ALD Applications
Room Grand Ballroom A-C - Session AA2-MoA

ALD for Solar Cells, Fuel Cells, and H_2 Storage

Moderators: Christophe Detavernier, Ghent University, Belgium, Nicholas Strandwitz, Lehigh University

4:00pm **AA2-MoA-11 Nucleation Layer for Atomic Layer Deposition Enabling High Efficiency and Flexible Monolithic All-Perovskite Tandem Solar Cells**, *Axel F. Palmstrom, G Eperon, T Leijtens,* National Renewable Energy Laboratory*; R Prasanna,* Stanford University*; S Nanayakkara, S Christensen, K Zhu,* National Renewable Energy Laboratory*; M McGehee,* University of Colorado Boulder*; D Moore, J Berry,* National Renewable Energy Laboratory

The emergence of metal halide perovskites as high efficiency, low-cost photovoltaic materials with a tunable band-gap has led to significant interest for perovskite-based tandems. Of existing perovskite-based tandem technologies, pairing wide-gap and low-gap perovskites in a monolithic all-perovskite tandem arguably offers the greatest potential by enabling efficiencies beyond the single-junction Shockley-Queisser limit with low-cost solution processing on a flexible, lightweight substrate. As of yet, efficiency of all-perovskite monolithic tandems has lagged behind perovskites paired with silicon or CIGS despite significant improvement to low-gap perovskite materials. A barrier to effectively combining state-of-the-art wide and low band gap perovskites in a monolithic tandem is the lack of a high-quality recombination layer that sufficiently protects an underlying perovskite thin-film to enable subsequent perovskite solution processing and minimal device shunting.

In this work, we aim to understand metal oxide growth by low-temperature atomic layer deposition (ALD) on C_{60} to develop improved recombination layers for all-perovskite 2T tandems. The effect of C_{60} surface modification with ultra-thin nucleophilic-containing materials is studied on ALD nucleation, growth, and film properties. We show, for multiple ALD systems, nucleophilic surface modification improves the water and dimethylformamide barrier properties of the grown oxide film. This strategy enables the fabrication of improved ALD recombination layers that are thinner and less laterally conductive (reduced shunting) than currently reported strategies. We demonstrate ALD-grown aluminum-doped zinc oxide (AZO) as an effective recombination layer for two-terminal all-perovskite tandems with efficiencies over 23% for rigid devices and 21% for flexible devices.

4:15pm **AA2-MoA-12 Perovskite Solar Cells Fabricated using Atomic Layer Deposited Doped ZnO as a Transparent Electrode**, *Louise Ryan,* M McCarthy, S Monaghan, M Modreanu, S O'Brien, M Pemble, I Povey, Tyndall National Institute, Ireland

Power conversion efficiencies of perovskite (PK) solar cells have rapidly improved in recent years obtaining efficiencies in excess of 20% [1]. Good absorption properties in the visible and infrared spectrum, high efficiencies and low fabrication costs have brought PK solar cells to the forefront. With single junction PK solar cells soon reaching theoretical efficiency limits a requirement for tandem cells, where materials of differing absorption characteristics convert a wider spectral range, is in demand. However, such tandem solar cells introduce fabrication complexities due to the thermal budget restrictions imposed by the complex layer structure [2].

Fluorine-tin oxide (FTO) and indium-tin oxides (ITO) are widely used transparent contacts in solar cells. However, the high deposition temperatures and energetic processes required for its production are detrimental to the fabrication of delicate perovskite based tandem solar cells and thus the need to find an alternative TCO is vital.

Here we have considered Ti-doped ZnO, produced by a ALD laminate doping method, as an alternative transparent contact and have incorporated it into perovskite solar cells in conjunction with an ALD-grown SnO_2 electron transport material. Detailed analysis of the influence of the growth process on the performance of the Ti-doped ZnO electrode is presented. Finally, the efficiency of the optimised perovskite solar cells are evaluated relative to the current state of the art.

[1] NREL: Efficiency Chart (2018). Https://www.nrel.gov/pv/assets/pdfs/pv-efficiencies-07-17-2018.pdf

[2] F. Sahli, et al.*, Nature Materials, 17(9) (2018) 820-826.

4:30pm **AA2-MoA-13 Metal Oxide Barrier and Buffer Layers by Atomic Layer Deposition and Pulsed-Chemical Vapor Deposition for Semi-Transparent Perovskite Solar Cells**, *Helen Hejin Park, T Eom, R Agbenyeke, S Yeo, G Kim, S Shin, T Yang, N Jeon, Y Lee, C Kim, T Chung, J Seo,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

For *n-i-p* structured semi-transparent perovskite solar cells, thermal evaporation has been a common technique to deposit the sputter buffer material, such as molybdenum oxide and tungsten oxide, to protect the organic hole transporting layer (HTL) from damage due to sputtering of the transparent conducting oxide. However, thermal evaporation does not guarantee stoichiometric and uniform pinhole–free coverage of films, leading to inefficient protection against sputtering and poor air stability. While there have been well-established buffer materials by atomic layer deposition (ALD), such as SnO_2, for *p-i-n* structured semi-transparent perovskite solar cells, this is not the case for *n-i-p* structured devices. In addition, thermal evaporation has also been commonly used to deposit a barrier layer at the perovskite/HTL interface to improve the fill factor and open-circuit voltage, however, ALD can provide more precise control and conformal coverage for this layer. In this presentation, we demonstrate metal oxide deposition techniques by pulsed-chemical vapor deposition and ALD in perovskite solar cells for the sputter buffer and barrier layers, which result in efficiencies over 16% for semi-transparent devices. Effects of the optical and electrical properties of barrier/buffer layers on the performance of working devices will be addressed, and the mechanisms involved in the enhanced performance and stability will also be discussed.

4:45pm **AA2-MoA-14 Particle Atomic Layer Deposition of Tungsten Nitride Environmental Barrier Coatings from Bis(t-butylimido)bis(dimethylamino)tungsten(VI) and Ammonia**, *Sarah Bull, A Weimer,* University of Colorado - Boulder

Ultra-thin tungsten nitride (WN) films were deposited by atomic layer deposition (ALD) on zirconia nanoparticles and yttria stabilized zirconia (YSZ) micropowders using a fluidized bed reactor. The film's intended use as a hydrogen barrier coating motivated the investigation of hydrogen diffusion in W using density functional theory (DFT) and differential thermal analysis (DTA). The lowest energy diffusion pathway was determined and the hydrogen charges at various sites along the pathway were calculated. DTA was used to investigate the efficacy of the W/WN films in preventing hydrogen attack. The temperature at which hydrogen reacted with the sample increased with film thickness, thereby indicating that the film inhibited this reaction. However, the existence of a hydrogen reaction peak in the thicker film indicated a material with greater than 2.0 eV energy barrier is necessary for a substantial decrease in hydrogen interaction with the substrate. This is the first study for ALD of WN on particles from bis(t-butylimido)bis(dimethylamino)tungsten(VI) and the use of ultrathin WN ALD films as environmental barrier coatings (EBCs) for high-temperature H_2 above 1000°C.

5:00pm **AA2-MoA-15 Atomic Layer Deposition on $Mg(BH_4)_2$: A Route to Improved Automotive H_2storage**, *Noemi Leick,* National Renewable Energy Laboratory*; K Gross,* H2 Technology Consulting LLL*; T Gennett, S Christensen,* National Renewable Energy Laboratory

In order to meet the U.S. Department of Energy requirements for on-board solid-state hydrogen (H_2) storage in fuel-cell powered vehicles, metal borohydrides are of particular interest. However, while materials such as magnesium borohydride, $Mg(BH_4)_2$, have a hydrogen capacity up to ~14wt%, challenges associated with hydrogenation-dehydrogenation cyclability need to be overcome. Specifically, improve the operating temperatures for adsorption/desorption; increase the hydrogen absorption-desorption kinetics; and eliminate the formation of the toxic diborane (B_2H_6). Prior research has indicated that nano-encapsulation (*e.g.* through graphene nanosheets) and chemical additives (*e.g.* catalysts) are areas of significance to address these challenges.

This work is the first to approach these two strategies simultaneously using atomic layer deposition (ALD). ALD coatings have been shown to protect and enhance heterogeneous catalyzed rates, as well as to precisely control the amount of chemical additive incorporated. In this project, metal-oxides (*e.g.* Al_2O_3, TiO_2, CeO_2), metal-nitrides (*e.g.* TiN, BN), pure metals (*e.g.* Ru, Pd) and combinations thereof were deposited by ALD on γ-$Mg(BH_4)_2$. We investigated how the deposition temperature, the use of water for some of these ALD processes and the composition of the additive affected the H_2storage properties of γ-$Mg(BH_4)_2$.

Compared to uncoated γ-$Mg(BH_4)_2$, we found that the ALD depositions lowered the H_2desorption temperature by 60–120 ˚C, doubled the desorbed gravimetric H_2capacity at temperatures below 250˚C, increased

the desorption kinetics by a factor of ~6, and suppressed the formation of B_2H_6 substantially during the dehydrogenation step. The ALD-modified γ-$Mg(BH_4)_2$was also explored with respect to the structure, the effects of the total hydrogen capacity, and catalytic effects. In this presentation we will discuss data supporting these results from temperature programmed desorption, pressure composition temperature manometric measurements, inductively coupled plasma mass spectrometry, nitrogen physisorption measurements, nuclear magnetic resonance, transmission electron microscopy and diffraction spectroscopy.

5:15pm **AA2-MoA-16 Plasmonic Mediated Hydrogen Desorption from Metal Hydrides**, *Katherine Hurst*, *A Gaulding, M Martinez, N Leick, S Christensen, T Gennett,* National Renewable Energy Laboratory

Excitation of plasmonic coatings deposited by atomic layer deposition (ALD) can provide important routes for tuning the performance of gas adsorption and desorption of hydrogen storage materials. Currently available hydrogen fuel-cell vehicles systems rely on hydrogen stored in compressed tanks at 700 bar. While this hydrogen storage system is partially fostering early-market deployment, the compressed gas system presents several practical challenges and expenses related to infrastructure and delivery that could limit widespread adoption. Metal hydrides are an important class of materials that can reach DOE system capacity targets for hydrogen storage. However, the gas uptake and release of hydrogen by metal hydrides requires high pressures and temperatures, and exhibits slow kinetics. It is well known that modification of a bulk hydride to the nanoscale phase, and the addition of catalyst additives can both greatly enhance the kinetics, lower operating temperatures, and increase cyclability. This work takes a unique route to alter the process of desorption through the incorporation of plasmonic materials into the hydride matrix. This allows for low-power-LED-illuminated systems to achieve the same rates of hydrogen desorption as radiative thermal heating

Specifically, recent work at the National Renewable Energy Laboratory has applied ALD to enable the use of plasmonic material coatings to alter the mechanism for hydrogen desorption. Through localized heating via surface plasmon excitation, the bulk thermal signature for hydrogen release can be significantly reduced. Furthermore, hydrogen desorption induced via plasmonic heating offers a completely new approach to using hydride materials. Temperature programmed desorption spectroscopy is used to monitor the kinetic changes associated with desorption by varying the conditions and type of plasmonic material introduced. The effects of partial coverages, ALD film thickness and crystallinity on the resonant plasmonic frequency are explored. This presentation will discuss advancements in enabling gas desorption via plasmonic excitation especially with respect to hydrogen carrier applications. These exciting results also point towards new applications for ALD in nano-scale photo-thermal processes.

5:30pm **AA2-MoA-17 Surface Modification of Solid Oxide Fuel Cell Cathodes by Atomic Layer Deposition**, *Dong Hwan Kim*, *H Choi, J Koo,* Korea University, Republic of Korea*; J Park, J Son,* Korea Institute of Science and Technology (KIST), Republic of Korea*; J Shim,* Korea University, Republic of Korea

Development of high-performance cathode is key to the commercialization of solid oxide fuel cells (SOFCs). Doped perovskite-type oxides including lanthanum strontium cobaltite (LSC) and lanthanum strontium cobalt ferrite (LSCF) are the most typical materials in practical SOFCs. However, degradation of LSC and LSCF from dynamic on-off operation at high temperature (600-1000 ºC) has been considered as the most serious technical obstacle. Many kinds of literature have reported that segregation of cations near the cathode surface leads to this degradation. Specifically, the A-site element of the cathode perovskite is subjected to electrostatic attraction to the surface due to excess oxygen vacancies on the cathode surface, which brings out the A-site element to segregate on the surface [1]. To solve this problem, we have proposed surface modification by atomic layer deposition (ALD) [2]. In this study, 1-4 cycles of ALD Al2O3 has been attempted on porous LSC to suppress the cation segregation and improve the surface redox kinetics. Performance of SOFCs with the ALD Al2O3-treated LSC cathodes has been evaluated in I-V-P and impedance. Finally, long-term stability at 500-600 °C has been examined in the potentio -static mode. In this presentation, the progress of this research will be shared in details.

[1] Cai et al. Chemistry of materials 24.6 (2012): 1116-1127.

[2] Choi et al. Advanced Energy Materials 8.33 (2018): 1802506.

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