

Thin Films

Room 115 - Session TF1-MoM

Thin Films for Energy Applications I: Green Fuels and Photovoltaics

Moderators: Alexander Kozen, University of Vermont, Blake Nuwayhid, Naval Research Laboratory

8:15am TF1-MoM-1 Unravelling the Role of Stoichiometry of ALD Oxygen Evolution Electrocatalysts on Their Activity, *Mariadriana Creatore*, Eindhoven University of Technology, The Netherlands **INVITED**

Production of green hydrogen is a key contributor to the energy transition, and the synthesis of cost-effective, earth-abundant oxygen evolution reaction (OER) electrocatalysts for H₂O splitting is presently subject of major investigation. In this contribution I will address the synthesis of two electrocatalysts, i.e., cobalt phosphate (CoPi) and nickel cobalt oxide (NCO), by plasma-assisted atomic layer deposition and discuss the merit of digital control over film stoichiometry to generate insight on the activation mechanisms of these electrocatalysts.

CoPi is prepared by combining ALD cycles of CoO_x from cobaltocene (CoCp₂) and O₂ plasma, with cycles of trimethylphosphate ((CH₃O)₃PO) followed by O₂ plasma. We show that the CoPi films undergo activation with increasing number of cyclic voltammetry (CV) cycles. During activation, the current density increases in parallel with a progressive leaching of phosphorous out of CoPi. These chemical changes proceed along with structural changes: measurements of the electrochemical surface area (ECSA) reveal that during activation, the ECSA of the film increases and that the electrochemical activity scales linearly with ECSA for all film compositions. Thus, the initial composition indirectly affects the activity of the catalyst by steering its restructuring during cycling and the ECSA is the sole parameter determining the activity of CoPi.

The second study addresses an ALD super-cycle based on CoCp₂ and nickel methylcyclopentadienyl (Ni^{(Me)Cp})₂ and an O₂ plasma. We observe a phase transition from Ni-rich rock-salt films to Co-rich spinel films at ~55 at.% Co. The transition is accompanied by an increase in the +3-to-+2 oxidation state ratio of the metal centers. Electrochemical analysis discloses a synergistic effect between Co and Ni metal centers, such that NCO films are more OER-active than Co₃O₄ and NiO. Moreover, rock-salt films continuously form an hydroxide phase during CV cycling, resulting in prolonged activation such that an optimal overpotential of 470 mV is observed for the 30 at.% Co film after 500 cycles. Instead, the presence of Co limits the bulk hydroxide formation, such that a constant performance at an overpotential of ~500 mV is observed for the spinel films. The activation process occurs in parallel with an increase in ECSA up to a factor 8 for rock-salt films. The improved OER activity of rock-salt films upon electrochemical activation indicates that the low-cobalt content films are a sustainable alternative to the more commonly investigated cobalt-rich films.

8:45am TF1-MoM-3 Stability of CsPbBr₃ Employing an Ultrathin Al₂O₃ Protective Layer, *F. Quintero-Borbon*, Centro de Investigación en Materiales Avanzados SC, Unidad Monterrey, Mexico; *J. Roy, L. Izquierdo-Fernandez, R. Wallace, M. Quevedo-Lopez*, Department of Material Science and Engineering, University of Texas at Dallas; *Francisco S. Aguirre-Tostado*, Centro de Investigación en Materiales Avanzados SC, Unidad Monterrey, Mexico

Lead halide perovskite nanocrystals, such as CsPbBr₃, have gathered significant interest due to their attractive optical properties and cost-effective production. However, their environmental stability remains a major challenge, hindering practical applications and scalability for commercialization. In this study, we propose an effective method to enhance the stability of CsPbBr₃ by depositing an ultrathin Al₂O₃ film using atomic layer deposition (ALD). The CsPbBr₃ was deposited on a glass substrate using closed space sublimation (CSS) from a 1:1 molar ratio of PbBr₂ and CsBr previously mixed powders. The Al₂O₃ was deposited from a TMA and H₂O sources using thermal ALD. This unique single layer protection structure significantly improves their resistance to moisture, and polar solvents. Notably, the modified surface exhibits chemical stability and stable photoluminescence (PL) intensity compared to the ordinary CsPbBr₃ surface. Additionally, X-ray photoelectron spectroscopy analysis shows a chemically abrupt Al₂O₃/CsPbBr₃ interface with high stability with respect to the water-soaked CsPbBr₃ surface. This research presents a promising approach for developing stable perovskite thin films with enhanced performance in various optoelectronic devices.

9:00am TF1-MoM-4 Deposition of Yb-doped Double Halide Perovskite Cs₂AgBiCl₆ for High-Efficiency Downconversion of Ultraviolet Photons, *Pulkita Jain, M. Tran, I. Cleveland, Y. Liu, S. Sarp, E. Aydil*, New York University

Halide perovskites, particularly those containing lead such as CsPbX₃ (X=Cl, Br, I), have emerged as a new class of materials for applications in optoelectronics. However, the toxicity of lead necessitates the pursuit of lead-free alternatives. Bismuth-based halide double perovskite Cs₂AgBiCl₆ has emerged as a promising candidate, but there are still conflicting reports and interpretations regarding this material's optical properties, such as its bandgap and the origin of its characteristic high-intensity visible orange emission. Here, we report on synthesizing Cs₂AgBiCl₆ thin films through reactive thermal evaporation and address these discrepancies. Specifically, we deposited Cs₂AgBiCl₆ thin films by co-evaporating CsCl, BiCl₃, and AgCl onto glass substrates, which, upon reaction on the substrate, yielded polycrystalline thin films. Film thickness and stoichiometry were controlled by controlling the evaporation fluxes of the precursors using quartz crystal microbalances. Typical film thicknesses were 100-400 nm. Optical characterization analysis of the thin films reveals a bandgap of 2.77 eV. X-ray diffraction (XRD) and Raman spectroscopy were used to verify the phase purity and structure of the perovskite as well as impurity phases when present. Steady-state and time-resolved photoluminescence (TRPL) measurement of emission lifetime gave insights into the origin of the orange visible emission. We propose a mathematical model of emission kinetics considering both defect and self-trapped exciton emissions. The high-fidelity fitting of the data with only a few adjustable kinetic parameters suggests both defect and self-trapped exciton emissions may be present, and their contributions may depend on the synthesis conditions, possibly settling the debate in the literature. We also doped the Cs₂AgBiCl₆ perovskite with Yb by co-evaporating YbCl₃ during film deposition to explore the possibility of downconversion and quantum cutting, the generation of two near-infrared photons from one ultraviolet (UV) photon. The perovskite host absorbs the UV photon and transfers its energy to Yb, which then relaxes (²F_{5/2}→²F_{7/2}) and emits photons (1.25 eV) in the near-infrared. Doping with Yb resulted in a photoluminescence quantum yield (PLQY) of 50%, the highest reported in the literature for Cs₂AgBiCl₆. We investigated various post-deposition treatments, such as annealing in air versus in a nitrogen-filled environment, and concluded that annealing in air, in the presence of moisture, results in the formation of bismuth oxychloride (BiOCl), confirmed by XRD and Raman spectroscopy. We hypothesize that BiOCl passivates non-radiative defects, aiding in achieving high PLQY.

9:15am TF1-MoM-5 Low-cost Grown a-Si:H Using Trisilane and its Application to Post Deposition Processes, *Benedikt Fischer, M. Nuys, S. Haas, U. Rau*, Forschungszentrum Jülich GmbH, Germany

Hydrogenated amorphous silicon (a-Si:H) films are used in a wide range of semiconductor devices. Especially in the current highly efficient solar cell techniques named silicon heterojunction (SHJ) solar cells and tunnel oxide passivated contact (TopCon) solar cells, they are used directly as passivation layer or as a precursor for recrystallized silicon films, respectively. However, for the growth of the a-Si:H films, techniques like plasma enhanced chemical vapor deposition or electronic beam evaporation with expensive vacuum technology are used. Here we show a new setup for the deposition of a-Si:H by atmospheric pressure chemical vapor deposition using liquid trisilane allowing a fast and cost-effective deposition process. By varying the deposition temperature, time and precursor amount we could set the H-content of the films to 0 - 10 %_{vol} and achieved a maximum photosensitivity of 10⁴ with a photoconductivity of 10⁻⁷ S/cm. By applying post deposition H treatments, a photoconductivity of 5 × 10⁻⁶ S/cm could be achieved, leading to a photosensitivity of almost 10⁵. The low H-content of the films allows annealing without blistering of the samples, especially for the films grown at a substrate temperature of ≥ 500°C. Therefore, we applied rapid thermal annealing to the films and achieved recrystallized silicon with conductivities up to 10⁻¹ S/cm. The results show that the as deposited thermally grown films already have a high film quality, indicated by the high photosensitivity. The application of post H-treatment can further improve the film quality, approaching the photosensitivity of high quality PECVD films. Both photoconductivity and photosensitivity can be further increased by improving the hydrogenation process, which was not optimized yet. In addition, the high conductivity achieved by the rapid thermal annealing experiments in comparison with state-of-the-art films show the applicability in TopCon solar cells. Further investigations regarding film doping and application of the polysilicon films for the passivation in combination with a tunnel oxide are in progress. These results, and the fact

Monday Morning, November 4, 2024

that the films were produced by a low-cost deposition system, make them highly promising for an industrial application in solar cells.

9:30am TF1-MoM-6 Optimization of DC Reactive Sputtering of NiO_x Transport Layer and Effects of Annealing Conditions on NiO_x film for Perovskite Solar Cells, *Firdos Ali, S. Gupta*, University of Alabama

DC reactively sputtered NiO_x was optimized as a hole transport layer for perovskite solar cell applications. We introduced the reactively sputtered NiO_x hole transport layer over a spin-coated NiO_x layer in solution-processed perovskite (MeO-2PACZ/MAPBI3-XClx) solar cells. The typical reactive hysteresis effects were not observed on the cathode voltage while varying the reactive gas flow during deposition, and this case may be explained by Berg's hysteresis model. We have investigated the unusual hysteresis behavior of the cathode voltage as a function of oxygen flow rate in argon, and correlated this with the deposition rate. The NiO_x films were infrared lamp annealed at various temperatures at high vacuum. Perovskite solar cells were fabricated using a solution processing method. A parallel set of devices were fabricated using hot-plate annealing of the NiO_x hole transport layer in atmosphere. The NiO_x thin films were structurally characterized using a variety of techniques: scanning electron microscopy (SEM), X-ray reflectivity (XRR), and X-ray diffraction. SEM studies were carried out to observe the surface morphology of the NiO_x film. A continuous film of NiO_x was observed at higher oxygen flows and lower deposition rates. XRD analysis on ITO/NiO_x thin films sputtered with various oxygen flows was carried out to study the crystal orientation and crystallinity. The effects of sputtered NiO_x deposition rate, film thickness, as well as annealing conditions on the solar cell efficiency were investigated. The power conversion efficiency was improved from 5% to 13.5 %.

9:45am TF1-MoM-7 Optimizing Sputtered Nickel Oxides as Hole Transport Layers and Their Applications for Perovskite Solar Cells, *Jae Won Kim, M. Kim, S. Lee*, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Nickel oxide (NiO_x) has garnered attention as an efficient hole transport layer (HTL) in perovskite solar cells (PSCs) due to its wide bandgap, which effectively blocks electron transfer, a compatible work function that aligns well with the energy levels of perovskite (PVK) materials, and adequate carrier mobility. This study explores the significant impact of NiO_x layer thickness on the electrical characteristics and efficiency of PSCs. The NiO_x layers were deposited using radio-frequency (RF) magnetron sputtering, a technique chosen for its capability to provide uniform thin films over large areas. By experimenting with NiO_x thicknesses ranging from 5 to 30 nm, it was determined that a 10 nm thick NiO_x layer yields the best performance.

Devices incorporating this optimal thickness demonstrated improved charge carrier extraction and transport properties, essential for achieving high-efficient PSCs. Photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements provide deeper insights into the charge dynamics within the PSCs. These analyses confirm that the 10 nm NiO_x layer facilitates a lower recombination rate and more efficient charge separation compared to thicker or thinner layers. Supporting these findings, transient photovoltage and photocurrent studies indicate faster charge extraction and prolonged carrier lifetimes, which contribute to higher power conversion efficiencies.

Moreover, energy band alignment investigations, including Hall measurement and ultraviolet spectroscopy, reveal that the 10 nm NiO_x layer optimizes charge transport from the perovskite layer to the HTL. The energy level offset between the valence band of NiO_x and PVK typically shows negative values, implying charge blocking at the interface; however, the 10 nm NiO_x layer displayed a minimal offset of 0.04 eV, resulting in efficient charge transport.

This paper significantly contributes to the field of photovoltaic research by highlighting the critical role of RF-sputtered NiO_x layer thickness in optimizing the performance of inverted PSCs. The findings suggest that precise control over the deposition of HTLs can lead to substantial improvements in PSCs efficiencies, offering a promising avenue for the development of more effective renewable energy technologies.

10:00am TF1-MoM-8 Tunable Sn_xS_y Deposition onto Functionalized Alkanethiolate Self-Assembled Monolayers by Chemical Bath Deposition, *Christopher Brewer, R. Woolard, T. Estrada, A. Walker*, University of Texas at Dallas

Tin sulfides (Sn_xS_y) are non-toxic and inexpensive materials with low band gaps, making them suitable for semiconductor applications and photovoltaic materials, such as solar cells. Sn_xS_y has three naturally occurring compositions, SnS, Sn₂S₃, and SnS₂, each with different

properties. The ability to control the stoichiometry of a Sn_xS_y deposit is of interest for devices like SnS solar cells, where Sn₂S₃ contamination reduces the device efficiency. Chemical bath deposition (CBD) is a low cost and scalable technique that can be used under ambient conditions to deposit Sn_xS_y onto a variety of substrates, including organic substrates. Alkanethiolate self-assembled monolayers (SAMs), functionalized with -CH₃, -OH, and -COOH terminal groups, are a readily available system, which can be used as a model organic substrate for deposition of Sn_xS_y by CBD. A CBD bath has multiple tunable components, including the solution pH, complexing agent, bases used, and sulfur source as the most common. Modification of any of the bath components, as well as the SAM functionalization, can control the deposit's major composition and phase. Using a mechanism based approach, we have been able to tune the bath chemistry to yield pure SnS deposits.

Author Index

Bold page numbers indicate presenter

— A —

Aguirre-Tostado, F.: TF1-MoM-3, **1**

Ali, F.: TF1-MoM-6, **2**

Aydil, E.: TF1-MoM-4, **1**

— B —

Brewer, C.: TF1-MoM-8, **2**

— C —

Cleveland, I.: TF1-MoM-4, **1**

Creatore, M.: TF1-MoM-1, **1**

— E —

Estrada, T.: TF1-MoM-8, **2**

— F —

Fischer, B.: TF1-MoM-5, **1**

— G —

Gupta, S.: TF1-MoM-6, **2**

— H —

Haas, S.: TF1-MoM-5, **1**

— I —

Izquierdo-Fernandez,, L.: TF1-MoM-3, **1**

— J —

Jain, P.: TF1-MoM-4, **1**

— K —

Kim, J.: TF1-MoM-7, **2**

Kim, M.: TF1-MoM-7, **2**

— L —

Lee, S.: TF1-MoM-7, **2**

Liu, Y.: TF1-MoM-4, **1**

— N —

Nuys, M.: TF1-MoM-5, **1**

— Q —

Quevedo-Lopez, M.: TF1-MoM-3, **1**

Quintero-Borbon, F.: TF1-MoM-3, **1**

— R —

Rau, U.: TF1-MoM-5, **1**

Roy, J.: TF1-MoM-3, **1**

— S —

Sarp, S.: TF1-MoM-4, **1**

— T —

Tran, M.: TF1-MoM-4, **1**

— W —

Walker, A.: TF1-MoM-8, **2**

Wallace, R.: TF1-MoM-3, **1**

Woolard, R.: TF1-MoM-8, **2**