Thin Films
Room 206 B W - Session TF1+EM-TuM
Thin Films for Energy III

Moderators: Su Gupta, University of Alabama, **Feng Yan**, Arizona State University

8:00am **TF1+EM-TuM-1 Atomic Layer Deposition of Metal Iodides**, ***Marianna Kemell***, *Georgi Popov, Alexander Weiss, Timo Hatanpää, Aida Heidari, Markku Leskelä, Mikko Ritala,* University of Helsinki, Finland **INVITED**

Metal iodide thin films have gained a lot of attention during the recent decade. Although their applications cover a variety of technological fields, majority of the research is motivated by photovoltaics.

Halide perovskites are the most studied metal iodides for photovoltaics. Single-junction cells made with abundant and low-cost materials and by inexpensive methods have shown high solar conversion efficiencies (>25%). The most studied halide perovskite is $CH_3NH_3PbI_3$, whereas fully inorganic perovskites such as $CsPbI_3$, and mixed compositions with tuned optoelectronic properties are under active research as well. The search for more stable materials on one hand and the concern caused by the toxicity of lead on the other hand have recently drawn attention also to other types of materials including Ag_2BiI_5 and $Cs_3Bi_2I_9$, for example. Halide perovskites are expected to find their main application in tandem solar cells with silicon, and the same may be true also for Ag_2BiI_5, $Cs_3Bi_2I_9$ and related materials.

Applications of halide perovskite and other metal iodide thin films require scalable and well-controllable deposition methods. The currently used methods are simple and low-cost but are difficult to scale up for industrial mass production of solar cells.

Atomic layer deposition (ALD) is well known for its unique controllability and excellent scalability and has therefore a lot to give also in the field of metal iodide films. We have developed, as the first team in the world, ALD processes for various metal iodides. We started by developing processes for the binary iodides PbI_2 [1], CsI [2], and SnI_2 [3]. All these processes use metal silylamides as the metal precursors and SnI_4 as the iodine precursor. The binary processes can be combined to make more complex materials: so far we have made the inorganic halide perovskites $CsPbI_3$ [2] and $CsSnI_3$ [3] by combining CsI with PbI_2 and SnI_2, respectively. $CH_3NH_3PbI_3$ can be prepared as well by exposing PbI_2 to CH_3NH_3I vapor [1]. We recently designed a new iodine source that produces anhydrous HI vapor on-site and overcomes thus the limitations of SnI_4 such as high cost and tin contamination in the deposited films. We have demonstrated the feasibility of the source by depositing CsI. Our recent results include the world's first ALD process for BiI_3, as well as the first experiments aiming to combine AgI and BiI_3 to ternary iodides.

References

[1] G. Popov et al., *Chem. Mater.* **31** 1101 (2019)

[2] A. Weiß et al., *Chem. Mater* **34** 6087 (2022)

[3] A. Weiß et al., *Chem. Mater*. **35** 8722 (2023)

8:30am **TF1+EM-TuM-3 Laser Raster Pattern Control for Uniform Deposition of Hybrid Organic-Inorganic Perovskites via RIR-MAPLE**, ***Joshua Ayeni***, *Adrienne Stiff-Roberts,* Duke University

Achieving uniform, scalable hybrid organic-inorganic perovskite (HOIP) deposition remains a key challenge, especially for pulsed laser deposition (PLD) systems [1]. Resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE), a variant of PLD, offers gentle deposition of complex, multi-component materials with excellent stoichiometric and structural integrity [2-3]. However, it is difficult to ensure consistent film thickness and spatial uniformity due to a limited understanding of how laser raster patterns (LRP) impact plume dynamics and film growth mechanisms. Despite its crucial role, the impact of LRP on the quality of films deposited by RIR-MAPLE remains underexplored.

This study aims to address these challenges by investigating the impact of LRP on film thickness, spatial uniformity, and optoelectronic properties of $(PEA)_2PbI_4$ thin films, paving the way for scalable industrial applications. $(PEA)_2PbI_4$, a two-dimensional hybrid perovskite known for its exceptional stability and tunable optoelectronic properties, holds promise for applications in light-emitting diodes, solar cells, and photodetectors [4].

Thin films were deposited under high vacuum conditions ($\sim 10^{-5}$ Torr) with five distinct raster patterns (A–E), each varying in mirror positions and rastering speeds to control material distribution. Film thickness and uniformity were measured by profilometry and scanning electron microscopy (SEM), revealing that LRP notably affects deposition outcomes. Patterns A and B produced the thickest films (305-385 nm) with lower radial thickness variations. Markedly, pattern B shows a moderate variation, offering a trade-off between film thickness and spatial uniformity. However, patterns D and E show greater non-uniformity, and C exhibits the largest spatial variation. These results show that variations in LRP greatly affect deposition rates and morphology, highlighting the need for systematic pattern optimization. The study emphasizes the role of plume overlap and local energy dispersion in controlling growth dynamics during deposition.

To enable predictive control over film properties, a simulation-based model is being developed to characterize the behavior of the plume generated under different LRP conditions. Characterizations such as XRD, XPS, PL, UV-Vis, and electrical measurements will be conducted to assess film properties and performance. By relating deposition conditions to intrinsic material properties, this study lays the foundation for scaling RIR-MAPLE to meet industrial demands for hybrid perovskite-based technologies.

This work is supported by the National Science Foundation under Grant No. NSF CMMI-2227551.

8:45am **TF1+EM-TuM-4 Role of Thermodynamics for Low-temperature Processing of Perovskite Chalcogenides: A Combined Approach of Density Functional Theory and Experiment**, ***Ramji Velayutham***, *Susmita Jana, Kumar Shwetabh, Birabar Ranjit Kumar Nanda, Surendra Anantharaman,* Indian Institute of Technology Madras, India

Semiconductors for optoelectronic devices are an ever growing topic of research for achieving cost-effective, solution-processable, and scalable techniques for applications in energy harvesting and generation. Compared to III-V semiconductors, metal halide perovskites have revolutionized photovoltaic and light emitting technologies as they meet most of the requirements mentioned above. Perovskites with ABX_3 structure where A-site can be organic or inorganic(MA, FA, Cs), B-site is inorganic, typically Sn or Pb, and X site can be halides (Cl, Br, I). Bandgap tuning by varying the composition and low-temperature synthesis are advantages of halide perovskites[1,2]. However, the chemical stability and presence of lead are major roadblocks for commercialization of these devices. On the other hand, perovskite chalcogenides with chalcogens provide enhanced stability compared to halide perovskites. The high-temperature phase formation and phase separation in these chalcogenide systems have gained significant attention for developing low-temperature processing of materials[3].Lowering the processing temperatures down to 350 °C has been achieved but not sufficient to develop flexible devices[4].

In this study, we have explored the possibility of synthesizing the perovskite chalcogenides at lower temperature compared to the literature reports. Using density functional theory, we investigate the thermodynamics of phase formation of perovskite chalcogenides, which are dictated by the configuration entropy and chemical potentials. These results are further verified by synthesizing the exact stoichiometric composition using the chemical vapour deposition technique. X-ray diffraction studies to unravel the phase formation at low-temperature will be presented. We will correlate the absorption and emission spectra from the experimental results with the DFT studies. Further, exciton dynamics at low-temperature from the perovskite chalcogenides will be discussed. We believe that our results will pave the way for introducing perovskite chalcogenides in flexible devices.

1. A. A. Zhumekenov, M. I. Saidaminov, O. F. Mohammed, O. M. Bakr. Joule. 5, 2027-2046 (2021).
2. C. He and X. Liu. Light Sci Appl 12, 15 (2023).
3. C. Wang, R. Nie, Y. Dai, H. Tai, B. Zhu, L. Zhao, Y. Wu, W. Guo, S. Il Seok. Energy Environ. Sci. 17, 1368-1386 (2024).
4. C. Comparotto, P. Ström, O. Donzel-Gargand, T. Kubart, J. J. S. Scragg. ACS Appl. Energy Mater. 5, 6335-6343 (2022).

9:00am **TF1+EM-TuM-5 Alloyed SnO2-Nb2O5 ALD Films for Energy Applications**, *Daniel Macayeal, Ian Christiansen, William Rekas, Madison Cooney, Elijah Burlinson, Yubin Han,* ***Alexander Kozen,*** University of Vermont

Perovskite solar cells are a promising alternative to silicon-based solar cells, however their current lifetimes and durability prohibit their commercial viability. One approach is to utilize ALD SnO_2 as a dual electron transport layer (ETL) and passivation layer applied using Atomic layer deposition

(ALD). ALD is a method ubiquitous in the semiconductor industry for growing thin film materials with atomic scale precision. Sequential alternating pulses of metalorganic and oxidation precursors are delivered to a reaction chamber and react to grow a film on the surface of a substrate. Using the metalorganic precursors TDMA-Sn and $Nb(OEt)_5$, and the oxidation precursors H_2O and O_3, we produced and characterized alloyed thin films of SnO_2, and Nb_2O_5. We will discuss how temperature and oxidation precursor selection impacts growth behavior, optical, and electrical properties of alloyed SnO_2-Nb_2O_5 thin films, and analyze phase evolution during alloyed film annealing through TTT diagrams. Lastly, we will examine the effect the alloyed $SnO_2$and Nb_2O_5 films have on perovskite solar cell performance by evaluating the open circuit potential, quantum efficiency, and degradation behavior.

9:15am **TF1+EM-TuM-6 Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Lead Halide Perovskite Thin Film Solar Cells for Space Applications***, **Charlie Chandler,*** University of Surrey, UK*; Dhilan Devadasan, Simon Bacon,* Thermo Fisher Scientific, UK*; Jae Yun,* University of Surrey, UK*; Hongjae Shim,* University of New South Wales, Australia*; Helen Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Tim Nunney,* Thermo Fisher Scientific, UK*; Mark Baker,* University of Surrey, UK

Perovskites are an exciting field of photovoltaic devices which can be used as solar cell materials for space applications. These devices have shown significant improvements over the last decade in both efficiency and stability. The stability of these devices within the deployed environment is a key area of interest. X-ray photoelectron spectroscopy (XPS) depth profiling of different spin-coated formamidinium lead Iodide ($CH_5N_2PbI_3$) based perovskite thin film solar cells, both pristine and following space environmental testing, have been performed. Depth profiling has been carried out using traditional monatomic and gas cluster ion beam (GCIB) bombardment and compared to profiles recorded using femtosecond laser ablation (fs-LA). A femtosecond laser with a 1030 nm peak wavelength and a pulse duration of 160 fs was employed. The monatomic and cluster ion sputtering depth profiles exhibited chemical damage due to preferential sputtering of C, N and I. Pb^0 was also observed in the Pb 4f spectrum as a preferential sputtering artefact. fs-LA XPS depth profiles fully retained the true chemical composition of the 500 nm thick perovskite layer [1]. Following different exposures to proton irradiation, fs-LA XPS depth profiling enabled changes in the perovskite chemical composition as a function of depth to be identified and correlated with solar cell performance. An additional propane-1,3-diammonium iodide ($PDAI_2$) surface treatment following perovskite deposition was shown to reduce the extent of ion beam damage due to self-healing.

[1] C.W. Chandler et al., Surface and Interface Analysis 57 (2025) 246–252

9:30am **TF1+EM-TuM-7 Ambient Degradation Mechanism in Halide Perovskite Cs2AgBiCl6 Revealed by ATR-FTIR***, **Pulkita Jain**, Seda Sarp, Eray Aydil,* New York University

Halide perovskites, such as $CsPbX_3$, are promising for optoelectronics but face challenges due to lead toxicity. Among these alternatives, $Cs_2AgBiCl_6$ has gained attention for its favorable optical properties and potential applications in light-emitting devices. In one potential application, $Cs_2AgBiCl_6$ is doped with $YbCl_3$, a well-known luminophore that enables downconversion and quantum cutting—a process where one ultraviolet photon generates two near-infrared photons. In this energy transfer mechanism, the perovskite host absorbs blue photons and transfers the energy to Yb ions, which then relax ($^2F_{5/2}\rightarrow{}^2F_{7/2}$) and emit near-infrared photons (1.25 eV). In our previous work, we demonstrated that phase-pure $Cs_2AgBiCl_6$ thin films required excess $BiCl_3$ during synthesis to prevent the formation of impurity phases. Using this optimized composition, our Yb-doped films achieved a photoluminescence quantum yield (PLQY) of 50%, attributed to downconversion. However, PLQY decayed to 30% within one week of exposure to ambient conditions. Hypothesizing that this degradation is a surface-related phenomenon, we implemented a surface passivation strategy on both the top and bottom surfaces of the films. This approach resulted in a remarkable increase in PLQY to 75%, which remained stable for over six months.We conducted a time-dependent ATR-FTIR study to investigate further the underlying mechanisms of PLQY decay in non-passivated films. Our findings revealed that water molecules adsorb onto the film surface upon exposure to air, reacting with excess $BiCl_3$ to form BiOCl and HCl. Concurrently, CO_2 is adsorbed, forming carbonic acid, which is facilitated by the presence of HCl. We observed an infrared absorption peak at ~1440 cm^{-1} in the FTIR spectrum, attributed to carbonate species, which emerged over time, reinforcing our hypothesis regarding surface reactions. To understand the role of excess $BiCl_3$, we deposited film with a stoichiometric amount of $BiCl_3$ on the ATR crystal and analyzed its FTIR spectrum. The results indicated that while carbonate formed, its intensity was significantly lower and did not change appreciably over time. Additionally, we examined passivated films on the ATR crystal, which exhibited similar behavior, suggesting that the observed carbonate formation is due to the presence of $BiCl_3$ and the formation of HCl upon its reaction with water vapor. This finding elucidates why PLQY remains stable in passivated films: the passivant protects the bulk from the ambient gases. These insights into the degradation mechanisms of Yb-doped $Cs_2AgBiCl_6$ thin films highlight the importance of surface passivation in enhancing long-term stability and performance.

9:45am **TF1+EM-TuM-8 High Rate Low Temperature Processing of Cu-chalcopyrite Semiconductors for Solar Cell Applications***, Thomas Lepetit,* Institut des materiaux de Nantes Jean Rouxel, France*; Nicolas Barreau,* Institut des Materiaux de Nantes Jean Rouxel, France*; Sylvain Marsillac, Deewakar Poudel,* Old Dominion University*; Thamer Alaoui, Leo Choubrac, Ludovic Arzel,* Universite de Nantes, France*; Fabien Pineau,* CNRS Photovoltaics, France*; **Angus Rockett**,* Colorado School of Mines, US

This talk describes a method to recrystallize Cu-chalcopyrite semiconductors during processing resulting in a greatly accelerated deposition process while retaining high material quality. While a number of flux materials were tested, AgBr was found to produce rapid recrystallization and greatly improved material properties in finished solar cells. Maximum process temperatures for $Cu(In,Ga)Se_2$ below 450°C with up to a 4x increase in deposition rate were demonstrated. Recent results have extended this work to ultrathin absorber (480 nm) deposited on transparent indium tin oxide back contacts. Related semi-transparent devices have achieved ~12% efficiency, providing the best device performances obtained to date for such thickness.

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