# On Demand

## ALD Applications
## Room On Demand - Session AA2

### Energy: Solar Energy Materials

**AA2-1 Synthesis of a Composite Dielectric With Conformal Coating of Aluminium Nitiride Over the Distribution of Titanium Nitride Nanoparticles, for Concentrated Solar Power Applications**, *Nikhar Khanna, M. El Hachemi,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Solar-thermal energy conversion is a promising technology that enables efficient energy harvesting from concentrated solar power (CSP). Recently, there is a lot of interest in metal -insulator based metamaterial absorbers due to complete hold on the permittivity and permeability of these absorbers. In our case the metamaterial absorber would consist of near homogeneous distribution of nanoparticles (Titanium Nitride) in a matrix of (Aluminium Nitride) to form a composite, and an omega shape resonator to couple the electric and magnetic field component of the incoming electromagnetic wave.

Electromagnetic wave absorbers have been investigated for many years with the aim of achieving high absorbance and tunability of both the absorption wavelength and the operation mode by geometrical control, small and thin absorber volume, and simple fabrication.

The present work involves the synthesis of a composite dielectric of approximately 1 μm thickness where nanostructure control is a very challenging task. In this work, we choose a bottom-up approach by constructing a stack of, TiN nanoparticles distribution over a substrate and then a layer of Aluminium Nitride of (85-90nm) thickness, and so on. Titanium nitride particles laid on Si wafer by wet chemical method are coated with conformal coating of Aluminium Nitride, via Plasma- enhanced Atomic Layer deposition. These components together form the dielectric, which helps in transporting the generated heat in the solar absorber. The control of the morphology at the nanoscale is primordial to improve the material's optical performance, thus in our case maximise the wave extinction inside the composite for the application as solar absorber. The optical properties of the dielectric are measured by ellipsometry and UV-Visible measurements.

In order to choose a composite that is best suited for our requirement, two types of composites were prepared. One with Titanium Nitride powder with particles in the range 20-30 nm with a layer of Aluminium Nitride on top of it, and the other with Titanium Nitride dispersions also with particles in the range 20-30nm with a layer of AlN on top. In both the cases, fewer clusters of 500nm to1um of TiN were present however, enough steps were taken to minimize these clusters into smaller particles.

In conclusion, the work presented here is the comparison of the two kinds of composites with their optical properties (n, k) measured by ellipsometer, and (absorbance, reflectance) measured by UV-Visible Spectroscopy.

**AA2-2** *Interface Chemistry in Metal Halide Perovskite/ALD Metal Oxide Systems, Andrea E.A. Bracesco,* C. Burgess, A. Todinova, Eindhoven University of Technology, Netherlands*; V. Zardetto,* Solliance Solar Research, Eindhoven, Netherlands*; D. Koushik, W. Kessels,* Eindhoven University of Technology, Netherlands*; I. Dogan,* Solliance Solar Research, Eindhoven, Netherlands*; C. Weijtens,* Eindhoven University of Technology, Netherlands*; S. Veenstra, R. Andriessen,* Solliance Solar Research, Eindhoven, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The conversion efficiency of perovskite solar cells, PSCs, has surpassed 25%.[1] The present PSC architecture includes organic charge transport layers, CTLs, which in certain cases limit the long-term stability and device's efficiency. Metal oxide CTLs, such as ALD metal oxides, are deemed valid alternatives. Among them, NiO and $SnO_2$, always processed prior to the synthesis of the absorber, are adopted as hole, HTL, and electron transport layers, ETL, respectively.[2,3] Instead, ALD processing directly on top of the perovskite is a major challenge yet to be solved. A well-known example is $SnO_2$: processed directly on perovskite leads to poor cell performance.[4,5,6] Instead, with the inclusion of an organic buffer layer, it leads to highly efficient and stable devices.

In this contribution[7], we systematically investigate the chemical changes occurring at a CsFAPb(I,Br)$_3$ perovskite (sub-)surface upon ALD growth of $SnO_2$ and $TiO_2$. $TiO_2$ is less investigated in literature, but it allows the comparison in terms of reactivity of the perovskite to similar ALD metalorganic precursors, namely tetrakis(dimethylamido)-Sn(IV) (TDMA-Sn) and TDMA-Ti(IV), with $H_2O$ as the co-reactant in both cases.

The bulk crystalline structure of the perovskite absorber is not affected by the ALD growth, as inferred by XRD analysis. Instead, XPS analysis reveals that the growth of $SnO_2$ is accompanied by the formation of molecular halide species at the perovskite/metal oxide interface. In parallel, the initial growth of $SnO_2$ is characterized by sub-stoichiometry and sub-gap defects present above its valence band maximum, associated to Sn(II) states, as observed by UPS. We speculate that a redox reaction involving Sn(IV) metal centers of the ALD precursor and halide anions in perovskite occurs, leading to the reported defects. These sub-gap states are expected to reduce the charge selectivity of $SnO_2$, since they can promote hole injection from the perovskite valence band to that of $SnO_2$, thus inducing non-radiative electron-hole recombination. The chemical changes and the decreased charge selectivity at the perovskite/$SnO_2$ interface support the poor performance of devices with $SnO_2$ grown directly on top of the absorber. As for $TiO_2$, instead, we observe limited chemical modifications. Devices employing $TiO_2$ directly grown on perovskite, show a promising (unoptimized) efficiency of 11%.

[1] J. Yoo et al., Nature 2021

[2] D. Koushik et al., J. Mat. Chem. C 2019

[3] Y. Kuang et al., ACS Appl. Mater. Interfaces 2018

[4]K.O. Brinkmann et al., Sol. RRL 2020

[5] A. F. Palmstrom et al., Adv. Energy Mater. 2018

[6] A. Hultqvist et al., ACS Appl. Energy Mater. 2021

[7] A.E.A. Bracesco et al., JVSTA 2020

**AA2-3 ALD of Lead Halide Perovskites**, *Jake Vagott*, K. Bairley, A. Castro Mendez, C. Perini, J. Correa-Baena, Georgia Institute of Technology

Perovskite solar cells (PSCs) have quickly risen in efficiency since their initial fabrication in 2009, with the current record power conversion efficiency (PCE) being 25.2% [1]. Quickly approaching the Shockley—Queisser limit of 33% for single-junction solar cells, stability and scalability research has become crucial. While solution deposition of the perovskite absorber layer by spin-coating has resulted in the highest efficiency devices so far, vapor deposition methods have shown promise and may help resolve both the stability and scalability problems that PSCs are currently facing. Atomic layer deposition (ALD), as a vapor deposition process, provides advantages such as fine thickness control, improved conformity, high uniformity, and ability to be incorporated into existing industrial processes such as roll-to-roll manufacturing. The stoichiometry of the perovskite may also be easily tuned through manipulation of the precursor doses. My work focuses on depositing perovskite through a two-step ALD/ molecular layer deposition (MLD) hybrid process, with ALD referring to the inorganic aspects of the process and MLD incorporating organic materials. The first step, which we have recently achieved, is to deposit a conformal lead iodide film which may be converted to methylammonium lead triiodide (MAPbI$_3$) through exposure to methylammonium iodide (MAI). For the lead precursor, Pb(dmamp)$_2$ was chosen as it is more volatile than other common lead precursors such as Pb(acac)$_2$ and has not shown signs of CVD—like growth which has been the case with Pb(tmhd)$_2$ [2]. HI (aq) was chosen as the iodine precursor due to its high vapor pressure and reactivity. The precursors involved are easily accessible through commercial means and do not require any additional processing before use. The second step, which we are currently developing, involves the introduction of a third precursor within every cycle of the previous recipe, which would allow for an effective ALD/MLD process for MAPbI$_3$. Once we are able to deposit highly uniform perovskite thin films by ALD/MLD, this will allow us the ability to deposit 2D perovskite passivation layers which will help improve stability by decreasing defects at the perovskite/charge transport layer interface. This will increase moisture and thermal stability in the PSCs while also being a scalable process.

**References**

[1] Yoo, Jason J., et al. "Efficient Perovskite Solar Cells via Improved Carrier Management." *Nature News*, Nature Publishing Group, 24 Feb. 2021

[2] Strnad, Nicholas. "ATOMIC LAYER DEPOSITION OF LEAD ZIRCONATE-TITANATE AND OTHER LEAD-BASED PEROVSKITES." *Thesis / Dissertation ETD*, Digital Repository at the University of Maryland, 2019.

**AA2-4 Atomic Layer Deposition of $Zn_{1-x}Mg_xO$ as Transparent Conducting Films for Chalcopyrite Solar Cells**, *Poorani Gnanasambandan,* Luxembourg Institute of Science and Technology (LIST), Luxembourg; *M. Sood,* University of Luxembourg; *N. Adjeroud,* Luxembourg Institute of Science and Technology (LIST), Luxembourg; *R. Leturcq,* luxembourg Institute of Science and Technology (LIST), Luxembourg; *S. Siebentritt,* University of Luxembourg

We investigate atomic layer deposited zinc magnesium oxide films with varying Mg content as transparent conducting films and as electron transport layers for chalcopyrite solar cells. Previous studies on the impact of $Zn_{1-x}Mg_xO$:Al as transparent electrodes and Mg doped ZnO thin films for the window layer of CIGS $Cu(In,Ga)(S,Se)_2$ solar cells employed co-sputtering, electrodeposition and ALD respectively [1][2][3][4]; these were limited to fixed composition and deposition temperatures. We examine the effect of $Zn_{1-x}Mg_xO$ films, deposited by atomic layer deposition (ALD) under different growth conditions, on the performance of high-bandgap solar cells based on $Cu(In,Ga)S_2$ absorbers.

Optimizing a ternary process by mixing two binary ALD process has its challenges [5]. We achieve high degree of control on composition by optimizing the growth conditions with varying deposition temperatures and supercycle parameters such as pulse ratios and bilayer period. With the advantage of low temperature and highly conformal thin film growth, we study ALD grown $Zn_{1-x}Mg_xO$ with x varying from 0.1 to 0.4 and elucidate the effect of doping on the band alignment, electrical and optical properties. By varying Mg content we were able to achieve 11% efficient $Cu(In,Ga)S_2$ solar cell with an open-circuit voltage of 941 mV.

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# Author Index

## Bold page numbers indicate presenter