ALD Applications
Room Van Rysselberghe - Session AA-MoM2

ALD for Solar Energy

Moderators: Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd., Paul Poodt, Holst Centre / TNO

10:45am **AA-MoM2-1 Atomic Layer Deposition for Silicon-Perovskite Tandem Cells*, Bart Macco*,** *N. Phung, E. Kessels, M. Creatore,* Eindhoven University of Technology, Netherlands **INVITED**

Solar cells are one of the pillars of the energy transition, where cells based on silicon wafers dominate this market of currently over 200 gigawatts per year. Though not widely known, ALD is now omnipresent in these silicon cells, where on the order of 10 billion wafers are coated with Al_2O_3 passivation layers per year, often using batch or spatial ALD.[1]

While silicon solar cells will dominate the market for the foreseeable future, the anticipated “next big thing” are so-called monolithic tandem solar cells which combine a silicon bottom cell and a perovskite top cell. These tandem cells have skyrocketed in efficiency to almost 30% (compared to 26.7% for silicon only), and have an incredible momentum both in R&D and pilot production.

These tandems cells are highly relying on functional thin films and as such this offers many more opportunities for ALD. Materials “beyond simple ALD Al_2O_3” are needed, including passivation, charge transport and buffer layers as well as tunnel recombination junctions with transparent conductive oxides. At the same time, the application has stringent demands such as extremely low cost, pinhole-free conformal films to avoid electrical shunts and often the need for processing on sensitive perovskite (e.g. max. temperature of ~100 ^{o}C). As will become clear, the distinct merits of ALD such as soft deposition, relatively low-temperature processing, conformality and excellent control over doping and stoichiometry are highly relevant in this field. This will be highlighted through selected case studies. These include ALD SnO_2, a well-established buffer layer which is present in most *(if not all)* recent record tandem cells, as well as recent innovations from our group being ALD NiO hole-selective contacts on the perovskite side [2] and ZnO:Al-based electron contacts on the silicon side.[3]

Finally, I would like to thank the whole PERCSpective consortium for their contributions.

[1] B. Macco, “What can Atomic Layer Deposition do for solar cells?,” *AtomicLimits.com*, 2019. https://www.atomiclimits.com/2019/10/15/what-can-atomic-layer-deposition-do-for-solar-cells-a-few-afterthoughts-from-my-ald-conference-tutorial/.

[2] N. Phung *et al.*, “Enhanced Self-Assembled Monolayer Surface Coverage by ALD NiO in p-i-n Perovskite Solar Cells,” *ACS Appl. Mater. Interfaces*, 2021, doi: 10.1021/acsami.1c15860.

[3] B. Macco *et al.*, “Atomic-layer-deposited Al-doped zinc oxide as a passivating conductive contacting layer for n+-doped surfaces in silicon solar cells,” *Sol. Energy Mater. Sol. Cells*, vol. 233, no. September, p. 111386, Dec. 2021, doi: 10.1016/j.solmat.2021.111386.

11:15am **AA-MoM2-3 ALD Al_2O_3/SiO_x Multilayers for c-Si Surface Passivation: Modification of Interface Properties by Voltage Stress and Plasma Treatments*, Armin Richter*,** *H. Patel, C. Reichel, P. Masuch, J. Benick, S. Glunz,* Fraunhofer ISE, Germany

Al_2O_3 is one of the most effective dielectric surface passivation layers for silicon solar cells. Due to the high amount of negative fixed charges, it is particularly suited for the passivation of p-type Si surfaces. However, other surface passivation schemes indicated recently that there is still room for improvement which becomes more and more important with increasing solar cell performance.

In contrast to single layers, multilayers with thicknesses of only a few nanometers of the individual layers open the opportunity to modify material properties on a nanometer scale. Multilayers of Al_2O_3 and SiO_2, for instance, have been studied recently for the application in MOSFETs because they allow to tune the flat-band voltage shift simply by varying the number of single layers in the multilayer. The origin of this voltage shift are dipoles, which are formed only at the SiO_2/Al_2O_3 interface with one polarity but not at the Al_2O_3/SiO_2 interface with the opposite polarity.

In this work we investigate systematically if such Al_2O_3/SiO_2multilayers are also beneficial for Si surface passivation. We used ALD to prepare the multilayer because of its ultimate deposition control and being at the same time industrially relevant. With CV measurements we studied the interface characteristics (interface defect density D_{it} and total effective fixed charge density Q_{tot}) to gain insights into the electronic properties of the multilayers.

Our results reveal that by varying, for instance, the number of layers in the stack or the deposition and post deposition anneal temperature, the surface passivation of the multilayers is very similar to that of Al_2O_3 single layers but not significantly improved. In fact, we found that Q_{tot} of the multilayers is actually even lower than that of the Al_2O_3 single layers. We studied further the influence of voltage stress. We found that it strongly effects Q_{tot} for both the multilayers and Al_2O_3 single layers and that voltage stress of the right polarity results in a significantly increase of Q_{tot}. However, too high voltage stress deteriorates D_{it}, i.e. the chemical passivation.

In addition, we studied also whether in-situ plasma treatments during the deposition of the multilayer effects its electronic properties. We found that especially H plasmas after the SiO_2 deposition results in a quite substantially improved surface passivation, significantly better than that of the Al_2O_3 single layer. A detailed analysis of the interface properties will be provided in the final paper. As such, our results indicate a promising way of improving the Si surface passivation. However, our results can be also interesting for other semiconductor devices.

11:30am **AA-MoM2-4 Atomic Layer Deposition of Aluminium Doped $Zn_{1-x}Mg_xO$ as Transparent Conducting Films for Photovoltaics*, Poorani Gnanasambandan*,** *N. Adjeroud, R. Leturcq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

We investigate atomic layer deposited aluminium doped zinc magnesium oxide films with varying Al content as transparent conducting films with tunable bandgap. While Aluminium doping of zinc oxide increases the electrical conductivity, it decreases the transmission due to absorption close to the band edge [1].On the other hand, with addition of Mg, the optical properties and bandgap of ZnO can be tuned making them well-suited for photovoltaic applications [2].

Most previous studies on aluminium doped zinc magnesium oxide (Al:ZMO) involved sputtering. While ALD has been used to investigate both aluminium doped zinc oxide (AZO) and magnesium doped zinc oxide (ZMO) [2][3], studies on Al:ZMO were limited to few ratios [4]. Also, the ALD studies fixed the Al-Zn doping concentration around 3% and varied the Mg doping. We aim to increase the electrical conductivity and tune the bandgap by varying both Al and Mg doping concentration.

Optimizing a quaternary process by mixing three binary ALD process involves immense challenges [5]. We achieve high degree of control on composition by optimizing the growth conditions with supercycle parameters such as pulse ratios and bilayer period. With the advantage of precise composition control, we study ALD grown Al doped $Zn_{1-x}Mg_xO$ with x varying from 0.2 to 0.3 and varying aluminium doping concentrations from underdoped to over doped cases. We elucidate the effect of doping on the band alignment, electrical and optical properties.

[1].Zhang, Wu, et al. "Tailoring of optical and electrical properties of transparent and conductive Al-doped ZnO films by adjustment of Al concentration." Materials Science in Semiconductor Processing 74 (2018): 147-153.

[2]. Törndahl, T., et al. ‘Atomic Layer Deposition of Zn1−xMgxO Buffer Layers for Cu (In,Ga)Se2 Solar Cells’. Progress in Photovoltaics: Research and applications 15.3 (2007): 225-235.

[3]. Peng, Qing, Anil U. Mane, and Jeffrey W. Elam. "Nanometer-Thick Mg x Zn (1–x) O Ternary Films for Photovoltaics." ACS Applied Nano Materials 3.8 (2020): 7732-7742.

[4]. Fleischer, Karsten, et al. Aluminium Doped Zn 1 − x Mg x O − a Transparent Conducting Oxide with Tunable Optical and Electrical Properties. Applied Physics Letters 101.12 (2012): 121918.

[5]. Mackus, Adriaan JM, et al. "Synthesis of doped, ternary, and quaternary materials by atomic layer deposition: a review." *Chemistry of Materials* 31.4 (2018): 1142-1183.

11:45am **AA-MoM2-5 An in-Situ Infrared Spectroscopy Study on the Influence of ALD SnO_2 on Formamidinium-Based Metal Halide Perovskite*, A.E.A. (Andrea) Bracesco*,** *J. Jansen, W. Kessels,* Eindhoven University of Technology, Netherlands*; V. Zardetto,* Solliance Solar Research, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The conversion efficiency of metal halide perovskite solar cells (PSCs) has reached 25.7%.[1] This record was achieved through engineering of the optoelectronic properties of the absorber and charge-selective and efficient interfaces between charge transport layer (CTLs) and the absorber. Recently, the focus has shifted towards the replacement of organic CTLs, often leading to parasitic absorption and long-term device instability. Metal oxides prepared by gas phase deposition methods, such as ALD, are prime candidates. The ALD merit of control over film stoichiometry, conformality and uniformity has led to several applications in PSCs. In this respect, ALD SnO_2, in combination with fullerene-based electron transport layers (ETLs), is the state-of-the art in p-i-n PSCs, imparting thermal and environmental stability to the device.[2] However, when attempting to replace the fullerene ETLs by ALD SnO_2 processed directly on the perovskite absorber, a poor device performance is observed, due to severe chemical changes imparted to the inorganic fraction of the perovskite, as previous XPS studies showed.[3,4]

In this contribution, we shift the focus of the investigation on the organic fraction of the perovskite absorber, specifically on the formamidinium cation (FA) in a $CsFAPb(I,Br)_3$ perovskite. By adopting in situ IR spectroscopy, we evaluate the effect that ALD processing conditions, such as substrate temperature, vacuum, and exposure to half and full ALD SnO_2 cycles (tetrakis(dimethylamido)-Sn(IV) (TDMA-Sn) and H_2O), have on FA IR spectral features. We observe that the cation is not affected by vacuum (10^{-5} mbar) and exposure to water half-cycles. Instead, prolonged exposure to a temperature range of 50-100°C (standard SnO_2 processing temperature on perovskite with/out the fullerene-based ETL) leads to the loss of N-H stretching modes. We speculate that FA deprotonates into formamidine, which is then released from the surface. Lastly, we report that the loss of FA, is also detected when the perovskite surface is exposed to a 500 ms pulse of TDMA-Sn. Moreover, the precursor-perovskite surface interaction leads to the formation of sym-triazine, i.e. a decomposition product of formamidine, which becomes trapped at the perovskite/SnO_2 interface. These studies enable to decouple the several effects of direct ALD processing on perovskite and highlight the major role played by the Sn-precursor in affecting the perovskite surface chemistry.

[1]H. Min et al., Nature,598, 444–450, 2021

[2]V. Zardetto et al., Sustainable Energy Fuels, 1, 30-55, 2017

[3]A. F. Palmstrom et al., Adv. Energy Mater., 8-23, 1800591, 2018

[4]A.E.A. Bracesco et al., JVSTA, 38, 063206, 2020

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