Thursday Morning, November 9, 2023

Surface Science Division
Room D136 - Session SS2+AS+TF-ThM

Thin Film Surface Chemistry

Moderators: Eric Altman, Yale University, **Zdenek Jakub**, CEITEC

11:00am **SS2+AS+TF-ThM-10 Ultrafast Exciton Dynamics of Phthalocyanine Films with Different Molecular Orientations***, **Hui Ung Hwang**, S. Kim, J. Kim,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea

Organic semiconductors (OSCs) have enormous potential in advanced optoelectronic devices, such as organic light-emitting diodes and organic solar cells. To achieve higher performance and functional versatility for these applications, a deeper understanding of the generation and relaxation mechanism of photoexcited excitons in molecular films is essential. In this study, we investigate the ultrafast dynamics of excitons in planar-shape molecules of phthalocyanines (Pc), which can adopt a lying-down or standing-up orientation depending on the substrate used, as shown in Fig. 1.[1] The distinct ionization-energy difference of more than 0.5 eV measured by photoelectron spectroscopy confirms that the Pc thin film on HOPG substrate grows in the lying-down direction and the Pc on ITO grows in the standing-up direction. Exciton energy and population from the molecules with these two different orientations are measured by time-resolved two-photon photoemission (tr-2PPE) with time resolution of 85 fs.In this measurement, we first pump a singlet exciton population in the Pc with a femtosecond pulse and probe its evolution as a function of delay time with an ultraviolet pulse. Singlet excitons have a variety of relaxation pathways, including diffusion between molecules, intersystem crossing to triplet states, and dissociation at the interface with metals. The tr-2PPE experiments show that the exciton relaxtion in Pc molecules with the standing-up geometry is dominated by exciton diffusionin the direction perpendicular to the substrate, resulting in relatively slow exciton relaxation. However, for Pc molecules in the lying-down geometry, the excitons undergo faster transfer to the metal interface due to aligned π-orbital overlap with neighboring molecules toward the substrate. These results imply that OSCs exhibit different exciton relaxtion dynamics depending on their orientation and suggest that for planar molecules like Pc, the lying-down geometry is more favorable for exciton transfer and dissociation to the metal interface.

11:20am **SS2+AS+TF-ThM-11 Understanding the Surface Chemistry of Oxide Thin Films by Isotope Labeling***, **Yingge Du**,* Pacific Northwest National Laboratory **INVITED**

Isotopic engineering is developing into a key approach to study the nucleation, diffusion, phase transition, and reaction of materials at an atomic level to reveal transport pathways, kinetics, and working/failure mechanisms of functional materials and devices. Understanding these phenomena leads to deeper insights into relevant physical processes, such as the transport and intercalation of ions in energy conversion and storage devices, and the role of active sites and supports during heterogeneous catalytic reactions. Likewise, isotopic engineering is being pursued as a means of modifying functionality to enable future technological applications. In this talk, I will present our work employing isotope labeling (e.g., ^{18}O and ^{2}H) during complex oxide thin films' (e.g., WO_3, $SrFeO_{2.5}$, and $La_{1-x}Sr_xFeO_3$) synthesis and post-growth processing to track the distribution and redistribution of the isotope tracers. Isotope-resolved analysis techniques with high spatial resolution, such as time-of-flight secondary ion mass spectrometry and atom probe tomography, facilitate the accurate quantification of isotopic placement and concentration in well-defined heterostructures with precisely positioned, isotope-enriched layers. These studies allow us to better understand the growth mechanisms, surface chemistry, and elemental diffusion under working and extreme conditions.

12:00pm **SS2+AS+TF-ThM-13 Interaction of Self-Assembled Monolayers with Atomic Oxygen During Area-Selective Atomic Layer Deposition***, **Silvia Armini**,* IMEC Belgium*; A. Brady Boyd,* School of Physical Sciences, Dublin City University, Ireland

Utilising self-assembled monolayers (SAMs) to achieve area-selective atomic layer deposition (AS-ALD) as an approach to bottom-up nanofabrication has recently gained significant attention from the nanoelectronics industry.

With the continued downscaling of feature sizes, top-down processing can no longer reach the challenging demands of the industry which requires conformal coating of high aspect ratio vias and a reduction in misalignment errors in multi-layered devices. In this work we attempt to imitate the effects of the ALD oxidation pulse experienced by the SAMs during the AS-ALD process by exposing two SAMs of different chain lengths and different functional groups, (3-trimethoxysilylpropyl)diethylenetriamine (DETA) and octadecyltrimethoxysilane (OTMS), to numerous controlled in-vacuo atomic oxygen exposures with subsequent characterisation by X-ray photoelectron spectroscopy (XPS). We monitor the sequential removal of the deposited monolayers with each successive atomic oxygen exposure for both SAMs. The etch rate is observed to be distinct for the different SAMs, the amino-terminated short chain DETA SAM reveals a linear etch rate while the longer chain OTMS SAM reveals an exponential etch rate. The results presented provide some insights into what characteristics are important for choosing the correct SAM for AS-ALD applications.

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