

Thin Films Division

Room A122-123 - Session TF+SS-ThA

Metal Halide Perovskites, Other Organic/Inorganic Hybrid Thin Films & Flash Session

Moderators: Mark Losego, Georgia Institute of Technology, Greg Szulczewski, The University of Alabama

2:20pm TF+SS-ThA-1 Tailoring Electrode-electrolyte Interfaces in Lithium-ion Batteries using Molecularly Engineered Functional Polymers, *Laisuo Su*, Carnegie Mellon University; *J Weaver*, National Institute of Standards and Technology (NIST); *M Groenenboom*, National Institute of Standards and Technology (NIST); *B Jayan*, Carnegie Mellon University **INVITED**

The performance and stability of lithium ion batteries (LIBs) depend on charge transfer and reactions at electrode-electrolyte interfaces (EEI), making interfaces design a key issue. Here we molecularly engineer this interface using conformal, functional polymer nanolayers via a novel vapor-based deposition technique. We demonstrate that poly(3,4-ethylenedioxythiophene) (PEDOT) nanolayer doubles the capacities of LiCoO₂ at high rates and extends its 4.5 V cycling life by 260%. The improved rate performance is enabled by high diffusion coefficient of Li⁺ in PEDOT measured from neutron depth profiling. Such behavior is further understood by density functional theory (DFT) simulation. The extended cycling stability comes from strong interactions between PEDOT and Co atoms, as suggested from X-ray photoelectron spectroscopy and DFT simulations. Additionally, in-situ synchrotron X-ray diffraction reveals that PEDOT uniformizes current distribution and improves LiCoO₂ structural stability during cycling tests. This work adds understanding and provides guidelines for designing the EEI for advanced LIBs.

3:00pm TF+SS-ThA-3 Chemoselective Adsorption of Alkyne-functionalized Cyclooctynes for the Formation of Si/organic Interfaces, *C Laenger, Julian Heep*, Justus-Liebig-University, Giessen, Germany; *P Nikodemiak, T Bohamud*, Philipps-University, Marburg, Germany; *P Kirsten*, Justus-Liebig-University, Giessen, Germany; *U Hoefer, U Koert*, Philipps-University, Marburg, Germany; *M Duerr*, Justus-Liebig-University, Giessen, Germany

Controlled organic functionalization of the Si(001) surface may play an important role in the efforts towards further miniaturization of silicon based electronic devices. The first step of such an organic functionalization in terms of organic molecular layer deposition on Si(001) would be the chemoselective adsorption of bifunctional molecules on silicon: whereas one functionality binds to the surface, the other stays intact for the attachment of further layers. This task, however, is complicated by the high reactivity of the dangling bonds with respect to almost all organic functional groups. As a consequence, bifunctional organic molecules typically react via both functional groups on the silicon surface. We solved this problem using cyclooctyne as the main building block of our strategy. The strained triple bond of cyclooctyne reacts via a direct reaction channel, in contrast to most other organic functional groups, which react on Si(001) via a metastable intermediate. This makes the latter ones effectively unreactive in competition with the direct pathway of cyclooctyne's strained triple bond [1].

In this work, we focus on the preparation of a functionalized organic layer on Si(001) using an alkyne-functionalized cyclooctyne, i.e., ethynyl-cyclopropyl-cyclooctyne (ECCO). If the ECCO molecule binds chemoselectively to the silicon substrate via cyclooctyne's strained triple bond, the terminal, linear triple bond of the ECCO molecule can be employed for the attachment of the second layer of molecules, e.g., via alkyne-azide coupling. We first show that the linear triple bond follows an indirect reaction pathway via a weakly bound intermediate. XPS and STM results then clearly indicate that ECCO adsorbs selectively on Si(001) via a [2+2] cycloaddition of cyclooctyne's strained triple bond. No indication for a reaction via the ethynyl group was detected. This chemoselectivity was observed for all coverages, starting from the isolated molecules up to saturation coverage of one monolayer [2]. The ECCO molecules can thus form an organic functionalization of the Si(001) surface which can be used for controlled attachment of further molecular layers.

[1] Reutzler, et al., J. Phys. Chem. C **120** 26284 (2016).

[2] C. Länger, et al., J. Phys.: Condens. Matter **31** 034001 (2019).

3:20pm TF+SS-ThA-4 Durability of Property Changes in Polyester Fabrics Infused with Inorganics via Vapor Phase Infiltration, *Kira Pyronneau, E McGuinness, M Losego*, Georgia Institute of Technology

Vapor Phase Infiltration (VPI) is a processing method for transforming polymers into organic-inorganic hybrid materials. During VPI, a polymer is exposed to vapor-phase metalorganic precursors that sorb, diffuse, and react within the bulk of the polymer to create new hybrid materials. VPI has been shown to modify properties such as the mechanical strength of spider silk, the thermal and UV degradation resistance of Kevlar, and the fluorescence of polyester. This study aims to better understand how VPI can change textile properties for industrial applications and the durability of these changes. To this end, polyester fabrics were treated with trimethylaluminum (TMA) and co-reacted with water in a custom-built vacuum chamber. The temperature of the treatment process was varied from 60°C to 140°C to establish a relationship between processing temperature, physicochemical structure, and material properties. Using thermogravimetric analysis (TGA), these infiltrated fabrics were found to have inorganic loadings between 5 and 8 weight percent, with a maximum inorganic loading at 100 °C (Figure 1). These results are consistent with our current understanding of precursor / polymer sorption thermodynamics and indicate that processing temperature can be used to control the loading of inorganics through both the diffusion rate and the sorption equilibrium. To examine the durability of this inorganic loading, wash fastness testing at 100°C for 90 minutes followed by TGA and SEM/EDX was used to determine the effects of high temperature wash cycles. These tests demonstrated that the inorganic loading remains even after intense laundering (Figure 2). To further characterize the durability of VPI treatment, known changes due to the VPI process were compared before and after washing. In particular, mechanical properties, fluorescence, and thermal degradation behavior were investigated. This talk will explore the wash-fastness of VPI treatments of polyester at different processing temperatures and the retention of enhanced properties relevant to the textile industry.

4:00pm TF+SS-ThA-6 Materials Synthesis and Device Fabrication for Novel Inorganic Perovskites, *Mingzhen Liu*, UESTC, China **INVITED**

In recent years, organic lead halide perovskite materials have attracted much attention due to their outstanding optoelectronic properties and low manufacturing cost. To improve the stability of perovskite solar cells, inorganic CsPbI₃ perovskite has been demonstrated as promising material for solar cells owing to the superb photoelectronic property and composition stability. However, the low stability of perovskite phase CsPbI₃ (α -phase) with an appropriate band gap under ambient environment hinders its practical application.

Here, we investigate new ways of synthesizing inorganic perovskite materials and optimizing the device stability through dimensional engineering. We tailor the three-dimension CsPbI₃ perovskite into quasi-two-dimensional Cs_xPEA_{1-x}PbI₃ perovskite, where an optimal Cs_xPEA_{1-x}PbI₃ film remains stable in α phase up to 250°C. Moreover, we further present an in-depth investigation of the so-called stable ' α -CsPbI₃,' especially the starting material hydrogen lead trihalide (HPbI₃, also known as Pbl₂:xHI) that is usually used for synthesizing α -CsPbI₃. We notice that the "mythical" HPbI₃, the often-assumed reaction product of HI and Pbl₂, does not actually exist. Instead, adding acid to DMF is known to generate a weak base dimethylamine (DMA) through hydrolysis, and with the presence of Pbl₂ the actual final product is believed to be a compound of DMAPbI₃. Our findings offer new insights into producing inorganic perovskite materials, and lead to further understanding in perovskite materials for solar cells with improved efficiency and stability.

4:40pm TF+SS-ThA-8 Carrier-Gas Assisted Vapor Deposition of Metal Halide Perovskite Thin Films, *Catherine Clark*, University of Minnesota; *E Aydil*, New York University; *R Holmes*, University of Minnesota

Hybrid organic-inorganic halide perovskites have emerged as an important class of optoelectronic materials with potential applications in photovoltaics and light emitting devices. One of the challenges in forming thin films of halide perovskites is controlling stoichiometry and morphology. We have designed and built a carrier-gas assisted vapor deposition (CGAVD) system capable of depositing halide perovskite thin films (e.g., CH₃NH₃SnI_xBr_{3-x}) with independent control over their stoichiometry and morphology. In our CGAVD system, an inert carrier gas (N₂) transports sublimed material vapors through a hot-walled chamber to a cooled substrate where they selectively condense and/or react. By separately controlling the precursor sublimation rate, *via* source temperature, and the transport rate to the substrate, *via* carrier gas flow

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rate, we realize fine control of species flux at the substrate and successfully co-deposit materials with very different vapor pressures (e.g. $\text{CH}_3\text{NH}_3\text{Br}$, SnBr_2). Four additional independent parameters (dilution gas flow, chamber pressure, gas temperature, and substrate temperature) can be varied to access a wide range of deposition conditions and film morphologies with controlled stoichiometry. To navigate the vast parameter space of CGAVD, we use an experimentally validated transport and reaction model, which informs the deposition parameter selections. We find that repeatable and spatially uniform deposition requires operating in a regime where solid source material is at equilibrium with its vapor and convective transport determines the flux of species arriving at the substrate. Importantly, we find that films grown using CGAVD have a stoichiometric “self-correcting” and robust operation window, wherein excess precursor flux during co-deposition is rejected from the film and a phase-pure perovskite film results. This is practically advantageous as it relaxes the need for balancing precursor fluxes exactly during co-deposition. We demonstrate the growth of $\text{CH}_3\text{NH}_3\text{SnI}_x\text{Br}_{3-x}$ thin films with a wide range of stoichiometries and morphologies. Specifically, by tuning the source material temperature (140 °C – 290 °C), the carrier gas flow rate (2 sccm – 100 sccm), the substrate temperature (8 °C – 70 °C), and the chamber pressure (350 mTorr – 10 Torr), we realize corresponding changes in grain orientation and grain size from <100 nm to over 1 μm . CGAVD is a promising approach to deposition of other halide perovskites and can potentially enable the growth of previously inaccessible morphologies and multi-layer perovskite films.

5:00pm TF+SS-ThA-9 Synthesis and Optical Properties of Organo-halide 2D Perovskites, *Misook Min, A Kaul*, University of North Texas

Organic-inorganic halide perovskite materials have attracted interest in recent years due to their excellent optoelectronic properties, such as high absorption coefficient, tunable band gap, small exciton binding energy. These advantages combined with the extremely low fabrication cost make this kind of material suitable as a light absorber for solar cells, light emitting diodes, field-effect transistors and photo-detectors [1]. Hybrid organic-inorganic perovskite described by the formula ABX_3 (A = organic ammonium cation, B = inorganic compounds, X = halide anion). Specifically, the iodide and bromide versions of $\text{CH}_3\text{NH}_3\text{PbX}_3$ have led to a breakthrough in various research fields. We report the scalable synthesis and properties of the 2D series of lead iodide $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_{n+1}\text{I}_{3n+1}$ ($n = 2, 3,$ and 4) perovskites [2]. The 2D $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_{n+1}\text{I}_{3n+1}$ were synthesized and materials characterization was conducted using atomic force microscopy (AFM), X-ray diffraction (XRD), and Photoluminescence (PL) spectroscopy. The crystal structure and surface morphology for $n = 2, 3,$ and 4 perovskites was validated using XRD and AFM, and the peak optical absorption was consistent with the composition-tunable bandgap for these formulations occurring at ~ 2.18 eV, 2.06 eV, and 2.03 eV. Our results show that hybrid organic-inorganic perovskites can be easily and efficiently prepared. Also, the hybrid organic-inorganic perovskites define a promising class of stable and efficient light absorbing materials for photo-detectors and other applications.

5:20pm TF+SS-ThA-10 Encapsulation of Perovskite Nanocrystal Solids using Metal Oxides - A Closer Look into Optical Properties, *Riya Bose, Y Zheng, T Guo, Y Garstein, A Malko*, University of Texas at Dallas

The performance (i.e., light harvesting, optical gain or emission outputs) of many optoelectronic devices (i.e., lasers, photovoltaics (PVs), light emitting diodes (LEDs), etc.) critically depends on the ability to deposit solution processed nanocrystals (NCs) into well-organized, close-packed solids with high photoluminescence quantum yields (PL QYs) and the long term stability of NC films. However, irrespective of the high quality of NCs or the passivation techniques used in solution, the deposition of NC multilayers as well as the exposure to the environment during solid state device fabrication often require or lead to changes in the NCs chemical environment, such as exchange/loss of ligands, which eventually lead to formation of trap states that decrease the PL QYs of NCs and are often detrimental to device performances. An attractive approach to protect the NCs' integrity is the use of atomic layer deposition (ALD) in which self-limiting surface reactions of the precursors allows conformal growth of the metal oxide layer with precise thickness control to encapsulate NCs. This process, though prevents the deterioration of NCs, is observed to decrease their PLQY significantly. To mitigate this issue, we recently developed an alternate gas phase deposition technique where a pulsed co-deposition of both metal and oxidant precursors at room temperature (RT) (reminiscent of chemical vapor deposition, CVD) is able to deposit uniform metal oxide (AlO_x) films, originating from gas-phase reactions in the immediate vicinity of the NC layer. Unlike conventional ALD, this method is observed to

preserve the optical properties, e.g., PLQY and lifetime of metal chalcogenide NCs film. With this new approach, we investigate the encapsulation of hybrid metal halide perovskite NCs, which have been at the forefront of recent optoelectronic materials research due to their high absorption coefficients, high charge carrier mobilities, balanced ambipolar transport properties, and easy solution processability. However, in spite of the exceptional upsurge in the lab scale device efficiency of perovskites in a remarkably short time frame, the practical application of the same in real world is restricted by their inherent instability. AlO_x deposition on perovskite nanocrystals with our modified approach not only retains the optical properties of the NCs, but also improves them, even at a single particle level, which paves the way for unique optoelectronic opportunities.

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