ALD Applications
Room Hall 3D - Session AA1-TuA

Energy: Solar Energy Materials II

Moderators: Arrelaine Dameron, Forge Nano, **Neil Dasgupta**, University of Michigan

1:30pm **AA1-TuA-1 Toward All-ALD Halide Perovskite Solar Cells**, *G. Popov, A. Weiss, M. Ritala, M. Leskelä, **Marianna Kemell**,* University of Helsinki, Finland **INVITED**

Halide perovskite solar cells show solar conversion efficiencies > 26 %, making them the most promising emerging photovoltaics technology. Halide perovskites have the general formula ABX_3 where most often A = $CH_3NH_3^+$, $CH(NH_2)_2^+$ or Cs^+, B = Pb^{2+} or Sn^{2+} and X = I^-, Br^- or Cl^-. Methylammonium lead iodide $CH_3NH_3PbI_3$ is a well-known example.

Commercialization of the halide perovskite solar cells is still impeded by challenges in upscaling. High quality perovskite layers can be made on small areas but the currently used methods are not suitable for large production volumes.

We have addressed the scalability issue by developing atomic layer deposition (ALD) processes for halide perovskites and other materials in perovskite solar cells. Our approach is based on ALD of binary halides, followed by their chemical conversion to the desired perovskites. As the first step, we developed ALD processes for the binary metal halides PbI_2 [1], CsI [2], SnI_2 [3], $PbCl_2$ [4] and $PbBr_2$ [4]. Prior to our work there were no ALD processes for iodides, bromides or chlorides. Using the binary halides as the starting points, we can deposit the halide perovskites $CH_3NH_3PbI_3$ [1], $CsPbI_3$ [2] and $CsSnI_3$ [3]. ALD-PbI_2 film is converted to $CH_3NH_3PbI_3$ by exposing it to CH_3NH_3I vapor, whereas ALD-CsI film can be converted into $CsPbI_3$ by exposing it to the ALD process of PbI_2, and to $CsSnI_3$ by exposing it to the ALD process of SnI_2. Combining these with the ALD processes of $PbCl_2$ and $PbBr_2$ enables compositional engineering as a route to fine-tuned properties.

In a halide perovskite solar cell, the perovskite layer is sandwiched between n- and p-type semiconductor films. ALD processes for various n-type materials are readily available, whereas p-type materials are more challenging. We have developed low-temperature ALD processes that enable deposition of p-type PbS [5] on $CH_3NH_3PbI_3$ at temperatures below 100 ºC, without damaging it. Furthermore, the PbS film also protects the $CH_3NH_3PbI_3$ film from degradation under ambient conditions, acting thus in a dual role as a functional layer and as an encapsulant. We have also developed a two-step process for p-type CuI [6] that is compatible with $CsPbI_3$. Our processes form the first steps towards making complete halide perovskite solar cells by ALD-based methods.

[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), [4] G. Popov et al., *Dalton Trans*. **51**, 15142 (2022), [5] G. Popov et al., *Chem. Mater.***32** 8216 (2020), [6] A. Weiß et al., *Adv. Mater. Interfaces***10**, 2201860 (2023).

2:00pm **AA1-TuA-3 Plasma-enhanced Atomic Layer Deposition of Tunable Cobalt Nitride Thin Films Enabled by Sequential N_2 Plasma Exposure**, ***Matthias Kuhl,*** Technical University Munich, Germany*; L. Kohlmaier,* Technical University Munich, Austria*; I. Sharp,* Technical University Munich*; J. Eichhorn,* Technical University Munich, Germany

Transition metal nitrides form an interesting class of materials due to their mechanical hardness, tunable electronic and magnetic properties, and catalytic activity. In this context, cobalt nitride is a promising material both in the semiconductor industry and for electrochemical (EC) energy conversion. Despite these potential applications, there are limited reports on depositing cobalt nitride via atomic layer deposition (ALD), especially at lower temperatures (<200 °C). Such low temperature processes would provide enhanced processing compatibility, including for photolithography, and aid in preserving high quality light absorber/catalyst interfaces for photoelectrochemical (PEC) energy conversion applications.

Here, we report on the low-temperature (100 - 200 °C) plasma-enhanced (PE) ALD of cobalt nitride using cobaltocene $CoCp_2$ as precursor and either NH_3 plasma or H_2/N_2 plasma as co-reactant. The deposition at low temperatures is enabled by introducing a subsequent N_2 plasma pulse at the end of each PE-ALD cycle to regenerate surface sites for the subsequent precursor adsorption. We analyze the film growth characteristics and material properties by in-situ spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Varying deposition temperature and plasma gas composition can be leveraged to tune the Co/N ratio and thus the material properties from semiconducting to metallic. Lastly, we applied the thin films as heterogeneous catalysts for the EC oxygen evolution reaction. Overall, this work highlights the use of PE-ALD as a promising approach for depositing metal nitrides with tunable film properties at low temperatures.

2:15pm **AA1-TuA-4 Hybrid Solar Cells Comprising Inorganic and Organic Materials Through Vapor Phase Infiltration**, *K. Ashurbekova,* 1. CIC nanoGUNE, Spain*; **Mato Knez**,* CIC nanoGUNE, Spain

Inorganic, organic and perovskite solar cells (SCs) have witnessed unprecedented progress in the past decade. Perovskite SCs, while highly efficient, encounter stability and toxicity concerns. Inorganic SCs excel in efficiency and durability but lack flexibility, prompting exploration of alternative technologies. In contrast, organic SCs offer flexibility, facing lower efficiency challenges. Despite the inherent limitations of each SC type, they have their own merits, promising a grand step forward if synergy is achieved. Combining the adaptability of organic SCs with the efficiency of inorganic ones may yield a hybrid versatile alternative. We are introducing new hybrid solar cell materials by applying vapor phase infiltration (VPI) to polymers.

We present a new hybrid materials set obtained after growing Sb_2S_3 and $Sb_2Se_3$by VPI inside the bulk and atop of diverse polymers including poly(triaryl amine) (PTAA), Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (PolyTPD), Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and Poly(3-hexylthiophene-2,5-diyl) (P3HT). PTAA, PolyTPD and PEDOT:PSS are excellent hole-transporting semiconducting materials, while P3HT is an efficient light absorber in the visible range. Metal chalcogenide light absorbent materials, such as Sb_2S_3 and Sb_2Se_3,have huge potential in photovoltaics owing to the suitable bandgap of 1.7 and 1.3 eV, and high light absorption coefficient above 10^4 and 10^5 cm^{-1}, respectively.For the VPI growth of Sb_2S_3 and Sb_2Se_3, $SbCl_3/H_2S$ and $SbCl_3/(Me_3Si)_2Se$ precursors were used, respectively. The hybridization process was monitored *in-situ* with a Quartz Crystal Microbalance (QCM). The monitoring allowed studying the saturation behavior of the VPI process and quantitatively controlling the loading of the inorganic precursors into the polymer. Scanning electron microscopy (SEM) showed infiltration in form of Sb_2S_3 and Sb_2Se_3 crystal growth throughout the whole polymer depth. TEM was used to examine the structure of the crystalline phase of the Sb_2S_3 and Sb_2Se_3 grown in the bulk and on top of the polymer. A complete photovoltaic characterization of a new set of hybrid materials, including thecurrent density–voltage (J–V) characteristic of SCs under illumination, power conversion efficiencies (PCEs) and the external quantum efficiency (EQE) of a device, was performed in 16 ITO pins SCs. Planar p-i-n SCs devices of the following structures were fabricated: ITO glass/polymer-Sb_2S_3//Sb_2Se_3 /ETL/Ag and ITO glass/polymer-Sb_2S_3//Sb_2Se_3/perovskite/ETL/Ag. C60/BCP was used as an electron transport layer (ETL). The results offer new solutions for sustainable solar energy.

2:30pm **AA1-TuA-5 Mitigating the Cross-Ion Migration Towards Perovskite Using a Conformal Layer of Alumina via Atomic Layer Deposition**, ***Mayank Kedia**, C. Das, M. Saliba,* Forschungszentrum Jülich GmbH, Germany

Atomic layer deposition (ALD) of aluminum oxide (Al_2O_3) layers is an established technique for encapsulation and stabilization of active materials against environmental stressors. This is particularly important for sensitive perovskite materials, that react with moisture, light, O_2, etc. during the device operation conditions. [1] At the same time, the role of the ALD-Al_2O_3 barrier layer between the perovskite and charge transport material still requires further analysis.

In this study, we demonstrate the surface coverage uniformity of a <1nm ALD-Al_2O_3 layer on bare perovskite at room temperature. [2] Such a sub-nanometer ALD-Al_2O_3 coverage on the different perovskite facets reduces surface defects enhancing the device performance from 19.2% to 20.1%. This ultra-thin layer of ALD-Al_2O_3 acts as a barrier layer for the diffusion of degraded byproducts of the aged spiro-OMeTAD preventing perovskite's transition to amorphous phases. Consequently, the ALD-Al_2O_3-based device retains 75% of its initial power conversion efficiency as compared to 10% for pristine devices after 180 days of shelf-aging, followed by 1000 min of maximum power point tracking under ambient conditions. Finally, this study deepens the mechanistic understanding of the ALD-Al_2O_3 as an impermeable layer, highlighting the multifaceted role of buffer layers in interface engineering.

References:

1. **Das, C.**, Kot, M., Hellmann, T., Wittich, C., Mankel, E., Zimmermann, I., Schmeisser, D., Khaja Nazeeruddin, M., and Jaegermann, W. (2020) Atomic Layer-Deposited Aluminum Oxide Hinders Iodide Migration and Stabilizes Perovskite Solar Cells. *Cell Rep Phys Sci*, **1** (7).
2. **Kedia, M.**, Das, C., **Saliba, M.**, (2024) Stabilizing perovskite solar cells using a conformal impermeable layer of alumina via atomic layer deposition. *(submitted)*

2:45pm **AA1-TuA-6 Thermoelectric Properties of Sb_2Te_3-based Ferecrystals based on Atomic Layer Deposition***, J. Yang, D. Shin, S. Lehmann, A. Bahrami, **Korneli Nielsch**,* Leibniz Inst. of Solid State and Materials Research / IFW-Dresden, Germany

Atomic layer deposition is a very versatile technology for the deposition of thin films with precise thickness control on large areas, non-planar surfaces and 3D objects. The chemical reaction is surface limited, well defined and works in most cases at low temperatures (RT to 250 °C). For a number of classical van der Waals 2D materials, there have been reports on ALD of transition metal dichalcogenide (TMDC) of MoS_2, SnS_2, WS_2 and WSe_2, which also included the electronic characterization as a field effect transistor (FET).

In this work, we have fabricated by atomic layer deposition (ALD) multilayers of layered materials based on topological insulators and van der Waals materials, called *ferecrystals.* These ferecrystals can be tailored to exhibit unusual properties such as high electrical conductivity or low thermal conductivity or magnetic properties. A detailed ferecrystal study was performed on ferecrytals of Sb_2Te_3 and SbO_x, which has been grown at the same temperature as single layers of Sb_2Te_3. Without post-annealing, the electrical and thermoelectric characterisation of the highly ordered samples have been performed with the ZT-chip setup. In general, the carrier mobility is very high >150 Vs^2/cm^2 and is even improved when the thickness of the Sb_2Te_3 layers is reduced and the number of SbO_x layers (typically 2 nm thickness) is increased. Detailed XRD investigations have been performed and an enhanced crystalline order is observed in the ferecrystal system compared to individual layers of Sb_2Te_3. We have grown ferecrystals based on Sb_2Te_3 and Sb_2Se_3 with tetrahedral and orthorhombic crystal structure, respectively. The p-type hole carrier concentration of Sb_2Te_3 films can be enhanced through the sublayer doping of Sb_2Se_3. The highest carrier concentration achieved was 2.5×10^{19} cm^{-2} when the thickness ratio of Sb_2Te_3 to Sb_2Se_3 was (4 nm/2 nm). Further reduction of the Sb_2Te_3 thickness resulted in a high Seebeck coefficient of 172 μV/K at room temperature.h

References:

1. J. Yang, A. Bahrami,X. Ding,P. Zhao,S. He,S. Lehmann, M. Laitinen, J. Julin, M. Kivekas, T.Sajavaara, **K. Nielsch**, „Low-Temperature Atomic Layer Deposition of High-k SbOx for Thin Film Transistors", Adv. Electron. Mater. 2022, 2101334.
2. J. Yang, J. Li, A. Bahrami, N. Nasiri, S. Lehmann, M. Cichocka, S. Mukherjee, **K. Nielsch**, „Wafer-scale Growth of Sb_2Te_3 Films via Low-temperature Atomic Layer Deposition for Self-Powered Photodetectors", ACS Appl. Mater. Interfaces 2022, 8, 2101334

3:00pm **AA1-TuA-7 Atomic Layer Deposition for Photoelectrochemical Solar Fuel Production***, **Lionel Santinacci**,* CNRS/Aix-Marseille Univ., France **INVITED**

Since H_2 is now considered as a key energy vector, its production through water electrolysis coupled to a renewable power supply is envisioned as a large-scale production scheme. In parallel to the various electrolysis approaches, H_2 and O_2 production from H_2O photoelectrolysis appears to be a more straightforward process. It has opened an attractive, though challenging, field of investigations that ultimately tackles direct water dissociation using an unbiased photoelectrochemical cell (PEC) under sunlight: solar fuel production. The recent remarkable conversion yield of 19%,[1] reported on unbiased PEC built with expensive and unstable III-V semiconductors (SCs) associated to platinoid catalysts, is very promising but the H_2 production remains more expensive than from fossil sources . The field needs therefore to significantly improve yield, stability and cost.

In the recent years, it has been shown that ALD can play a valuable role to address such challenges. Photoelectrodes can be significantly improved by (i) surface structuring inducing a better light harvesting and a higher active surface area, (ii) by co-catalysts improving the reaction kinetics and enhancing the photocurrent and (iii) by protective films extending the electrode lifetime. ALD exhibits key advantages to achieve such improvements and recent literature has shown numerous successful examples of photoelectrode modifications. ALD is, indeed, known to be well-suited to conformally coat nanostructured surfaces with either continuous pinhole-free layers or uniform particle collections. After a short reminder on the basics of water photosplitting (principle, materials of interest and current challenges), this review will therefore show how ALD can be implemented in the field. Although it is a minor application, specific materials can be synthetized by ALD but the mains uses of this technique consist of fabricating nanostructured electrodes, deposit co-catalysts, passivate or modify the semiconductor/electrolyte junctions and prevent corrosion. In most cases, materials combination is the appropriate way to reach better performance and durability and ALD is, of course, a good tool for such approach.

[1] W.-H. Cheng et al, ACS Energy Lett. (2018) 3, 1795

Author Index

Bold page numbers indicate presenter