Atomically Engineered Oxide Heterostructures for Solar Water Splitting Catalysis

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Abstract
  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 breakthrough more than 40 years ago [1, 2]. However, the general approach of using polycrystalline samples for the study has hindered identifying the microscopic key factors limiting the efficiency.

  In this 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 catalysts. For this exploratory project, we work on: (1) identifying the role of the space charge region in the photocarrier separation process by systematically controlling the thickness and doping density in epitaxial thin films, (2) fabrication of atomic scale surface dipole layers to tune the energy band alignments at the electrolyte/oxide interface, and (3) basic characterization of intrinsic carrier transport properties of visible light harvesting photocatalysts.

  For all of our studies, the crucial step is the fabrication of heterostructures in a controlled and reproducible manner. We have 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 temperature dependent resistivity, Hall effect, combined with photoluminescence (PL) measurements, we have identified that oxygen vacancies are the source of the n-type carriers in TiO_2 and that their 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. Based on these results, we grew polar stacking layers ($LaAlO_3$) on the surface of anatase TiO_2 to act as surface dipoles. Initially, the growth of $LaAlO_3$ layers on top of TiO_2 resulted in severe degradation of the underlying TiO_2 thin films. By optimizing the kinetics of growth in PLD, we succeeded in forming high quality $LaAlO_3/TiO_2$ heterostructures suitable for photoelectrochemical characterizations.

Introduction
  Based on our expertise of atomic-scale growth of complex oxide heterostructures, our objectives for this project are to study and isolate the critical factors limiting solar water splitting efficiency and to establish a platform for designing optimal heterostructure catalysts.

  Solar water splitting is achieved by photo-generation of electron-hole carriers inside the catalyst, which are transported to the catalyst surface to reduce or oxidize water. 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 catalyst 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 propose that single crystalline *oxide heterostructures* can provide the experimental platform to develop this understanding and the design principles that can greatly enhance conversion efficiency.

(i) Inefficient charge separation

We propose a systematic study to isolate the dominating factor limiting the charge separation by photoconductivity and photo-voltammetry as a function of film thickness. This maintains fixed surface area and structure, and isolates thickness reduction effect on the photocarrier transit time. Space charge effects will be controllably studied (1) by varying the uniform doping density, and (2) by using interface "modulation doping", whereby the electrostatic boundary conditions induced at the substrate-film interface dope mobile carriers.

ii) Slow chemical reaction rate at the catalyst surface

A fundamental limitation of many solar water splitting catalysts is the position of the semiconductor band edges with respect to hydrogen/oxygen reduction potentials. We will epitaxially grow ultra-thin layers of charge polar stacks which will act as a dipole at the oxide/electrolyte interface to engineer the band edge positions without affecting the bulk oxide properties. This is an application of the technique we have successfully developed in controlling Schottky barrier heights at all-oxide metal-semiconductor interfaces.

iii) Ineffective use of the solar spectrum in the visible

Recently, nitrogen doping in oxides have proven to be an effective way of reducing the band gap in oxides. However, due to the difficulty in obtaining single crystals, fundamental materials properties have not been studied in detail. If time allows, we will focus on partial nitridation of our oxides thin films and characterize their intrinsic physical and photoelectrochemical properties.

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 catalysts including pn-junction catalysts 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 rage $0.2 < x < 0.9$ 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 electrochemical 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 electrolyte solution.

Results

In order to form a concrete basis for this project, we focused on the growth of epitaxial anatase TiO_2 thin films and heterostructures.

Anatase titanium dioxide (TiO_2) is one of the main oxide semiconductors we use throughout this project. 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.

60 nm thick anatase TiO_2 thin films were grown on $LaAlO_3$ (001) substrates by PLD. The substrate temperature and the oxygen partial pressure were fixed at 700 ºC and 1×10^{-5} Torr, similar to previous reports [8]. The growth rate, namely the film thickness per deposition time, 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 were confirmed by x-ray diffraction (XRD).

The temperature dependent resistivity (ρ - T) of the films for various growth rates is shown in Fig. 1(a). A metal-to-insulator transition was observed as r decreased from 18.3×10^{-3} nm/s to 6.6×10^{-3} nm/s, while the opposite behavior was found for 6.6×10^{-3} nm/s $\leq r \leq 1.9 \times 10^{-3}$ nm/s. The resistivity at $T = 300$ K, $\rho_{300 K}$, as a function of r peaks around a value of $r \sim 5\text{-}7 \times 10^{-3}$ nm/s as shown in Fig. 1(c). This peak coincides with the minimum in the carrier density obtained from Hall measurements [Fig. 1(c)]. The

maximum change in the carrier density is nearly two orders of magnitude, contrasting with a marginal variation in the electron Hall mobility [Fig. 1(b)].
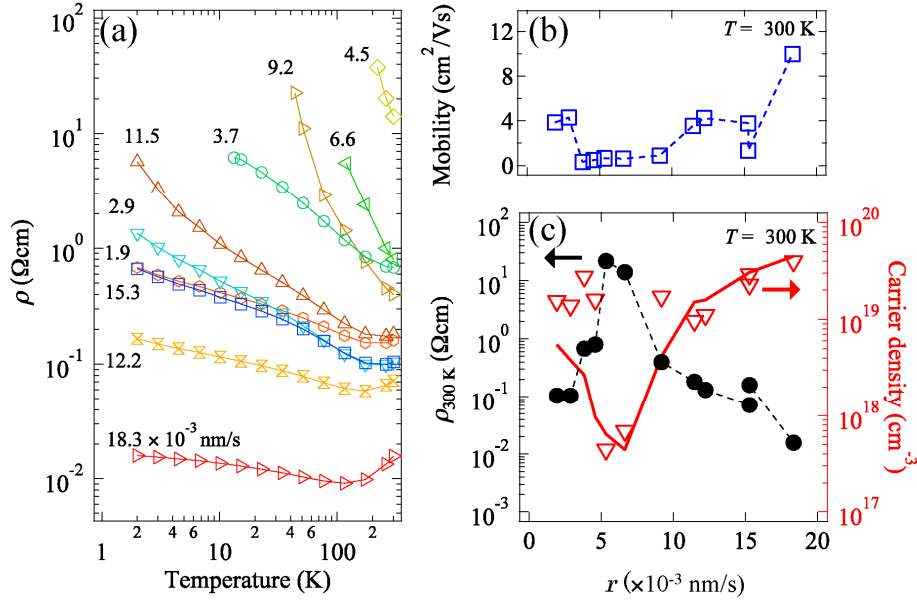
Figure 1: (a) ρ - T curves of anatase TiO_2 thin film for various growth rates, r. Numbers correspond to the growth rate ($\times 10^{-3}$ nm/s). (b) Hall mobility, (c) carrier density and resistivity at $T = 300$ K, $\rho_{300 K}$, as a function of r. The dashed lines are guides for the eye. The solid line is the calculated carrier density from the coupled rate equation.

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 evidence for the variation in $V_O^{\bullet\bullet}$ at different r.

The growth rate dependence of $V_O^{\bullet\bullet}$ can be understood by considering the dynamics of the oxidation process in detail. 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(d).
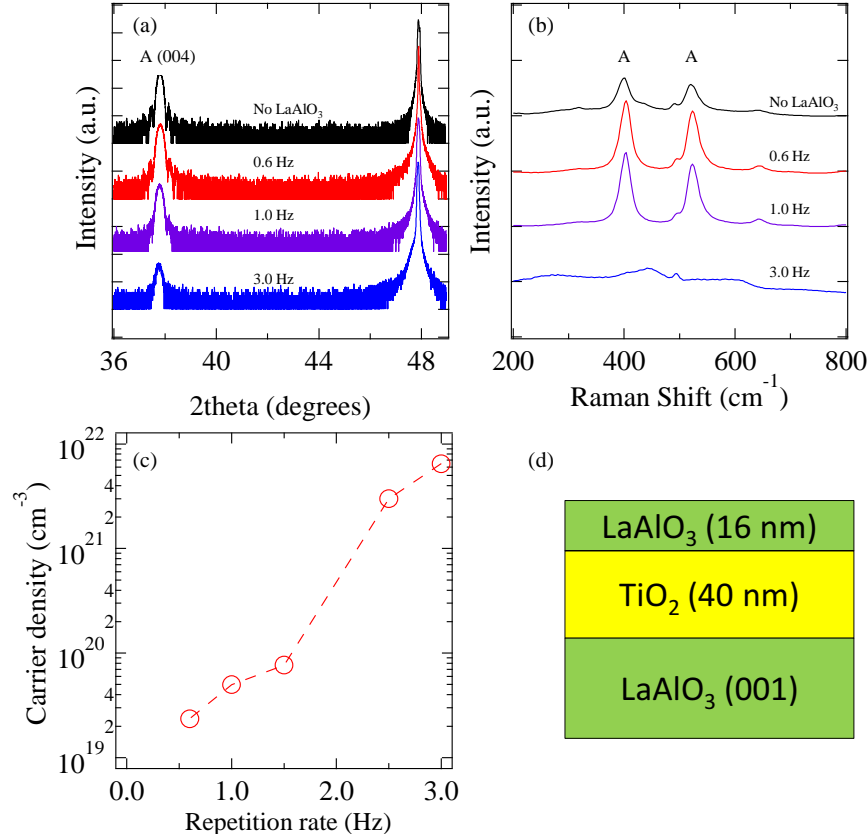
Figure 2: (a) The XRD pattern, (b) Raman shifts, and (c) carrier density from Hall measurements of the $LaAlO_3/TiO_2/LaAlO_3$ (001) heterostructures grown at repetition rates of 0.6, 1.0, 3.0 Hz. "No $LaAlO_3$" correspond to single layer of TiO_2 grown at 1.0 Hz. (d) A schematic diagram of the grown heterostructures. "A" corresponds to anatase TiO_2 specific peaks in (a) and (b).

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, potentially modifying the oxide/electrolyte interface band alignment.

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, we employed a defect control technique similar to the one mentioned above. 40 nm thick TiO_2 films were deposited on $LaAlO_3$ (001) substrates at a laser repetition rate of 1.0 Hz followed by 16 nm of $LaAlO_3$ layers at different laser repetition rates. The XRD patterns of the heteorestructures indicate that the quality of the TiO_2 thin films improve at slower repetition rate. This trend was confirmed more clearly from the Raman shift shown in Fig. 2(b). By conducting Hall measurements of the heterostructures at room temperature, an exponential increase in the carrier density was confirmed as a function of the laser repetition rate. These results suggest extraction of oxygen atoms from the TiO_2 to the $LaAlO_3$ layer is the origin of the degraded TiO_2 films

for the samples grown at fast repetition rates. By reducing the laser repetition rate, the surface $LaAlO_3$ 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.

We believe that the current progress forms a solid basis for the photoelectrochemical characterizations planned in the remaining time of this project.

Progress
This exploratory project pursues fundamental new ideas for photocatalyst development; however, the approaches taken would not be the direct implementation at commercial scale. Rather, the insights gained may guide development of cost effective implementations such as core-shell nanostructures. The use of highly idealized yet realistic structures will allow for fundamental progress in understanding the essential features governing the wide range of behaviors reported for polycrystalline oxide catalysts. Current commercial H_2 production by non-fossil fuels is only 4% (primarily electrolysis), for already a very large market [11]. Advances in solar water splitting have potential to be a game-changing fuel for a range of applications, such as H_2 vehicles.

Future Plans
The remainder of the research project will focus predominantly on the electrochemical characterization of heterostructures to test their ability as effective photocatalysts. These will include: (1) TiO_2 film thickness dependent study for charge separation efficiency, (2) surface dipole tuned $LaAlO_3/TiO_2$ heterostructures for the study of oxide/electrolyte band alignments, and if time allows, (3) synthesis and basic transport studies of epitaxial oxynitrides including $LaTiO_2N$ and $TiO_{2-x}N_x$.

Publications and Patents

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