LABORATORY DIRECTED RESEARCH AND DEVELOPMENT
INTERFACIAL PHOTOELECTROCHEMISTRY USING OXIDE HETEROSTRUCTURES

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<td>Proposal Term</td>
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Abstract

This project proposes the initiation of a new direction within SLAC to establish a research platform for developing functional electrodes in photoelectrochemical applications using atomic scale controlled epitaxial oxide heterostructures. Exploiting the well-defined nature of our structures, the focus will primarily be to identify the critical factors in water photoelectrolysis and demonstrate new strategies to improve its efficiency based on electrostatic boundary conditions.

Summary of Proposal

Description of Project

Oxide semiconductors have been the primary candidate for hydrogen production using water photoelectrolysis. However, the yield still remains insufficient for commercial use despite its long history. One cause restricting the progress is the use of polycrystalline samples in the majority of the studies. Effects of crystalline orientation, particle size, and surface band alignments are typically not isolated, with experiments varying multiple parameters limiting fundamental understanding necessary for significant progress.

We propose that epitaxial oxide heterostructures, grown with atomic precision using pulsed laser deposition (PLD), can provide the experimental platform to develop structures that can greatly enhance the yield. The use of highly idealized yet realistic structures will enable to identify and independently evaluate the essential features reported for polycrystalline samples. Furthermore, basic strategies to develop new design principles for the electrodes are proposed based on manipulating the electrostatic boundary conditions at oxide heterointerfaces. The technical approach proposed here can be applied more generally to study complex-oxide/electrolyte electrochemistry on firm grounds.

Expected Results

Using well-defined oxide heterostructures, we expect to: (1) identify the rate-limiting steps for each elemental process in water photoelectrolysis, (2) perform a “proof of principle” operation of conceptually new design strategies to improve the yield, and (3) critically evaluate the potentials of multi-elemental oxides by comprehensive study of materials intrinsic and photoelectrochemical properties. These results will initiate strategic programs within SLAC that will synergize the expertise from spectroscopy and first-principles calculations.
Proposal Narrative

Purpose/Goals

The water photoelectrolysis reaction to hydrogen and oxygen involves multiple processes; photo-generation of electron-hole carriers inside the semiconductor, transportation of carriers to the surface, and reduction/oxidation of water. There are two major approaches in the research field, macroscopic and microscopic approaches. The macroscopic approach involves materials exploration and development working predominantly with polycrystalline specimens targeting maximum overall efficiency. The microscopic approach focuses on studying the mechanisms behind each elemental reaction process using single crystalline specimens. It would be ideal if the two approaches could develop in a concerted manner, however this is restricted primarily due to the limited range of samples available for microscopic studies.

In this proposal, we propose to bridge between the two approaches using oxide epitaxial heterostructures as the platform for the study of water photoelectrolysis. Given the highly kinetic growth realized in PLD, we expect to grow a far larger range of oxide thin films in single crystalline form with well-defined surface structures. Furthermore, the growth technique allows fabrication of artificial heterostructures controlled on the atomic scale, providing ways to modify surface and interfaces with great degree of freedom.

Approach/Methods

We will focus on improving the three fundamental factors limiting the practical implementation of water photoelectrolysis: i) Inefficient charge separation, ii) Slow chemical reaction at the semiconductor surface, and iii) Ineffective use of the solar spectrum in the visible.

i) Inefficient charge separation

High recombination rate of photocarriers reduces the number of photocarriers reaching the reaction sites. This can be suppressed by introducing space charge regions via dopants, particle size reduction, or mobility improvements. In polycrystals, these effects occur simultaneously since the particle size is often controlled by the sintering temperature which inevitably changes the defect density.

We propose to isolate each factor by studying the photoconductivity and the photoelectrochemical behavior of semiconductors with precisely controlled film
thickness. This maintains a fixed surface area and structure, and isolates size reduction effect in the photocarrier transit time. Our preliminary results using archetypal semiconductor (anatase TiO₂) suggest that the minority carrier diffusion length, generally recognized as a materials specific property, is varying as a function of its thickness. We will examine the space charge effects by varying the dopant density of the oxides to comprehensively understand the role of size reduction in the charge separation process.

ii) Slow chemical reaction at the semiconductor surface

The band edge positions of the oxide semiconductor relative to the H₂ and O₂ reduction potentials determine the thermodynamic driving force for the reaction. The capability to arbitrarily tune these positions while maintaining the semiconductor bulk property will give large flexibility to improve the reaction rate. Our approach is to introduce oxide surface dipole layers at the oxide/electrolyte interface thereby modifying its band alignment. Our recent progress in tuning the barrier height over 0.8 eV at metal/oxide semiconductor interfaces and the confirmed chemical stability of the surface dipole layers give firm ground to test this approach in photoelectrochemical environment.

iii) Ineffective use of the solar spectrum in the visible

Search for effective dopants to reduce the band gap of oxides to harvest a larger portion of the solar spectrum has been an important theme. The recent progress in partial substitution of nitrogen in many oxides has proven to be a promising strategy. Given the difficulty in controlling and stabilizing nitrogen in large volume crystals, we will use epitaxial thin films to systematically control the nitrogen content and characterize the electronic as well as photoelectrochemical properties of these new semiconductors.

**Specific Location of Work**

The research activities will be conducted at SLAC, SIMES Building 40 and Stanford University campus using the currently installed PLD growth systems, structural, and photoelectrochemical characterization capabilities.

**Anticipated Outcomes/Results**

We expect to demonstrate that the use of epitaxial oxide heterostructures with well-defined surface structure, thickness, dopant density, and clean interfaces can be a new platform to study and develop new water photoelectrolysis systems. By critically designing structures, we aim to isolate and resolve some of the major rate limiting factors by applying concepts we have established in the study of epitaxial oxide interfaces.
Accomplishments to date

1. Band alignments tuning at electrolyte/oxide interfaces

We aim to control the semiconductor band edge positions appropriately with respect to the hydrogen/oxygen evolution potential by forming ultrathin oxide surface dipole layers on top of the oxide photoelectrodes. The feasibility of this technique was examined in a model system consisting of LaAlO$_3$ (001) ultrathin surface dipole layer on top of an anatase TiO$_2$ oxide photoelectrode. We have succeeded in stabilizing the LaAlO$_3$/TiO$_2$ heterostructure, which was previously reported to be unstable when grown under UHV conditions. The key to this achievement was to carefully control the growth rate of the LaAlO$_3$ thin film to minimize oxygen extraction from the underlying TiO$_2$ layer. Using these heterostructures, we first confirmed the effectiveness of surface dipoles by forming metal/semiconductor Schottky junctions. From thorough characterization of the Schottky barrier height, SBH, we clearly observed a linear decrease over 0.8 eV by depositing ~1 nm of surface dipole layers. Furthermore, the chemical stability of these structures was tested in basic solution which showed negligible degradation. The outcome of this study will ultimately enable to decouple several major constraints imposed in searching for effective photoelectrode materials.

2. Intrinsic effect of electrode thickness on water photoelectrolysis

The balance between photon absorption and the ease of charge transfer between the cathode and the anode are two important factors defining the efficiency of water photoelectrolysis. Charge transfer efficiency is strongly related to the lifetime of the photogenerated carriers which can be affected by for example bulk scattering, back contact interface barrier, as well as surface reaction kinetics. Here we use epitaxial thin films with fixed surface and bulk properties, and independently varied the electrode thickness to study the intrinsic effect of charge transport on the efficiency of the device. Compared to previous studies in polycrystals, this approach enables to isolate key parameters that are limiting the overall device efficiency. By varying the thickness of TiO$_2$ (001) thin films from 34 nm to 186 nm for a fixed dopant density, the incident photons to current efficiency (IPCE) increased in a step-wise manner, while the flat-band potential remained constant. The critical thickness where the IPCE shows an abrupt increase corresponds approximately with the thickness where the TiO$_2$ thin film structurally relax from the underlying substrate LaAlO$_3$ (001), suggesting the importance of lattice strain on IPCE. Further experiments including optical characterization and doping dependence are planned.
VITA (Lead Scientist)

Yasuyuki Hikita, Associate Staff Scientist

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Education
2007  Ph.D. in Science, University of Tokyo, Japan.
2003  M.S. in Science, University of Tokyo, Japan.
2001  B.S. in Engineering, University of Tokyo, Japan.

Positions
-  Associate Staff Scientist, SIMES, SLAC National Accelerator Laboratory (2011 -).
-  Assistant Professor, Dept. Advanced Materials Science, University of Tokyo, Japan (2007- 2011).
-  Research Assistant, Center of Excellence for “Applied Physics on Strong Correlation”, University of Tokyo, Japan (2004-2007).

Honors
-  Japan Society of Applied Physics Young Scientist Award for the Presentation of an Excellent Paper (2007).

Research interest
Application of atomic scale engineering in oxide heterostructures to electrochemistry, probing complex oxide artificial interfaces for electronic device applications.

Selected Publications (total 55 publications, 1 book chapter, $h$-index = 16, >770 citations)

**Budget Explanation**

The budget ($125k for year 2, $125k for year 3) includes cost for personnel, materials and supplies, and travel. Personnel includes salary for PI, Yasuyuki Hikita, at 20% and post-doctoral associate, Kazunori Nishio, at 50% for years 2 through year 3. Materials and Supplies are projected at $25.7k for year 2, and $22.4k for year 3. Travel expenses are projected at $1.5k for years 2 and 3 for the PI to present at domestic conferences. Please see accompanying budget for details.
Approvals

Signing indicates you have reviewed the contents of this proposal, and support its submission to the LDRD process. Signatures are **required**.

Business Planner

Department Chair/Division Manager

Associate Laboratory Director