Strained TiO_2 Photoanodes

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Objectives:

Our goal is to develop strain-modified TiO_2 suitable for use as a high efficiency photoanode in the photoelectrochemical production of hydrogen. The strain is primarily responsible for reducing the band gap of the TiO_2, thereby increasing the absorption of solar energy. The focus of our efforts is the design and fabrication of a substrate that is both compatible with the film growth process and capable of imparting large tensile stresses into the TiO_2.

Technical Barriers*:*

The most general technical barrier for the photolysis of water is the lack of a photoelectrode that is both a stable and efficient component of a photoelectrochemical cell[1]. There exists several technical barriers specific to our particular approach to this problem. Little to no information is available regarding the stress generation during the thermal oxidation of titanium substrates with a non-planar topography. Furthermore, transferal of patterns onto titanium substrates is increasingly difficult as the feature sizes decrease into the micro and nanometer regimes.

Abstract

Our goal is to develop strain-modified TiO_2 suitable for use as a high efficiency photoanode for the photoelectrochemical production of hydrogen. The strain is primarily responsible for reducing the band gap of the TiO_2, thereby enhancing its absorption of solar energy. At present, we have demonstrated a process that reduces the band gap of TiO_2 by approximately 0.3 eV and realizes a concomitant (5-6X) increase in solar-to-hydrogen conversion efficiency. Our theoretical modeling results indicate that properly applied pressure can reduce the band gap by 68.5 meV/GPa. In order to physically strain the TiO_2 film, we thermally oxidize a titanium foil substrate with a non-planar topography. To design the topography of the substrate, we are investigating the stress generated during thermal oxidation of titanium by making small modifications to the default behavior of the Florida Object Oriented Process Simulator (FLOOPS). Fabrication of the features is being pursued primarily through wet etching of a masked

substrate. We have preliminary results that demonstrate the feasibility of microcontact printing (μCP) as an effective means to transfer etch masks to the titanium foil. As these processes mature we anticipate further improvements to our conversion efficiency that our theoretical modeling indicates is possible.

Progress Report

Over the course of the funding period, we have progressed in all major aspects relating to our main objectives. Our present solar-to-hydrogen conversion efficiency is several times greater than it was at the program's inception. We have also advanced our computer modeling and material fabrication and characterization tools to guide and accelerate our progress.

Our present electrode fabrication process was carefully developed to randomly pattern the substrate topography with structures that have feature sizes ranging from the micro to nanometer scale. Creation of these topographic structures, combined with our optimization of the thermal oxidation parameters, represents a simple and powerful means of creating an efficient and stable photoelectrode. These samples are capable of hydrogen production when illuminated by light with energy as low as ~2.9 eV as opposed to the typical[2] 3.2 eV. A direct comparison to electrodes with more planar topographies credits our process with a 5-6X increase in solar-to-hydrogen conversion efficiency.

Computer modeling plays a key role in two aspects of our work. We have a Linux based workstation equipped with several state-of-the-art scientific modeling and simulation codes. Both the Quantum Espresso[3] and Abinit[4] codes allow us to study the physics of the strained semiconductor. This has allowed us to quantify the stress/strain relationship to the band gap shift. For anatase TiO_2 we expect the band gap to change at a rate of 68.5 meV/GPa of total pressure. To design the strained TiO_2 electrode we have patched the FLOOPS[5] code in order to successfully port it to our computer architecture. This is a finite element modeling tool that allows us to approximately simulate the thermal oxidation of titanium and calculate the film stresses associated with a non-planar topography. We have also developed our own post-processing code to interpolate the stress solutions at the nodes into a smooth image. Our FLOOPS scripts periodically sample the solution data during a thermal anneal simulation and the resulting images are used to animate the time progression of the stressed film formation.

Fabrication of the TiO_2 electrode is divided into formation of the film and formation of the substrate topographical features. After exhaustive experimentation with several methods of creating TiO_2 thin films, we have achieved our most robust results via thermal oxidation of titanium substrates. Our work has identified and optimized several key variables of this process. Given our film formation process, the substrate is required to be titanium foil. Controlled modification of the surface topography of titanium at the micro and nanometer scale is required to implement our electrode designs. Our facilities and staff expertise are most equipped to fabricate these structures by transferring etch masks to the substrate. We have demonstrated that μCP[6,7] is a viable means to achieve this objective. To date we have identified an inking material capable of forming a self-

assembled monolayer on the substrate that also remains stable when subjected to a variety of suitable etchants.

Future Directions

Our basic objectives and premise remain unchanged as we advance our technology. Our intention is to further increase the film stresses to realize larger band gap reductions, and hence, greater solar-to-hydrogen conversion efficiencies. We expect to achieve this through refinement of our present processing methods, although alternatives will also be explored.

Electronic structure modeling will continue as needed. The versatility of this tool may predict and explain a variety of phenomena associated with the semiconductor physics. However, the majority of the modeling efforts will focus on the FLOOPS process simulations. A sensible algorithm will be required to optimize several dependent variables that describe the topography. This will be especially critical as models are extended to three dimensions. Additionally, given that FLOOPS was developed to model silicon-based technology, more work is needed to adapt the code to our titanium-based work.

Fabrication of the electrodes designed using FLOOPS is our ultimate objective. We will continue our refinement of the μCP method to transfer patterns to the titanium substrate. However, this approach is primarily a means of replication. Suitable master patterns must be fabricated with alternative methods. However, known techniques are readily available for this purpose, and are comparatively simple because many of our specific constraints are lifted during master fabrication. Master fabrication will proceed by wet etching masked silicon wafers. Silicon can be etched highly anisotropically by potassium hydroxide, allowing the wet etch of very deep topographical features. We will consider mask transfer using both UV lithography and self-assembled block copolymers[8]. This should allow adequate flexibility for master production. We will also investigate the feasibility of applying these methods directly to the titanium substrates.

Considerable work remains with respect to experimental characterization of the electrodes. Most of our effort has involved electrochemical methods such as photocurrent and impedance spectroscopy. We expect to expand our characterization through a variety of techniques. Regular scanning electron microscopy will be performed to provide feedback for our fabrication processes. This instrument will also be equipped to perform energy-dispersive x-ray spectroscopy (EDX). This will verify the adsorption of the inking material from the μCP process as well as measurement of the TiO_2 stoichiometry. Potential stress measurements will also be investigated through micro- and/or nano-Raman spectroscopy[9]. These techniques will all serve to aid and verify our current results and future progress.

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