g.* batteries, photovoltaics, organic semiconductors and OLEDs, chemical sensors.Furthermore, optical UV filters also improve the energy resolution, further enhancing the appeal of LEIPS over traditional IPES.

Like any surface science technique, the quality of LEIPS data depends on both the instrumentation and sample preparation. Here, I will discuss the material requirements and limitations for successful LEIPS measurements, several of which differ from more common techniques such as XPS, SPM, or electron microscopy.I will also present LEIPS data from taken at the interface between two metals and explain those results using calculated trajectories of the electron beam.Finally, I will illustrate a key difference between LEIPS, which probes the true unoccupied electronic density of states, and optical methods, such as optical spectroscopy or EELS which measure the joint density of states, by presenting LEIPS spectra of an excitonic 2D material.

[1] Yoshida, H; "Near-ultraviolet inverse photoemission spectroscopy using ultra-low energy electrons" *Chem. Phys. Lett.* **539-540**, 180-185, (2012)

[2] Lida, S.; Terashima, M; Mamiya, K; Chang, H. Y.; Sasaki, S; Ono, A; Kimoto, T; Miyayama, T; "Characterization of cathode-electrolyte interface in all-solid-state batteries using TOF-SIMS, XPS, and UPS/LEIPS" *J. Vac. Sci. & Tech. B*, **39**, 044001, (2021)

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