Thin Films
Room 206 B W - Session TF2-MoA
Thin Films for Energy II

Moderators: Marianna Kemell, University of Helsinki, Finland, **Alexander Kozen**, University of Vermont

4:00pm **TF2-MoA-11 Interface Engineering for the Highly Efficient Antimony Chalcogenides Thin Film Energy Devices*, Feng Yan,*** Arizona State University **INVITED**

Antimony chalcogenide (Sb_2X_3, X=S, Se, Te) thin film solar cells have garnered significant interest due to their optimal bandgap, high absorption coefficient, and earth-abundant constituent elements. Interface engineering plays a pivotal role in optimizing the performance of these solar cells, as the interfaces between different layers critically influence charge carrier dynamics. This talk focuses on systematically investigating and engineering interfaces in Sb_2X_3-based thin film solar cells to enhance their efficiency and stability. Precise control over interface properties was achieved by employing techniques such as sputtering and chemical bath deposition (CBD). The introduction of buffer layers, passivation treatments, and surface modifications were explored to mitigate recombination losses and improve charge extraction. Advanced characterization methods including X-ray photoelectron spectroscopy (XPS), were utilized to analyze the interfacial properties and their impact on device performance. The findings highlight the critical importance of interface quality and the potential of tailored interface engineering to unlock higher efficiencies in antimony chalcogenide thin film solar cells. This work provides a pathway for further optimization and commercial viability of Sb2X3 solar cells, contributing to the advancement of sustainable photovoltaic and photoelectrochemical technologies.

4:30pm **TF2-MoA-13 Developing R32 Barium Nickelate Thin Films for Catalysis*, Ian Graham,*** Georgia Institute of Technology*; Kayla Chuong, Anna Österholm, Lauren Garten,* Georgia Institute of Technology, USA

The oxygen evolution reaction (OER) is the rate limiting step inhibiting the production of fuel from water.[1,2] Barium nickelate (BNO) is a promising catalyst, due to a tunable oxygen stoichiometry without significant structural changes to the crystalline phases. Tuning oxygen stoichiometry in transition metal oxides can modulate the band structure and increase catalytic activity.[3] The *R*32 phase of BNO is proposed to exhibit increased OER catalytic activity due to a theoretically predicted e_g orbital filling of Ni near the optimal value of 1.2 for OER.[1] However, the range of stoichiometries, and therefore Ni oxidation states, that the *R*32 phase of BNO can exhibit are not yet known.

Here, we stabilized the *R*32 phase of BNO in thin films using a $BaNi_{0.93}O_{2.68}$ target by pulsed laser deposition (PLD) on (0001) Al_2O_3 substrates. The films were deposited at a substrate setpoint temperature of 400 °C, oxygen partial pressures ranging from 0.012-0.091 mbar, and a laser fluence of 2.5 J/cm^2. X-ray diffraction shows that the films are solely (100) oriented and only the *R*32 phase is observed over this range of partial pressures. Energy dispersive X-ray spectroscopy reveals that the film stoichiometries range from $BaNi_{1.10}O_{2.26}$ to $BaNi_{1.03}O_{2.14}$. The range of stable oxygen stoichiometries is further increased by post annealing in an oxygen atmosphere beyond those available by PLD. X-ray photoelectron spectroscopy indicates the presence of Ni^{2+}, Ni^{3+}, and Ni^{4+}. Four-point probe measurements show an increase in resistivity with increasing oxygen stoichiometry; decreasing oxygen stoichiometry to $BaNi_{1.03}O_{2.14}$ resulted in a conductivity of 0.161 S/m. Then films were deposited on conductive (111) Nb:$SrTiO_3$ substrates for impedance spectroscopy, dielectric, and piezoelectric measurements. The piezoelectric response was measured using laser doppler vibrometry in an $e_{11,f}$ wafer flexure system. Impedance spectroscopy results further show the role of oxygen vacancies migration on the electronic and ionic conductivity.

References

1) Lee et al., *J. Am. Chem. Soc.* **2016**, 138 (10), 3541–3547.

2) Plevová et al., *Journal of Power Sources* **2021**, 507, 230072.

3) Wang et al., *ACS Catal.* **2018**, 8 (1), 364–371.

4:45pm **TF2-MoA-14 Exploring the Effect of Dopant Proximity to the Electrolyte-Surface Interface on the Activity and Selectivity of Metal Oxide Anodes for Water Oxidation*, Jacob Kupferberg,*** *Igor Messias, Pietro Papa Lopes, Alex Martinson,* Argonne National Laboratory

The activity and selectivity of water oxidation catalysts is dependent on the available active sites at the electrolyte-catalyst interface. In doped metal oxide systems, enhancements in activity and selectivity can result from either the replacement of host matrix surface sites with dopant atoms or from the influence of buried dopants on the surface. In this study, we use atomic layer deposition to control the depth of a single layer of dopant buried in a comparatively inert metal oxide matrix like TiO_2 or SnO_2. The dopants used include MnO_x and Fe_2O_3, materials that have been characterized by a high activity for the 4-e^- water oxidation. Annealing was found to be a critical processing step to enable the dopant to enhance the activity of the electrode. The water oxidation activity of the electrode diminished linearly with dopant depth until the material activity was identical to that of the host matrix. This change in activity occurred despite the maintenance of a stable reversible set of peaks in CV corresponding to the redox behavior of the dopant material. The reversibility of these peaks was rather correlated to the overall thickness of the catalyst film. Increasing the thickness of the catalyst film reduced overall activity but also enhanced the stability of the catalyst at higher applied potentials. It was also found that the coverage of the dopant could enhance the selectivity of the electrode to oxidize water to H_2O_2 relative to the dopant metal oxide or the host metal oxide.

5:00pm **TF2-MoA-15 Sputter Deposition of Composite Membranes for High Performance Hydrogen Purification*, Cameron Burst,*** Colorado School of Mines*; Thomas Fuerst,* Idaho National Laboratory*; Doug Way, Colin Wolden,* Colorado School of Mines

Ultrahigh purity hydrogen is essential in many fields including semiconductor processing, fuel cells, and fusion energy.Palladium-based foils offer high flux and perfect selectivity for hydrogen purification, but are prohibitively expensive for many applications. BCC metals like vanadium (V) and niobium (Nb) are ~600X less expensive and offer an order of magnitude greater hydrogen permeability, but require the application of a catalyst to efficiently dissociate and recombine molecular hydrogen and protect V and Nb from uptake of nonmetal impurities. In this work sputter deposition is used to fabricate composite membranes to unlock the full potential of BCC metal foils. Pd is a great catalyst, but will rapidly interdiffuse with BCC metals. In the first strategy we deposit a TiN interdiffusion barrier between Pd and the underlying V foil.TiN was deposited via reactive sputtering, and films with the desired (200) orientation were obtained in the metallic regime at 400 °C with the application of a 200 V bias. The permeability of thin-film TiN was determined with palladium-based sandwich structures. TiN layers up to 10 nm resulted in a minimal decrease in flux (~20%) relative to a freestanding PdCu foil, which was attributed to the interfacial resistance. Composite Pd|TiN|V|TiN|Pd membranes exhibited permeability values up to three times greater than pure palladium, exhibiting stability at 450 °C for over 100 h. However, the membranes were unstable at 500 °C, which was attributed to the instability of the thin Pd layer and loss of catalytic activity. The second strategy involved using sputter–deposited TiO_2 as a catalyst layer. It was found that anatase TiO_2 was an excellent catalyst for H_2 activation, producing composite membranes that achieved theoretical permeability at 500 ºC.After 20 hours of operation these membranes begin to display a slow decline in performance. Extensive materials characterization techniques are employed to understand the underlying reasons driving performance and to further improve the stability of these composite membranes.

5:15pm **TF2-MoA-16 Nano Layers, Tera Goals : Atomic Layer Deposition of Ruthenium for the future Hydrogen Economy*, Swapnil Nalawade,*** *Shyam Aravamudhan, Mengxin Liu, Dhananjay Kumar,* North Carolina A&T State University

Atomic layer deposition (ALD) enables angstrom level control over material synthesis, making it a powerful platform for engineering catalytic thin films. In this study, we report the deposition of ultrathin Ruthenium (Ru) films on TiO2 substrates with (100),(101) and (110) orientations via thermal ALD using organometallic precursor ($Ru(ETCP)_2$) and oxygen as co-reactant. The process yield conformal, uniform and highly crystalline as confirmed by X ray photoelectron spectroscopy (XPS) and X ray diffraction (XRD). XRD showed hexagonal closed packed structure and XPS confirmed the binding energy of $Ru3d_{5/2}$ is associated with $Ru^{(0)}$. Electrochemical evaluation demonstrates hydrogen and oxygen evolution reactions in 0.1 M H_2SO_4, achieving enhanced catalytic activity for Ru on TiO2(110) which also exhibited lower charge transfer resistance in EIS plot. Tafel slopes also highlighted different kinetics for different Ru films. To understand surface chemistry and guide future refinement, first principles density functional theory (DFT) calculations will be employed to explore reaction mechanisms to unravel the energetics and rate limiting steps during growth of Ru films. DFT will help in understanding precursor-ligand decomposition, oxygen interaction and surface termination dynamics during the ALD cycle. This integrated experimental-computational approach illustrates how nanoengineered Ru films can play pivotal role in enabling next generation clean energy infrastructure to achieve terawatt scale hydrogen production.

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