Atomically Engineered Oxide Heterostructures for Solar Water Splitting Catalysis

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Abstract

The solar water splitting reaction to hydrogen and oxygen provides a means of energy storage as well as producing feedstock for industrial chemical synthesis, thereby reducing fossil-fuel-derived hydrogen. Oxide semiconductors have been the primary materials candidate since the major breakthroughs more than 40 years ago [1, 2]. However, the general approach of using polycrystalline samples for their study has hindered identifying the microscopic key factors limiting the efficiency.

In this exploratory project, our emphasis is on using atomic scale controlled epitaxial oxide heterostructures as the platform to study and develop fundamental concepts in improving the efficiency of solar water splitting devices. Our goals are (1) to identify the dominant effect of size reduction in photoanodes by systematically controlling the thickness in epitaxial thin films, and (2) to fabricate atomic scale surface dipoles using ultrathin oxides to ultimately tune the energy band alignments at the electrolyte/electrode interface.

We succeeded in controlling the carrier density in epitaxial undoped TiO_2 thin films over two orders of magnitude by tuning the deposition rate during pulsed laser deposition (PLD) growth. From electrical and optical characterization, we identified that oxygen vacancy density is sensitively tuned by the balance in the exposure time of the adsorbed precursors with respect to the subsurface oxygen out-diffusion time constant. This formed the basis for our systematic photoelectrochemical characterization of TiO_2 photoanodes. Furthermore, we grew polar stacking layers ($LaAlO_3$) on the surface of anatase TiO_2 to act as surface dipoles which was confirmed by characterizing the Schottky barrier heights in $Pt/LaAlO_3/TiO_2$ heterostructures using well-established semiconductor device characterization techniques.

Introduction

Our objectives are to study and isolate the critical factors limiting solar water splitting efficiency and to establish a platform for designing optimal heterostructure devices.

Solar water splitting is achieved by photo-generation of electron-hole carriers inside the photon absorbing semiconductor, which are transported to the electrode surface to reduce or oxidize water, often with the aid of an efficient catalyst. The current best achievable efficiency of ~2.5 % [3] is far below the ~10 % yield needed for applications,

giving negligible contribution to current commercial hydrogen production. Three principal factors limiting the practical implementation of solar water splitting are: *i)* Inefficient charge separation, *ii)* Slow chemical reaction at the oxide surface, and *iii)* Ineffective use of the solar spectrum in the visible. Despite the many efforts to address these challenges, the majority of experiments use polycrystalline materials. The effects of surface crystalline orientation, particle size, doping, and modifications of the near-surface band diagram are typically not isolated, with experiments varying multiple relevant parameters. Thus, there is great difficulty in developing a fundamental understanding necessary for significant progress. Here we use single crystalline *oxide heterostructures* to provide the experimental platform to develop this understanding and the design principles that can greatly enhance conversion efficiency.

Background

The study of solar water splitting using *epitaxial oxide heterostructures* is still rare compared with the mainstream of research using polycrystalline specimens. However, the following two reports present growing interest in using epitaxial thin films as a new platform for designing catalysts exploiting the well-defined surface and bulk structures.

The first report [4] is the fabrication and photoelectrochemical characterization of epitaxial Rh-doped $SrTiO_3$ (Rh:$SrTiO_3$) thin films. The band gap was reduced from the original 3.2 eV ($SrTiO_3$) to 2.1 eV ~ 2.6 eV depending on the oxidation state of Rh (Rh^{3+} or Rh^{4+}). From cyclic voltammetry under light, it was shown that Rh:$SrTiO_3$ showed *p*-type behavior producing H_2 at cathodic polarization which was absent for the normal *n*-type Nb-doped $SrTiO_3$ substrates. Despite its low yield, the demonstration of *p*-type behavior in $SrTiO_3$ opens new possibilities to design solar water splitting devices including *pn*-junctions with better chemical stability.

The second report [5] is the reduction of band gap in α-$Fe_{2-x}Cr_xO_3$ thin films grown on Al_2O_3 (0001) substrates. Despite the larger band gap for α-Cr_2O_3 (3.0 eV), the band gap of α-$Fe_{2-x}Cr_xO_3$ was almost constant at ~1.7 eV in the range $0.2 < x < 0.9$, smaller than α-Fe_2O_3 (2.1 eV). A detailed growth study of these thin films revealed the stable phase boundaries between α-Fe_2O_3 and Fe_3O_4 in the T-P_{O2} phase diagram [6]. Although photoelectrochemical characterization is yet to be performed, α-$Fe_{2-x}Cr_xO_3$ promises to be a good candidate for solar water splitting catalyst given its small band gap and the expected chemical stability in aqueous solution.

Results

We have made three major achievements as explained below.

1. Control of defects in epitaxial oxide thin film heterostructures

In order to form a concrete basis for this project, we focused on the growth of epitaxial anatase TiO_2 thin films and heterostructures. In all of our studies, it is essential that the carrier density and mobility of the semiconductor are controlled precisely and reproducibly. Generally, such properties are most sensitive to oxygen vacancies formed according to the thermodynamic conditions during synthesis. Therefore, the ability to control oxygen vacancies independently from the thermodynamic constraints is inevitable,

especially given the similar thermodynamic stability of anatase and rutile phases [7]. Here we conducted a systematic growth study of undoped anatase TiO_2 thin films, varying the growth deposition rate, r, and characterized their structural and electronic properties by transport and optical measurements.

Anatase TiO_2 thin films were grown on $LaAlO_3$ (001) substrates by PLD [8]. The growth rate was controlled by the laser fluence and the laser repetition rate. All film surfaces showed surface roughness of less than 1 nm, and growth of single phase epitaxial anatase TiO_2 (001) thin films was confirmed by x-ray diffraction. The resistivity at $T = 300$ K, $\rho_{300 K}$, as a function of r peaks around a value of $r \sim$ 5-7 $\times 10^{-3}$ nm/s as shown in Fig. 1. This peak coincides with the minimum in the carrier density obtained from Hall measurements. In order to confirm the origin of the carriers, PL measurements were performed at $T = 10$ K. By carefully analyzing the PL spectra for each r, oxygen vacancy ($V_O^{\bullet\bullet}$) coupled peak intensity traced a similar trend with the carrier density obtained from Hall effect, giving an independent measure for the variation in $V_O^{\bullet\bullet}$ at different r.
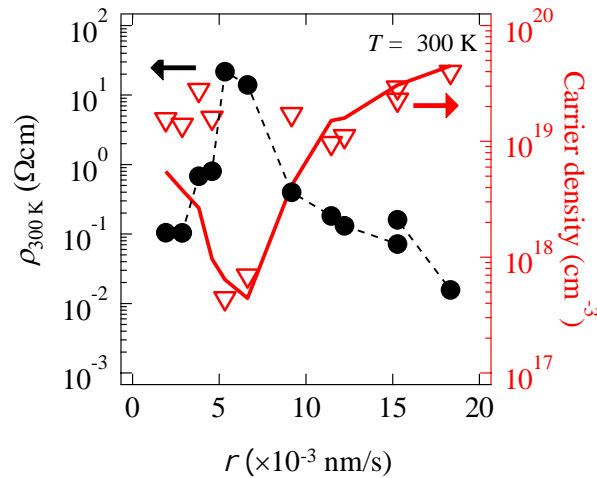

Figure 1: Carrier density and resistivity at $T = 300$ K, $\rho_{300 K}$, as a function of the growth rate r. The dashed line is a guide for the eye. The solid line is the calculated carrier density from the coupled rate equation. (Publication [1].)

The growth rate dependence of $V_O^{\bullet\bullet}$ can be understood by considering the dynamics of the oxidation process. When the highly oxygen deficient ablated TiO_{2-x} precursors adsorb on the growth surface, the adsorbed precursors oxidize until the next layer of precursors are deposited. At high deposition rate, the adatoms freeze on the lattice sites before being oxidized, producing highly oxygen deficient thin films. As the deposition rate decreases, the adatoms will have more time to reoxidize, leading to smaller $V_O^{\bullet\bullet}$ density. However, calculations have shown that in equilibrium, the *subsurface* of TiO_2 (001) favors a more reduced state than the top surface [9]. Therefore, when the adatoms have long enough exposure time to extract oxygen atoms from the subsurface to reach equilibrium, the layers are expected to be oxygen deficient except for the topmost layer.

By solving a coupled rate equation for $V_O^{\bullet\bullet}$ density, we were able to quantify the variation in $V_O^{\bullet\bullet}$ density, which explains the trend observed in Fig. 1.

2. *Fabrication of dipole engineered heterostructures*

Based on these defect-controlled TiO_2 thin films, we fabricated (001)-oriented $LaAlO_3/TiO_2$ heterostructures to manipulate the surface dipoles on the TiO_2 surface. Here, depending on the termination layer of $LaAlO_3$ on TiO_2, a surface dipole of $(LaO)^+$-$(AlO_2)^-$ or $(AlO_2)^-$-$(LaO)^+$ forms on the TiO_2 surface, effectively modifying the electron affinity of the TiO_2 thin films.

Despite our well-defined TiO_2 thin films, deposition of $LaAlO_3$ layers lead to a severe degradation of the underlying TiO_2 thin films as reported previously [10]. In order to stabilize both materials, the growth rate was carefully controlled. $LaAlO_3$ layers deposited at different laser repetition rates on $TiO_2/LaAlO_3$ (001) heterostructures indicated that the quality of the underlying anatase TiO_2 thin films improve at slower repetition rate and the in-plane Hall measurements revealed an exponential increase in the carrier density as a function of the laser repetition rate. These results suggest that the extraction of oxygen atoms from the TiO_2 to the $LaAlO_3$ layer is the dominant origin of the degraded TiO_2 films when $LaAlO_3$ films are grown at fast repetition rates. By reducing the laser repetition rate, the $LaAlO_3$ surface will have sufficient time to incorporate the molecular oxygen in the atmosphere rather than extracting oxygen from the underlying TiO_2, resulting in reduced $V_O^{\bullet\bullet}$ density in TiO_2.
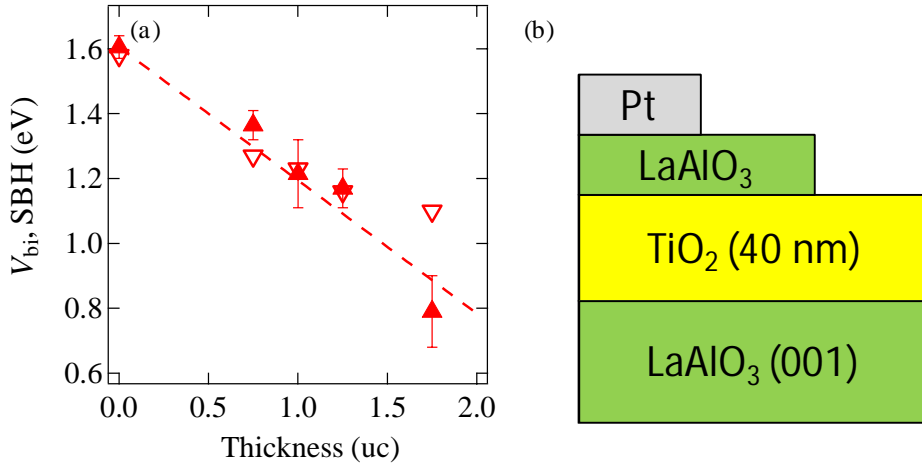

Figure 2: (a) Built-in potential, Schottky barrier height as a function of dipole layer thickness. Open symbols: V_{bi} from capacitance-voltage, closed symbols: SBH from internal photoemission. (b) A schematic diagram of the dipole engineered Pt/[$LaAlO_3$]/TiO_2 Schottky junctions.

We studied the effect of surface dipole through characterization of the Schottky barrier heights (SBH) at the Pt/[$LaAlO_3$]/TiO_2 junctions (Fig. 2). The barrier heights

obtained from capacitance-voltage and internal photoemission measurements agree well and a linear decrease over 0.8 eV with the $LaAlO_3$ thickness was confirmed, indicating that the $LaAlO_3$ layer is effectively acting as an electrostatic dipole. We note that the present demonstration at polycrystalline (Pt)/single crystalline ($LaAlO_3/TiO_2$) interface shows that utilizing oxides as charge stack layers in the ultrathin limit is a generic way of controlling band offsets not restricted to perovskite/perovskite interfaces [11].

3. Photoelectrochemical characterization of oxide heterostructures

Photoelectrochemical characterization of epitaxial anatase TiO_2 thin films was conducted to evaluate their intrinsic properties as photoanodes. Here we focused on how the properties evolve as a function of the film thickness in the (001) orientation. Despite the long history of TiO_2 photoanodes, a systematic photoelectrochemical study of (001) oriented anatase TiO_2 thin films has been limited [12].
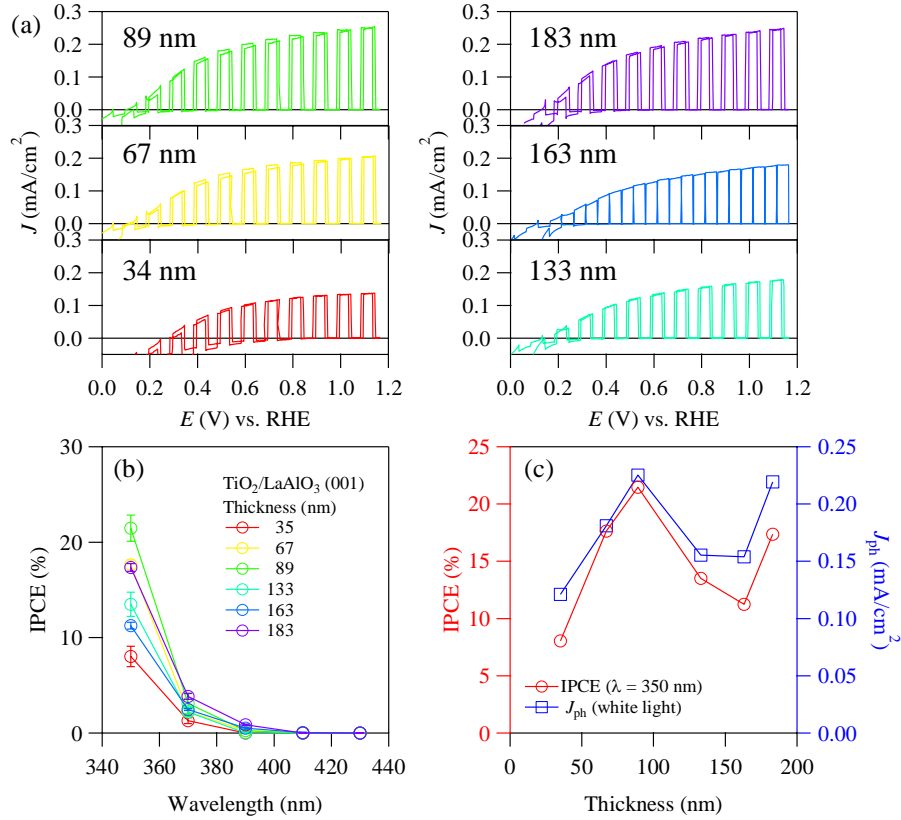

Figure 3: (a) Photocurrent under 900 W/m^2 of chopped white light irradiation for various thicknesses of TiO_2 thin films. (b) IPCE for various thicknesses of TiO_2. (c) IPCE at incident wavelength of 350 nm and photocurrent density under white light irradiation as a function of thickness. In both cases, photocurrent measured under +0.8 V vs. RHE.

Semiconducting TiO_2 thin films with thickness between 34 – 183 nm were grown on $LaAlO_3$ (001) substrates with pre-deposited Nb-doped TiO_2 back contact. The measurements were conducted using a solar simulator (wavelength 200 – 1010 nm) for white light irradiation under pH = 13.

The onset of the photocurrent was 0.1 V vs. RHE independent of thickness showing saturation under anodic potential [Fig. 3(a)]. The photocurrent density at +0.8 V vs. RHE increased in a step wise manner between 34 nm and 89 nm and 163 nm and 183 nm [Fig. 3(c)]. From electrochemical impedance measurements in the dark, the flat-band potential showed small variation with thickness, E_{fb} = -0.25 ~ -0.30 V vs. RHE which is slightly smaller than reported for (101) orientation in single crystals with comparable dopant density [13]. The incident photon to current conversion efficiency (IPCE) was measured at +0.8 V vs. RHE using a monochromatic light as shown in Fig. 3(b). For all thicknesses, IPCE rapidly decreased as the incident photon energy approached the band gap of TiO_2 (380 nm). The thickness dependent IPCE at 350 nm showed similar trend to the photocurrent density, close to a three-fold increase from 34 nm to 89 nm followed by a decrease and a further increase at 183 nm.

Since the film thickness used in this study is always shorter than the light penetration depth [14], we believe that the increasing trend in IPCE with film thickness is mainly due to increased absorbed photons. Considering the lattice relaxation of the thin films occurring at ~150 nm, the observed minimum in IPCE is likely related to the modulation of the hole diffusion length associated with the lattice relaxation of the thin films. Although a microscopic understanding requires further characterization, we believe that these results demonstrate the effectiveness of utilizing epitaxial thin film heterostructures for photoelectrochemical studies to elucidate the intrinsic properties of candidate photoanode materials.

Conclusions

With recent discoveries in highly efficient solar water splitting materials and proposed heterostructure devices, the materials and structures are becoming increasingly more complex, often masking the dominating factors responsible for the observed efficiency. Through this project, our approach of utilizing epitaxial heterostructures combined with semiconductor characterization techniques have demonstrated to be very powerful in addressing fundamental materials and interfacial properties that may have not been fully controlled previously. The key findings such as kinetic control of defects and its effectiveness in synthesizing multilayered structures are applicable to a broad range of oxides of interest, ultimately serving to increase the efficiency of solar hydrogen production and hence contributing to reduction in green house gas emission.

Publications and Patents

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