

Thin Film

Room: 111 - Session TF+EN-WeM

ALD for Energy

Moderator: Jesse Jur, North Carolina State University, Angel Yanguas-Gil, Argonne National Lab

8:00am **TF+EN-WeM1 Photovoltage Design for ALD Metal Oxide Protected Solar-Water-Splitting Photoanodes**, Andrew Scheuermann, J.P. Lawrence, K.W. Kemp, O.L. Hendricks, Stanford University, A. Walsh, I. Povey, M.E. Pemble, P.K. Hurlley, Tyndall National Institute, C.E.D. Chidsey, P.C. McIntyre, Stanford University

Metal oxide protection layers for photoanodes may enable the development of large-scale solar fuel and chemical synthesis. ALD-TiO₂ is the most widely used material because of its excellent stability under water oxidation conditions and potential for high electrical conductivity both as an ultrathin film and with thicknesses exceeding 100 nm [1-3]. However, the most conductive ALD-TiO₂ films exhibit poor photovoltages of ~ 400 mV and less [3]. Even assuming near-ideal fill factors, these voltages fall far short of the values needed for viable water splitting devices. Photovoltage optimization is especially difficult to achieve in MOS photoanodes because of the presence of a defective metal oxide protection layer and a defective semiconductor/oxide interface in the device structure. Therefore, understanding how to optimize photovoltage and stability is of utmost concern for the advancement of the field.

Here we report a novel observation of photovoltage loss associated with charge transfer in these metal-oxide protected devices, and by eliminating it, achieve photovoltages as high as 630 mV, the maximum reported to date for single-junction water-splitting silicon cells. The loss mechanism is systematically probed in MOS Schottky junction cells compared to buried junction p⁺n cells, revealing the need to maintain a characteristic hole density at the semiconductor/insulator interface. A capacitor model that predicts this loss is developed, and is related to the dielectric properties of the protective oxide, achieving excellent agreement with the data. From these findings, we extract design principles for simultaneous optimization of charge transfer resistance and interface quality to maximize the photovoltage of metal-oxide protected MOS water splitting devices.

[1] Y.W. Chen, et al. *Nature Mat.* 2011, **10**, 539-544.

[2] A. G. Scheuermann, et al. *Energy Environ. Sci.* 2013, **6**, 2487-2496.

[3] S. Hu, et al. *Science* 2014, **344**, 1005-1009.

Supplemental Figure 1 | Charge transfer in three cell types for water splitting applied to silicon: Shows the Type 0 Semiconductor-Liquid (SL), Type 1 Metal-Insulator-Semiconductor (MIS), and Type 2 p⁺n junction. The density of states on either side of the oxides and the excitation splitting position with respect to these layers play a crucial role in mediating efficient charge transfer. These effects are so strong that Type 0 protected silicon cells exhibit essentially no photovoltage, Type 1 nSi cells show a linear photovoltage loss with oxide thickness, and Type 2 cells--where the hole concentration on the Si/SiO₂ interface is always high--exhibit record photovoltages at all oxide thicknesses and pH values studied.

8:20am **TF+EN-WeM2 Activity and Thermal Stability Enhanced Platinum catalysts with Nano-scale Oxide Coating via Atomic Layer Deposition**, Kun Cao, J.M. Cai, B. Shan, R. Chen, Huazhong University of Science and Technology, Wuhan, China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For most catalytic applications, sintering of Pt NPs is undesired since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs for CO oxidation. The active oxide coated catalysts have additional metal-oxide interfaces which may further improve the catalytic activity besides good sintering resistance. We use cobalt oxide, cerium oxide and nickel oxide as the active oxide encapsulations. Compared with aluminum oxide reference samples, these active oxides have been reported as much better materials with synergetic effect for Pt catalysts. The thickness of the metal oxide film is controlled by varying the number of ALD cycles. CO oxidation measurements were carried out in a micro flow reactor designed for planar model catalysts. Our results indicate that cobalt oxide coated Pt nanoparticles demonstrating the highest activity towards CO oxidation, and the optimal coating thickness is around 1nm. At the same time the coated catalysts have good thermal stability up to 750°C under

atmospheric conditions. The enhancement of catalytic activity may originate from the active oxygen at the Pt/cobalt oxide interface, further Co (II) sites show better synergetic effect compared with Co (III) sites.

8:40am **TF+EN-WeM3 Passivation of Highly-doped c-Si Solar Cell Surfaces by Atomic Layer Deposition**, Bas van de Loo, Eindhoven University of Technology, Netherlands, J. Melskens, Eindhoven University of Technology, G.J.M. Janssen, ECN Solar Energy, K.R.C. Mok, L.K. Nanver, Delft University of Technology, A.H.G. Vlooswijk, Tempres Systems, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) of Al₂O₃ has been successfully implemented in silicon solar cell manufacturing, predominantly to passivate defects at the lowly-doped back surface of p-type solar cells. However, also for the passivation of highly-doped n⁺ or p⁺ type surfaces, present in e.g., high efficiency n-type solar cells, ALD films and stacks might become feasible. Yet, for such surfaces, the level of passivation strongly depends on the doping concentration and surface conditions. To allow for an even wider implementation of ALD-based passivation schemes in industrial solar cells, the work presented in this contribution aims to understand the passivation of highly-doped n⁺ and p⁺ type regions.

First of all, we observed that the passivation of boron-doped (p⁺) Si surfaces highly depends on the doping process and the fixed charge density Q_f in the passivation layer. For instance, when a boron-rich layer (a B₂Si₃ compound) was remained after the doping process, the surface passivation by ALD Al₂O₃ severely deteriorated. The formation of this undesirable layer could be avoided by using an oxidizing ambient during the drive-in of boron, although this results in a significant reduction in boron doping density at the surface. The latter impaired the level of passivation when Q_f was virtually zero, such as for ALD SiO₂/ Al₂O₃ stacks. Importantly, the level of surface passivation offered by ALD Al₂O₃ films remained high under these circumstances, due to the strong negative Q_f.

Next, for phosphorous doped (n⁺) Si surfaces having surfaces densities of 10¹⁸-10²⁰ cm⁻³, the passivation by dielectrics containing a negative Q_f such as ALD Al₂O₃, can be severely compromised, as the negative Q_f increases the minority carrier (i.e., hole-) concentration at and near the surface. Moreover, the negative Q_f can invert the n⁺ Si surface, which triggers (undesirable) increased recombination at low injection levels and parasitic shunting. For those n⁺ Si surfaces, it is demonstrated that ALD stacks such as SiO₂/ Al₂O₃ and HfO₂/ Al₂O₃ are promising alternatives to Al₂O₃ single layers, due to the absence of a negative Q_f. These stacks are particularly interesting from an industrial point of view, as they can make ALD viable for the passivation n⁺ Si surfaces.

Lastly, ALD-based passivation schemes also have the potential to fully replace the heavily-doped n⁺ and p⁺ Si regions in solar cells. In this new field of 'passivating contacts', the significant recombination losses in the highly-doped regions can be avoided due to accurate band-alignment. Preliminary but promising results on novel electron-selective, passivating stacks of HfO₂ and TiO₂ by ALD will also be presented.

9:00am **TF+EN-WeM4 Low Temperature Plasma-Assisted Atomic Layer Deposition of TiO₂ Blocking Layers for Organo-Metal Halide Perovskite Solar Cells**, V. Zardetto, Eindhoven University of Technology, The Netherlands, F. di Giacomo, G. Lucarelli, T.M. Brown, A. di Carlo, S. Licoccia, A. D'Epifanio, University of Rome "Tor Vergata", Italy, W.M.M. Kessels, Mariadriana Creatore, Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) offers accurate control in terms of film thickness, chemical and opto-electrical properties. This is extremely appealing for the novel class of mesoscopic solar cells (SCs), where the several interfaces between the absorber, charge transport layers and electrical contacts require the control of selected charge transfer and charge recombination processes.

Organo-metal halide perovskite SCs presently catalyze the interest in the PV community due to the remarkable increase in device performance in the last three years. Recently, thermal ALD processes have been applied for the deposition of TiO₂ blocking layers (BLs) in glass-based perovskite SCs[1]. Plasma-assisted ALD allows to extend the process window down to temperatures compatible with conductive plastic substrates. Therefore, in this work we investigate the role of plasma-assisted ALD TiO₂ BLs deposited on ITO/PET substrates for a CH₃NH₃Pb_{1-x}Cl_x perovskite SC. The BLs are required to avoid the charge recombination process at the interface between the transparent conductive oxide layer and the perovskite and/or the hole transport layer. They have been prepared [2] in a remote plasma reactor (FlexAL™) at 150 °C using a heteroleptic alkylamido precursor Ti(Cp^{Me})(NMe₂)₂, exposure step alternated with an O₂ plasma exposure.

Very low open circuit voltage ($V_{oc} = 50\text{mV}$) and efficiency ($\eta = 0.01\%$) have been measured in the absence of the blocking layer. In this case, the analysis of dark current-voltage measurements revealed the lack of diode-like behavior and a significant exchange current ($7\text{ mA}\cdot\text{cm}^{-2}$). The introduction of thin TiO_2 layers brought to an increment in all the photovoltaic parameters (J_{sc} , V_{oc} and FF), with a saturation in electrical efficiency for a TiO_2 thickness above 5.5 nm. The saturation in the anodic branch of the JV curve ($V > 0$) for ALD layers thicker than 5.5 nm points out that at this thickness the ALD layer is compact and therefore it suppresses the charge recombination processes. Dark current-voltage measurements have highlighted the decrease of exchange current and dark reverse current ($V < 0$) up to three orders of magnitude with respect to the device without BL. The maximum performance of 9.2% on ITO-PET and 12.9% on ITO-Glass was achieved with 11 nm-thick TiO_2 BL, overcoming the efficiency achieved with conventional sol-gel-deposited TiO_2 BLs (respectively, 4% and 8% on the two substrates).

[1] M. Grätzel, *Nature Materials*, 13, 838–842 (2014).

[2] F. Di Giacomo and V. Zardetto et al, *Adv. Energy. Mater.* 1401808 (2015)

9:20am **TF+EN-WeM5 Ultra-thin transition Metal Oxide-titania Alloy Coatings for Water Oxidation by Atomic Layer Deposition**, *Olivia Hendricks, C.E.D. Chidsey, P.C. McIntyre*, Stanford University

Synthesizing chemical fuels from solar energy requires a source of electrons. The most obvious choice for generating these electrons is the oxidation of water. The oxygen evolution reaction, however, is kinetically challenging, requiring significant overpotentials even with the best noble metal catalysts. At these positive potentials, preserving catalyst stability becomes a key concern. In industrial chlor-alkali electrolysis, which requires similarly positive potentials, the issue of catalyst durability was solved with the development of the dimensionally stable anode (DSA). Today's DSAs consist of a mixed $\text{TiO}_2/\text{RuO}_2$ coating prepared by thermal decomposition of appropriate precursors on a Ti substrate (Over, H. *Chem. Rev.*, 2012, 112, 3356). The TiO_2 imparts stability by preventing Ru dissolution, while the RuO_2 imparts sufficient activity and conductivity to the electrode. We report on the fabrication of an ultra-thin analogue to the DSA by atomic layer deposition (ALD) of ruthenium and TiO_2 . We hypothesize that a conformal ALD coating of this type on nanostructured electrodes can optimize both the catalytic activity and durability for water oxidation while minimizing the use of transition metal components that have very limited Earth-abundance.

Both TiO_2 and Ru can be deposited simultaneously in our ALD reactor. Thus, by changing the relative number of ALD cycles for each precursor, we can achieve precise control of the catalyst content within the films. Preliminary results suggest that enhanced stability is achieved through the alloying process after annealing. The alloyed films also exhibit overpotentials that are competitive with pure ALD-Ru films deposited on a TiO_2 protective layer, even at relatively low Ru content. By decorating the TiO_2 surface with Ru ions at an optimal areal density, ALD alloying has the potential to achieve efficient catalysis of oxygen evolution from water while minimizing usage of the noble metal catalyst.

9:40am **TF+EN-WeM6 Atomic Layer Deposition of Nickel-Iron-Oxide Catalysts for Photoelectrochemical Splitting of Water**, *Adrie Mackus, K.L. Pickrahn, J.G. Baker, S.F. Bent*, Stanford University

The splitting of water to form hydrogen using sunlight as the source of energy has been actively researched in recent years to enable the production of green alternatives to fossil fuels. One of the main challenges in this technology is to develop a photoanode that (i) absorbs sunlight, (ii) has the ability to catalyze the oxygen evolution reaction (OER), (iii) is chemically stable in the aqueous electrolyte, and (iv) is made of earth-abundant materials. A strategy to synthesize an improved photoelectrochemical cell is to decouple these functions by conformally coating (e.g. by atomic layer deposition, ALD) a catalytic and protective layer on a nanostructured light-absorbing material.¹

In this work, we investigate ALD of NiO and NiFe_xO_y films and their use as catalysts for the OER. The material NiFe_xO_y was chosen because it is one of the most promising OER catalysts. The NiFe_xO_y films were deposited using an ALD process that combines NiO ALD (NiCp_2 , O_3) with Fe_2O_3 ALD (FeCp_2 , O_3) in a supercycle. Alternatively, NiFe_xO_y films were prepared by soaking ALD-grown NiO films in Fe-containing KOH electrolyte.² Using the latter approach, the best results were obtained when the electrode was preconditioned in Fe-poor KOH, causing the smooth and compact NiO film to partly exfoliate, which increases the number of electrochemically accessible Ni sites. Synchrotron-radiation X-ray diffraction was employed to investigate the phase of the material as a function of the deposition conditions. Moreover, the catalytic activity of the films for the OER was investigated by cyclic voltammetry (CV). It was found that incorporating Fe

in the NiO films enhances the activity for OER significantly with a 10-fold increase of the turnover frequency.

1. T.M. Gür, S.F. Bent, and F.B. Prinz, *J. Phys. Chem. C* **118**, 21301 (2014)

2. Y.T. Chong, E.M.Y. Yau, K. Nielsch, and J. Bachmann, *Chem. Mater.* **22**, 6506 (2010)

11:00am **TF+EN-WeM10 From Atom to Solid: The Structure of Amorphous ALD Thin Films and Nanolaminates**, *Angel Yanguas-Gil*, Argonne National Laboratory **INVITED**

Atomic Layer Deposition is currently being used for a wide range of energy applications, such as photovoltaics, artificial photosynthesis, energy storage, and power semiconductor devices. In many cases the films are either very thin, well below 10 nm, or either doped or laminate materials, in which a second constituent is intercalated every few cycles.

Given the low deposition temperatures compared to other thin film processes, one of the key questions is how the microstructure of ALD materials differs from their bulk counterparts. This fundamental question of how atoms transition from isolated clusters or single monolayers to a local coordination environment characteristic of the bulk has important technological implications. Answering this question will allow us to better understand the performance of these materials as well as what makes ALD materials different, and in some cases better, to materials synthesized using other techniques.

In this talk I will discuss the impact that chemistry has on the properties and microstructure of very thin ALD films and nanolaminates of oxide dielectrics, semiconductors, and transparent conductors, comprising ZnO , HfO_2 , and $\text{M:Al}_2\text{O}_3$ nanolaminates. By combining synchrotron X-ray characterization techniques such as X-ray Absorption Fine Structure (XAFS) and Pair Distribution Function (PDF) with in-situ techniques such as QCM and FTIR, my talk will focus on two particular problems: the evolution of coordination environment and the emergence of long-range order from the first monolayer and during the early stages of growth, and the impact that the interaction between dopant and host have in the microstructure of doped and laminate materials.

11:40am **TF+EN-WeM12 Inorganic Functionalization of Colloidal Quantum Dot Solar Cells through ALD Infilling**, *Axel Palmstrom, P. Santra, S.F. Bent*, Stanford University

Colloidal quantum dot (CQD) solar cells are of great interest due to the tunable nature of the quantum dot light absorbers through size, composition and interface engineering, together with the potential for low-cost fabrication through solution processing techniques. Lead chalcogenide CQD devices have recently gained traction with rapidly improving efficiencies (>9%). Great strides have been made with organic ligand functionalization of the quantum dot surfaces to enhance CQD transport properties; however, these devices often suffer from poor long-term stability and are still limited by carrier lifetime and mobility. Atomic layer deposition (ALD), a technique that allows for conformal coating of nanostructured surfaces, has been used to improve stability and mobility of CQD solar cells by growing oxides within the quantum dot film. In this work, we explore the inorganic functionalization of CQD solar cells through combinations of ALD materials, including Al_2O_3 , ZnO , NiO and other oxide materials, in thin (~30 nm) devices to ensure infilling throughout the entire device. With the proper choice of ALD oxide, short circuit current density and overall efficiency could be enhanced by 70% and 10% respectively relative to the non-infilled control CQD device. We will discuss the effects of ALD inorganic functionalization on surface passivation and carrier mobility as well as methods to implement ALD infilling on thicker devices in order to ultimately push the limits of CQD solar cell performance.

12:00pm **TF+EN-WeM13 Integrating Atomic Layer Deposited Lithium-Containing Thin Films for Lithium-ion Battery Applications**, *J. Cho, Trevor Seegmiller, J. Lau, L. Smith, J. Hur, B. Dunn, J.P. Chang*, University of California at Los Angeles

Lithium-ion (Li-ion) batteries have demonstrated their performance in portable electronics for many years. Li-ion batteries also have the potential to be miniature power sources for microelectromechanical systems (MEMS) through 3-dimensional (3D) battery architectures. In order to fabricate a fully functional 3D Li-ion microbattery, an ultra-thin, highly conformal electrolyte layer is required to fully coat 3D electrodes. Lithium aluminosilicate ($\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$, LASO), a solid oxide Li-ion conductor, synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications due to its adequate ionic conductivity ($1 \times 10^{-7}\text{ S/cm}$) in thin film applications as well as improved electrode stability.

The self-limiting nature of ALD allows precise thickness and composition control when applied to complex metal oxides. This results in a highly conformal and pinhole-free coating on complex structures, including high

aspect ratio 3D electrodes. Lithium tert-butoxide (LTB), trimethylaluminum (TMA), tris(tert-butoxy)silanol (TTBS), and tetraethylorthosilicate (TEOS) were precursors used to synthesize LASO by ALD. LASO films ranging in thickness from 6 to 12 nm exhibited Li-ion conductivity from 8.2×10^{-8} to 1.4×10^{-9} S/cm. The LASO films were also deposited on anode and cathode materials for evaluating their integration into solid state Li-ion batteries. A Li-ion half-cell consisting of LASO-coated 2D carbon anode showed reversible electrochemical behavior with coulombic efficiency reaching 98%.

Current research on Li-ion batteries is directed at creating next generation anode materials. Both silicon and germanium have received considerable study due to their high theoretical volumetric capacity (8444 A h L^{-1} for $\text{Li}_{15}\text{Si}_4$ and 7366 A h L^{-1} for $\text{Li}_{15}\text{Ge}_4$ respectively). Upon lithium intercalation, however, these anode materials undergo large volumetric expansion (~300% for Si) which compromises their mechanical integrity. We have started to carry out *in situ* transmission electron microscopy (TEM) studies in which the structural effects of lithium intercalation and deintercalation on silicon/germanium (Si/Ge) alloy nanowires conformally coated with LASO electrolyte are characterized. These *in situ* TEM studies show 40% radial expansion of the $\text{Si}_{0.4}\text{Ge}_{0.6}$ alloy upon lithium intercalation, and morphological changes upon deintercalation, with the LASO film preserved on the nanowire.

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