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Impedance spectroscopy study of $SrTiO_3$ pulse laser deposited photoelectrodes

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ABSTRACT

Strontium titanate (STO) is an oxide that has found application in several technological areas and is a candidate electrode for photoelectrochemical cells (PECs). In this study, STO thin films were prepared via pulsed laser deposition to function as PEC electrodes. Effects of post-deposition annealing in a reducing environment on the photocatalytic activity of these electrodes are characterized by measurements of optical and electrochemical properties of the films. These observations are used to obtain insight into how the crystal and electronic properties of these electrodes are affected by the annealing process. Low annealing temperatures produce non-crystalline STO films that exhibit low photocatalytic activity. Annealing at 500 °C and higher allowed the formation of crystalline STO, which showed substantially higher ultraviolet-driven photocurrent densities. Electrochemical impedance spectroscopy reveals large decreases in charge transfer resistance that is associated with improved performance of these films. Oxygen evolution at these electrodes was confirmed with a rotating ring-disk electrode setup. Porous versions of the STO films were investigated to evaluate the effect larger surface area can have in enhancing the water oxidation performance.

1. Introduction

Photoelectrochemical cells (PECs) provide a potential solution to some of the fundamental problems faced by solar power, particularly its variability. By using solar radiation to create a fuel, PECs could effectively bottle solar energy allowing it to be shipped and used wherever and whenever it is needed. Various architectures and fuel products have been proposed for PECs. This work is concerned with water-splitting via an illuminated, semiconductor photoanode that drives oxygen evolution in series with a dark electrode that catalyzes hydrogen evolution. The properties of the semiconductor electrode play an essential role in the performance of the PEC. Optical bandgap, band-edge positions, electrochemical stability, and dielectric properties of the material are particularly important for sustaining the reaction. Due to their properties, several metal-oxide semiconductors have been considered for constructing photoanodes for PECs.

Strontium titanate (STO) has been investigated for use in these electrodes because of its high electrochemical stability. Single-crystal STO was first used for photoelectrochemical applications in the 1970's and had the distinction of catalyzing a water-splitting reaction with no external applied bias [1,2]. Single-crystal STO has been investigated as a photoelectrode in a variety of studies [1–6] as has STO in thin film forms [7–13]. Its band structure and dielectric properties are however not ideal for water-splitting, and their tuning via doping remains a topic of interest. The simplest methods for doping STO are accomplished during the growth process or through a post-growth annealing step. In earlier work with single-crystal bulk STO, electrodes are often annealed at temperatures ranging from 800 °C to 1100 °C in hydrogen atmospheres to improve its charge density and electrical conductivity. Annealing temperatures reported in literature for STO thin film photoelectrodes range from 450 °C to 1100 °C. Notably, high temperature anneals in reducing environments have been shown to create oxygen vacancies in the STO lattice resulting in electron donor states and increased conductivity [14,15]. There is some evidence that interstitial hydrogen doping also occurs during these anneals and creates shallow donor states [15,16].

The annealing conditions for STO films have been shown to influence crystallinity, band-structure, dielectric properties, and optical properties of STO films [14,15,17–28], all important factors on the photocatalytic performance of STO photoanodes. Nevertheless, published accounts on the photocatalytic properties of reduced STO films lack methodical studies of annealing temperature effects but instead

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have focused on alternative doping strategies (other metal impurities) or unassociated electrode properties (i.e. adsorbed catalyst). In a previous investigation we showed the effects of annealing in different environments (atmosphere, O_2, H_2/Ar) on STO electrodes specifically for dye-sensitized PECs [29]. In that case, the study of performance change with annealing temperature was limited by the substrate stability – i.e. transparent fluorine doped tin oxide.

Below we present a systematic study on the effects of post-deposition annealing temperature on two properties of STO films that strongly effect their performance as PEC photoanodes, namely optical bandgap and electrical impedance. A pure titanium substrate is employed allowing STO films to be annealed at higher temperatures than conventional STO thin films in literature. We have found that higher annealing temperatures are correlated with lower electrical impedance and narrower optical bandgaps in STO films, and furthermore these changes are associated with large improvements in performance for these films as PEC photoanodes under ultraviolet (UV) illumination. We have also identified a minimum temperature requirement for the annealing step to achieve STO films that exhibit band structures similar to single-crystal STO. In this investigation, both flat and porous films were fabricated under similar conditions and tested to investigate the role of the electrode morphology in electrochemical performance. This work definitively shows how the material physical property changes correlate to improvements in photocatalytic performance of STO films.

2. Experimental details

STO films were grown with a PVD Products pulsed laser deposition system (NanoPLD) at room temperature from a sintered STO target (PVD Products, 99.9% pure). Titanium substrates were used for electrochemical measurements while silicon and fused silica were used to create twin samples for optical measurements. An O_2 back pressure of 1 Pa was used to make flat, dense films. Porous films were grown by depositing first a 20 nm flat, dense film and then proceeding with porous growth at 30 Pa O_2 back pressure. The dense underlayer was used to ensure the Ti substrate could not have direct contact with the electrolyte during the photoelectrochemical experiments. Post-deposition annealing was done in a 2.5% hydrogen (balance gas argon) atmosphere using an MTI Corporation OTF-1200× tube furnace. Post-deposition annealing temperatures varied from 300 °C to 700 °C for different samples with the temperature being maintained for 2 h.

Prior to selecting titanium metal as the substrate, we noted that high temperature anneals in a 2.5% hydrogen atmosphere dramatically decreased the conductivity of a number of substrates considered for this study. Fluorine-doped tin-oxide, silver foil, glassy carbon, and high-conductivity silicon (As-doped) were all degraded under this reducing atmosphere. The titanium substrate proved to be the best though it also showed increased (×100) resistivity at annealing temperatures ≥700 °C, presumably from a surface reaction/compositional alteration. This change in conductivity for anneals at 700 °C was also eliminated by coating the metal substrate with Al_2O_3, before STO film deposition, on all sides except the side that supports the STO film. Al_2O_3 deposition was done via atomic layer deposition. It was found that a 10 nm thick Al_2O_3 coating was sufficient to prevent increases in substrate resistivity on the back side of the substrate.

Spectroscopic optical characterizations were made with two different techniques. A J.A. Woollam V-Vase spectroscopic ellipsometer with an HS-190 monochromator light-source was used to determine optical constants by fitting data to a multi-oscillator model (J.A. Woollam, W-Vase software). A custom setup incorporating a light source (Spectral Products, ASBN-W series) integrating sphere (Labsphere), and monochromater (SpetraPro) was used to independently determine the film absorption. Samples for spectroscopic ellipsometry and reflection measurements were grown on silicon wafer substrates (100). Samples for absorption measurements were deposited on fused silica. X-ray diffraction (XRD) measurements were performed with a Rigaku SmartLab X-Ray Diffractometer (Cu source, 1.5418 Å, 0.02 °/s) for STO films on fused silica. Samples on the titanium substrates were too small for the XRD spot size to obtain reliable data but could have produced Ti-rich STO films.

Electrochemical impedance spectroscopy (EIS) curves and UV-illuminated photocurrents were measured using a Rotating Ring-Disk Electrode (RRDE) setup (Pine Instruments AFMSRCE) with the disk electrode replaced by the titanium substrate. A platinum wire counter electrode and double-junction Ag/AgCl reference electrode were used to complete the electrochemical cell. In the case of RRDE a platinum ring electrode surrounds the disk electrode. Current at the ring electrode is monitored for changes correlated to illumination of the disk working electrode. The platinum ring electrode had no applied bias for these experiments except in the case of oxygen measurements via RRDE. Electrolyte for photocurrent measurements was at pH 5.8 with 0.2 M $LiClO_4$ in an acetate buffer. A CH Instruments Model 760E Bipotentiostat was used to collect electrochemical data. EIS curves were taken with a voltage oscillation amplitude of ± 5 mV at twelve points per decade frequency. When a potential bias was used with EIS measurements the system was allowed to equilibrate before.

For porous films it was preferable to make films as thick as possible to maximize surface area while maintaining structural integrity. To meet both requirements porous films were grown to 650 nm total thickness. As porous electrodes have delicate 3D structures that can be damaged by loading into the RRDE setup, electrodes for these films were constructed by connecting the titanium substrate to a wire using a conductive epoxy (Chemtronics CW2400) and then covering the connection and exposed titanium with a stable, electrically resistive epoxy (Hysol E-00CL). Flat films on Ti substrates were also made into electrodes with this technique to obtain comparable measurements.

Illumination for electrochemical measurements was provided by a continuous wave solid-state laser from Crystal Laser with 375 nm wavelength. Light intensity was controlled by adjusting laser-to-sample distance and with neutral density filters. For measurements in the RRDE setup laser intensity at the sample was approximately 4.0 ± 0.1 mW/cm^2 while measurements in the sealed cell had intensity 1.7 ± 0.1 mW/cm^2 at the sample.

3. Results and discussion

3.1. Photocurrent measurements

Initially we considered a possible relationship between film thickness and photocurrent generation, therefore a series of films were created ranging from 20 nm to 1 μm thick and post-annealed at 700 °C. The results, summarized in Fig. 1.a, show that photocurrent slightly peaked at a thickness of 40 nm. The underlying cause of this peak performance at 40 nm thickness is not obvious, as optical absorption and electrical resistance could both be functions of the geometric dimensions. Electrochemical impedance spectroscopy was used to examine these films. EIS on illuminated films showed only small differences in impedance for films of different thickness (Fig. 1.b). Given the photocurrents were all also within a factor of two from each other, this is a relatively small effect compared to what will be shown results from the annealing conditions (below), therefore we conclude that film thickness in the explored range did not have a substantial effect on performance. The 40 nm thickness was maintained for the subsequent investigations into annealing effects.

Photocurrent measurements of these films under the conditions described above were done for films annealed at several temperature setpoints. Fig. 2 shows that films annealed up-to and below 300 °C exhibited < 0.1 μA/cm^2 photocurrent densities. Annealing above that point resulted in significant improvements in photocurrent densities, with a ~10^4 factor increase for the best film which was annealed at 700 °C. Incident photon-to-electron conversion efficiency (IPCE) for the film annealed at 700 °C under these conditions (0 V bias vs. Ag/AgCl,