

Schottky Tunnel Contacts for Efficient Coupling of Photovoltaics and Catalysts

Investigators

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Abstract

This interdisciplinary project investigates the performance of nanoscale metal-insulator-semiconductor (MIS) contact structures that electrically couple optimized catalysts to high quality semiconductor absorbers in photoelectrochemical (PEC) cells, while chemically protecting the absorbers from oxidation during solar-driven water splitting. In the initial funding period, we have investigated the effects on water oxidation performance of varying the TiO₂ thickness (grown by atomic layer deposition – ALD) in the MIS structures. Uniform films of atomic layer deposited TiO₂ are prepared in the thickness range ~1-12 nm on degenerately-doped p⁺-Si yielding water oxidation overpotentials at 1 mA/cm² of 300 mV to 600 mV in aqueous solution (pH 0 to 14). Electron/hole transport through Schottky tunnel junction structures of varying TiO₂ thickness was studied using the reversible redox couple ferri/ferrocyanide. The dependence of the water oxidation overpotential on ALD-TiO₂ thickness, with all other anode design features unchanged, exhibits a linear trend corresponding to ~21 mV of added overpotential at 1 mA/cm² per nanometer of TiO₂ for TiO₂ thicknesses greater than ~2 nm. For thinner TiO₂ layers, an approximately thickness-independent overpotential is observed. The linear behavior for anodes with thicker TiO₂ layers is consistent with the predicted effect of bulk TiO₂-limited electronic conduction on the voltage required to sustain the current density across the TiO₂/SiO₂ insulator stack.

We have also designed and are now assembling a small ALD reactor to investigate precursor chemistries for deposition of RuO₂-TiO₂ alloy layers that combine the capabilities of an efficient oxygen evolution reaction (OER) catalyst and a chemical protection layer for an underlying silicon absorber. Our goal is to minimize utilization of RuO₂, a rare, but very efficient, OER catalyst.

Introduction

In this GCEP program, we will apply our recently demonstrated approach¹ for protecting otherwise-unstable semiconductor surfaces in aqueous electrolytes to achieve efficient and stable photoelectrolysis of water using crystalline and amorphous, earth abundant semiconductors. Atomic layer deposition can be used to synthesize ultra-thin and pin-hole free TiO₂ films that allow facile carrier transport from a Si anode to an overlying nanoscale metal catalyst/electron transfer mediator.¹ Without the ALD-grown layer, a Si anode rapidly oxidizes destructively during water oxidation. The Ir/TiO₂/SiO₂/Si nanocomposite anodes function as Schottky tunnel junctions, in which the ultrathin insulator prevents pinning of the silicon Fermi level that would otherwise occur at a metal/silicon interface.

We will use ALD to grow chemically protective oxide layers and form Schottky tunnel contacts on several different earth-abundant semiconductors. We will study the efficiencies of photovoltaic energy conversion and photosynthetic production of hydrogen and oxygen from water with optimized catalysts. Of particular interest is a photoelectrochemical cell using stable Schottky tunnel contacts to both a photoanode and photocathode, thus providing two photovoltages in series to drive the device. This can constitute a *much simpler-to-fabricate two-junction solar cell*, more suitable for *large-scale application* than solid state multijunction cells, but using the same principle of selective absorption of different portions of the solar spectrum by semiconductors with different bandgaps. Closely coupling of experimental capabilities in the two PI's laboratories will help us establish the design rules, fabrication methods and photoelectrochemical performance of single-junction and two-junction PS and PV devices employing nanocomposite Schottky tunnel contacts. Our goal is to demonstrate simultaneous protection of the respective semiconductors from oxidation/dissolution while achieving unpinned Fermi levels in the semiconductors, rapid electronic transport across the oxide layer and highly efficient electrocatalysis at the oxide-electrolyte interface.

Background

In the past year, two studies have been reported that have bearing on our ongoing and planned research. Seger et al.² reported on the ability of TiO₂ thin films (~ 100 nm thickness) to protect p-Si photocathodes. Because of favorable conduction band alignment, the TiO₂ provides little barrier to electron transport from the cathode to the water interface for proton reduction to hydrogen. These results are relevant to our work because they suggest the potential to use ALD-TiO₂ or related materials to stabilize photocathodes made from Si or other high-quality semiconductor absorbers in two-junction PEC's.

Strandwitz et al.³ have reported on the properties of ALD-grown MnO₂ layers as an OER catalyst and chemical protection layer for n-Si photoanodes. Although large photovoltages (as high as 550 mV, similar to those observed in our work on ALD-TiO₂ protected n-Si) are reported, MnO₂ layers that do not have high overpotentials for water splitting were not sufficiently protective to prevent oxidation of the Si photoanode. This suggests that ALD-MnO₂ may not be a viable choice as a catalytic protective layer of high-quality absorbers.

Results

As a tunnel barrier, the thickness of the ALD-TiO₂ is a key parameter for the performance of protected anodes. We recently completed an investigation of the relationship between this ALD-TiO₂ thickness and the required overpotential to drive 1mA/cm² through the device.

Titanium dioxide layers were deposited by ALD on Si (100) wafers coated with ~1.5 nm of a chemical oxide (SiO₂) layer as-received from the wafer vendor. The TiO₂ film thickness ranged from 1.2 nm to 11.6 nm. The TiO₂ thickness was measured using a Gaertner ellipsometer calibrated by cross-sectional transmission electron microscopy (TEM) analysis. TEM results for TiO₂ layers of thickness ~2, 5, and 12 nm, respectively,

are shown in Figure 1, indicating a uniform and continuous film with no evidence of the catalyst layer mixing into the TiO₂ layer that would provide an alternative mechanism to transfer charge through the insulating oxide layers of the anode. Another indication of reliable ALD depositions is a stable growth rate. Over the entire thickness series investigated, the mean growth rate variation was less than 0.1 Å/cycle. The reproducibility and uniformity of this deposition technique indicates the promise of using ALD for electrochemical device applications, where both very thin and uniform films are required.

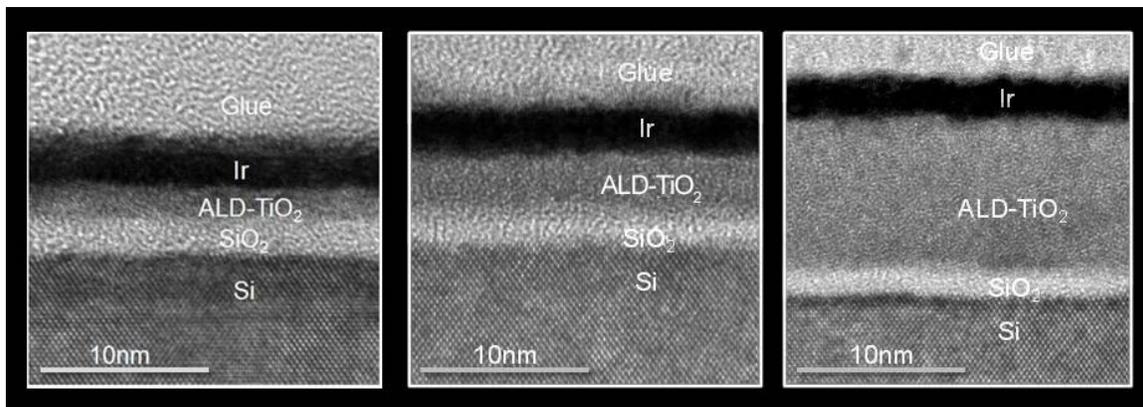


Figure 1: Transmission electron micrographs of three ALD-TiO₂ films of thickness 2 nm, 5 nm, and 12 nm from left to right.

Increasing the thickness of the ALD-grown TiO₂ oxide layer is expected to decrease the charge transfer efficiency of the anode, indicating the importance of an ultrathin layer for facile electronic carrier transport between the oxygen evolution catalyst and the semiconductor absorber. Indeed, the overpotential for water-oxidation required for devices to operate at 1 mA/cm² increases with increasing TiO₂ thickness for thicknesses greater than ~ 2 nm. Interestingly, the overpotential is relatively constant, at a value of 300 mV to 350 mV, for anodes with 0 to 2 nm of ALD-TiO₂, suggesting that the thickness of TiO₂ is not rate-limiting for the water oxidation reaction in this oxide thickness regime.

As shown in Figure 2, there are two distinct regimes: (1) From 0 to ~ 2 nm, where the trend is relatively independent of thickness and (2) from ~2 nm to 12 nm where the trend is linear with a slope of ~21 mV/nm of TiO₂, interestingly similar to the slope observed for the half peak-to-peak splitting of the ferri/ferrocyanide redox cyclic voltammograms. The conduction mechanism for ultrathin TiO₂, the first thickness regime, was previously indicated as direct tunneling, supported by the temperature independence of the conductivity, while anodes with thicker TiO₂, characteristic of the second regime in Figure 2, show a clear temperature dependence suggesting a more bulk limited, thermally-activated conduction mechanism.¹ Through this recent work and an investigation of the band diagram of the bilayer oxide TiO₂/SiO₂, this bulk-limited conduction mechanism has been further explicated, showing that a linear trend is expected with the slope equal to the characteristic value of the field in the TiO₂ needed to

drive 1 mA/cm^2 . Taking the slopes in Figure 2, this corresponds to a field of 200-250 kV/cm and an effective ALD-TiO₂ resistivity of $1\text{-}2 \times 10^8 \Omega\cdot\text{cm}$.

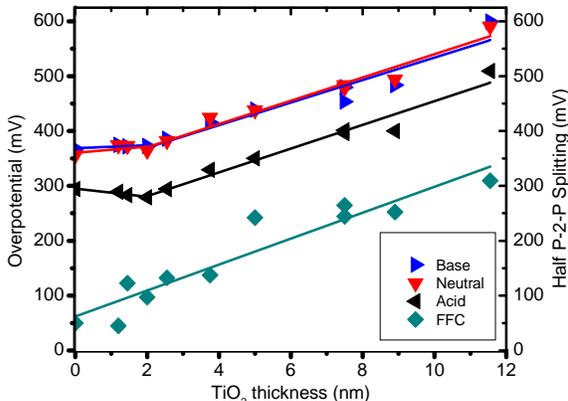


Table I: Linear regression analysis data for measured overpotentials as a function of TiO₂ thickness in all four solvent systems.

Solvent system	Linear slope (mV/nm of TiO ₂)	Linear correlation (R ²)
Base	20.6	0.92
Neutral	21.2	0.97
Acid	21.7	0.96
FFC	23.6	0.90

Figure 2: Left: Overpotentials for water oxidation at 1 mA/cm^2 and ferri/ferrocyanide half peak-to-peak splitting as a function of TiO₂ thickness. Table I gives the results of the corresponding linear regression analysis of these four trends. For water oxidation, the linear regression is applied to the regime from 2 nm to 12 nm of TiO₂.

In summary, the key findings are that 1) total overpotentials are quite low for these ALD-grown MIS anode structures, and 2) the overpotential penalty per nanometer of added TiO₂ thickness (e.g. for increased chemical stability) is modest. For ALD-TiO₂ thicknesses greater than ~ 2.0 nm, the effective overpotential for water oxidation increases linearly as the TiO₂ thickness is increased in accordance with a bulk-limited conduction mechanism that requires a characteristic E-field in the TiO₂ layer to maintain a given water oxidation current across the metal-insulator-semiconductor anode. For ultrathin TiO₂ films in which direct tunneling can dominate charge transport, the minimum overpotential and reaction rate are relatively independent of TiO₂ thickness and are apparently dominated by the kinetics of the water oxidation on the catalyst surface.

A second major research effort involves developing optimal catalysts for the oxygen evolution reaction. Noble metals such as ruthenium, iridium, and their oxides are the most efficient catalysts for water oxidation.⁴ Given their high cost, however, it is important to understand how these noble metals can be most efficiently and effectively used. We plan to investigate ALD surface alloying of RuO₂ with TiO₂. By decorating the TiO₂ surface with Ru ions at an optimal areal density, we hope to optimize the turnover frequency for oxygen evolution by achieving surfaces with the same electrocatalytic current density as planar 2D catalyst layers, but with a fraction of the noble metal usage. Such a 2D-alloyed electrode represents a modern, ultra-thin analogue to the thick film dimensionally stable anodes (DSAs) used widely in industry for brine electrolysis. Alloys of RuO₂ and TiO₂ have previously been investigated for catalytic oxygen evolution, and based on those results, we expect maximum electrocatalytic activity per Ru atom near 30 mol% RuO₂.⁵ The procedure for depositing RuO₂ and TiO₂ using ALD has already been established.^{1,6} To create alloys, we will vary the pulse cycles for each metal oxide

between 0 and 100% to create electrocatalyst of varying composition.⁷ Stanford hosts an impressive collection of instruments for materials characterization, including scanning electron microscopy, Rutherford backscattering, X-ray diffraction, X-ray reflectivity, and inductively coupled plasma atomic emission and mass spectroscopies. These techniques will allow us to fully characterize the surface structure and composition of the alloys. In addition, cyclic voltammetry (CV) will be used to study water oxidation current as a function of applied potential in the light and in the dark, as well as in acidic, basic, and neutral solutions. CV will also be used to characterize charge transport between ALD-grown RuO₂-TiO₂ alloys and standard redox couples in aqueous solution. Finally, chronoamperometry and chronopotentiometry will be used to monitor the lifetime of the resulting electrodes.

Once we understand how electrode composition affects electrocatalytic activity, we will attempt to template Ru ions at a fixed distance from one another using novel ruthenium precursors. We predict that hard-donor anionic oxygen ligands will be displaced by Ti-O bonds under the hydroxylic conditions of ALD, while neutral aromatic amine ligands will be preserved. Therefore, bridging amine ligands in a dinuclear ruthenium precursor could be used to separate two Ru atoms at a fixed distance during their incorporation into the alloyed catalyst. Our goal is to develop a ruthenium ALD precursor that can yield templated dimeric Ru sites films using a milder oxygen source, such as H₂O, as opposed to oxygen gas. For example, a potential precursor will be prepared from ruthenium trisacetylacetonate and 2,2'-bipyrimidine.⁸ The distance between Ru atom centers can be varied by using different bridging amines. After securely anchoring the Ru atoms in place, we will remove the bridging ligand by aggressive oxidation, for instance with an oxygen plasma. If successful, this strategy will allow us to determine the "ideal" Ru-separation for catalytic oxygen evolution. Precise control over Ru atom placement should yield enhanced catalytic activity compared to random alloys.

In order to rapidly screen novel precursors, we are designing a new, customized ALD reactor specifically for this purpose. The schematic of the proposed reactor is shown in Figure 3. The deposition chamber is a Pyrex tube encased in a ceramic heater with temperature capabilities of 500°C or higher. A 3-way switching valve will be used to direct the flow of nitrogen directly to the chamber, as during a purge pulse, or through one of the bubblers, as during a precursor pulse. The water line is kept separate to prevent unwanted reactions within the lines. The system is designed to easily incorporate multiple precursor inlets, though only one will be used initially. Furthermore, to maintain the precursors and lines at a constant temperature, the entire system is encased in an oven designated by the dotted line boundary in Figure 3. The valves are pneumatically actuated and rated to approximately 200°C, which allows precursors to be heated to higher temperatures than what is commonly seen in the literature. By placing nearly all of the system components within the oven, we can achieve enhanced temperature uniformity and easily control precursor vapor pressure. Overall, we have attempted to minimize system components in order to focus on the chemistry of ALD, rather than the process engineering. We will test our system with well known ALD precursors, such as trimethyl aluminum (Al₂O₃ deposition) or tetrakis(dimethylamino)-titanium (TiO₂ deposition), both of which have been studied extensively in our lab.

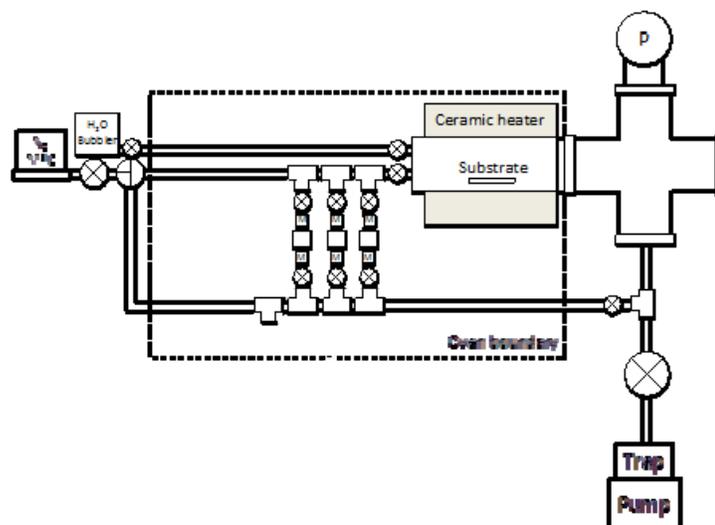


Figure 3: Schematic of ALD reactor design for the screening of novel precursors. Manual valves are designated with an “M.” The dotted line represents the oven boundary. The “P” designates the location of the pressure gauge.

Progress

Our observation that only a modest increase in OER overpotential occurs per nm of additional ALD-TiO₂ deposited onto n-Si substrates is exciting, and suggests the potential to effectively engineer simultaneous chemical protection and efficient solar-driven water oxidation kinetics. This is essential for making a viable PEC-based solar fuel synthesis technology incorporating high quality photovoltaic materials such as (normally unstable) Si, III-V and II-VI semiconductors. Detailed endurance studies are underway to determine the trade-offs between stability and MIS anode structure more quantitatively.

Future Plans

The mechanism of electronic carrier conduction across TiO₂ layers thicker than ~ 2.5 nm remains poorly understood. A more detailed understanding of this topic will allow us to assess the effects of RuO₂ alloying (for efficient catalyst utilization) on facile photogenerated hole transport to the anode surface. Our planned experiments will include both solid-state and electrochemical cell measurements to determine conduction mechanisms across the MIS structures and their effects on the measured photovoltage as we vary anode design parameters. We will also investigate the effects of OER catalyst coverage on stability and the overpotential for water oxidation. These studies will include both patterned metal catalysts deposited by sputtering or evaporation, and ALD-grown RuO₂ catalysts grown as partial surface layers or alloys during ALD of the TiO₂ protective tunnel oxide. Finally, in the next year, we will focus more of our efforts on ALD-oxide protected photocathodes, with particular emphasis on amorphous Si thin film absorbers to provide much greater photovoltages in two-junction cells combined with crystalline Si Schottky junctions.

Publications and Patents

None to report.

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