Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+HC+LS+VT-WeM

Multiphase Interfacial Analysis and Imaging

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

8:00am **CA+HC+LS+VT-WeM-1 Probing the Impact of Nanoscale Defect Sites in Perovskite Photovoltaic Films with Time-Resolved Photoemission Electron Microscopy**, ***Keshav Dani***, 1919-1 Tancha, Kunigami-kun, Japan **INVITED**

Hybrid perovskite photovoltaic devices have rapidly emerged as promising contenders for next generation, low-cost solar cell technology. Yet, the presence of defect states critically impacts device operation, including device efficiency and potentially long-term stability. Understanding the nature of these defects, and their role in photocarrier trapping, requires techniques that are capable of probing ultrafast photocarrier dynamics at the nanoscale.

In this talk, I will discuss the development of time-resolved photoemission electron microscopy (TR PEEM) techniques in my lab [1, 2], applied to hybrid perovskite solar materials. Thereby, we directly visualize the presence of the performance limiting nanoscale defect clusters and elucidate the role of diffusion in the charge carrier trapping process [3]. By correlating PEEM measurements with other spatially resolved microscopies, we identify different types of defects that form, and study how passivation strategies may have a varied impact on them [4]. Finally, we show that these defect can act as seeds for degradation [5].

[1] M. K. L. Man, *et al.* Imaging the motion of electrons across semiconductor heterojunctions. *Nature Nanotech.***12**, 36 (2017).

[2] E. L. Wong, *et al.* Pulling apart photoexcited electrons by photoinducing an in-place surface electric field. *Science Advances***4**, eaat9722 (2018).

[3] T. A. S. Doherty*, A. J. Winchester*, et al.Performance-limiting trap clusters at grin junction in halide perovskites. *Nature***580**, 360 (2020). *equal authors

[4] S. Kosar, et al. Unraveling the varied nature and roles of defects in hybrid halide perovskites with time-resolved photoemission electron microscopy. *Energy Environ Sci*. 14, 6320 (2021)

[5] S. Macpherson, et al. Local Nanoscale Phase Impurities are Degradation Sites in Halide Perovskites. *Nature* DOI: 10.1038/s41586-022-04872-1 (2022)

8:40am **CA+HC+LS+VT-WeM-3 Correlating Structure and Chemistry Using Ambient Pressure Photoemission and X-Ray Scattering**, ***Slavomir Nemsak***, Lawrence Berkeley Laboratory Advanced Light Source **INVITED**

In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) will be also discussed.

References

[1] H. Kersell et al., Ambient Pressure Spectroscopy in Complex Chemical Environments, 333-358 (2021).

[2] H. Kersell et al., Rev. Sci. Instr. 92, 044102 (2021).

[3] H. Kersell et al., Faraday Discussions, accepted (2022).

[4] H. Kersell et al., Synchr. Rad. News, accepted (2022).

9:20am **CA+HC+LS+VT-WeM-5 Gating of the 2D Hole Transport in Diamond by Subsurface Charges**, *E. Strelcov,* ***Andrei Kolmakov***, NIST

The unique electronic, physical, and thermal properties of diamond make diamond-based FETs one of the most prospective devices for high-frequency power electronics. Transfer doping of hydrogenated diamond is a common process to form 2D conducting channels in diamond FET. The electron /hole transport of such a device is sensitively dependent on near-surface scatters including charged traps.

Here, using SEM (EBIC) and AFM Kelvin probe force (KPFM) microscopies we report on imaging of the hole transport in narrow conducting channels as a function of the density and depth of near-surface charges. We demonstrate the gating effect induced by trapped charges and discuss the methods to minimize these effects.

9:40am **CA+HC+LS+VT-WeM-6 Development of 0–D Argon Collisional Radiative Model conjoined with Optical Emission Spectroscopy between 1 mTorr to 760 Torr**, ***Tag Choi***, *N. Abuyazid, D. Patel,* University of Illinois at Urbana-Champaign*; D. Jacobson,* LytEn. Inc*; S. Keniley, S. Dubowsky, D. Barlaz, D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

Optical emission spectroscopy (OES) is a non-invasive plasma diagnostic, which can be utilized with 0-dimensional argon collisional radiative model (Ar CRM) to understand dynamics of excited and charged argon species and determine plasma parameters in the system. This work aims to study rate coefficients of excited and charged argon species, calculate their densities over time and verify the theoretical results with experimental optical spectra in a wide range of pressure regimes. The model considers various types of collisions such as electron and atom excitation/ionization, photon emission, diffusion, penning ionization, and excimer formation. A merit function is used to obtain a better correlation between the theoretical and experimental densities of the various argon species. This allows the model to get a more accurate estimate of the electron temperature and the densities. Various plasma sources are used such as a low pressure inductively coupled plasma (ICP) source, dielectric barrier discharge (DBD), and microwave discharges, to produce different types of plasmas at pressure ranges of 10 – 50 mTorr and 1 – 760 Torr. The optical emission spectra and Langmuir probe measurements are collected for verifications on a low pressure ICP source and DBD discharge. For the verification of atmospheric microwave discharge, OES data is collected for temperature calculations from Specair and the model. Different plasma sources produce different electron temperatures and densities. The ICP source, DBD and microwave discharge have electron temperatures (T_e) of 2 – 5 eV, 1 – 3 eV, and 0.4 – 0.6 eV and electron density (n_e) of 1E16 to 1E18 m^3, 1E18 to 1E21 m^3, and 1E19 to 1E22 m^3 respectively. A methane and argon gas mixture are introduced to the microwave discharge to understand how plasma parameters differ from a pure argon environment.

11:00am **CA+HC+LS+VT-WeM-10 Atomic-Scale Modeling of Bismuth and Argon Clusters Sputtering of Water/Vacuum Interfaces**, ***Zbigniew Postawa***, *M. Kański, C. Chang, S. Hrabar,* Jagiellonian University, Poland **INVITED**

Modeling of water/vacuum interfaces should consider the high vacuum pressure of water. First, there is continuous evaporation of the liquid into the vacuum chamber, which must be considered. This phenomenon poses a significant challenge for conventional experimental techniques. Yang *et al.* presented a way to reduce the impact of this phenomenon by using a microfluidic channel [1]. This approach uses an ion beam to drill a 2-3 µm window in the channel wall, exposing the liquid flowing below. Such an arrangement allows for maintaining a low base pressure (~10^{-7} mbar) in the measuring chamber. This technique has already been used to study photochemical reactions, biofilms, and liquid-liquid interfaces by secondary ion mass spectrometry or secondary electron microscopy [2]. Recently, another approach minimizing the effect of high vacuum pressure of water that uses a graphene cell encapsulating a liquid was proposed in studies with transmission electron microscopy [3].

Recently, we have developed a new ReaxFF potential parameterization for modeling C/H/O systems designed directly for sputtering simulations [4]. This parametrization is up to 3 times faster than standard ReaxFF. New force-field allowed us to perform molecular dynamics computer simulations of water and graphene-covered water systems sputtered by bismuth and argon clusters. The mechanism of molecular emission from these two systems is investigated. The effect of the projectile size and the influence of the protecting graphene sheet on the emission process is discussed.

References

[1]L. Yang, X.-Y.*et al*., Lab on a Chip, 11, 15, 2481, 2011, doi: 10.1039/c0lc00676a.

[2] X.-Y. Yu,, J. Vac. Sci.Technol. A, 38, 040804, 2020, doi: 10.1116/1.5144499.

[3] S. M. Ghodsi *at al.*, Small Methods, 3, 5, 1900026, 2019, doi: 10.1002/smtd.201900026 *and references therein*.

[4] M. Kański *at al.*, J. Phys. Chem. Lett. 13, 2, 628, 2022, doi: 10.1021/acs.jpclett.1c03867.

Acknowledgments

The work has been supported by Polish National Science Center Grant 2019/33/B/ST4/01778 and the PLGrid Infrastructure.

11:40am **CA+HC+LS+VT-WeM-12 Finite-Elements Modeling of Solid-Electrolyte Interfaces in Through-Membranes Imaging and in-Liquid Scanning Probe Experiments*, Alexander Tselev,*** Department of Physics & CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal **INVITED**

Studies of the physicochemical processes at the interfaces between solids and electrolytes interfaces require *operando* multi-parametric measurements with chemical and electric potential sensitivity, in-depth selectivity, as well as with a high lateral resolution. A number of experimental techniques were implemented for this purpose. In this talk, we will describe applications of finite-elements (FE) modeling to elucidate and interpret microscopic imaging and measurements with liquids ranging from non-polar ones to decimole electrolyte solutions. This includes probing through graphene membranes with the use of microscopy and spectroscopy tools based on high-energy beams—X-rays and electron beams, as well as low-energy probing with the use of scanning probe techniques. Scanning probe techniques can be implemented both with probes in liquids and with probes separated from the electrolytes by membranes. We will discuss liquid-solid interface probing by the Kelvin probe force microscopy (KPFM) through graphene membranes as well as by near-field microwave microscopy through dielectric membranes. Furthermore, models for piezoresponse force microscopy and KPFM with probes immersed in electrolytes will be presented. Support of this work by the project CICECO-Aveiro Institute of Materials, financed by national funds through the FCT/MEC (Portugal) and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement is acknowledged.

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