

NEW STRATEGIES FOR APPLICATION OF DEFECT ENGINEERING TO TiO_2 BASED
PHOTOCATALYTIC MATERIALS

BY

DAVID EITAN BARLAZ

DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Chemical Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2017

Urbana, Illinois

Doctoral Committee:

Professor Edmund G. Seebauer
Professor Angus Rockett
Professor Paul Kenis
Assistant Professor David Flaherty

ABSTRACT

There is good reason to believe the performance of semiconductor metal oxides for catalytic applications may be improved through the application of principles related to defect engineering. Specifically, TiO_2 has already demonstrated promise as a catalytic material for environmental remediation by photocatalysis in aqueous media as well as water splitting for hydrogen fuel production by photo/electrocatalysis. There remain a number of major hurdles preventing widespread implementation of such technologies related to the material's optoelectronic properties.

Previous applications of defect engineering to these hurdles have yielded a variety of point dopants which narrow the band gap to include portions of the visible spectrum, but carrier lifetime is reduced as the same dopants act as recombination centers. Dopant free defect engineering has demonstrated that the amorphous synthesis route has a direct result on the native carrier concentration of a polycrystalline finished production through the manipulation of medium range order; this control has enabled an improved drift current to drive minority carriers to the free surface, but has fallen short of its goal. Heterostructuring has produced some innovative material combinations that place band edges of complimentary materials close to redox potentials of desired reactions, but there are many limitations including difficulties with material selection, interfacial charge transfer, cost, and stability.

This thesis endeavors to introduce and advance three distinct efforts within the spectrum of applicable defect engineering techniques. In dopant free material, the relationship between annealing temperature and final material properties of polycrystalline anatase TiO_2 was explored. The soak temperature had a strong effect on crystallite size with a variation of about a factor of 2 with the larger ones being of a length scale comprising the majority of film thickness. However, there was no corresponding changes in density or carrier concentration. This demonstrated that measurements of crystallite size may not be used as a direct estimate of grain sizes. As grain size (viewed by film density) did not alter, there was no benefit with regard to carrier concentration through the removal of free surface area within the material.

Attempts at reducing fully oxidized material by annealing in a hydrogen atmosphere produced thermally grown Magnéli phases without affecting the bulk crystallinity. These phases appear to have grown along grain boundaries through the removal of oxygen in the form of water. Because these phases form a separate contact with the substrate and top contacts, their effect of film carrier concentration is not perceivable until the filaments are fully formed, after which any further changes to the bulk material are obscured. Reversibility by thermal methods did not have good success possibly due to limitations to the diffusivity of molecular oxygen.

Lastly, a new heterostructure design was explored to better understand the dominant mechanisms of minority carrier transport. In this system, SrRuO_3 , a strongly correlated metallic oxide is used as a visible light absorber. Both electrons and holes must transverse a rectifying interfacial barrier before crossing a TiO_2 layer to a catalytic free surface. Minority holes avoid the need to tunnel or be excited beyond the TiO_2 band edges via an interfacial surface defect. From the interface, their transport to the free surface is governed largely by diffusion as evidenced by a linear dependence of activity on TiO_2 thickness and a weak band bending at the interface indicating little to no built in electric field. The performance of the material in an amorphous state was comparable to an epitaxially grown counterpart suggesting a robust system amenable to further development in lower cost systems. Performance was a bit under an order of magnitude below polycrystalline thin film TiO_2 catalysts.

ACKNOWLEDGMENTS

בס"ד

An expert is a man who has made all the mistakes which can be made, in a narrow field.

~Niels Bohr

I would like to thank my advisor, for his endless guidance and patience in the lab and for all the opportunities he provided outside the lab. I would like to thank my lab mates over the years for their aid in the lab and many useful discussions about lab and life. My undergraduates, Rickard Shin and Byeongjin Kang for their efforts. Thanks to Bruno Giuliano Nicolau for all his help with sputtering. I must think Kyle Webb in the mechanics shop for aid in repairs and many useful tips on vacuum equipment maintenance. The same goes to Mike “Hodge” Harland in the machine shop for aid with many challenges around the lab and great conversations besides.

The staff around campus were at many times indispensable to my success, they are too many to name all. In particular Mauro Sardela, Julio Soares, Rick Haasch, and Scott MacLaren of MRL deserve special thanks. Hearing of Scott’s passing so close to my defense was a major blow as he was such a giant in his field. Dane Sievers is an immense help with electrical testing and deserves an incredible amount of thanks for all his hours spent in the lab and office. His conversations will fill my ears for years to come when I am in need of guidance. Off campus I must thank Dr. Tiffany Kaspar at Pacific Northwest National Lab for teaching me a great deal about XPS interpretation. Thanks to Dr. Mingzhao Liu of Brookhaven National Lab for his aid in SrRuO_3 synthesis.

Special thanks to all my friends and family who made graduate school special and tolerable; Brian Rosen, BJ Slater, Lawrence Valverde, Naftali and Tali Rothstein, and YD Schwartz to name a few. Thanks to everyone I brewed beer, mead, and wine with; and for foraging around town with me. Special thanks to Marissa, Salem and Zev for coming into my life during graduate school, sorry you are stuck with me now.

TABLE OF CONTENTS

Chapter 1: INTRODUCTION.....	1
1.1 Motivation & Defect Engineering	1
1.2 Titanium Dioxide	3
1.3 Defect Engineering of TiO_2	4
1.4 Correlated Metallic-Oxides and SrRuO_3	6
1.5 Key Questions.....	8
Chapter 2: EXPERIMENTAL METHODS.....	10
2.1 Synthesis of TiO_2	10
2.1.1 Layer by Layer Deposition	10
2.1.2 Annealing.....	13
2.2 Synthesis of SrRuO_3 thin films	13
2.2.1 Electrical & Optical Characterization of SrRuO_3	14
2.3 Morphological Characterization	15
2.3.1 X-Ray Reflectivity & Diffraction	16
2.4 Electrical Characterization of TiO_2	17
2.4.1 Electrical Measurements.....	18
2.4.2 Carrier Concentration Determination	19
2.5 Atomic Force Microscopy	20
2.6 X-ray Photoelectron Spectroscopy	21
Chapter 3: EFFECT OF ANNEALING TEMPERATURE ON MORPHOLOGY AND CARRIER CONCENTRATION	23
3.1 Medium Range Order	23
3.2 Previous Work Concerning Medium Range Order.....	24
3.3 Experimental Results	25
3.4 Conclusions.....	28
Chapter 4: EFFECT OF HYDROGEN ANNEALING ON ANATASE TiO_2	30
4.1 Introduction.....	30
4.2 Key Questions	32
4.3 Experimental Design.....	33
4.4 Physical Characterization Results.....	33
4.5 Electrical Characterization Results	37
4.6 Reversibility.....	40

4.7 Conclusions.....	41
Chapter 5: SYNTHESIS AND CHARACTERIZATION OF STRONTIUM RUTHENATE.....	43
5.1 Introduction.....	43
5.2 Amorphous & Epitaxial SrRuO ₃ Synthesis	44
5.3 Physical Characterization Results.....	45
5.4 Optical Absorption Results.....	49
5.5 Conductivity Results.....	50
5.6 Conclusions.....	52
Chapter 6: PERFORMANCE OF TITANIUM DIOXIDE/STRONTIUM RUTHENATE HETEROJUNCTION PHOTOCATALYST IN DEGRADATION OF METHYLENE BLUE	53
6.1 Introduction.....	53
6.2 Heterojunction Band Structure and Charge Transfer.....	56
6.3 Methylene Blue Degradation	60
6.4 Photocatalysis Measurement Apparatus	63
6.5 Methylene blue degradation test conditions	66
6.6 TiO ₂ synthesis and thickness measurements.....	67
6.7 Photocatalytic Results.....	69
6.8 Conclusions.....	73
Chapter 7: DETECTION OF INTERFACIAL BAND BENDING AT THE TITANIUM DIOXIDE/STRONTIUM RUTHENATE INTERFACE BY X-RAY PHOTOELECTRON SPECTROSCOPY	75
7.1 Interfacial Band Bending.....	75
7.2 Reference Spectra & Fitting Constraints	78
7.3 TiO ₂ /SrRuO ₃ Interface.....	81
7.4 Discussion.....	83
7.5 Conclusions.....	84
Chapter 8: REFERENCES.....	85
APPENDIX A: LIQUID PHOTOCATALYSIS REACTION CELL	95
APPENDIX B: SOLAR SIMULATOR OPERATION INSTRUCTIONS	98
APPENDIX C: XPS CONSTRAINTS	100

CHAPTER 1

INTRODUCTION

1.1 Motivation & Defect Engineering

Among the many challenges facing the large scale adoption of technologies that support sustainable living is the high cost associated with adoption. This cost may come from a number of sources including material, fabrication, transportation, installation and maintenance. Encouragingly, some metal oxides such as TiO_2 offer promise as a viable material for many sustainable energy technologies when high earth abundance leads to low material cost. However, the design and fabrication of efficient catalytic materials from TiO_2 requires a better understanding and manipulations of the performance of these materials at an atomic scale necessitating the use of defect engineering.

Defect engineering refers to the effort to manipulate the concentrations, spatial distributions, and types of atomic-scale defects in a material. Defect engineering formed the basis for the birth of microprocessors as it was discovered that many transistors could be fabricated on a chip with a density many orders over that of a tube transistor device. The term ‘defect’ in a crystalline material can encompass a huge variety of types ranging from point defects in a crystal lattice caused by the removal, translation, or addition of either a native or foreign atoms to clusters of defects as shown in Figure 1¹.

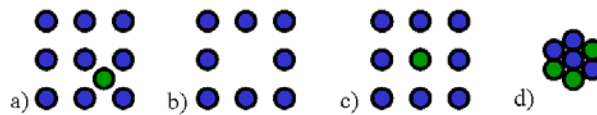


Figure 1: Examples of interstitial (a), vacancy (b), substitutional point defects (c) and defect clusters (d).

The foundation for defect engineering was that the conductivity, resistivity, capacitance, and other electronic properties of crystalline materials could be precisely tuned by controlling the type and/or

concentration of both native and non-native defects in the material. Defect engineering is often an important component of a related practice called “band engineering” that refers to the manipulation of the electronic band structure of a semiconductor, especially the energies of the valence and conduction bands. While the fields are distinct, electronic band structure is heavily influenced by the presence of defects, and often changes to band structure will be the primary physical manifestation of an intentionally manipulated defect. For the purposes of this thesis, we will generalize defect engineering to include both defect and band engineering, but the similarity should be noted when reviewing the literature on either subject.

In the case of integrated circuits, the primary crystalline material used was Silicon. The invention of the Czochralski process to produce low cost, highly single crystalline, high purity silicon wafers led the majority of defect engineering efforts to focus on the introduction of foreign atoms (dopants) both during growth and later via high energy ion implantation. Current defect engineering efforts in silicon on the side of single crystal purity work includes annealing procedures to remove low level carbon-oxygen complexes². Advanced ion implantation research includes a crystalline-to-amorphous transformation to lower the energy required for ion implantation³, as well as efforts to apply ion implantation techniques to new silicon structure such as nanowires⁴.

The expansion of defect engineering to new silicon structures has paralleled development of other defect engineering techniques as well as entry of defect engineering to new materials. Techniques have expanded to include not only the addition of *ex-situ* dopants, but *in situ* doping, other growth controls, annealing controls including atmospheric composition. In addition to single crystals, defect engineering is also studied in bulk forms of multicrystalline, polycrystalline and amorphous materials. As length scales decrease in electronic devices and nanostructuring becomes popular in catalytic materials, defect engineering is increasingly important to the understanding of interfaces between materials.

The effort to apply defect engineering to electronic materials beyond single crystal Silicon has been successful in many materials systems. Defect engineering and spectroscopy efforts have also

been made in two dimensional materials such as graphene⁵ and hexagonal boron nitride^{6,7}. Manipulation of nitrogen vacancies in diamond has led to opportunities in quantum computing^{8,9}. Attempts have so far been made to dope GaAs and ZnO nanowires with both transition and rare earth metals, for use in spintronic and luminescence devices⁴. Ion implantation for improved luminescence properties has been similarly sought in other materials used in light emitting diodes (LEDs) such as GaN¹⁰. Defect engineered HfO₂ has been under investigation as a possible magnetic semiconductor for use in memory devices; the switching speeds of memory units are closely correlated to concentrations of oxygen vacancies¹¹.

1.2 Titanium Dioxide

The material of choice for our defect engineering investigations in Titanium Dioxide (TiO₂). There is a constantly growing body of literature surrounding TiO₂ since the discovery of its photocatalytic properties¹². It is under investigation for use throughout materials research as a photocatalyst, other areas of heterogeneous catalysis, as well as a catalyst support. It is stable in a number of typical operating environments being highly insoluble. It is inexpensive to obtain, and benign to both humans and the environment. Lastly, it is amenable to a wide variety of synthesis techniques for both the production of thin films and nanoparticles.

Despite the immense interest and investment in the development of TiO₂ as a catalyst, a great deal remains to be investigated. In its native anatase form, it is highly *n-type* with an electrically active carrier concentration of about 1×10^{17} charges/cm³. It also exhibits several polymorphs or varying catalytic activity with the more active being the kinetically favorable but thermodynamically unstable anatase phase. When exposed to temperature above about 700 °F, the more thermodynamically favorable rutile phase begins to form in this films¹³.

Defect engineering has been accomplished to a degree in anatase TiO₂. A variety of substitutional defects have been successfully incorporated by various groups with varying success in

altering reaction rates in test systems¹⁴. Substrate choice has been shown to affect catalytic activity¹⁵. Dye sensitization has been accomplished but without producing the desired degree of improvement^{16,17}. Other reports demonstrate the varying of morphological properties with variations in synthesis and processing which are similarly correlated to changes in reaction rate^{18,19,20,21,22}.

We hypothesize that TiO₂ can become a more viable photocatalytic material with principles of defect engineering applied to its growth and processing. Precise control of carrier concentration may allow the TiO₂ to be tuned to individual reactions or processes. In certain photocatalytic systems, lowering carrier concentration increases carrier lifetime which is key to improved quantum yield¹⁴. The combination of TiO₂ and a strong light absorbing material has been shown to produce improved photocatalytic activity as a heterojunction photocatalyst²³. The treatment of TiO₂ nanoparticles with hydrogen has also been demonstrated to improve photocatalytic activity via increased light absorption by thermal²⁴ and plasma treatment²⁵.

1.3 Defect Engineering of TiO₂

The application of defect engineering to catalytic materials, such as TiO₂, has received comparatively less attention to electronic materials, such as silicon. The expansion of nanotechnology has driven researchers to focus on improving surface area to weight or volume ratios while minimizing the loading of precious metals on supports. Many of these supporting materials are metal oxides due to the need to remain stable under intense heat. Additionally, some transition metal oxides have also found uses in gas phase reactions due to their unique acid-base properties, though the connection between charge carrier concentrations and acid-base charge balance is often overlooked despite being established for several different semiconductors^{26,27}. More recently defect engineering of V₂O₅ demonstrated a link between the ability to tune the fermi level²⁸ and surface potential²⁹ of the material, its acid-base properties, and its thermal catalytic performance.

Defect engineering in TiO_2 is difficult because of special challenges in carrier concentration metrology³⁰, the dearth of dopants having shallow donor or acceptor levels³¹, the effects of poorly-controlled concentrations of native point defects serving as donors or acceptors^{32,33} and the dominant effects of charged defects at grain boundaries³¹. The need for defect engineering to resolve these issues is becoming increasingly recognized^{34,35} although the primary efforts for TiO_2 (for photocatalysts^{36,37} and memristors³⁸) focused on doping for many years.

To avoid the problems inherent to metal oxide doping, this laboratory and others have developed dopant free defect engineering techniques including the discovery that film thickness^{31, 39} can control defects that influence carrier concentration propagating into improved rates of photocatalysis⁴⁰ and supported metal catalysis⁴¹. This technique relied on the removal of grain boundary space usable for charge accumulation thus restricting its use to polycrystalline materials. Treatment of thin films with a remote oxygen plasmas has been shown to affect surface potential with similar success in photocatalysis improvement⁴². Other examples of surface modification of TiO_2 achieved without dopants includes the use of templating to control surface site coordination⁴³, and *ex situ* treatment with TiCl_4 gas to alter surface crystallinity⁴⁴. The ability to perform defect engineering on TiO_2 via surface modification is promising due to its applicability to both thin film characterization systems as well as nanoparticles or other high surface area structured arrays.

Another method that TiO_2 has been improved without the use of dopants is through heterostructuring⁴⁵. This can mean several different things depending on the issue being addressed. For example, TiO_2 surfaces have been decorated with coupled co-catalysts such as Pt or MoS_2 that improve electron hole separation⁴⁶. This introduces issues of cost and stability while failing to solve the issues inherent to TiO_2 being a wide band gap semiconductor that does not absorb visible light⁴⁵. Similar to dopants, dye-sensitization allows for the possibility of improved light absorption while also raising the possibility of better aligning band edges to the redox potentials of reactants⁴⁷, or to electrode potentials in

photovoltaics⁴⁸. However, inherent issues of charge carrier motilities and lifetimes, along with persistent issues with sensitizer stability and regeneration has minimized the impact of this strategy⁴⁵.

A more aggressive approach is the formation of a mixed composite comprised of TiO_2 and a second material that may address multiple challenges to TiO_2 performance. An elegant example of this may be found in composite nanoparticles of $\text{LaVO}_4/\text{TiO}_2$. Here, the LaVO_4 acts as a light absorbing layer, co-catalyst, and provides improves band edge alignment for the degradation of benzene⁴⁹. Stability concerns are minimized relative to the leaching of an organic dye or the clustering of precious metals on the TiO_2 surface. Further development of charge transfer style heterostructured photocatalysis will require better understanding and attention to the contact between the two distinct materials including the formation of rectifying junctions and interfacial defects.

1.4 Correlated Metallic-Oxides and SrRuO_3

The advancement of metal oxide research has led to a significant growth in the investigation of more complex metal oxides, typically involving 3-4 different atomic species before consideration of dopants. The perovskite crystal structure (ABX_3 with 'X' typically being oxygen) has been of particular interest to many researchers due to the cubic symmetry of both the A and B atoms. Relative ion sizes for this crystal structure are quite stringent. As a result, any distortion due to doping may lead to significant changes in physical properties. This sensitivity to dopants, or other sources of lattice irregularity such as epitaxial mismatch, raises significant possibilities for defect engineering research.

Synthesis of these perovskite crystal structures can be difficult to achieve without high performance synthesis techniques such as Pulsed Laser Deposition (PLD) and Molecular Beam Epitaxy (MBE). There is also a very limited number of substrates that can meet the tight matching requirements for epitaxial growth of perovskite thin films. The most popular substrate for research on perovskite thin film device is SrTiO_3 (STO). An insulator intrinsically, STO can be made a conductor with Nb doping at less than 1% atomic concentration while retaining its crystallinity. STO single crystals are manufactured

commercially, but in wafers much smaller than silicon wafers currently achieve. One bright spot for high throughput processing of perovskite materials is the discovery that STO will grow epitaxially on single crystal silicon (001) surfaces and can be used as a buffer layer for further epitaxial growth of other materials such as TiO_2 ^{50,51}.

Perovskite materials have found potential application in many areas of electronic materials research. Notable examples include the use of N_d doped LaAlO_3 to produce a narrow emission continuous wave IR laser⁵². BaTiO_3 has demonstrated useful ferroelectric properties⁵³. PbTiO_3 and LiNbO_3 have been shown to act as piezoelectric materials^{54,55}. For a review of catalytic use of perovskites, a recent review by Grabowska highlights the explosion in the identification of candidate materials⁵⁶. A more unusual application of perovskites has been the discovery of photovoltaic⁵⁷ and photocatalytic⁵⁸ properties when the 'X' element of the crystal structure is a methyl group rather than oxygen.

Among the many perovskite materials of interest, SrRuO_3 (SRO) requires extended discussion. It is of particular interest because of its unique optical and conductivity properties as a "strongly correlated metal oxide". Despite being a metal oxide, it possesses carrier concentration and conductivity properties nearer to a metallic conductor. Optically, it has a low reflectivity and absorbs strongly in the visible portion of the spectrum, with a band gap loosely akin to that of a semiconductor. Physically, the (010) facet of SRO is a close match for both the (001) cubic facet of STO substrates as well as the (004) facet of anatase TiO_2 . This is of interest to the photocatalysis community as it created the possibility of improving the performance of TiO_2 through the use of a high efficiency light absorbing layer of SRO underneath a thin catalytic capping layer of TiO_2 . Early research showed promise surpassing activities of both commercial Degussa P25 TiO_2 powders and N-doped TiO_2 nanopowders^{23,59}.

A multitude of applications for the use of SRO have been investigated. The material has demonstrated promise for use in all-oxide magnetic tunnel junctions⁶⁰ and other spin-electronic devices⁶¹. As a model material, SRO interfaces with SrTiO_3 and other perovskites has been used as a material

system for simulating^{62,63} and studying⁶⁴ two-dimensional electron gases. The ability of SRO to absorb heavily in the visible spectrum has made it a candidate material for heterojunction photocatalysis studies as well²³. For a complete review of the properties of SRO, along with other applications including electrode materials, see Reference [65].

The decision to incorporate SRO into the heterojunction device structure is motivated by the need for a model system with exceptional visible light absorption. The high cost of ruthenium would make it a poor material choice for large scale photocatalysis applications, though this cost becomes less significant if this heterostructure were to be redeveloped at a later stage for electrocatalytic or photoelectrocatalytic purposes where activity is expected to be significantly greater. A practical heterojunction photocatalysis device structure could easily make use of other correlated metallic oxides with similar properties.

Despite its close epitaxial match with SrTiO₃, well controlled synthesis of SrRuO₃ has proven to be a difficult challenge in the past for several reasons. The first is that several other stable crystalline materials of the same elements exist, namely Sr₂RuO₄ and Sr₃RuO₇, meaning that deposition rates of the metals and background oxygen content may all require independent control. Bulk single crystals of both Sr₂RuO₄ and Sr₃RuO₇ have been produced using the float zone method⁶⁶, but the same study failed to produce SrRuO₃. Epitaxial thin films of SRO have been produced using RF magnetron sputtering at elevated temperature in an argon oxygen mixture⁶⁷; the authors of this study did not say whether the sputtering was done from a single strontium-ruthenium oxide ceramic target or co-sputtered from independent Sr and Ru targets. SRO epitaxial thin films have also been produced by PLD at elevated temperature in oxygen⁵⁹.

1.5 Key Questions

This thesis contains a combination of three distinct efforts to apply principles of defect engineering to amorphous and anatase TiO₂. The key questions to be answered in each of these three

efforts are somewhat disparate and will be discussed at greater length in their respective chapters. One feature that may be introduced is that insights gathered here represent similar placement with regards to a technology readiness level, specifically, all will be represented within the first three levels. TiO_2 has already demonstrated proof of concept level readiness for photocatalytic needs (level 4). However, the development of new defect engineering tools for TiO_2 require the discovery and understanding of newly discovered physical phenomena within the material.

The first effort is an attempt to manipulate the transformation from amorphous to polycrystalline material via annealing temperature to minimize the native *n-type* carrier concentration. The second is the treatment of fully oxidized polycrystalline films by annealing in a low pressure atmosphere of hydrogen in attempt to passivate oxygen vacancies. In both cases, the removal of negatively charged defects would allow better transport of holes to a free surface to catalyze a reaction.

The third is the combination of TiO_2 and SrRuO_3 in a heterojunction device structure to take advantage of favorable optoelectronic properties of the later for photocatalysis. This system offers a unique opportunity to raise a large number of interesting scientific questions about heterostructured materials. These questions can be broken down into four categories, a) the effect of a capping layer on the electronic structure of the SRO bulk, b) the effect the TiO_2 -SRO interface on charge transfer, c) the effect of the SRO on charge transport in the TiO_2 , and d) whether the TiO_2 free surface/liquid interface is affecting by any of the former. We will focus primarily on questions ‘b’ and ‘c’ within the third effort.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Synthesis of TiO_2

TiO_2 can be synthesized into thin films by a wide variety of methods. The most popular within the Integrated Circuit (IC) industry is by some type of Chemical Vapor Deposition (CVD). CVD allows for precise control over film deposition rates, temperatures, pressures, and doping concentrations if desired. The result is spatially uniform films and good repeatability with regard to control of final film morphology, crystallinity, and electronic properties. As a result, techniques adapted from the IC industry are most applicable to defect engineering efforts in thin films.

2.1.1 Layer by Layer Deposition

Atomic Layer Deposition (ALD) represents a sub-set of CVD techniques. In both cases, a synthesis chamber is fed gas phase precursor(s) at controlled rates. The chamber is operated in vacuum to prevent contamination or unintentional doping of the film. The primary difference between CVD and ALD is that the former delivers multiple precursors simultaneously to the chamber with deposition time and sample temperature being the only controllable growth variable. ALD by comparison, is a layer-by-layer, self-limiting growth technique in which the precursors are fed to the chamber in individual alternating pulses with a purge between each pulse. In true ALD, pulses and purges are timed such that the growth is a single atomic layer or less per pulse ensuring uniform film growth. In the case of polycrystalline or epitaxial film growth, this helps to ensure a highly crystalline product. When synthesizing amorphous films, the low growth rates are not inherently required for the process, and pulses can be increased to produce growth rates of several nm/cycle in a pseudo-ALD layer-by-layer technique.

Although the deposition rate of an amorphous film has a measureable effect on the morphological properties and carrier concentration of a final polycrystalline film⁶⁸, we believe that a pseudo-ALD process will be sufficient for the films required in these studies. We have no reason to expect a significant variation in the properties of the films in their amorphous phase with regard to optical and electrical conductivity which will be the most important properties when testing photocatalytic properties. Similarly, the final crystallinity of an epitaxially regrown film should not be dependent on the presence of sub-critical nuclei in the amorphous phase.

The precursor of choice is titanium tetra-isopropoxide (TTIP), shown in Figure 2. Though a liquid at room temperature, TTIP produces an appreciable vapor pressure according to Equation 1 when heated⁶⁹, and can thus be delivered to the chamber via a carrier gas such as N₂.

$$\log(P_v)[\text{Torr}] = 9.465 - 3222/T [\text{K}]$$

Equation 1: Vapor Pressure of TTIP

Though it degrades slowly with time and exposure to light, it is stable in the absence of moisture. It is unique among many metal organic precursors as it has multiple decomposition pathways depending on temperature and the choice of oxidizing agent as a 2nd precursor.

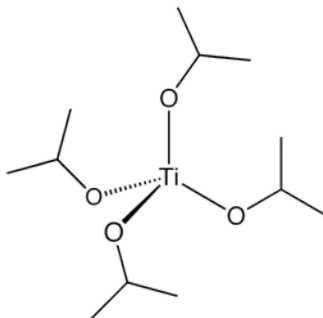


Figure 2: Structure of TTIP - Ti(OC₃H₇)₄

TTIP will decompose upon heating above about 100 °C without such an agent though higher temperatures (above ~165 °C) are favored for TTIP decomposition to avoid unoxidized carbon contamination of the sample^{70,71}. The use of an oxidizing agent is the simplest method for eliminating carbon; others have avoided it by using an evaporated Ti layer to begin deposition rather than expose Si to the TTIP directly⁷².

Oxidizing agents can be selected based on synthesis temperature, but selection rules are flexible.

Common agents include O_2 gas, and H_2O or H_2O_2 fed by a carrier gas from a bubbler. Water has limited reactivity below $150\text{ }^\circ\text{C}$ ⁷³, but above that it is a good agent as it is insensitive to temperature⁷⁴, safe to use, and easy to provide in excess leaving TTIP as a limiting reagent. TTIP will decompose above about $100\text{ }^\circ\text{C}$ to produce propane and water without an oxidizing agent making water the lower limiting factor in regards to deposition temperature.

Conversely to water, TTIP has an upper limit as far as deposition is concerned. Above about $300\text{ }^\circ\text{C}$, the decomposition product shift to include more isopropanol and eventually to propene^{70,75}. This shift coincides with the precursor sticking to adsorption sites. Lowering surface mobility in this way prevents true self-limiting growth necessary for ALD. Additionally, the rapidity of the decomposition precludes an oxidizing agent being able to participate due to the purge time. Above about $340\text{ }^\circ\text{C}$, TTIP will begin decomposition in the gas phase especially when not shielded from self-collisions by a carrier gas⁷⁶.

Antimony doped Si(100) wafers (Silicon Quest International) with n-type resistivity of $0.013\text{ }\Omega\cdot\text{cm}$ were used as substrates for polycrystalline TiO_2 work. Heterojunction device were grown on $SrTiO_3$ single crystals (MTI Corporation) either as received or with 60 nm of $SrRuO_3$ deposited by DC sputtering or Pulsed Laser Deposition (PLD). Substrates were degreased by successive sonication and rinsing in acetone and isopropanol, before drying with compressed N_2 . Silicon substrates were etched in 48% HF (Sigma Aldrich) (1 min) and rinsed in deionized water (1 min) to remove the native SiO_2 layer that otherwise acts as an undesired insulator.

All water used in the etching processes, as well as during synthesis was minimum $18\text{ Mohm}\cdot\text{cm}$ deionized water produced by the deionized water still (Barnstead E-pure D4641) in the Kenis lab group.

Detailed explanations of the Layer by Layer (pseudo-ALD) deposition chamber may be found in Master's and Doctoral thesis of David Barlaz and Meredith Kratzer Sellers respectively.

2.1.2 Annealing

Synthesized films can be amorphous or polycrystalline depending on synthesis temperature. Crystallinity may be achieved by annealing in a tube furnace (Barnstead Thermolyne F79300) under an ambient atmosphere. The programmable furnace allows films to be annealed at a specified ramp rate for specified time before turning off and allowing samples to cool. This furnace is capable of ramp rates up to approximately 60 °C/min.

When annealing in a controlled atmosphere and/or under vacuum was desired, samples were annealed in a 0.5 liter six-way cross vacuum annealing chamber. The sample was mounted to a low resistivity silicon carrier wafer (SQI, same as above) using a zirconia based (Aremco CeramabondTM 516) ceramic adhesive cured at 200 °F for two hours in air. The carrier wafer was attached to copper leads using tungsten foil and resistively heated with up to 30 Watts of DC power. The temperature of the sample was monitored via a k-type thermocouple pressed on the sample surface on the same feedthrough as the copper leads. Other ports included a viewing port, a leak valve connected to a H₂ compressed gas cylinder, and a gate valve with a pressure monitor attached leading to a Welch 1405 belt drive rough pump.

Atmospheric annealing may also be accomplished using temperature programmed X-Ray Diffraction (TP-XRD). Diffractometer details may be found in Section 2.3.1 X-Ray Reflectivity & Diffraction below. When TP-XRD is performed, the samples are mounted on a 1*1 inch silicon carrier wafer with Aremco 516. A custom sample stage includes a resistive heater which the carrier wafer is mounted to. Ramp rate and temperature are controlled through the diffractometer software, all annealing occurs in an ambient atmosphere.

2.2 Synthesis of SrRuO₃ thin films

SrRuO₃ was deposited two different ways in this thesis, both on undoped SrTiO₃ substrates. The first was from a single strontium-ruthenium oxide ceramic target by DC sputtering on the Illinois campus. The chamber was pumped to an unknown base pressure below 1*10⁻⁵ Torr before deposition.

Sputtering took place in 4 mTorr of a 60:40 Ar:O₂ mixture at room temperature. At a power of 15 W, a 60 nm film of SRO required 4 hours of deposition. All films produced by this method were amorphous. *Ex situ* annealing in air was performed on some samples in the same furnace described above to attempt solid phase epitaxial regrowth of the SRO.

The second method was performed at Brookhaven National Lab by PLD using a PVD Products PLD/MBE 2300 with a 248 nm KrF excimer laser. Deposition occurred from a single strontium-ruthenium oxide ceramic target at 750 °C in 200 mTorr of oxygen. All samples produced by this method were epitaxial.

2.2.1 Electrical & Optical Characterization of SrRuO₃

Due to differences in physical properties of amorphous and crystalline SRO, there was a need to estimate the relative degree to which photogenerated charge carriers would be produced and transferred to the TiO₂ capping layer. To accomplish this, optical transmittance measurements over the visible region were made using a Varian Cary 5G Spectrophotometer. Measurements were taken in both diffuse and direct modes to determine the effect of the unpolished substrate backside. Samples were mounted against a 2.5 mm through hole to ensure that only the film area was measured.

Electrical characterization measurements were made using a Jandel 4PP with the RM 3000 test unit. Conductivity values are not measured directly using a 4PP, rather a sheet resistance value is calculated from the current applied and voltage produced in units of $\Omega/\square$. Resistivity is then calculated using Equation 2.

$$\rho = R_s * t$$

Equation 2: Determination of resistivity using sheet resistance measured by 4PP.

Where ρ is bulk resistivity, R_s is the sheet resistance, and t is the thickness of the layer being measured. Conductivity is the reciprocal of resistivity, and estimations of carrier concentrations may be made from this value if desired. Care must be taken when performing 4PP on layered materials that the layer being

measured is the only conductive layer, is continuous, and forms an ohmic contact with the tips of the 4PP apparatus.

If the sample geometry is significantly different from a square, correction factors to the sheet resistance value may be applied. However, in the case that the distance between the farthest probes is less than half the distance from the probes to the edge of the sample, the shape factor does not make a significant difference. Additionally, the measurements performed in this thesis were for the purpose of comparing samples so absolute values were not of significant use.

All measurements were repeated both under ambient light, as well as under dark conditions. Dark conditions were obtained by placing aluminum foil sheets over the measurement apparatus. In general, this did not significantly affect measured values of resistivity as photogenerated carriers comprise a relative minority of free carriers in a metallic material. Only dark measurements are reported.

2.3 Morphological Characterization

While a single wavelength Ellipsometer is sufficient for films of known refractive index, it becomes a tool of limited value for polycrystalline thin films, films thin enough that optical properties no longer resemble the bulk, or films on highly reflective surfaces such SrRuO_3 , or very rough substrate or film surfaces. Films with thicknesses below about 10 nm are difficult to characterize with X-Ray reflectivity or spectroscopic ellipsometry unless they are smooth at both interfaces to within 1 nm. Such films may require cross sectional Scanning electron microscopy to provide accurate thickness measurements without the use of Transmission electron microscopy. Polycrystalline films tend to have varying refractive index, and even a small change (1%) can introduce significant inaccuracy to thickness measurements. In addition to more accurate thickness measurements, other morphological data for thin films is typically learned through the use of non-destructive X-ray based techniques.

2.3.1 X-Ray Reflectivity & Diffraction

Morphological data were acquired through the use of a PANalytical X-ray diffractometer. The Copper X-ray source operated at 45 kV and 40 mA. The detector was a PIXcel High Speed Line detector capable of 25 million counts per second per strip. For X-ray reflectivity scans, a 1/32 degree slit is used with the divergence slit, X-ray diffraction scans use a 1/2 degree slit.

X-ray reflectivity (XRR) data were analyzed for bulk density as well as thickness. Density was determined one of two ways depending on the quality of the scan. The most direct method is as follows¹. The experimentally determined critical angle of total external reflection, θ_c , is related to the bulk density of the film ρ according to Equation 3. θ_c is obtained from the angle at which the XRR spectral intensity is half of the plateau value⁷⁷.

$$\frac{\theta_c^2}{\rho} = \frac{r_e \lambda Z N_A}{\pi A} = F$$

Equation 3: Density as a Function of Critical Angle

F is constant for a given material and irradiating beam. From literature sources, r_e is the classical electron radius (2.82×10^{-15} m), λ the x-ray wavelength, Z the atomic number, N_A Avogadro's number, and A the mass number⁷⁸.

The PANalytical X-ray Reflectivity software package can also determine density and thickness through a simulation method where the two parameters along with surface roughness are varied by the user to match the experimental data. In cases where simulation was used, thicknesses agreed with the previous method to within either 1 nm or 2% of total thickness.

X-ray diffraction (XRD) data were analyzed using MDI JADE software. Peak identification was done using JCPDS cards 21-1272 and 21-1276 for anatase and rutile phases respectively. JCPDS cards 35-0734 and 43-0472 were used for SrTiO_3 and SrRuO_3 respectively. Scherrer's formula (Equation 4) is used by the software to determine individual crystallite sizes.

$$D = \frac{0.9\lambda}{B \cos(\theta)}$$

Equation 4: Scherrer's formula

From the instrument, $\lambda = 0.15406$ nm. Additionally, $\beta = B - b$, where B is the observed FWHM and b is the instrument function determined from the broadening of the monocrystalline silicon diffraction line. Peak broadening was assumed to be solely a function of crystallite size as microstrain and temperature effects are expected to be negligible for room temperature measurements¹.

Without a more direct visualization method, determination of grain size is not possible. Crystallite size is therefore used as a type of proxy for grain size in polycrystalline material with the assumption that they are at least partially correlated. Grain sizes may be directly visualized using Transmission electron microscopy if required⁷⁹.

2.4 Electrical Characterization of TiO₂

Defect engineering desires to control the concentration of electrically active defects in a material. This is a non-trivial matter in TiO₂ and indeed much of the literature seeks to explain catalyst performance solely in terms of morphological properties as a work around. TiO₂ has a relatively high bandgap (3.2 eV), and forms a Schottky diode with many metals. This makes Hall effect measurements difficult, and traditional Four Point Probe (4PP) measurements nearly impossible.

To overcome this, carrier concentration is derived from Mott-Shottky plots taken from Capacitance-Voltage sweeps of TiO₂ thin films built into an electrical circuit with the metal contacts and the silicon substrate. The device structure and protocol first developed in this research group^{1, 80} has been altered to avoid the use of InGa eutectic. Updated details of the diode fabrication process may be found in the master's thesis of David Barlaz⁸¹ and recent literature⁶⁸ while a schematic of the final device structure may be seen in Figure 3.

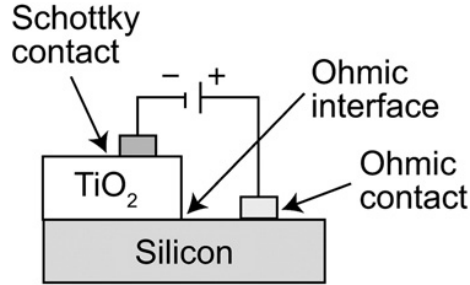


Figure 3: Schematic of the Al/TiO₂/Si/Al Mott-Schottky diode test structure.

2.4.1 Electrical Measurements

Electrical measurements are carried out on a probe station with four Signatone S-725 micropositioners, each connected to a dedicated 3 lug BNC triaxial cable for connection to instruments. Each micropositioner was equipped with a 1.25" SE-T tungsten probe tip with a tip diameter of 5.0 μm , and a shaft diameter of 25 mm. Measurement control and data collection were performed using a Shottky diode testing program within Agilent IC-CAP Device Modeling Software.

I-V sweeps were carried out using a Agilent B2900A Series Precision Source/Measure Unit. For a given sample, a sweep was taken using two Al/Si ohmic contacts to ensure that they demonstrated ohmic behavior and were of sufficiently low resistance. A typical sweep would be 400 data points from -0.5 V to 0.5 V. One of these contacts would be used in series with a TiO₂/Al contact for a second *I-V* sweep to demonstrate diode like behavior and determine the location of the diode's breakdown point under reverse bias. A typical sweep would be 800 data points from -10 V to 10 V with device breakdown typically occurring between -2 V and 2 V.

C-V sweeps were obtained using a Agilent E4980A Precision LCR Meter. Up to three TiO₂/Al contacts would be tested for each sample depending on the integrity and placement of the contacts. A typical sweep would be 500 data points between -1.5 V and 2.5 V with a frequency of 1 MHz. Two sweeps were obtained for each sample. The first with is taken using default instrument settings with a "medium" integration time for each data point. The second increased the integration time

to “long” and added a 5 ms hold at each data point. This later scan was to help ensure that scan data did not have any transient behavior caused by the rapidity of testing.

2.4.2 Carrier Concentration Determination

The extraction of carrier concentration values from C - V data is not trivial. Typical C - V sweeps can be divided into five regimes. On the two extremes, the device is in ‘breakdown’, which is to say that a sufficiently high voltage has been applied that the circuit ceases to act like a capacitor in series with a resistor and behaves like a series of resistors. In the middle behavior is divided into accumulation, depletion, and inversion regimes. Figure 4a shows a typical C - V plot for a Al/TiO_2 diode¹.

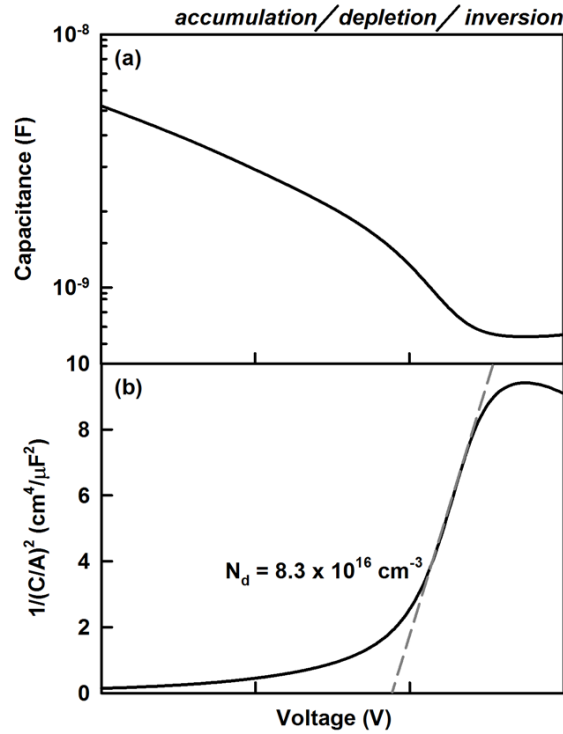


Figure 4: a) C - V data and b) Mott-Schottky plots for a Al/TiO_2 device.

In the accumulation regime (typically $V < 0$), positive charges accumulate in the TiO_2 at the interface from the bulk. This coupled with a reduction in positive charge on the Al side produces a higher capacitance. In the depletion region ($0 < V < V_{\text{FB}}$) the reverse occurs. Positive charges from the bulk Al are pushed to the interface while positive minority carriers in the TiO_2 are drawn away creating a

negatively charged depletion layer at the TiO_2 side of the interface. These oppositely charged interface sides lower the capacitance. Inversion ($2V_{FB} < V$) occurs as negative charge carriers from the TiO_2 bulk are now pushed to interface increasing capacitance.

In the depletion region, the device obeys the Mott-Schottky Equation below.

$$\frac{1}{C^2} = \left(\frac{2}{q\epsilon_0\epsilon N_D A^2} \right) \left(V - V_{FB} - \frac{kT}{q} \right)$$

Equation 5: Mott-Schottky Equation

C is the capacitance across the semiconductor/metal interface, ϵ_0 is the permittivity of free space, ϵ is the dielectric constant for the semiconductor ($\epsilon_{\text{TiO}_2} = 55^{82}$), V is the applied voltage, V_{FB} is the flat band voltage, kT/q is the potential from thermal generation of electron hole pairs, A is the contact area, and N_D is the net donor concentration. Equating net donor concentration and carrier concentration is valid for applied potentials which are low enough to form the generation of ions in the solid. N_D can be extracted by plotting $1/C^2$ v. V and determining the slope in the depletion region as seen in Figure 4.

2.5 Atomic Force Microscopy

ALD, Sputtering, and PLD are all known for their ability to produce highly uniform, smooth thin films regardless of the material being deposited. However, when working with material layers of decreasing thickness, even small non-uniformities become more likely to affect the performance of a device. This is especially true of catalytic materials where activity is typically normalized and reported in units of activity per unit of real surface rather than bulk area. For this reason, if it necessary to produce at least a rough estimate of surface roughness to ensure that sample to sample variation is minimal and does not cause catalytic activity data to become meaningless.

A useful characterization technique for this is Atomic Force Microscopy (AFM). AFM is a technique where a hard tip with an extremely fine point (< 10 nm) is rastered across a surface, either dragging or tapping, while at least one other measurements are taken. The simplest and most common of these is a height measurement made by reflecting a laser onto the backside of the cantilever arm holding

the tip. One thing that has led to the notoriety of AFM is the ability to achieve resolution of a single atomic radius in the vertical direction when measuring sharp steps on surfaces. AFM is a parent technique to many other characterization tools where other measurements are made simultaneously using tip bias, sample bias, other photostimulation, etc.

The Asylum Research MFP-3D™ AFM tool was used for AFM measurements. Tips were Budget Sensors BS-Tap300Al tapping tips with a lateral resolution of approximately 8 nm when new. All measurements were performed in tapping mode where the tip is rapidly waved in the vertical direction by a series of piezoelectric motors. This helps prevent rapid tip degradation from dragging across a hard surface and also helps reduce the buildup of organic contaminants on the tip which impede measurements. Surface roughness measurements, and other analyses, were performed using the Igor Pro software package used to control the AFM.

2.6 X-ray Photoelectron Spectroscopy

The basis behind X-ray Photoelectron Spectroscopy (XPS) is that for every element and every bond type, there will be a signature energy associated with the transition of an electron from a core shell to the vacuum level. Electrons are excited and ejected by a beam of X-Ray photons of known energy, and the kinetic energy of the ejected electrons is measured using an electron energy analyzer. The binding energy of these electrons is given by Equation 6.

$$KE = h\nu - BE - \phi$$

Equation 6: Determination of Binding Energy from Kinetic Energy of a free electron.

where the energy of the incoming X-Ray photon is given by $h\nu$ and ϕ is the work function of the material, or the energy between the Fermi level and the vacuum. Binding energy is defined in XPS as the energy difference between the Fermi level and core shell energy level. Typical XPS data will be plotted on a binding energy scale with a reverse order x-axis so that when reading a plot from left to right, the kinetic energy will be increasing.

The practical limit to XPS with regard to material thickness is the escape path of the ejected electron. The signal gained versus depth drops off significantly above one mean free path for an electron making XPS primarily a surface characterization technique. Typically depths for XPS profiling will be in the range of 2-10 nm, often less than 5 nm.

The SRO deposited by room temperature sputtering was done with a single SRO ceramic target. Because deposition of Sr and Ru cannot be controlled independently, a mechanism for comparing the stoichiometry of the finished film is required. XPS provides a relatively quick way to obtain chemical composition near the surface of the film to within a few atomic percent. Minimal data fitting and processing is needed. The deposited films are expected to be homogenous, so a near surface composition is a good proxy for bulk film composition, especially where ratios of metal elements are concerned.

The second use for XPS in this project is the determination of interfacial band bending at a shallow buried interface. Because of charge compensation at a heterojunction, the redox state of elements in the atomic layers closest to the junction may differ significantly from the bulk material. XPS is capable of capturing this phenomenon in the form of peak shifting and broadening when the buried interface is less than the mean free path of an electron from the surface (~ 5 nm for TiO_2). Details of the technique can be found in Chapter 6.

All XPS measurements were performed on a Kratos Axis ULTRA instrument with a pass energy of 40 eV, excitation by monochromatic Al $K\alpha$ radiation. Samples were sonicated in acetone, sonicated heavily in IPA, and dried with dry N_2 before being scanned to prevent significant surface contamination. Samples were mounted with copper clips on the surface as the semiconducting nature of the TiO_2 can lead to charging. All samples were grounded and data were collected with charge compensation off. The metallic nature of the SRO was sufficient to prevent significant charging when grounded despite the insulating nature of the STO substrates. All data fitting and analysis was performed using the Casa XPS software package.

CHAPTER 3

EFFECT OF ANNEALING TEMPERATURE ON MORPHOLOGY AND CARRIER CONCENTRATION

3.1 Medium Range Order

The final microstructure of a polycrystalline film is in and of itself complex, there is also another regime of crystallinity that must be accounted for when studying the crystallization of an amorphous material. Typically, crystallinity in films is detected by spectroscopic techniques such as XRD. This technique can produce a lot of noise especially with films with significant surface roughness meaning that the smallest crystal detectable will be on the scale of several to tens of nanometers containing dozens to hundreds of unit cells. Many nominally amorphous materials contain a shorter range crystallinity that forms under growth conditions but is not detectable by commonly available spectroscopic methods. This level of order is not necessarily energetically stable over long periods of time. However, if a nominally amorphous film begins crystallization soon after growth, this medium range order may allow nuclei for larger stable crystallites to form more quickly. This regime of crystallinity has been given several different terms in the literature, several of which are introduced below. For simplicity, in subsequent sections of the present work this regime of crystallinity will be collectively referred to as “medium range order” or MRO.

Nanoscale order in the form of “subcritical nuclei” in amorphous titania-silica glass has been detected using neutron scattering data assisted by computational techniques⁸³. Experimental techniques have been developed for detecting nanoscale order using Fluctuation Transmission Electron Microscopy⁸⁴ in some disordered solids with some complimentary computational work⁸⁵ by the Abelson group at U. of Illinois.

The presence of “medium range order” in the form of subcritical nuclei in CVD-deposited amorphous TiO₂ was noted by our group in a photo-assisted surface diffusion experiment⁸⁶. Here subcritical nuclei were present throughout an amorphous titania film, and the film was exposed to low level UV light through a patterned photo mask. In areas exposed to the light, critical nuclei grew as mobile surface atoms migrated to the subcritical nuclei. Furthermore, the shape of the final crystallite was controllable by varying the pattern of the photo mask. If the same level of medium range order detected at the surface by Kondratenko *et al.* is present in the bulk of our amorphous titania films, it may have a noticeable effect on the final crystallized form.

3.2 Previous Work Concerning Medium Range Order

This results in this chapter are an extension of an effort to discover and manipulate medium range order in amorphously deposited TiO₂ during crystallization to the anatase phase. Previous results are contained in the Master’s thesis of David Barlaz. There details of experiments in which the deposition rate, deposition temperature, and ramp rate used during annealing were altered.

The effects of deposition rate and temperature closely followed each other as a single parameter, the mobility of deposited atoms, was altered. At lower deposition rates and deposition temperatures, each ‘layer’ of atoms has a greater degree of freedom initially before being covered. This allows for some of these sub-critical nuclei to form in a highly dense and relatively ordered amorphous material. Upon crystallization, these films exhibited significantly (~ 15%) greater density and reductions in carrier concentration of about ½ an order of magnitude. The explanation was that the presence of medium range order at the outset of crystallization by annealing allowed for fewer, larger grains to form with less void space between grains leaving fewer internal surfaces for oxygen vacancies to form and store charge.

The effect of annealing ramp rate was less straightforward. As ramp rate was increased, monotonic increases were observed in both crystallite size and bulk density. The explanation was that the

MRO present in the film was able to grow rapidly into stable crystallites upon annealing, and that this rapid growth outcompeted the growth of randomly seeded nuclei in the remaining amorphous material. However, there was the corresponding change in carrier concentration. No explanation was able to be given for this without the tools available. It is possible that the increase in crystallite size does not translate as well to grain size as hypothesized and that enough pore space continued to exist allowing oxygen vacancies space to maintain their stability.

3.3 Experimental Results

To examine the effects of steady annealing temperature that converts amorphous material to anatase, films were grown at 200 °C and 2.25 nm per cycle to thicknesses of 80 or 250 nm. Ramp-up was done at 20 °C min⁻¹ to temperatures between 400 and 650 °C. Figure 5 shows a sharp increase by a factor of two in crystallite size as the annealing temperature rises from 400 to 450 °C. Error bars are taken from JADE peak fitting results, the added curve is hand drawn, serving only to guide the eye.

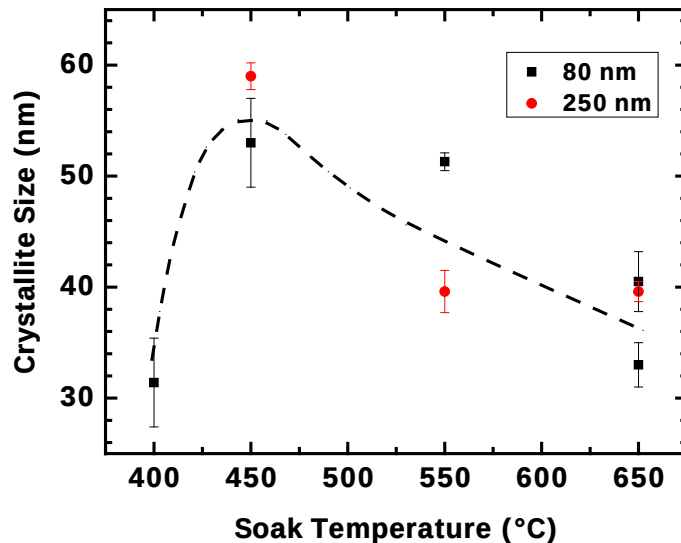


Figure 5: Variation in anatase [101] crystallite size with annealing temperature.

The crystallite size decreases gradually for further temperature increases back to approximately the original value. Despite significant scatter in the data, Figure 6 shows no perceptible change in bulk

density over the range of annealing temperatures tested. Error bars represent a 2% uncertainty around the determined value typical to density measurements made with PANalytical software packages.

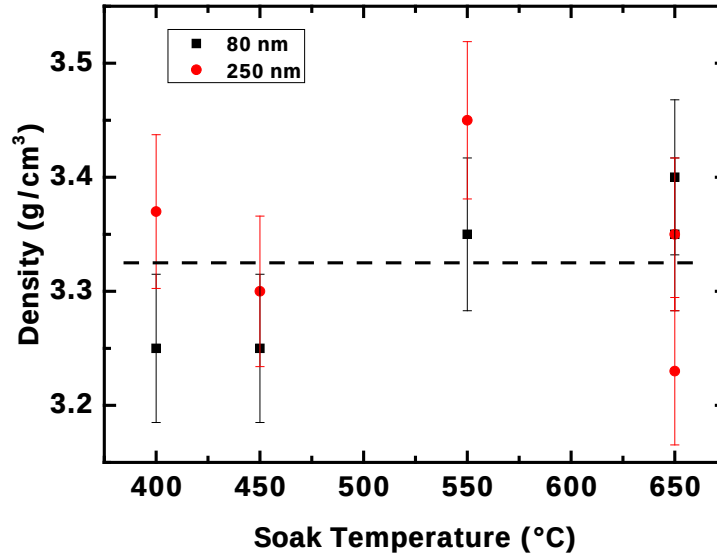


Figure 6: Variation in bulk density with annealing temperature.

Figure 7 compares the thickness variation of the carrier concentration for the two annealing temperatures. The data for 550 °C hint at a slightly stronger thickness variation than for 450 °C. However, given the substantial scatter, the results in do not provide an adequate basis for conclusively distinguishing a difference between the two annealing temperatures. Accordingly, a single line has been employed to correlate the data phenomenologically based on trends seen in the literature^{31,68}.

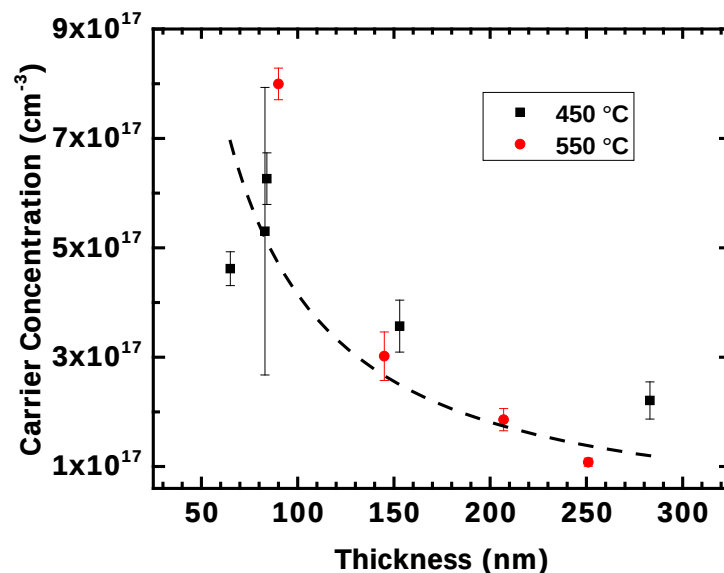


Figure 7: Variation in carrier concentration with thickness for annealing temperatures of 450 °C and 550 °C.

Carrier concentration data are not shown for 400 and 650 °C for partially unknown reasons. XRD of the 400 °C films showed normal peak intensities for a polycrystalline TiO₂ film. However, film conductivity was below a level needed to perform either I-V or C-V measurements. New Al contact fabrication did not rectify the issue which persisted across all samples annealed at 400 °C. The conclusion was that either a degree of crystallinity or oxidation required to make grains conductive with each other was not met. This would potentially be of use if an application were discovered in which crystallinity without conductivity was required.

Samples annealed at 650 °C also exhibited conductivity issues which were not rectified by fabrication of new Al contacts. One likely explanation is that the increased temperature allowed for diffusion of oxygen from either the atmosphere, the TiO₂, or both into the silicon substrate creating an insulating barrier. This is supported by an outlier peak observed in the XRD pattern for one sample annealed at 650 °C (Figure 8) and nowhere else.

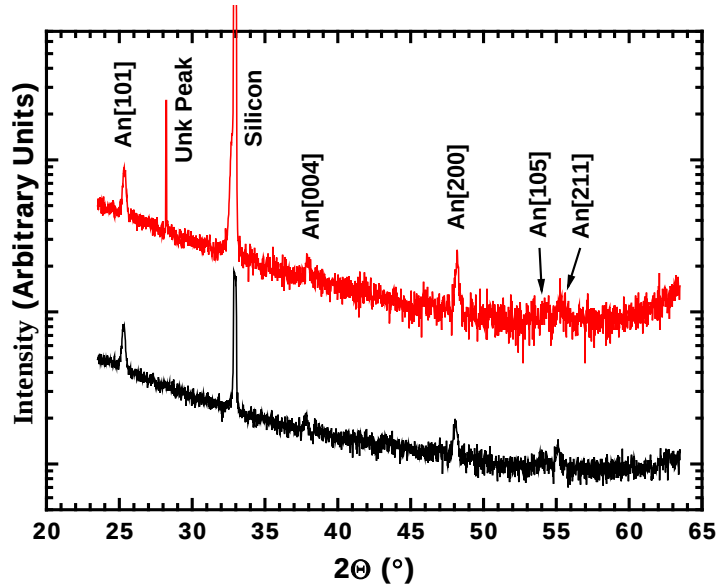


Figure 8: XRD patterns of samples annealed at 650 °C (red) and 550 °C (black). The unknown peak at 28.2° is attributed to a Silicon-Titanium oxide material. All other peaks attributed to anatase TiO₂ of Silicon substrate.

The peak does not match diffraction patterns for any phase of TiO₂; it does match diffraction patterns for several Si-Ti-O compounds that could result from an interfacial reaction between the silicon and titanium in the presence of heat and excess oxygen. Why this peak would appear, and no other peaks associated with any of these materials is likewise an unknown. What may be said is that all of the Si-Ti-O compounds discovered are believed to be insulating which is consistent with the probe station data. Why crystallinity would appear in one sample but not another is likewise unknown but suffice it to say that an amorphous mixture of Si, Ti and O would also be expected to form an insulating layer.

3.4 Conclusions

Increasing the final annealing temperature exerts no clear effect on density or N_d , but induces large and non-monotonic variations in crystallite size. Evidently any time or temperature dependence of the donor concentration for the polycrystalline material originates on a time scale less than the 24 annealing time used here, and the experimental range of temperatures. There was no compelling explanation for the complicated behavior of crystallite size. It seems reasonable that competing kinetic and perhaps diffusional processes are probably at work, either during the latter stages of the ramp phase

(whose length depends upon the final temperature) or early in the constant-temperature phase. While the variation in crystallite sizes lends further credence to the presence to medium range order in amorphous TiO_2 , the soaking temperature of the annealing process does not appear to be an appropriate method for future manipulation for purposes of defect engineering.

CHAPTER 4

EFFECT OF HYDROGEN ANNEALING ON ANATASE TiO₂

4.1 Introduction

The tools for defect engineering on the bulk properties of metal oxides are limited without the use of dopants. In the case of polycrystalline anatase TiO₂, the presence of oxygen vacancies creates an *n-type* material which can only be healed to a limited extent through film densification. It has been noted that these vacancies tend to aggregate at grain boundaries, void spaces, and other free surfaces within the material where the local energy landscape is different^{31, 68}. Building from this, it is conceivable that oxygen vacancies could be passivated or removed by the addition of a new species just at grain boundaries. If these defects are healed, the bulk properties of the material would be altered without the need to perform defect engineering in the bulk as is commonly performed with dopants. Similar techniques have already been demonstrated in rutile TiO₂ single crystals^{87,88} and ZnO single crystals^{89,90} where dangling bonds, surface polarity, and other specific surface sites/defects acted as gateways for dopants to enter the near surface bulk.

Polycrystalline materials retain significant porosity, so a treatment gas should not have difficulty accessing significant area of grain boundaries within the bulk material. Additionally, the treatment gas will need to be reactive with the TiO₂ without the addition of a liquid phase catalyst such as a strong acid. The adsorption of a number of different gases have been studied on TiO₂ surfaces⁹¹, though a great deal has yet to be done with regard to understanding their reactivity as a means of passivating oxygen vacancies. Oxygen has been shown to diffuse along grain boundaries and react with vacancies at high oxygen pressure in coarse grained rutile TiO₂, while at low pressures both coarse

grained rutile and finer grained anatase lost oxygen through the formation of titanium interstitials along grain boundaries⁹². Other promising candidates may include hydrogen and halides group elements. On rutile TiO₂, Cl₂ has been shown to adsorb to Ti⁴⁺ ions⁹³ and bridging oxygen atoms⁹⁴ at the surface and preferentially fill oxygen vacancies⁹⁵.

Hydrogen has a much longer, but more complex history with metal oxides. Diffusion of hydrogen in ZnO, and the effects on conductivity^{96,97}, was studied as far back as the 1950s due to the luminescence of ZnO. This work has continued with the aim of modifying ZnO conductivity for use as a transparent conducting oxide (TCO) using both hydrogen gas⁹⁸ and plasma⁹⁹. As TiO₂ research expanded, UHV studies showed that molecular hydrogen did not interact strongly with rutile TiO₂ surfaces¹⁰⁰, but that atomic hydrogen would adsorb at room temperature¹⁰¹, with oxygen vacancies acting as adsorption sites¹⁰². Despite the perceived low reactivity, rutile surfaces were shown to have all bridging oxygen sites hydroxylated at elevated temperature after treatment with hydrogen gas¹⁰³, and Diebold is quick to point out that this hydroxylation is unlikely to be present under normal synthesis conditions⁹¹.

Hydrogen annealing of TiO₂ has already received some interest from the electronic materials community as TiO₂ is considered a candidate electrode material for batteries and fuel cells where corrosion is a major concern^{104,105}, as well as non-volatile memory applications due to its thermal stability and unipolar switching mechanism^{106,107}. In all cases, the conductivity change is attributed to the reduction of the TiO₂ along grain boundaries or other free surfaces resulting in the production of a Magnéli phase composed of Ti_nO_{2n-1} where 'n' is typically 4-5. Memory applications have favored electroforming the Magnéli phase using electrodes sandwiching thin films of anatase¹⁰⁸ or brookite¹⁰⁹ TiO₂ under bias with good reversibility under reverse switching bias. Electrode applications have favored hydrogen annealing as spatial resolution of filaments is not as crucial and high throughput processing of nanoparticles to be immobilized on other electrode substrates at a later point is desired. Magnéli phase

formation was successful by this route in both anatase¹⁰⁵ and rutile¹¹⁰ nanoparticles. In the later, bulk crystalline Ti_4O_7 appeared in XRD patterns with the sample material taking on a black color.

In more recent photocatalysis research, a major discovery was made that annealing anatase TiO_2 nanoparticles in high (20 bar) pressures of hydrogen gas for extended periods of time significantly increased photocatalytic activity turning nanoparticles from white in color to black^{111,112}. Electron spin resonance data attributed the improved activity to light absorption due to the formation of a Ti^{3+} defect¹¹² ostensibly at the free surface though TEM experiments show the formation of an amorphous shell at the edge of the bulk crystalline nanoparticle. Similar results were demonstrated in rutile TiO_2 using photoelectrochemical electrodes annealed in hydrogen²⁴. This intensive treatment process was quickly improved upon with comparable results were achieved at lower pressures, and much shorter processing times, using a hydrogen plasma of anatase nanoparticles; again seeing improved photocatalytic performance, coloring the material black and producing a thin amorphous shell atop a crystalline core^{25,113}.

4.2 Key Questions

Throughout the work on catalytic materials, several things are not addressed. Possibly the most important as regards materials stability is one of reversibility. If oxygen is removed from a crystalline material as water, will oxygen gas be able to oxidize the Magnéli phase back to TiO_2 ? With the exception of the rutile particles, no bulk TiO_2 is ever completely reduced leaving a crystalline TiO_2 core. Because the Magnéli phases are conductive, can a meaningful carrier concentration be extracted from such material? If the material still behaves like a bulk semiconductor except for the Magnéli phase filaments, could this be manipulated as a new tool for defect engineering? Could the ability to reduce large areas by annealing in controlled atmospheres offer advantages to electroforming processes where metal contacts would have to be etched off before a catalytic material would be ready to use?

While reversibility questions may be tested on nanoparticles, carrier concentration measurements are much better suited to thin films systems. Thermal production of Magnéli phases in thin films has not been previously reported for hydrogen annealed TiO₂. This will serve as a useful point of comparison to the intensive annealing conditions on the order of days first used in the production of black TiO₂ nanoparticles.

4.3 Experimental Design

Thin films of TiO₂ were grown by pseudo-ALD to thicknesses of 100 nm on HF etched *n*-type silicon. All samples were annealed at 550 °C for 24 hours as per the normal oxidation routine described earlier. Samples were then cleaved by scribing the backside, one part was left in its oxidized form while the other was annealed further in a hydrogen atmosphere using the controlled atmosphere chamber described in Chapter 2. The chamber was purged with hydrogen and the pressure was allowed to stabilize at the intended value before heating began. Pressures ranged from 10 to 100 mTorr, temperature was held constant at 550 °C. Heating ramp rates were not easily controlled; sample heating typically took 30 minutes or less and cooling typically occurred over the course of an hour in vacuum with the hydrogen leak valve closed.

After annealing was complete, Al contacts were sputtered to thicknesses of approximately 100 nm as described in Chapters 2 and 3. In some cases Al contacts were removed after probe station testing. These contacts were removed by etching in 0.1 M NaOH for several minutes until sample appeared free of Al. Samples were rinsed heavily in DI water afterwards and degreased in acetone and IPA before any further characterization was performed.

4.4 Physical Characterization Results

To determine whether the hydrogen treatment caused any bulk crystallinity alteration, XRD was performed on samples before after annealing. A representative pattern can be seen in Figure 9. In addition to the substrate peak at 33°, anatase TiO₂ peaks can be seen at 25° (101), 48° (200), and 55°

(211) with negligible changes in intensity or peak shape before and after treatment. Therefore, any effect that the hydrogen has on the TiO_2 is likely to be taking place at grain boundaries and free surfaces without the creation of a significant amount of amorphous material, or in the bulk in the form of point defects that do not change bulk crystallinity at low concentrations.

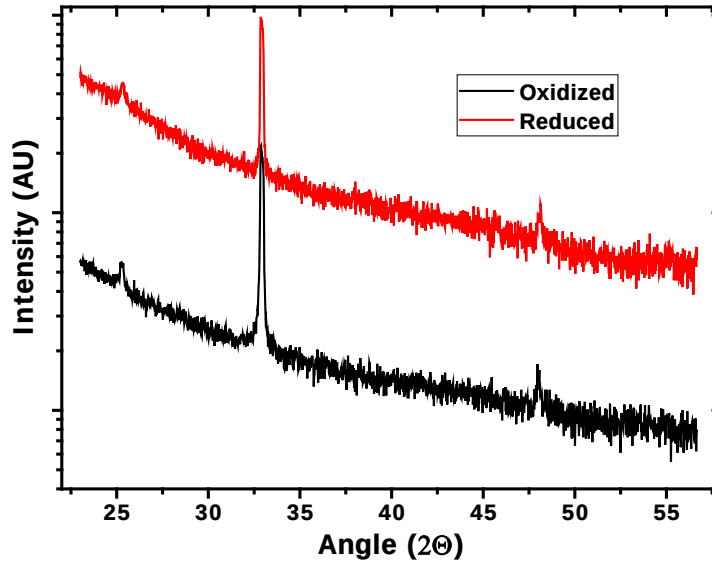


Figure 9: XRD pattern of 100 nm film before (oxidized) and after (reduced) exposure to 8 hours of 100 mTorr H_2 at 550 °C.

Despite the consistency in bulk crystallinity, some samples displayed significant visible changes upon annealing. These changes were at least partially correlated with the power required to heat the sample to 550 °C. All samples were backed by identical carrier wafers, however, there was significant variability in the quality of the contact between the wafer and the copper leads. The wafers were regularly abraded and the leads were wrapped in W foil to assist in making a good electrical connection. Despite this, the power required varied from about 15 W to close to 30 W. Samples requiring high power were more likely to have an altered appearance, a representative sample of which may be seen in Figure 10. The small fractal patterns on the surface are significantly larger than the average crystallite size. They were generally not visible through the Al contacts, suggesting that they are in the bulk of the film, or spread across the surface. An immediate theory for their appearance is

redepositing of Si from the carrier wafers which were heated to over 800 °C in order to produce a temperature of 550 °C at the sample top surface. Whether they are comprised of SiO₂, a silicon carbide, or a polysilicon hydride is unknown, but failure to remove them could seriously impact the integrity of electrical characterization efforts.

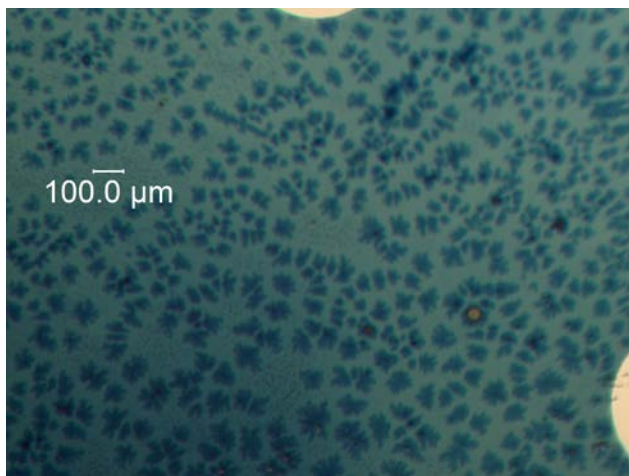


Figure 10: Optical image of hydrogen annealed sample requiring high power. Depth of focus is lost in top right and bottom left corners as the sample was not mounted flat on its carrier wafer. Sputtered Al contact can be seen in the bottom right and top center.

To determine the composition of these surface features, survey scans using XPS were performed on a number of samples, with and without the visible change. As seen in Figure 11, samples show a significant surface coverage of silicon and carbon deep enough to mask the majority of the Ti 2p signal. The sample was then sputtered by an *in situ* ion beam for 3 minutes. This time should remove approximately 5 nm of material. After sputtering was completed, the signals from both silicon and carbon are in line with the background, while peaks associated with TiO₂ become stronger in intensity. The unidentified peak at 248 eV may be a W 4d peak associated with the conductive sample mount or another chamber piece affected by the ion beam. This confirmed that the surface decoration was from the carrier wafer and did not diffuse into the bulk of the sample where it would affect electrical characterization. Surface contamination by silicon compounds can be etched using strong bases without affecting the TiO₂.

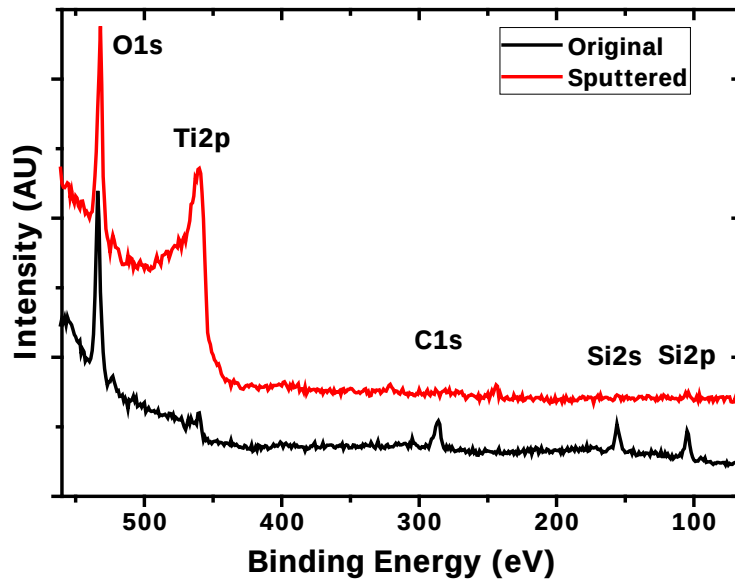


Figure 11: XPS of Hydrogen annealed sample as received and after sputtering.

The final question to be answered on the physical side is whether the hydrogen affects the concentrations of either Ti or O in the film. To help answer this, Secondary Ion Mass Spectroscopy (SIMS) was performed on a sample before and after exposure to hydrogen. The approximate atomic concentrations for Ti can be seen in Figure 12; note, some offset is expected between the samples due to instrument stability issues at the time the measurements were taken. In the oxidized film, no trend in concentration is visible as expected. The reduced film does show a slight trend with an order of magnitude drop in concentration close to the surface; this may be explained by the presence of surface contamination. What is more difficult to explain is why the concentrations do not fully return to untreated levels until much deeper in the film. It is unlikely that H_2 would remove significant Ti from the film; TiH_4 is the primary compound that could form, and it is an unstable gas. Conventional diffusion behavior would expect oxygen to be depleted near the surface rather than being drawn up from deeper in the bulk. The profile is too deep for surface contamination to explain the entire trend, it is possible that instrument instability is partially at fault.

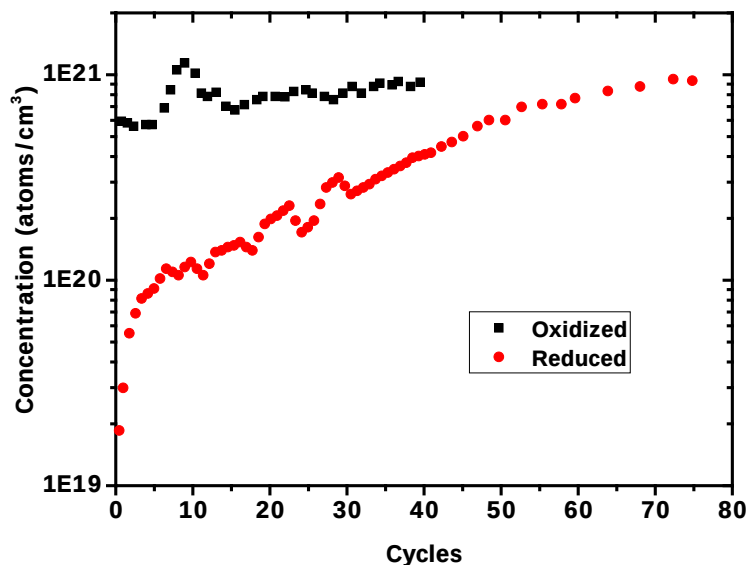


Figure 12: SIMS depth profile of Ti atomic concentration.

Unfortunately, the question of oxygen concentrations could not be answered by this method. The SIMS uses oxygen ions as a bombardment source both during milling and sampling. As a result, any oxygen concentration measured would be a measurement of beam intensity and not sample composition. Hydrogen signals are detectable by SIMS, but because of their light mass, accurate concentrations are difficult to obtain. Indeed, significant and nearly constant hydrogen signals were recorded by the SIMS for both samples that may most easily be attributed to H₂ background in the chamber operating at UHV conditions. A small but constant Si peak was discernable for both samples that is indicative of a pinhole(s) somewhere in the otherwise continuous film. A similar Al peak was also detected and was attributed to the sample holder/mask used by the SIMS errantly being milled due to instrument drift.

4.5 Electrical Characterization Results

One set of samples were annealed for 3 hours in a 10 mTorr H₂ atmosphere. These samples displayed no significant differences in the shapes of their IV and CV data. Carrier concentrations for the oxidized and reduced sample halves were all in the range of expected values for anatase TiO₂ of that thickness ($\sim 6 \times 10^{17} / \text{cm}^3$). Variations between the oxidized and reduced samples were on the order of 5%

which is well within experimental error common to these measurements as seen by the scatter in Reference [68].

Annealing pressures were then increased to 100 mTorr and annealing times were varied from under 2 hours up to 8 hours. The contrast was stark as seen in Figure 13. Samples annealed for 3 hours or longer have IV curves that are not rectifying unlike their oxidized counterparts. There is an ill-defined transition that occurs between 2 and 2.5 hours where the breakdown at negative bias is clearly missing, as is the rectifying loss of current at positive bias. Nonetheless, the junction is clearly not fully ohmic as the IV curve is bowed heavily away from linear behavior. The behavior shows minimal hysteresis between forward and reverse sweeps. The CV curves lose the characteristic shape belonging to rectifying junctions shown in Figure 4. Some have irregular shapes that are not consistent across samples, but most just appear heavily flattened as there is no longer any variation in capacitance of an ohmic junction with bias.

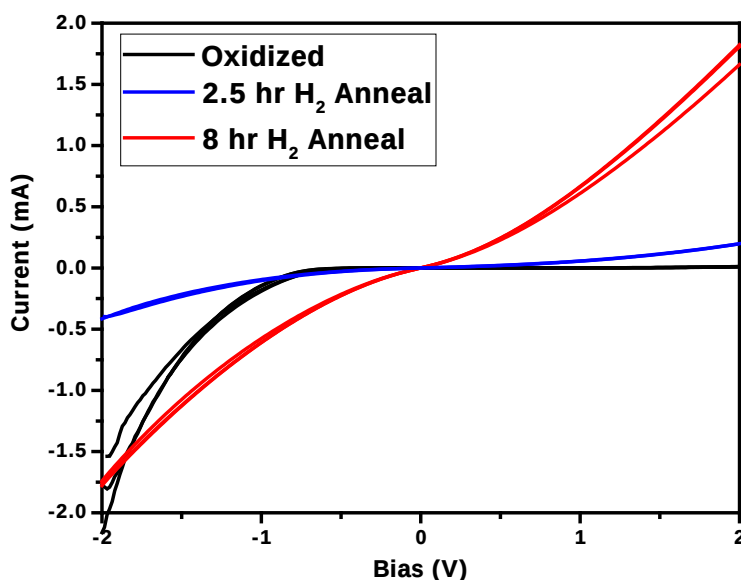


Figure 13: Representative IV curves of oxidized, partially reduced, and heavily reduced TiO₂. Forward and reverse curves are shown for each sample.

To ensure that the phenomena was unique to the contacts on the TiO₂ side and not related to the backside contacts, pad-to-pad measurements were taken by moving the probe on an Al/Si contact to

another Al/TiO₂ contact. IV curves from these measurements were also nearly linear albeit at a noticeably higher resistance, compare the 8 hour data in Figure 13 to Figure 14. This may be explained as the thickness of TiO₂ that current must traverse has doubled in this measurement. Without a rectifying junction, the TiO₂ is the greatest contributor to the overall series resistance of the circuit shown in Figure 3. Variation between contacts and hysteresis are both negligible as evidenced by the total overlap of plotted data in Figure 14.

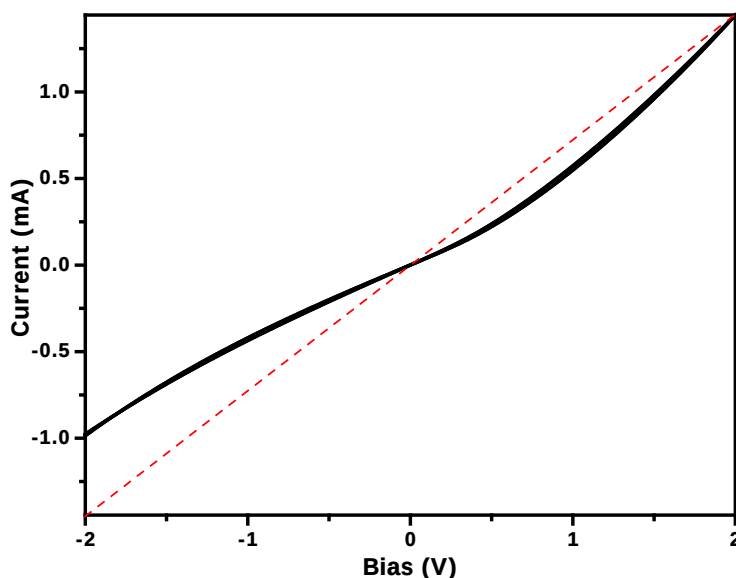


Figure 14: IV curves from pad-to-pad measurements on 8 hour reduced TiO₂. Two measurements are shown with forward and reverse sweeps overlaid. The measurements shared one common pad and one uncommon pad. Red dashed line sits at a 45° angle and is meant as a guide to the eye.

As mentioned in the previous section, there was a concern about the presence of Si species on the surface. It is unlikely that these species would produce the response seen here with TiO₂ apparently making an ohmic contact with a metal. The surface contamination would be heavily oxidized and SiO₂ is a known insulator so no ohmic connection with the Al would be expected. If enough silicon built up on the surface, it is hypothetically possible that some conductive layer could form which would bridge the contacts through pin holes in the film to the substrate and this circuit would be ohmic in nature. To test for this or any other effects of the surface contamination, Al contacts were removed with caustic etches as described above and redeposited at a later time. New contacts showed the same behavior

indicating that the surface contamination did not interfere with the type of contact the TiO_2 formed with the Al.

In a similar vein, selected samples were subjected to 4PP measurements. Oxidized samples consistently failed to produce a signal as the voltages required were out of range of the instrument. This is expected of TiO_2 as the W tips form a rectifying contact with the material⁸⁰. Those reduced in H_2 showed some conductivity, though it was inconsistent across samples and often required many attempts to make a stable contact. Values for resistivity were significantly lower than the reference Si substrate indicating that when an electrical contact was made, the majority of the current was passing through the TiO_2 film laterally as opposed to through the thickness of the TiO_2 , into the substrate, and back through the TiO_2 beneath another probe.

The results above are consistent with the formation of thermally produced Magnéli phases along the grain boundaries of the TiO_2 . The physical and electronic properties are comparable to electroformed Magnéli phases in thin film TiO_2 with regard to bulk morphology and ohmic contacts with metals¹⁰⁸. As the reduction occurs primarily along grain boundaries, the hydrogen has only to diffuse through these pores rather than the bulk material. Once in the pore, the hydrogen can react anywhere along the path ways allowing filaments to form which transverse the film. Given that the grain sizes will be a fraction of the size of the Al contacts, a large number of these filaments should be in contact with any given contact. As the Magnéli phases are metallic in nature, they are likewise able to form ohmic, or very leaky diodes, contacts with the underlying *n-type* silicon. The ability to form a good contact with the 4PP apparatus was likely dependent on whether the probe contacted a filament as those probe tips are significantly smaller.

4.6 Reversibility

The literature on electroformed Magnéli phases mentioned above focuses heavily on the bias required to switch the material back to rectifying, and the number of cycles that the material can undergo

before reversibility fails. In thin film electrode sandwiches, the reduced material must lose oxygen, but the oxygen cannot travel far and may be simply absorbed by the adjacent bulk TiO_2 material. In the case of the thermally grown Magnéli phases, it is likely that the reduced material loses oxygen in the form of water vapor that is able to diffuse out of the pore through which it entered. It is unclear whether molecular oxygen will be able to follow the same diffusion path, or what its adsorption and reactivity will be with a Magnéli phase.

To test this, select films had their contacts removed by caustic etch and were annealed in air for the length of time at the same soak temperatures that they were subjected to a reducing environment. Annealing protocols were the same as those discussed earlier. The results were spurious with no consistent trend across different annealing times. A selection is shown in Figure 15. Some samples return to rectifying behavior with a drop in current indicating that the contact between the Si substrate and TiO_2 is being oxidized in addition to the Magnéli phase (Figure 15a). Other samples display nearly identical behavior, or at least retain a non-rectifying profile similar to the partially reduced sample shown in Figure 13.

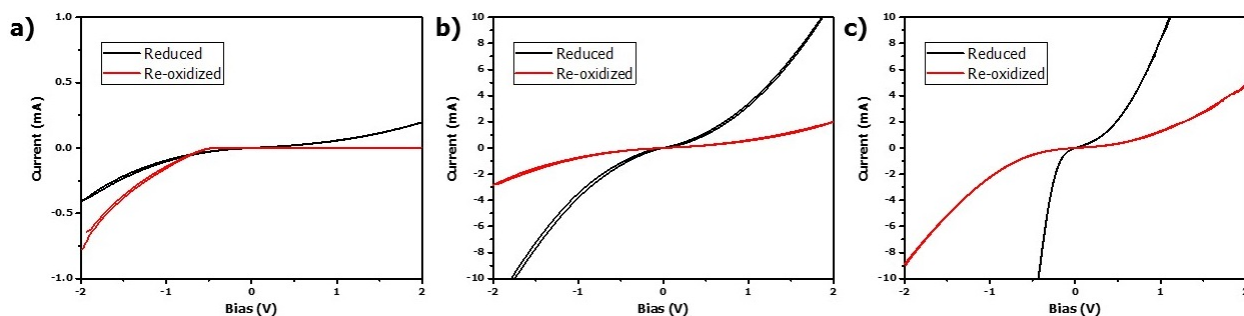


Figure 15: IV curves of re-oxidized Magnéli phases. 'a' and 'c' are each 2.5 hour anneals, 'b' is 2 hour.

4.7 Conclusions

Magnéli phases can be produced by thermal methods in thin films with comparable properties to those produced by electroforming. The reducing conditions are not nearly as time or energy intensive as the processes used to form Magnéli phases in nanoparticle systems. While the reversibility is

poor compared to electroforming, the stability is good and could be useful to applications where Magnéli phases are desirable but the deposition and removal of a counter electrode for the electroforming process could cause issues for subsequent contacts, such as in battery and photovoltaic applications. If the electrode fabrication step could be avoided, it is possible that an anneal in hydrogen would not significantly increase fabrication time as well and can be performed in large quantities. Despite this, the use of hydrogen appears ill suited for the control of carrier concentration for purposes of tuning material properties for photocatalytic applications.

CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF STRONTIUM RUTHENATE

5.1 Introduction

The synthesis of a material containing more than a single atomic species frequently poses a challenge to researchers and industrial designers alike. In the case of metal oxides, controlling the relative oxygen stoichiometry is a challenge as oxygen may be incorporated into the final material by several means. For example, when synthesizing TiO_2 from TTIP, oxygen can be incorporated exclusively from the precursor⁷², from an oxidizing agent such as water, and from annealing in an oxygen rich environment.

Controlling stoichiometry becomes significantly more challenging when there are three or more atomic species such as the case of SrRuO_3 . In addition to oxygen, the ratio of Sr:Ru must be controlled independently for high quality films to be produced. Despite the fact that Sr and Ru differ by only six protons, Sr is an alkali earth metal while Ru is a transition metal. Their atomic radii differ by nearly a factor of two, and their relative reactivity with oxygen is altered strongly by their differing valence states. Sr belongs to a group of elements that oxidize rapidly in the presence of oxygen. One implication of this reactivity is that use of sputter deposition for synthesizing oxide films containing Sr must accommodate high resputter rates of Sr off of the sample in the presence oxygen.

To add to this challenge, the SrRuO_3 synthesized on campus is done using a single SrRuO_3 target. Frequently triatomic and more complex materials being synthesized from solid sources such as sputter targets will have a target for each metallic element to be incorporated into the final film so that their deposition rates may be tuned somewhat independently. Given that Sr and Ru each have difference

masses and electron affinities, their abilities to be sputtered, deposit on a substrate, and avoid being re-sputtered by oxygen atoms will all be different.

This leaves several strategies for adjusting the Sr/Ru ratio of the deposited film. Although resputtering of Sr would be reduced by the removal of oxygen gas from the plasma, it would require the film be oxidized by an *ex situ* anneal, the protocol development for which would be challenging as one would then have to contend with Sr and O diffusion from the substrate as well as the free surface while trying to achieve uniform oxygen stoichiometry throughout. Removal of Sr or O from the substrate interface would likely affect epitaxial regrowth as well. A much better established strategy is to increase the total pressure during film growth; this reduces the average energy of oxygen ions or radicals that reach the substrate thereby reducing the degree to which Sr will be resputtered from the surface^{114,115,116}. However, these studies were all performed at elevated temperature, so changes sticking probability and other factors may be at play. If final oxygen stoichiometry is significantly off of specification, adjustments may also be made to the gas ratios at a constant total pressure. An alternate strategy to reduce the energy of oxygen atoms near the substrate is to increase the distance between the sputter target and substrate¹¹⁴. This option is not available to us as the sample mount only allows for rotation. The final strategy for reducing oxygen atom energy is to perform off-axis sputtering^{117,118}. This method does not reduce the energy of oxygen atoms directly, but rather assumes that the majority of their momentum will be perpendicular to the target. Rotating the sample mount so that the substrate is nearly parallel to the path of sputtered material leaving the target means that the only oxygen atoms striking the surface will have momentums with small perpendicular components that will not cause significant resputtering of Sr. The disadvantage to this is that deposition rates of all material drop significantly.

5.2 Amorphous & Epitaxial SrRuO₃ Synthesis

Because SrRuO₃ is somewhat unique in its band structure and metallic characteristics, it is unknown whether or to what degree amorphous material will retain these properties. In order to

determine the suitability of amorphous SRO for characterization of the photocatalyst, various physical and electronic properties of a representative sample were compared to an equivalent epitaxial sample. Samples were synthesized as described in Chapter 2. Amorphous samples were grown to a thickness of 60 nm. Thicknesses were estimated using sister samples of silicon wafer pieces with a line of photoresist across the sample. After developing the sister sample, the height of the film could be measured by profilometry. The accuracy of this measurement method was confirmed by XRR. Epitaxial samples grown at Brookhaven National Lab were given sister samples where TEM was used to determine precise thickness values.

After growth, several amorphous SRO samples were annealed to temperatures between 850 °C and 1100 °C for up to 2 hours in either the tube furnace or using the TP-XRD stage both described in Chapter 2 to attempt Solid Phase Epitaxial Regrowth. No epitaxial samples from Brookhaven received any post-synthesis processing.

5.3 Physical Characterization Results

AFM scans were performed on representative samples of amorphous, annealed and epitaxial samples. The surfaces of the amorphous and epitaxial samples are comparably smooth with surface roughness values on the order of 2 nm as seen in Figure 16. The amorphous sample that was annealed takes on a roughened surface with the appearance of small raised dots of material on a smooth background. It is not known whether the background here is bare substrate, or a second phase within the film. The relative height difference from the peak tops to the floor bottom is on the order of the total original film thickness.

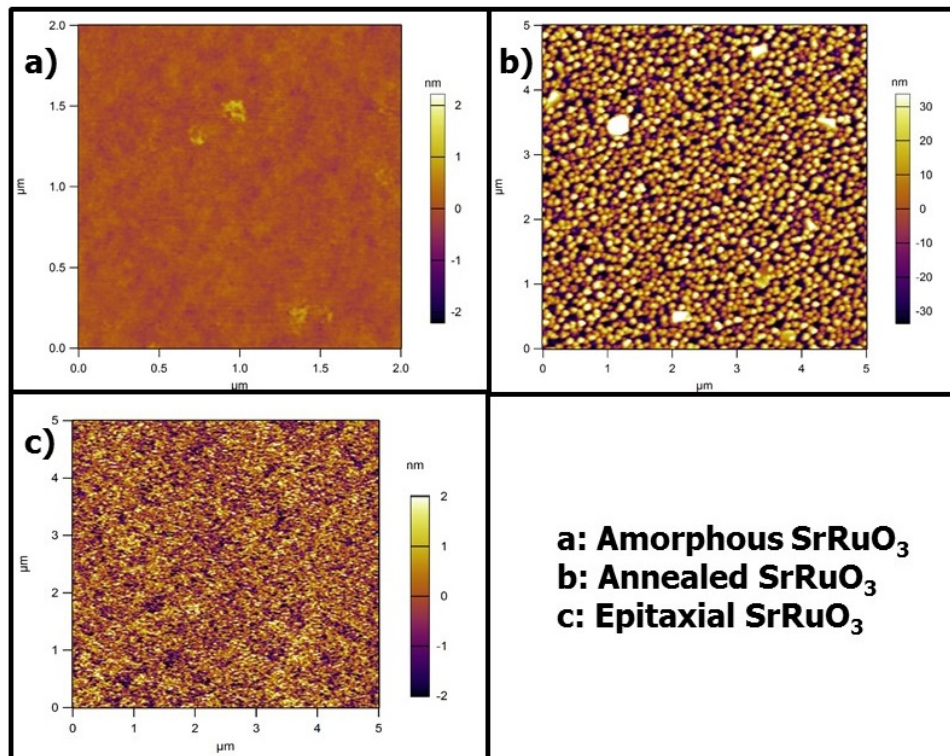


Figure 16: AFM micrographs of SrRuO₃. Note differences in scale bars.

An SEM image of the annealed sample can be seen in Figure 17. The annotations on the image point out several things of note.

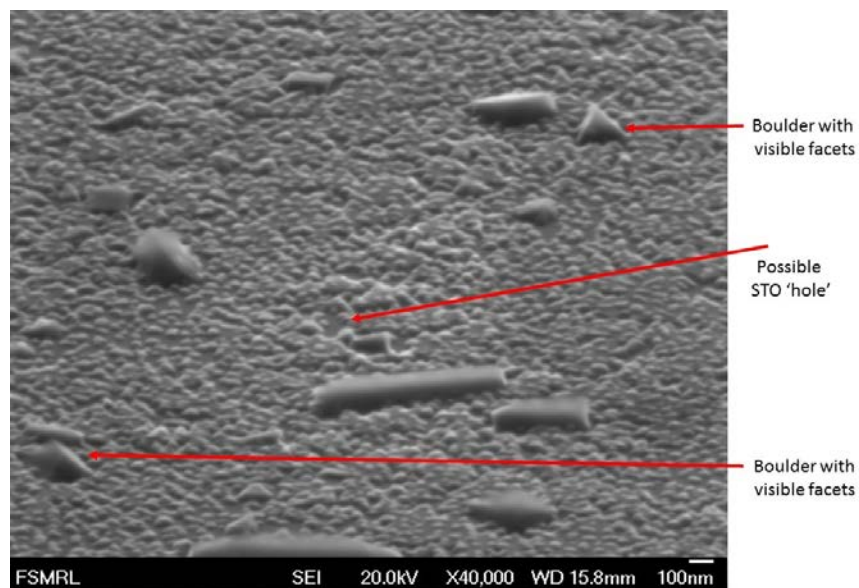


Figure 17: SEM micrograph of annealed SrRuO₃.

The first is the presence of highly faceted islands among the smaller surrounding islands too small to see any form of faceting. The second is the presence of incredibly smooth sections between some islands that suggest the annealing process caused a partial delamination of the film revealing a bare STO substrate. These bare regions were too small to perform Electron Backscatter Diffraction or another spectroscopic elemental identification technique to confirm the presence of STO.

The crystallinity suggested by Figure 17 is confirmed by the asymmetric shoulders on the STO substrate peaks of the annealed SRO sample in Figure 18. The amorphous SrRuO_3 has no identifiable peaks other than the substrate peaks; the peaks at 20, 24, 27, 28 and 32° are from the ceramic adhesive used to mount the sample for TP-XRD and may be ignored. As the sample was annealed, the shoulder at lower angle grew as the sample crystallized in small, highly strained, epitaxial regions. Although these regions are epitaxial, they do not form a contiguous film as will be demonstrated later. The epitaxial film shows fully separated SRO peaks alongside the substrate peaks.

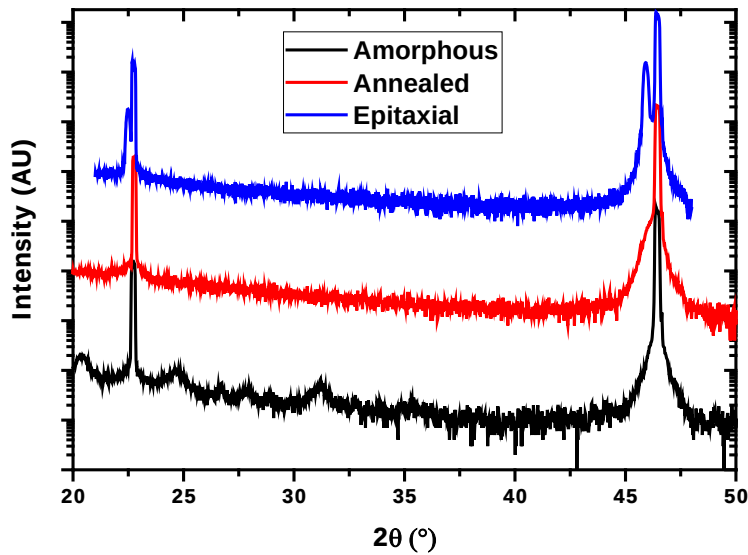


Figure 18: XRD 2θ-Ω plots of SrRuO_3 thin films on SrTiO_3 . Visible SrTiO_3 substrate peaks are at 22.8° (100) and 46.5° (200); SrRuO_3 peaks are at 22.6° (020) and 46.2° (040).

A number of factors may contribute to the failure of a film to undergo complete solid phase epitaxial regrowth. The most common impediment is a dirty interface which disrupts the crystal lattice

from the perspective of the film to be crystallized. This could explain bare patches, but is not likely the case as all samples were degreased by sonicating in acetone and IPA before final rinses in either IPA or distilled water. A more likely explanation comes from the lack of control over the stoichiometry of the amorphously deposited SRO as the deposition source is a single SRO target, elemental compositions of the amorphous film as determined by XPS is in Table 1. Better control over stoichiometry would prevent the preferential segregation of Sr to the epitaxial islands and allow the entire film to epitaxially regrow in a uniform manner.

Sample	Composition %			Approximate Ratio
	Sr	Ru	O	O:Ru:Sr
Deposition Pressure				
4 mTorr	8.6	24.9	66.6	3:1:0.15
12 mTorr	5.1	25.6	69.3	3:1:0.07
4 mTorr (off-axis)	Negligible Deposition			

Table 1: Elemental compositions of amorphously deposited SrRuO₃ films.

The increase in total pressure did not improve the control over stoichiometry as desired. It appears that another factor is dominating the Sr deposition or resputter rate. This is most likely attributable to the deposition temperature. At higher temperatures, the Sr will oxidize rapidly in the presence of oxygen possibly making it more resistant to resputtering. The compositions of films deposited by off-axis sputtering could not be determined as films were too thin and of too poor a quality to perform meaningful characterization on. The author suggests that this be tried again at a later date at a higher sputter power. Oxygen pressure and Ar:O₂ ratio was not manipulated to preserve the Ru:O ratio.

The Ru:O ratios in Table 1 are consistently close to the expected values for a SrRuO₃ film. It is therefore likely that the nanostructured epitaxial film seen in Figure 16b and Figure 17 is close to a proper stoichiometric ratio while the regions surrounding those crystalline islands contain some RuO_x suboxide of indeterminate crystallinity. The oxidation states are likely close to that of RuO₂ as the films were annealed under atmospheric conditions and allowed to oxidize in the same manner the TiO₂ films do as described above.

5.4 Optical Absorption Results

Results of the transmission experiments described above for the samples can be seen in Figure 19. The data were collected using a 3.5 mm through hole with the detector set to collect directly transmitted light in addition to diffuse scattered light. This was necessary for two reasons. The first is that the goal of the transmission experiment is to determine the total light absorbed by the sample, so all light not absorbed must be accounted for. Second, the backside on the STO substrate is not polished, so while scattering is consistent across samples, collecting only directly passed light reduces the signal by over an order of magnitude. For all SRO samples, reflected light is expected to be consistent and negligible because the samples were uniformly dark in color to the naked eye. The sharp drop in transmittance around 380 nm may be interpreted as the band gap of the SrTiO_3 .

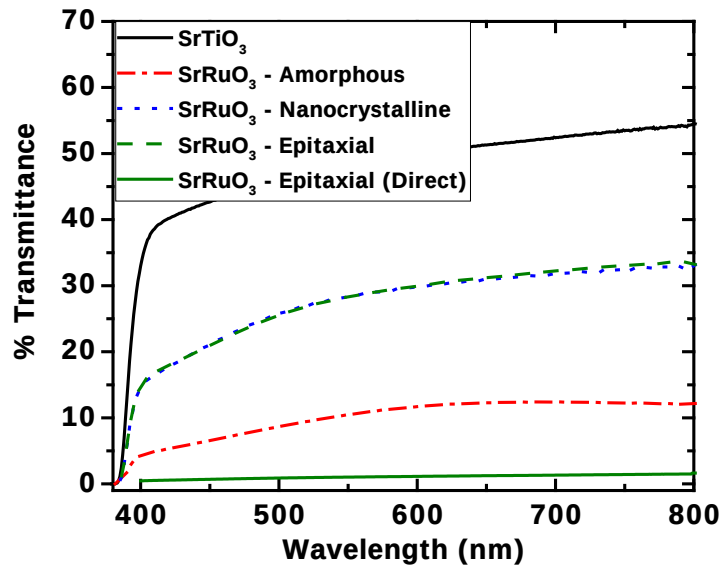


Figure 19: Transmittance data for SrRuO_3 film types. Solid green line (direct light) shown for comparison to epitaxial SrRuO_3 film. Scattering from film backside is responsible for artificially low measured transmittance and is not indicative of absorption of light.

It is important to note, the measurement of transmittance and absorbance does not indicate the final-state energy of the photogenerated carriers absorbed by the SRO film. Whether they barely reach band edges and immediately recombine, or exist as hot carriers and tunnel significant lengths within the SRO or substrate is not known.

Several results may be interpreted from the data. The most important item of note is the exceptional performance of the amorphous SRO relative to the crystalline films for possible photocatalysis. The absorbance of the film over the visible range is approximately twice that of epitaxial material. One reasonable explanation for this is that the energetic states of the amorphous material are not tightly pinned as they are in a crystalline material. As a result, the band gap may not be as well defined for the amorphous material and absorption across a number of wavelengths may be improved.

The second major result is the insignificant difference in optical absorption performance between the nanocrystalline annealed sample and the epitaxially grown sample. The flat areas seen in Figure 17 suggested that a significant portion of the substrate had little to no film coverage. If this was the case, one would expect performance with regard to light absorption to suffer. We do not have a comparison sample of RuO_x suboxide to use as a comparison for the nanocrystalline material. Rather we are forced to assume that the majority of the light absorbed by the film is done in the epitaxial crystalline regions and the combined performance of the amorphous ruthenium heavy regions and bare substrate regions more or less offset each other. RuO₂ is a difficult material to characterize without knowing its exact composition and crystallinity. A transition from metal to dielectric behavior has been reported as the material goes from crystalline to amorphous¹¹⁹. In the amorphous state, the band gap of RuO₂ has been reported between 2.2 [120] and 2.4 [121] eV; this is higher than SRO, but well short of the STO substrate.

5.5 Conductivity Results

Independent from the ability act as a light absorbing layer, the SRO must also provide efficient transfer of charge to the TiO₂. This takes place in several steps. The first is that the SRO itself must be conducting enough that these charges reach the interface before recombining. The second is overcoming the rectifying barrier at the TiO₂ interface. Direct quantitative measurements of this transfer are difficult as the substrate is insulating and the electron microscopy techniques, such as Ballistic

Electron Emission Microscopy (BEEM) and Electron Beam Induced Current (EBIC), require a completed circuit to be made across the layers of the sample and were not possible with available resources.

Determination of the metallic conductivity of the SRO films was performed using a Four Point Probe (4PP) as described above, the results of the measurements are compiled in Table 2. Listed sheet resistance values are averages of measurements at 100 μ A, 500 μ A and 1 mA on 2-3 distinct spots on the sample. Typical variations in measured values was on the order of 1% so standard deviations values were not calculated or reported separately.

Sample	Sheet Resistance ($\Omega/\square$)	Resistivity ($\Omega\cdot\text{cm}$)
Substrate SrTiO_3	Too Insulating	
Amorphous SrRuO_3	155	$9.2\cdot 10^{-4}$
Nanocrystalline SrRuO_3	Discontinuous Film	
Epitaxial SrRuO_3	43	$2.8\cdot 10^{-4}$

Table 2: Summary of 4PP data on SrRuO_3 films.

Sheet resistance values may be converted to resistivity (and conductivity) values using the thickness of the film and a shape factor. In the case of these samples, the probes were far enough from the edge of the sample that no shape factor corrections are needed. As expected, the STO was too insulating to take a 4PP measurement; the W probe tips likely created a rectifying barrier with the STO. This is helpful as it assures the integrity of future measurements of SRO films as all of the current will be known to be passing through the film and not the substrate.

As suggested by Figure 17, the nanocrystalline film does have significant regions between the epitaxial crystals leaving an essentially discontinuous film. This is confirmed by the 4PP measurements as the sample failed to form a stable bias within acceptable current ranges. Regardless of the RuO_x or bare substrate material between the islands, they are not conductive as a metal would be. This means that any TiO_2 capping layer above the bare regions would not be taking advantage of the metallic properties of the SRO to receive photogenerated carriers in those regions.

5.6 Conclusions

The epitaxial material appears to be well suited for use as a light absorbing layer in a heterojunction photocatalyst based on its absorption of light across the visible spectrum and its metal like conductivity. The question becomes to what degree does an amorphous SRO films that is significantly non-stoichiometric retain this unusual conductivity. We have already seen that the amorphous material has approximately double the light absorbing capacity of the epitaxial material. The 4PP data indicates a conductivity that is significantly lower than the epitaxial film, but only by a factor of 3, not the orders of magnitude that typically separate metals and semiconductors; for reference, the difference in electrical conductivity between undoped amorphous and polycrystalline silicon may be six orders of magnitude¹²². It would appear that the amorphous material does retain this abnormal conductivity to a significant degree. This is crucial for two reasons. The first is the underlying assumption regarding charge transfer from the SRO to the TiO_2 requiring the production of hot carriers. If the conductivity and optical properties are comparable, it is plausible that hot carriers will be produced as before and the amorphous material may be used as a light absorbing layer in the subsequent heterojunction device structures. The second is that if photocatalytic performance is comparable, it may open new research directions for metal oxides. The identification of metal oxides that possess unusual properties in crystalline form should be then tested to see if any of these properties are retained in the amorphous state. If so, metal oxide based devices could be produced at low cost and energy intensity as amorphous materials typically require less extreme synthesis conditions with regard to temperature and impurity tolerances.

CHAPTER 6

PERFORMANCE OF TITANIUM DIOXIDE/STRONTIUM RUTHENATE HETEROJUNCTION PHOTOCATALYST IN DEGRADATION OF METHYLENE BLUE

6.1 Introduction

Semiconductor photocatalyst and electrocatalyst devices are attractive options for tackling the large scale clean energy demands that will face the next generation. The materials are often cheap and abundant relative to precious metal catalysts, such as Pt and Re, and are amenable to a variety of deposition and structuring techniques. A favorite in the crowd has been TiO_2 for its demonstrated ability to produce hydrogen and oxygen gas from liquid water¹². Since the discovery of its photocatalytic properties, ongoing efforts to improve its performance have led researchers down a variety of paths, though there is an increasing desire to use TiO_2 in some form of heterostructured device structure in order to tune material selection to a specific catalytic process or reaction environment. This has necessitated a parallel effort in the identification of new materials for both cathode/anode^{123,124,125,45}, and light absorbing materials^{45,59}.

A heterojunction may be defined as the contact between any two dissimilar semiconductors. This heterojunction may take many shapes, the additional material may form small phase separated pockets with a TiO_2 bulk, it may be surface decoration on a TiO_2 free surface, or a TiO_2 substrate. The development of a heterojunction photocatalytic device seeks to solve one or more limitations inherent to the use of TiO_2 as a photocatalyst. Common goals are to reduce the band gap/stimulate photocarrier production, improve carrier separation/lifetime, increase reactivity of a surface species, or act as an electrode for an electrocatalytic portion of the process. A useful summary of heterojunction photocatalysis strategies can be seen in Figure 20.

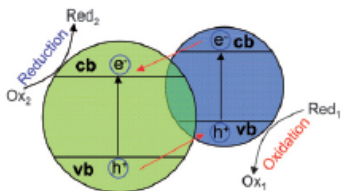
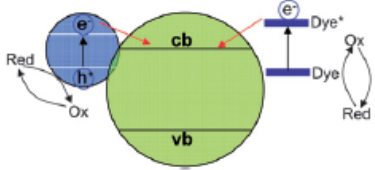
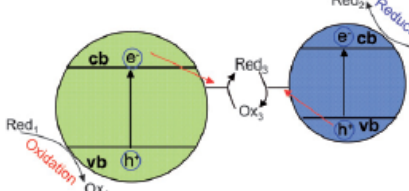
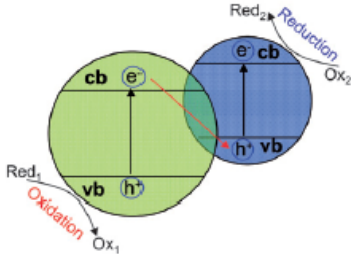
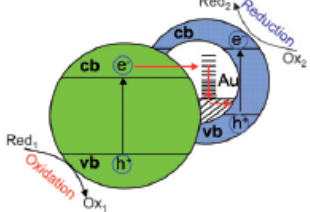
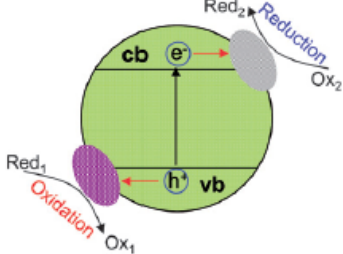
Mechanisms	Representative systems	Key issues
Traditional charge-carrier transfer 	CdS/TiO₂,¹³³ Bi₂S₃/TiO₂,¹³⁴ PbS/TiO₂,¹³⁵ Cr-doped In₂O₃/Cr-doped Ba₂In₂O₅,¹³⁶ Co₃O₄/BiVO₄,¹³⁷	● Suitable band electronic structure ● Intimate contact between two phases ● Interface atomic structure ● Efficiency ● Lowered redox potential of transferred electrons and holes ● PN junction
Sensitization 	N719/TiO₂,¹³⁸ H₂PtCl₆/TiO₂,¹³⁹ Cu₂O/TiO₂,¹⁴⁰ CdSe/TiO₂,¹⁴¹	● Limited to sensitizers with potential higher than the CB level of semiconductors ● Redox-couple electrolyte needed to regenerate sensitizers ● High stability of sensitizers required ● Requires good contact and high conductivity of photocatalyst particles, and high surface area for sensitizer adsorption
Indirect Z-Scheme 	RuO₂/WO₃,¹⁴² Pt-WO₃/Pt-SrTiO₃ (Cr-Ta-doped),¹⁴³ rutile/anatase TiO₂,³⁰ RuO₂-TaON/Pt-TaON,¹⁴⁴ Pt-CaTaO₂N/WO₃,¹⁴⁵ together with their redox mediators Fe²⁺/Fe³⁺, I⁻/IO₃⁻, Br⁻/BrO₃⁻	● Semiconductor pairs with suitable electronic structure ● Suitable redox mediators in solution ● Keeping reduction and oxidation reactions on different semiconductors ● Electrons and holes with higher redox potential ● Potential to split pure water ● Very low efficiency at current stage
Direct Z-Scheme 	WO₃/dye-sensitized TiO₂,¹⁰ ZnO/CdS¹⁴⁶	● Very hard to find suitable semiconductor pairs ● Intimate contact between two phases ● Excellent interface carrier transfer required ● No need for redox mediators in solution ● Electron and hole with higher redox potential
Vectorial electron transfer 	TiO₂-Au-CdS²⁸	● Electron and hole with higher redox potential ● Design of semiconductor-metal-semiconductor framework with suitable geometric and electronic structure
Co-catalyst coupling 	Co-catalyst: Pt, RuO₂, NiO, Rh-Cr₂O₃, MoS₂,⁵⁹	● Creating more efficient reactive sites for hydrogen and oxygen ● Understanding and designing highly efficient co-catalysts ● Extending light-response range of photocatalysts is important ● Shaping photocatalysts ● Ohm/Schottky contact

Figure 20: A summary of traditional heterojunction structures for photocatalytic processes. Reproduced from Reference [45].

A major feature in the above figure is that none of the strategies use the primary catalyst material (such as TiO_2) as both the cathode and anode. At first glance, this may appear somewhat odd as anatase TiO_2 is known to have reasonable charge separation capabilities given its indirect band gap¹²⁶. It may be explained one of several ways depending on the application. In the case of water splitting, or any other endothermic reaction, the reverse (undesirable) reaction would likely be favored by a single reactive surface. For other reactions, the second material allows for the possibility of a selection of band edge positions for one of the half reactions. Using the example of water splitting, the Conduction Band Minimum (CBM) of TiO_2 matches closely with the redox potential of hydrogen, see Figure 21, the redox potential for oxygen is over 1 eV away.

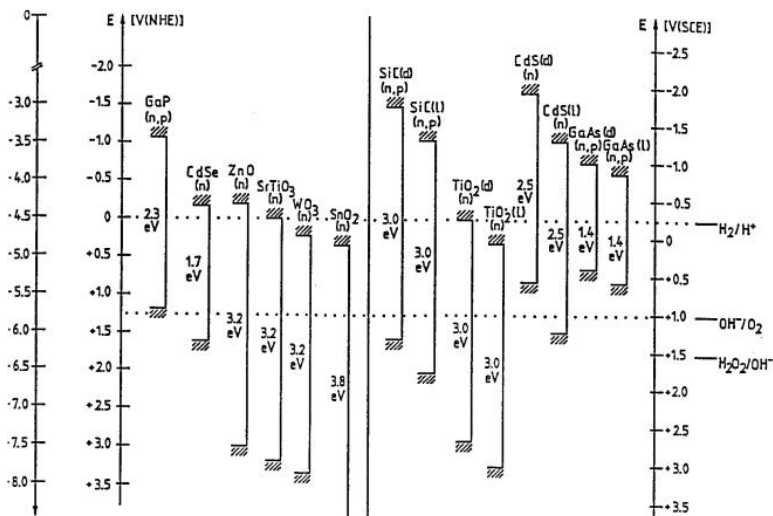


Figure 21: Position of energy bands of various semiconductors in the dark (d) and in light (l) with respect to the electrochemical scale. Reproduced from Ref [127].

If a single TiO_2 surface is used, achieving changes in band edge positions at the free surface without an external bias is difficult. Bi_2S_3 and CdS have both been employed in this manner providing a Valence Band Maximum (VBM) closer to the redox potential of oxygen and other organic pollutants¹²⁸.

Several of these strategies seek to address the poor light absorption capabilities of TiO_2 . Both ‘Sensitization’ and ‘Direct Z-scheme’ use a second material to absorb light. In the case of sensitization, the dye will be degraded by the process and must be regenerated making large scale durable

systems difficult to design. The Direct Z-scheme does not require regeneration, and improves electron-hole separation by having each half of the redox reactions occur on different surfaces; reactivity will likely become limited by the reactivity of the second material. Finding a material whose VBM closely matches the redox potential of the oxidation reaction is challenging even with the help of dopants in tunable materials such as correlated oxide materials. Add on the requirements of stability in a specific environment and a catalytically active surface and the design often becomes untenable.

One possible solution to these design challenges is to use the second material exclusively for light absorption and have the material completely encased in a protective layer of TiO_2 , a schematic for which is shown in Figure 22. In addition to the material being an efficient light absorber, it must form an electrical contact with TiO_2 that enables both electrons and holes to move across the interface. The material needs to have minimal effect on the transport of holes within the TiO_2 . Native anatase TiO_2 is heavily *n-type* ($\sim 10^{17} / \text{cm}^3$), so while free electrons are typically plentiful at the free surface, hole transport to the surface requires either enough holes to be produced that diffusion current is sufficient, or a strong drift current resulting from strong upward band bending in the TiO_2 shown in Figure 22 by the curved solid black lines. Other considerations include lack of reactivity or diffusivity of species between the second material and TiO_2^* , material and processing costs, and chemical stability[†].

6.2 Heterojunction Band Structure and Charge Transfer

SrRuO_3 is a strong candidate material to test the viability of a heterojunction design where the second material will be responsible for the majority of light absorption. As mentioned previously, epitaxial or single crystal SRO can form a heteroepitaxial interface with anatase TiO_2 which provides

* Diffusion of Sr, Ru, and Ti not a significant concern at temperatures a photocatalyst would be expected to experience (ie: below the boiling point of water for an aqueous system).

† Due to the thin nature of the TiO_2 capping layer, pin holes and other film discontinuities are a certainty.

ideal contact between the materials with a minimum of defects that could cause scattering and/or act as recombination centers for electron-hole pairs. SRO also demonstrates strong light absorption in the visible region of the spectrum, see Figure 19. There are two notable limitations to using SRO. The first is that because the SRO has metallic conductivity, it has an effective *n-type* carrier concentration at least three orders of magnitude greater than TiO_2 . As a result, there should exist a depletion region on the order of > 100 nm in the TiO_2 to allow interfacial charge compensation to occur. This may give rise to unusual band structures when the TiO_2 is significantly less thick than the expected depletion region that will in turn create a strong drift current in one direction. This will be discussed at length in Chapter 7.

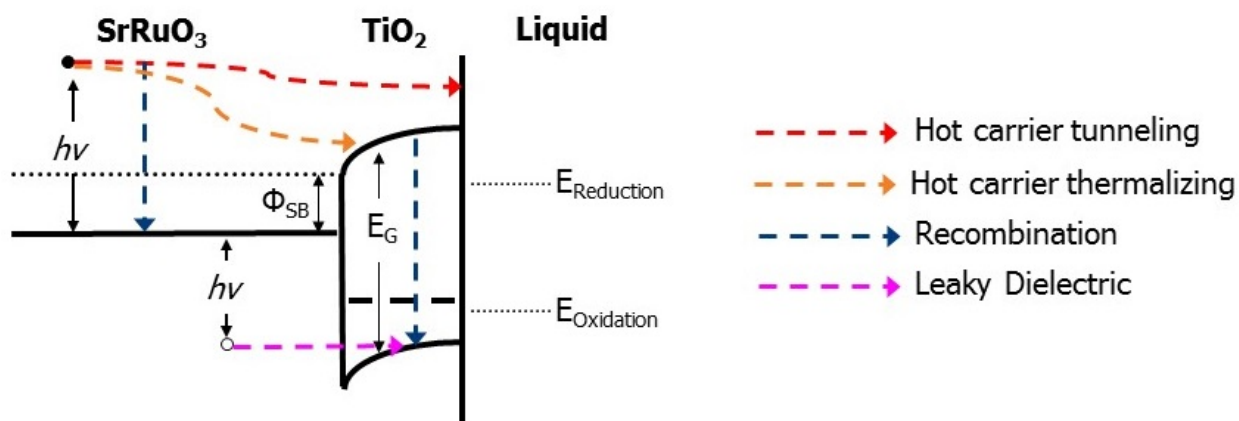


Figure 22: Schematic of a $\text{TiO}_2/\text{SrRuO}_3$ Heterojunction photocatalyst. Band positions are not drawn to scale. Dashed line in TiO_2 is a Quasi-fermi level for thermalized holes. Redox potentials shown in liquid designate water splitting half reactions.

The second major intrigue is that SRO does not possess a traditional band gap, but rather has a nearly continuous density of states close to its Fermi level¹²⁹. This has been represented in Figure 22 by a single metal like work function of 4.1 eV (straight black line). Due to the position of this work function, a Schottky barrier forms at the interface with a barrier height of approximately 1.3 eV (Figure 22, Φ_{SB})²³, a significant barrier for an electron to overcome. Based on a 3.2 eV band gap for TiO_2 , the electronic barrier for a hole would be an even greater 1.9 eV. Hot carriers from the SRO have been proposed as a possible mechanism for driving carriers across the interface²³ with a transit time on the order of 10^{-12} to 10^{-14} seconds^{130,131}. A hot carrier refers to any carrier that has been excited beyond the

relevant conduction or valence band edge. The excess kinetic energy gives the carrier an effective temperature, thus ‘hot’, greater than the temperature of the material. Unfortunately, detection of hot carriers at the interface is difficult, so their effects must be felt and studied in the bulk. Hot carriers have been shown to be capable of driving redox reactions in certain systems where thermal carriers cannot^{132,133}. In such a system, the redox potential of the species cannot align with the Fermi level and remains outside the band edges at the semiconductor free surface. This can happen either because a) the band edges are well pinned, b) because they can bend, but not far enough to encompass the redox potential (Figure 23, Reduction reaction), or c) they are bent in the opposite direction of the redox potential (Figure 23, Oxidation reaction).

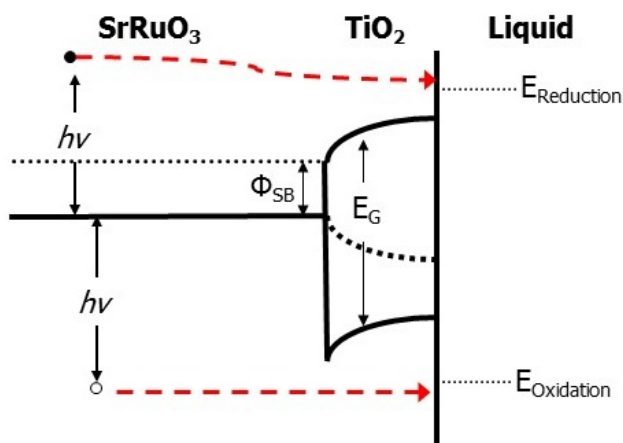


Figure 23: Hot carrier photocatalysis.

More commonly, hot carriers will thermalize to their relevant band edges and continue to exist as thermal carriers (Figure 22, orange lines). These carriers are still mobile and will have lifetimes similar to those of other photogenerated carriers regardless of whether it is a single material system or a heterojunction device; thermal carrier recombination is shown by the blue lines in Figure 22. In the case of a heterojunction device where hot carriers overcome an interfacial barrier, the question arises of whether they thermalize at the interface, or deeper in the TiO₂ bulk. Hot carriers are subject to drift currents in electric fields in the same manner that thermal carriers as shown in Figure 22, but over a significantly shorter time frame. Hot carriers typically have lifetimes before thermalization on the order

of 10^{-13} to 10^{-11} seconds^{134,135,136} whereas thermal carriers can have lifetimes before recombination anywhere from 10^{-9} to 10^{-6} seconds^{130,137}. Regardless of whether hot carriers are swept by an internal electric field, or are allowed to diffuse freely, their lifetimes in the TiO₂ bulk is expected to be brief. This leaves an open ended question as to how far into the TiO₂ bulk they are hot. The distance is affected not only by lifetime, but mean free path as well. Hot and thermal electrons have smaller effective masses than their hole counterparts so diffusion lengths can vary negligibly to three orders of magnitude¹³⁴. Taking a round literature estimate of 15 nm¹³⁴ for diffusion length of a hot electron (without crossing an interface), it is reasonable to expect that there will be a significant population of hot and thermalizing electrons in the first ~10 nm of the TiO₂ film in addition to fully thermalized electrons. As a result, the system does not obey an energetic distribution of thermalized electrons as another illuminated device such as a photovoltaic device might. Because of this, Figure 22 was drawn without a Quasi-fermi level or demarcation level for the electrons in the TiO₂.

Given the significant barrier to the movement of holes across the interface, an alternate mechanism may be required. Tunneling is a realistic probability for movement across the interface, but does not explain transport to the TiO₂ free surface. Literature measurements of tunneling path lengths for holes in TiO₂ give an upper limit of about 2 nm¹³⁸; photocatalytic activity observed in TiO₂ capping layers of a similar length scale has been attributed to tunneling holes¹³⁹. A second option for moving the holes across the interface would be presence of an interfacial defect, or near interfacial in the TiO₂, that is capable of receiving the holes near the valance band of the TiO₂ shown in Figure 22 by the pink arrow. This proposed defect state creates a situation where the interface acts as a leaky dielectric¹⁴⁰ and has been used to explain hole transport across interfacial barriers including SiO₂/Si systems¹⁴¹ as well as a number of TiO₂/Si heterostructures^{142,143}. The transit time for a hole across an interface by a leaky diode mechanism is estimated to be on the order of 10^{-12} seconds¹³¹, the transfer time for a hole to an OH species on the surface is on the order of 10^{-9} to 10^{-10} seconds^{144,127}, and recombination will occur on the order of 10^{-8} seconds¹³¹. From this we may say that the rate of transport is greater than the rate of

recombination which means the thermion limit will be reached¹⁴⁵. As a result, holes in the TiO₂ will be fully thermalized, an equilibrium concentration will form under illumination that may be represented by a Quasi-fermi level shown in Figure 22 by the dashed black line in the TiO₂. A demarcation level could also be used here, but it would be difficult to place as the precise energies at which holes are likely to be trapped is unknown.

6.3 Methylene Blue Degradation

In order to determine the ability of photogenerated carriers in the SRO to perform meaningful catalytic work at the TiO₂ free surface, a benchmark reaction is needed. For this, the degradation of methylene blue dye (Figure 24) was used. Methylene blue (MB) is an organic dye common to textile production and analytical chemistry. It has gained significant use in photocatalysis research following the discovery that TiO₂ is an effective catalyst for mineralization of the dye¹⁴⁶ which has led to an ongoing effort to determine the degradation mechanism on TiO₂ surfaces^{147,148}. The primary disagreement is whether the center ring opens first, as shown in Figure 24, or whether the amine groups are de-methylated and removed and the ring opening is the last step before full mineralization. This is potentially a significant difference in that the amine removal will significantly increase the pH of the solution affecting future degradation rates, for that reason, many MB studies are performed on dilute solutions as we have done here. Additionally, the two decoloration steps are associated with the opening of the central ring, so reporting a catalytic activity based on decoloration does not reflect the total number of catalytic electron-hole pairs produced by the catalyst. In general, the literature reports activity in this manner, probably for ease of reporting and comparison.

While variants of the mechanism exist in the literature, first order kinetics are generally agreed upon, and the reaction is catalyzed by a hole (h^+), or another species produced by a hole and H₂O such as an OH[•] radical or OH⁻ ion. Hole catalyzed path ways are consistently invoked for MB degradation on a variety of other catalysts including CeO₂ nanoparticles¹⁴⁹, ZnFeAl composites¹⁵⁰, and

plasma treated water¹⁵¹. The use of MB as a benchmark reaction has a number of advantages when selecting a reactant. It is not volatile, it is relatively non-toxic when compared to common organic pollutants, and may be procured free of heavy metal contaminations known to poison catalytic surfaces. This allows it to be used as a model molecule for other degradation of more toxic materials such as toluene¹⁵². It has a strong absorption peak in the visible range at 665 nm making its concentration easily monitored by inexpensive visible light spectroscopy equipment.

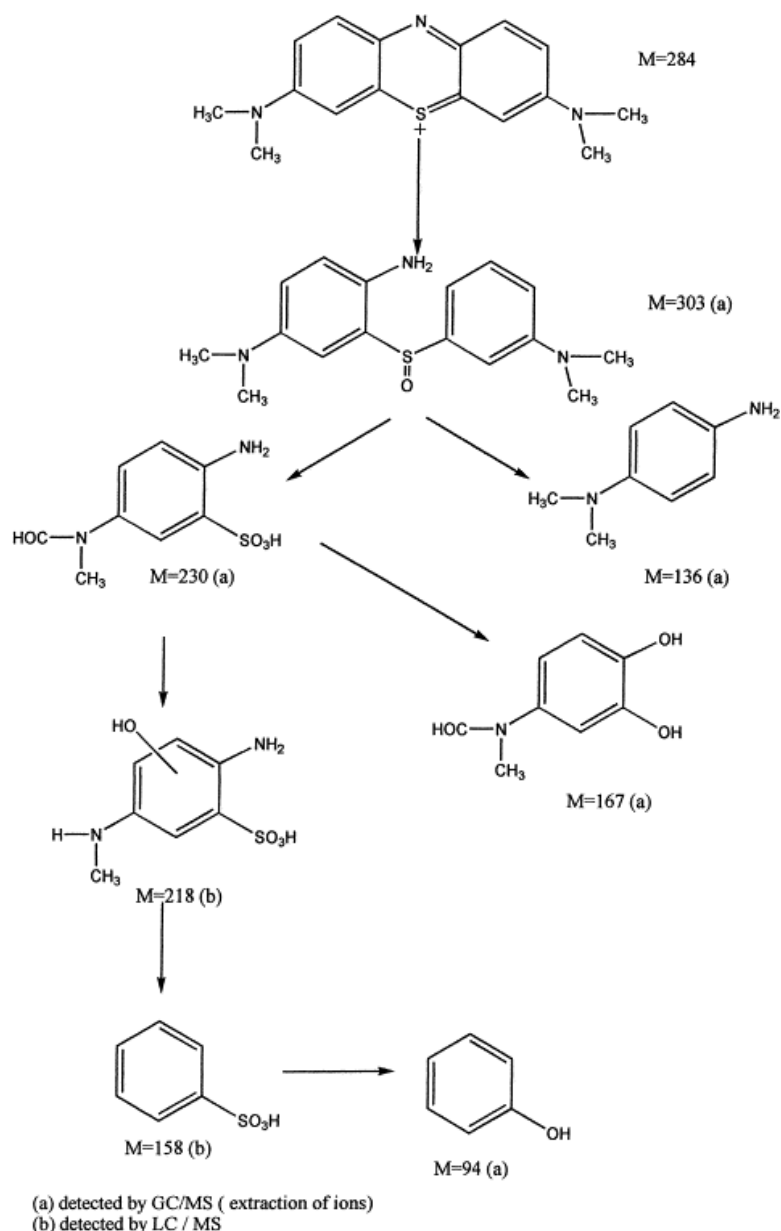


Figure 24: Schematic of Methylene Blue degradation path way with decoloration in the first elementary step, reproduced from Reference [147].

Several disadvantages to the use of MB degradation are known as well. It's mineralization products include strong acids which affect its degradation rate¹⁵³. It will degrade under strong visible and UV light sources including the spectroscopy equipment used to monitor its concentration. Alternate pathways to its degradation can also produce different responses to light absorption including the formation of dimers¹⁵⁴. Both of these concerns are relatively minor in dilute solutions where the dye

exists only as a monomer (dimers form at higher concentrations). Unless the degradation reaction is run to complete mineralization, the changes in pH will be relatively minor and will not significantly affect the overall degradation rate. Lastly, the degradation that results from the spectroscopy measurement device can be accounted for using data where no other catalyst is present.

6.4 Photocatalysis Measurement Apparatus

Photocatalysis experiments were performed using a Newport solar simulator. The apparatus is equipped with a 300 W Xe arc lamp producing $3,760 \text{ mW/cm}^2$ full AM1.5G spectrum light. Between this light source and the sample is an AM1.5G filter and condenser lens to produce filtered light with a $\lambda_{\text{OD2}} = 416 \text{ nm}$ longpass glass filter (which removes more than 99.97% of light with energy above the band gap of TiO_2). The final intensity of the light on the TiO_2 surface has been estimated at approximately 3280 mW/cm^2 by other users²³.

The apparatus is equipped with a recirculating flow reactor for the thin film sample and the MB dye solution. The path of the dye can be seen in the schematic shown in Figure 25. Starting from a reservoir that is open to the air, the solution is drawn by the pump and forced through a cell containing the sample exposed to the filtered solar simulator light. The dye then passes through a z-flow cell which provides a 1 cm path length for the spectrometer measuring dye concentrations before the solution returns to the reservoir. The cell is mounted vertically with the liquid ports close to the top and bottom to prevent air bubbles from accumulating in the cell on the light path in front of the sample.

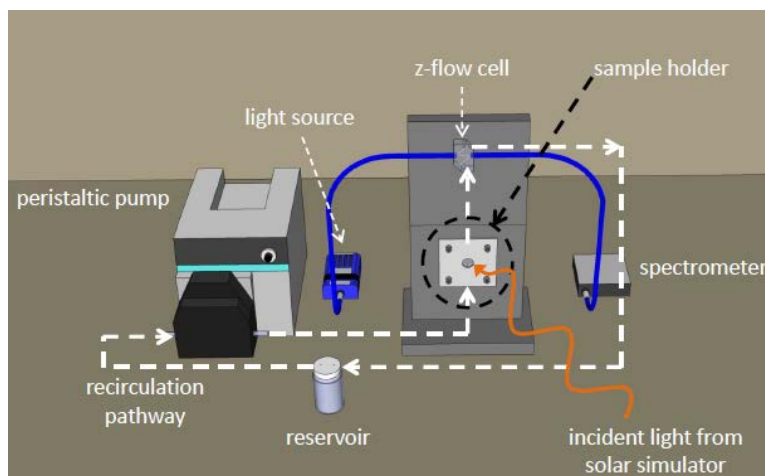


Figure 25: Schematic of the recirculating photocatalysis reactor.

The individual components of the reactor system are as follows:

- Masterflex L/S peristaltic pump with L/S 16 tubing
- Custom fabricated sample holder (details to follow)
- FIA-1000 Z-flow (Plexiglas) cell with 1 cm path length
- Ocean Optics LS-1 light source with fiber optic cables
- Ocean Optics USB4000 spectrometer
- Teflon tubing and 30 mL Erlenmeyer flask

The sample mount was custom fabricated based on several needs. Like the tubing used, it must not absorb significant dye from the solution, nor may it contribute to its degradation. It should not expose the MB solution to light unnecessarily, restricting the spot size to the spot size of the exposed sample. It must be sealed against leaks while mounted vertically for an extended period of time. It also must be easily disassembled, cleaned, and reassembled between samples. Through consultation with the machine shop, the schematic seen in Figure 26 was fabricated.

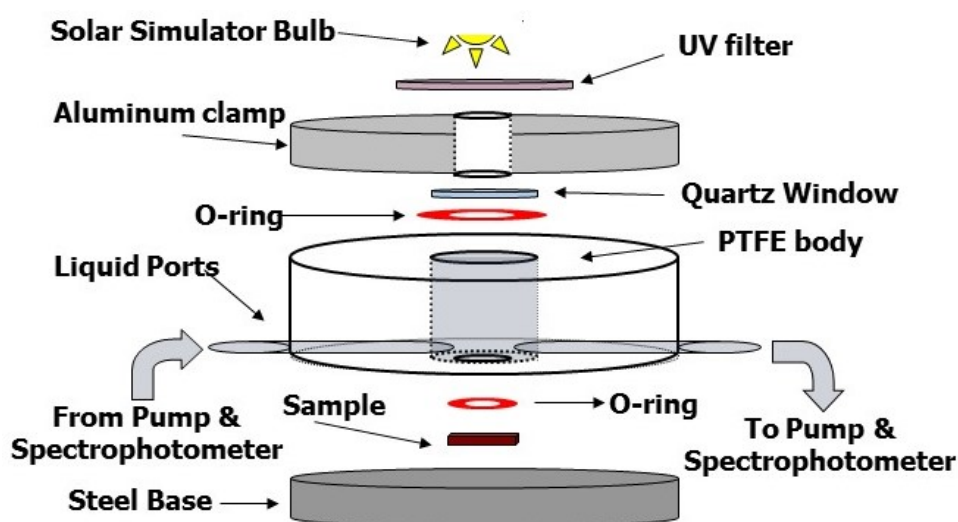


Figure 26: Schematic of liquid cell for photocatalysis measurements. Sizes in figure are not to scale.

The frame of the cell is made from stainless steel. The six threaded screws are machined to be flush with the base on the backside so that the cell will sit flat against any surface. The main body of the cell is made from machined Teflon. This body has a 2 mm diameter through hole which allows light and the MB solution to reach the sample surface below. The sample is sealed to the main body by an O-ring placed in a groove on the back side. This O-ring size was the determining factor in setting the through hole diameter as the ring must sit entirely on the substrate (a 5*5 mm square). The 2 mm diameter through hole is the maximum illuminated area allowable while still having a Teflon O-ring groove strong enough to support the thumb screw compression. Inside the body, the main liquid cell is a cylinder of diameter 1 cm and height 5 mm. At the base of this cell are liquid ports where 18 gauge stainless steel tubes which seal to the external Teflon tubing are placed. The top of the body has a second O-ring groove to seal with a 1/16" thick quartz window (Chemglass Life Sciences CGQ-0600-01). This window is held in place by an aluminum cover with a 2 mm diameter through hole centered above the through hole in the main body. This prevents undesired illumination of the MB solution except where necessary above the active sample area. This 2 mm through hole sits easily in the 3*4 mm oval shaped focus spot from the condenser lens of the Xenon lamp. The window provides liquid sealing when the sample, body and window are compressed by six thumb screws above the aluminum cover. The quartz

grade was selected for its minimal absorption in the visible spectrum. Computer-aided design drawings (CAD) of the cell pieces can be found in Appendix A.

6.5 Methylene blue degradation test conditions

A complete set of instructions for operating the Solar Simulator can be found in Appendix B. The dye solution was prepared each time from a stock solution of MB that was approximately 5 ppm. Each sample run used 15 mL (by weight) of a 1 ppm (3.17×10^{-6} M) MB solution diluted using the same DI described for TiO₂ synthesis in Chapter 2. Absorbance measurements are processed from the raw intensity signal for the spectrometer. The dye solution was recirculated at a rate of about 10 mL/min. With the reservoir open to the atmosphere, the dye solution was allowed to equilibrate for 2 hours to ensure that the solution was fully saturated with oxygen. When the lamp is on, the reaction is typically run for 8 hours. When data collection is finished, the system is flushed for at least 30 minutes with DI water to ensure no absorbed dye remains behind. Removable components are washed in DI water and dried under dry N₂ gas.

Full spectrum intensity and absorbance data are collected at intervals of one minute. Strip charts are formed from these of intensity and absorbance at 665.03 nm where MB absorbance is maximized. Data processing involves normalizing the raw absorbance data to an initial concentration of 1 ppm at the beginning of the solar simulator exposure. The relation between MB dye concentration and absorbance is linear, so normalized absorbance data can be interpreted directly as concentration of undegraded MB dye. The spectrometer does not measure the concentration of intermediate degradation products, and pH was not monitored separately to estimate the degree to which the dye was fully mineralized. As is commonly done in the literature, all activity data reported here will be strictly measurements of decoloration while the total activity of the catalyst is likely to be several times higher based on the number of elementary reaction steps in the proposed path ways.

6.6 TiO₂ synthesis and thickness measurements

TiO₂ capping layers were grown on amorphous and epitaxial SRO samples described in Chapter 5. Growth chamber settings used a 2 second pulse of TTIP and H₂O to overcome incipient film nucleation issues observed for shorter precursor doses. SRO samples were successively sonicated and rinsed in Acetone and IPA before being dried by blowing dry N₂. Due to the small sample sizes, they were adhered to similarly cleaned Si wafer pieces using silver paint (Ted Pella Leitsilber 200) which was dried in a 40 °C furnace for 10 minutes before being loaded into the TiO₂ deposition chamber.

Due to the thin nature of the TiO₂ films being grown, several issues with accurately measuring film thicknesses presented themselves. It was desired by the author to avoid performing TEM on each sample to obtain thicknesses due to the number of samples, the preparation time involved, and the necessity to sputter coat samples with metal during preparation as TiO₂ is too insulating for FIB use. The Rudolph Research single wavelength ellipsometer routinely failed to converge when the standard program for a film of known refractive index was used. This may have been due to the thin nature of the TiO₂, or the unusual optical properties of the underlying SRO. It is worth noting that the single wavelength ellipsometer did not return consistent or accurate film thickness measurements for SRO films without capping layers. The Woollam VAS spectroscopic ellipsometer encountered similar issues. When modeling of the data was attempted in order to obtain a thickness from the fits, it was discovered that standard TiO₂ optical constants were not sufficient as they appeared to vary at low thicknesses. Because accurate thicknesses were not available for reference samples, we could not produce new optical constants on our own.

XRR was the most successful technique in measuring film thicknesses. X'Pert Reflectivity modeling software indicated that the expected fringes for films under 20 nm would be on the order of 0.5 degrees in width on a 2Theta-Omega scan so the step size used was relatively large (0.25°) with dwell times per step increased until the signal to noise ratio was reasonable (~20 seconds/step). With these scan settings, the critical angles of both the TiO₂ and SRO films were frequently visible (Figure 27), though

the thickness fringes of the SRO were often poorly defined. As there was no significant variation in thickness, density, or surface roughness for the SRO films, particularly the epitaxial films, SRO fringe visibility was not of concern. Additionally, the small area of the samples provided an additional challenge as the beam length is of a similar or greater length than sample lengths. To accommodate this, scans were performed using two different beam heights using beam blockers placed in the front of the X-Ray optics. The standard beam height (beam #10) was about 1 cm, while the smaller beam height used (beam #5) was about 0.5 cm. Performance across the two beam sizes varied by sample. Whichever beam height provided data with less noise was used for analysis.

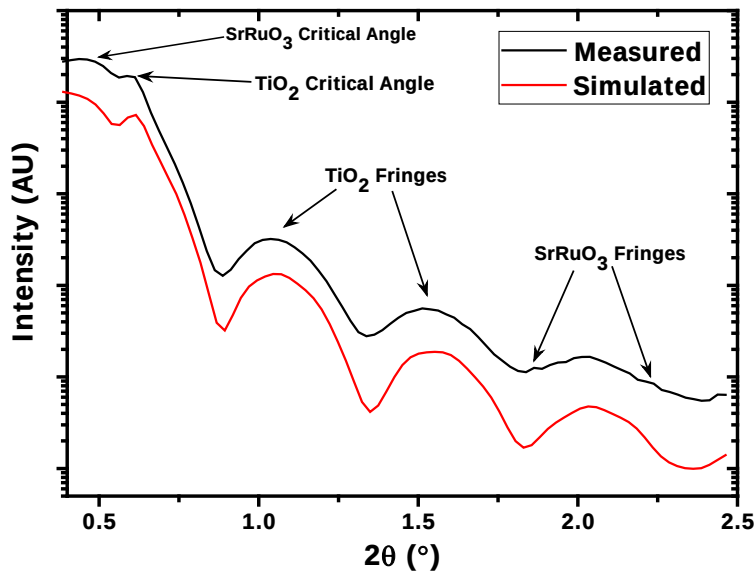


Figure 27: Representative XRR of a thin TiO_2 capping layer on an SrRuO_3 light absorbing layer. Simulated data is shifted vertically for ease of viewing.

Each sample had its TiO_2 thickness measured by two separate fitting methods, both using the X'Pert Reflectivity software. The first is a user defined fringe separation measurement in which users tell the software the location of the critical angle and at least two fringe peaks or valleys. The spacing is then used to calculate a thickness independent of material properties without providing information on density or surface roughness. The second method uses a built in modeling capability that uses material data to produce a simulated data set given basic material properties. Users then adjust inputs of material

thickness, density and roughness until the simulated data matches the overlaid experimental data. This method is significantly more time intensive and its efficacy depends heavily on the noise in the experimental data. Density of materials in the relevant thickness ranges is often poorly estimated but this does not prevent users from getting reliable fits for thicknesses as the density primarily affects the position of the critical angle and not the spacing of thickness fringes. In the example shown in Figure 27, density values were as much as 30% lower than single crystal values to obtain the displayed fit. Thickness values obtained by this method agree with the first method typically returning values by about 5% higher than the first method. For purposes of this work, reported thicknesses will be those obtained by the first method. Surface roughness estimations obtained by this method were in good agreement with AFM calculations on the order of 1-2 nm at most. As roughness was consistent across all samples, it is believed to stem primarily from the roughness of the SRO and not from the TiO₂. As a result, roughness values will not be reported for each sample.

The thinnest sample successfully measured by this method was 6.5 nm in thickness. This leaves an open question of how to interpret samples where the TiO₂ fringes were not discernable amongst the noise. One explanation to offer is that they are thinner, and that sample roughness is sufficient to prevent a clear signal. The alternative is that they are above this thickness and were abnormally rough for an unknown reason.

6.7 Photocatalytic Results

The overall degradation rate of MB is known to be pseudo-first order regardless of which path way mentioned above is followed. A first order rate would produce an exponential decay while a zeroth order would produce a linear decay. A linear decay may appear visible without curve fitting over the 8 hour run time used here. An exponential decay shape often becomes clearly visible at significantly longer time periods, see Reference [23] Supporting Information, Figure S6 for a comparable catalyst loading and dye concentration.

The decoloration of MB by various thicknesses of amorphous TiO_2 on 60 nm of amorphous SRO can be seen in Figure 28. A limited number of samples are shown as the absorbance data is noisy due to known fluctuations in the spectrometer and possible bubbles in the solution. What may be immediately seen is that clear differences in activity are visible between samples with thinner TiO_2 being the better performer by a little under 10% after 8 hours. The decay trend appears linear as expected over the run time.

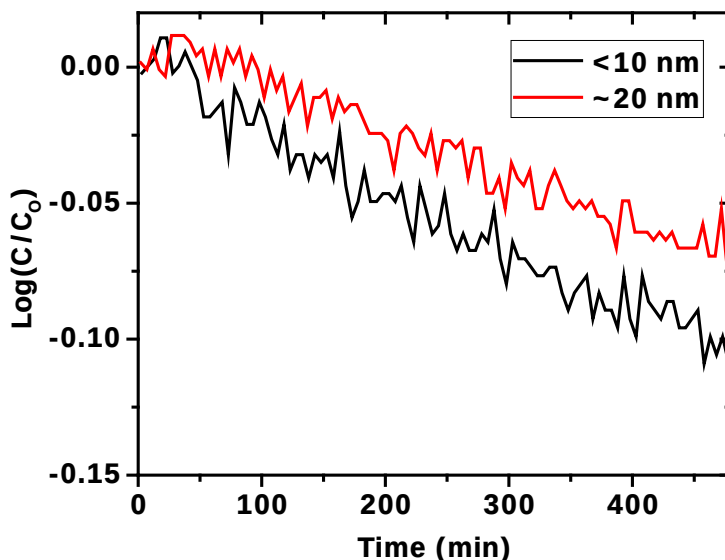


Figure 28: Decoloration of MB on a- TiO_2 /a-SRO. Thicknesses of TiO_2 are estimates due to uncertainties in the XRR data for these samples.

An equivalent data set may be seen in Figure 29 for amorphous TiO_2 of various thicknesses over epitaxial SRO. As with the amorphous SRO data, a subset of the samples are shown for ease of viewing due to the noise in the data. One thing that is immediately striking is that the amorphous SRO performs as well as the epitaxial material to within a few percent based on the final concentrations of dye for the 6.5 and 16 nm samples. Additionally, a major example of spectrophotometer drift can be seen in the 6.5 nm sample from 200 minutes to 350 minutes.

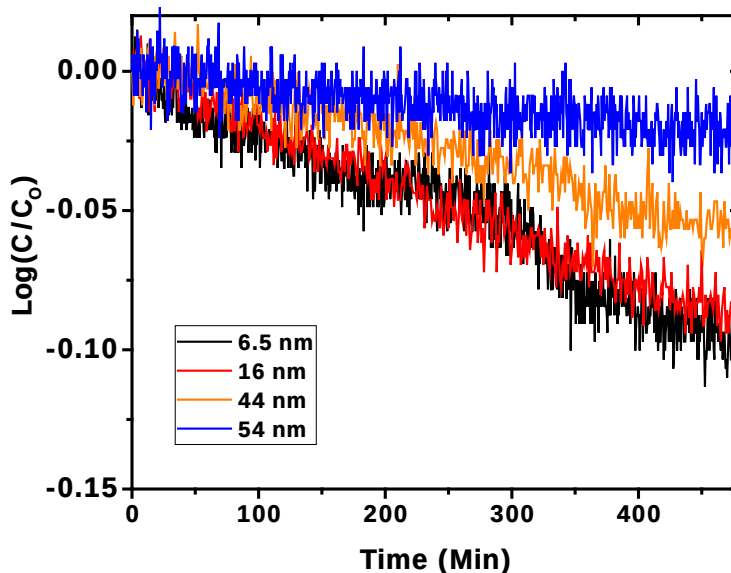


Figure 29: Decoloration of MB on a-TiO₂/e-SRO for various thicknesses of TiO₂.

In order to treat the data more quantitatively, rate constants were extracted from the data. Both first order and zeroth order fits were performed on the normalized absorbance data in order to check for any evidence that the degradation was not happening according to the expected pseudo-first order model. These values for 'k' were calculated forcing the y-intercept to be equal to 1 PPM. In reality, dye loading varied slightly as dye was being pipetted from a stock solution on the order of 0.2% across all samples. Rate constants were re-calculated from the logarithm scale plots shown using linear fits based on first order kinetics. These values for the overall reaction rate constant 'k' can be seen in Table 3. In order that the data may easily be compared to other MB degradation experiments, the units for k were subsequently converted to units more common to the literature for heterogeneous catalysis such μmol of MB/hour*gram of catalyst used for porous material and μmol of MB/hour*cm² as used for thin film materials. The weight of catalyst involved may be taken from the combined weight of TiO₂ and SRO that lies beneath the 2 mm round active area of the reactor cell. The SRO is a static 60 nm and a single crystal of known density (6.489 g/cm³). The TiO₂ is amorphous and of unknown density. In Reference [23] a single crystal density of 4.23 g/cm³ was used for epitaxially grown TiO₂, however, this TiO₂ was only 10 nm in thickness making the use of a bulk density potentially problematic. An estimated density of 3.2

g/cm^3 was also used for the weight based activity calculation. This value comes from a rough average of TiO_2 densities reported by the XRR simulations when fitting raw data to extract thickness, as well as from a slight underestimation of densities for polycrystalline material grown to greater thicknesses but at the same growth rate by the same chamber in Reference [68], Figure 2 ($\sim 1 \text{ nm/cycle}$).

TiO_2 Thickness (nm)	$k \cdot 10^3 \text{ (1/min)}$	$k \cdot 10^{-3} \text{ (1/hr)}$	$k \text{ (}\mu\text{mol/(hr}\cdot\text{g))}$		$k \text{ (}\mu\text{mol/(hr}\cdot\text{cm}^2\text{))}$
			Single Crystal TiO_2	Amorphous TiO_2	
6.5	0.205	12.3	438	468	0.0182
15.5	0.155	9.3	305	356	0.0139
16	0.190	11.4	372	436	0.0170
27	0.109	6.54	199	258	0.0100
31	0.087	5.22	150	200	0.0078
44	0.117	7.02	182	269	0.0105
54	0.048	2.88	70	110	0.0043

Table 3: Determination of overall rate constants for amorphous TiO_2 /epitaxial SrRuO_3 samples based on first order kinetics fit ($\text{Log}(C/C_0) = -kt$).

When the absorbance data was normalized to the actual starting concentrations, calculated values for k did not change by more than 1% and are not reported separately here. The total dye loading on a mol basis was included when calculating the catalyst weight activity.

Figure 30 shows the same values for k plotted versus thickness of TiO_2 . The values in thickness stretch from approximately the mean free path of an electron to several diffusion lengths for a thermal hole. A linear trend is apparent from the data.

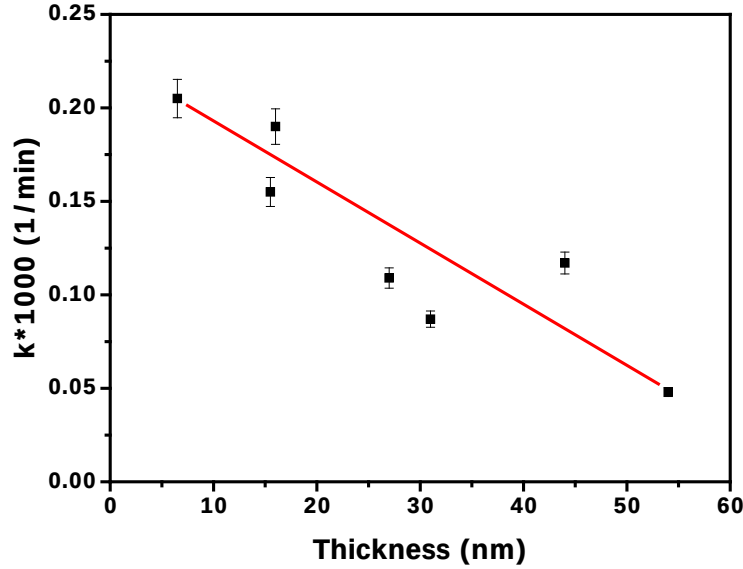


Figure 30: Experimental k values. Error bars shown are 5% of the calculated value and were chosen based on the signal/noise in the absorbance data. A hand drawn line has been added as a guide to the eye.

As demonstrated in Reference [23], this heterojunction structure has the ability to significantly outperform current industry standards such as Degussa P25 nanoparticles. Our results outperform their sample comprising of 10 nm of epitaxial TiO_2 over 60 nm of epitaxial SRO by about a factor of 3 on a per weight basis before correction for dye degradation due to light. The results are less promising when compared to other TiO_2 thin film experiments. The best performing sample reported by Ong *et al.* showed activity half an order of magnitude higher for thin film TiO_2 under UV light on a surface area basis⁴⁰.

6.8 Conclusions

The linear dependence of catalytic activity on film thickness alone does not answer the overarching question of whether hole transport through the TiO_2 is limited by diffusion or drift current. The degree to which the TiO_2 is depleted will likely be a strong function of thickness as depletion width varies with the square root of the permittivity of the material. We expect that the permittivity of the TiO_2 is changing with thickness as the optical properties at the thicknesses used here did not match well with bulk values. If a truncation approximation for the degree to which the TiO_2 is depleted is employed, the

electric field arising from the interface would in turn become a strong function of film thickness. In this sense, a drift current model is not unreasonable. The better charge compensation that occurs with increased thickness drives the magnitude of the electric field down and sweeps fewer holes to the surface. Unfortunately, the direction of the electric field is not known. It is possible that the field could be in a disadvantageous direction, promoting electrons to the free surface and keeping holes close to the interface. This is unlikely as the redox potentials of the water splitting half reactions should force the TiO_2 band edges to be bent up at the free surface as shown in Figure 22. A more simple explanation would be simply that the TiO_2 at all the thicknesses above is heavily depleted and that electric field strength is insignificant with the band edge positions at the TiO_2 free surface staying independent of the work function of the SrRuO_3 . In this view, activity drops off linearly with thickness as photogenerated holes diffuse randomly across the TiO_2 recombining randomly with the majority carrier electrons in the TiO_2 . To decide between these opposing models, more information about the strength of the electric field at the interface is needed. We will endeavor to address this question in Chapter 7.

CHAPTER 7

DETECTION OF INTERFACIAL BAND BENDING AT THE TITANIUM DIOXIDE/STRONTIUM RUTHENATE INTERFACE BY X-RAY PHOTOELECTRON SPECTROSCOPY

7.1 Interfacial Band Bending

Charge transfer over a near interface depletion region is required to balance the difference in fermi levels between two semiconductors, or in the case of a metal-semiconductor junction the work function of the metal and fermi level of the semiconductor. Interfacial band bending is a major artifact of this process of charge neutralization. There reason to explore the presence of this band bending is a twofold. First, it can lead to very strong electric fields close to the interface which can propagate across a thin catalytic layer. These fields would play a significant role in a drift current affecting both minority and majority carrier transport. Second, if band edges are bent significantly at the interface, the magnitude of an interfacial electronic barrier may also change which would have consequences for the discussion as to whether hot carriers are required to explain the photocatalytic events described in Chapter 6.

The width of the depletion region may be estimated by solving the Poisson equation in one dimension, the form of which can be seen in Equation 7.

$$W_d \cong \left[\frac{\epsilon_r \epsilon_o}{q} \left(\frac{N_A + N_B}{N_A N_B} \right) (V_{BI} - V) \right]^{1/2}$$

Equation 7: Depletion Width estimation from one dimensional Poisson equation

Here, ϵ_r is the relative permittivity of the material of interest, ϵ_o is the permittivity of free space, N is the free carrier concentration of the two materials, V_{BI} is the built in voltage resulting from the interfacial electronic barrier, such as a Schottky barrier, and V is the applied bias to the system if any.

The width will be greater on the side of lower carrier concentration, though actual widths vary significantly. Depletion widths in TiO_2 in a junction with *n-type* silicon can vary from < 10 nm to tens of nm as doping levels in the silicon are decreased. Junctions between TiO_2 and a metal will be tens of nm or larger. The degree to which this charge compensation process occurs in heterojunctions where one layer is significantly below the predicted depletion width is an important question and an area of research for metal oxide catalyst researchers where the catalytic layer is the thin layer of interest²⁸.

Measuring the degree to which charge compensation occurs in a semiconductor layer that cannot be fully depleted is difficult. In a thick layer on one side of a typical junction, the depletion width will be storing charge in a material essentially identical to the rest of the bulk. In a thin layer, another interface or free surface may also assist with charge compensation. What can be observed is the changing of the charge state of material layers very close to the interface by way of XPS.

When significant shifts occur in the position of the Fermi level within the sampling depth of the XPS instrument, the signature signal from the core shell ejection will change. Typically, this leads to a broadening of the Full Width at Half Maximum (FWHM) of the XPS peaks where the x-axis is the binding energy of the observed electron. When the position of the Fermi level is not pinned to the positions of the band edges, a broadening of the peak is indicative of band bending. A greater degree of band bending is observed as increased broadening. Slight differences in peaks symmetry may be indicative of which direction the band bending is occurring, however, this requires the peak not be overlapping with any nearby peaks that obscure peak shape in any way. An excellent example of this technique may be found in publications by Scott Chambers group at Pacific Northwest National Lab, a replication of which can be seen in Figure 31.

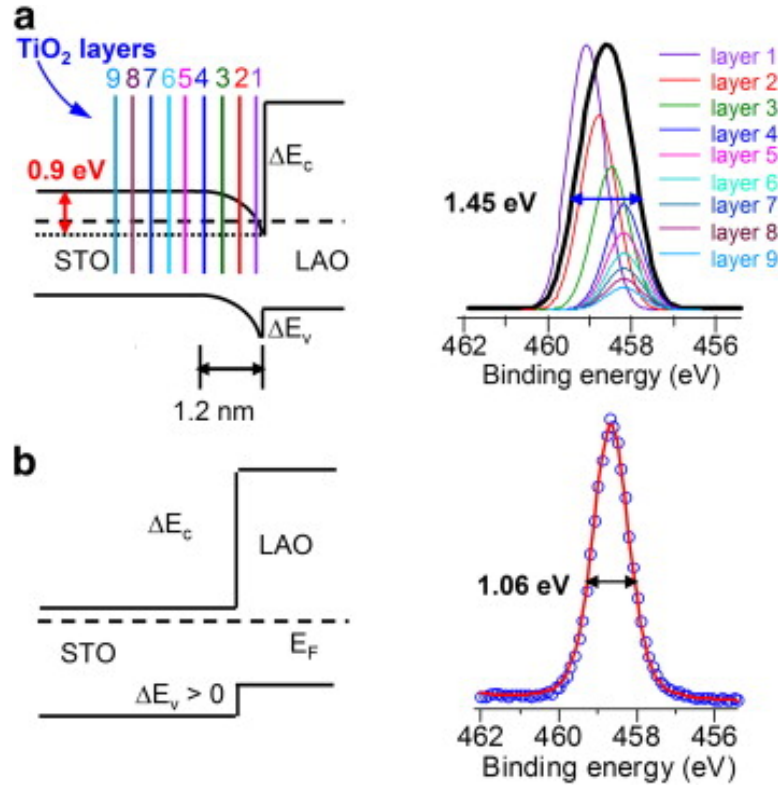


Figure 31: Reproduced from Reference [155]. a) Simulation of the effect of band bending on Ti 2p 3/2 line shape at a LaAlO₃/STO (001) heterojunction. The first four TiO₂ layers below the interface are shifted and attenuated to simulate 0.9 eV of band bending over 1.2 nm of STO. The black solid is the composite signal and exhibits a FWHM of 1.45 eV. (b) The actual Ti 2p 3/2 peak which exhibits a FWHM of 1.06 eV, indicating a near flat-band state.

By measuring the peak broadening of a core shell electron belonging to the top layer of a very thin layered material, band bending at the interface may be estimated using first principles calculations and generating composite pictures of expected peak shape^{155,156}. If the positions of core shell electrons are significantly different for each atomic species on either side of the interface, band bending may be measured on both sides by looking at shifts in binding energies for core shell positions and valence band positions for each species, and solving for changes in Fermi level positions algebraically as seen by Equations 2-5 in Reference [155].

7.2 Reference Spectra & Fitting Constraints

In order to detect band bending, a reliable measurement of the FWHM of reference TiO_2 material must be obtained. First a sample of amorphous TiO_2 was grown on silicon to a thickness of approximately 90 nm with the same growth conditions as used in Chapter 6. This is significantly greater than the predicted depletion width of a $\text{TiO}_2/n\text{-type}$ silicon junction, so the FWHM of the TiO_2 peak will be representative of the TiO_2 bulk and any charged surface states. The XPS spectra of the Ti 2p peaks are shown in Figure 32. It may be assumed that there will be no significant difference between the contributions of surface states in the reference and interfacial samples. Should processing variations led to different surface states, the change in FWHM would render the reference sample not useable. If variations are expected, changing the angle of the X-Ray source relative to the sample may help probe this as a more glancing angle will sample shallower depths of the sample. Comparison of this glancing angle peak to a higher angle peak would display the effects of surface states to the FWHM of the Ti 2p reference peak. This check was not performed as the thin nature of the samples that follow in the next section required that the X-ray incidence angle was kept high to ensure the entire film was sampled, especially at close to the interface, so surface sensitive comparisons would be difficult.

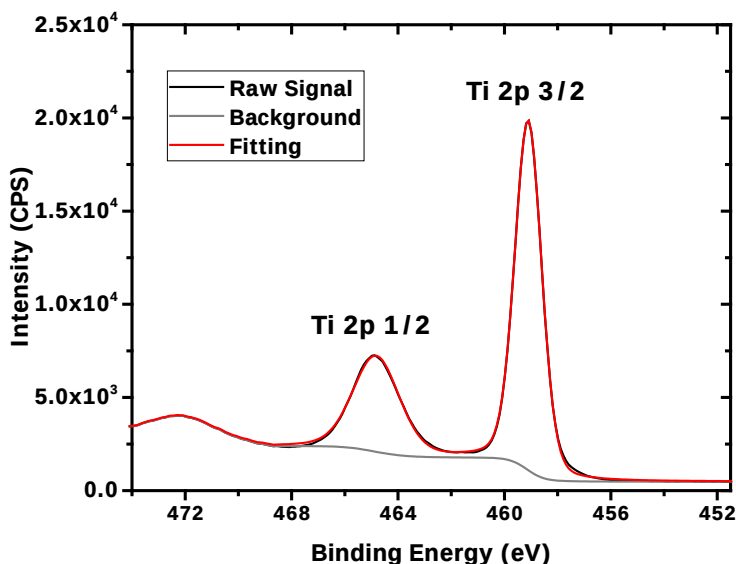


Figure 32: XPS spectra for amorphous TiO_2 reference sample.

The Shirley background was fit from 451.5 to 468.6 eV to encompass both the Ti 2p 1/2 and 3/2 peaks. The plasmon centered around 472 eV could not be easily fit with a Shirley background and was not necessary to obtain information about the Ti 2p peaks. With regard to the fitting of sample peaks, several constraints may be taken from this reference spectra. First, the Ti 2p peaks are both highly symmetrical as expected. The line shape SGL(20) was used to fit both peaks. This produces two further constraints on future fits. The ratio of the areas of the peaks is expected to remain constant for any similar material regardless of changes to peak shape or width. Additionally, the spacing between the peaks will remain constant regardless of other changes to the surrounding material. A summary of peak fitting information may be found in Appendix C.

Reference samples of amorphous and epitaxial SRO were measured in a similar matter. For SRO, the Ru 3p peak is the only elemental peak that is not heavily convoluted with another peak belonging to either strontium, ruthenium, oxygen, or carbon. The Ru 3p peak of a 60 nm amorphous SRO reference can be seen in Figure 33.

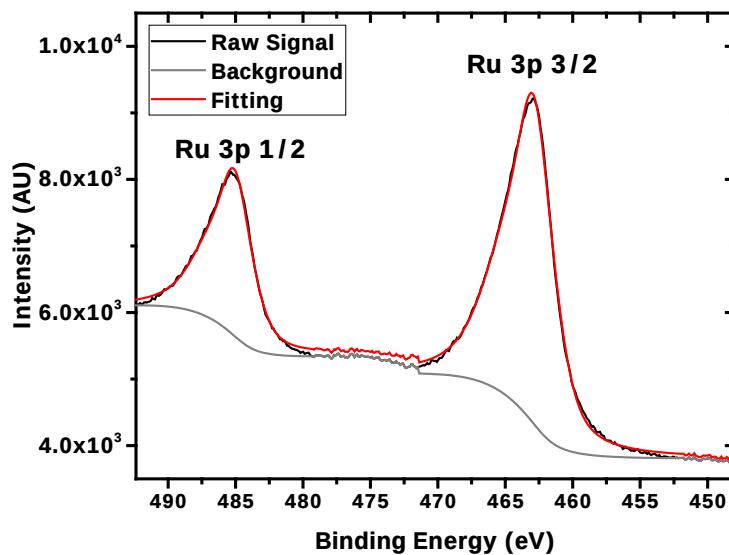


Figure 33: XPS spectra for an amorphous SrRuO₃ reference sample.

Unlike the Ti 2p peaks shown above, the Ru 3p peak has a noticeable asymmetry with a tail at higher binding energy. In order to accommodate the width of the peak, the Shirley background was extended

beyond the range used for Ti 2p and divided between two distinct regions. The line shape A(0.2,0.6,0)SGL(50) produces good fits for both the Ru 3p peaks with an area ratio of 2.3:1. This is the major constraint to be extracted from the reference spectra of amorphous SRO. The signal will be attenuated by a TiO₂ capping layer, but as signal is lost, asymmetry and total area should not vary. FWHM may be attenuated by capping layers differently, so it will not be as reliable of a constraint even though peak asymmetry is not expected to vary. If this were a true semiconductor-semiconductor heterojunction, the asymmetry would be expected to shift in accordance with peak broadening. However, because the SRO is metallic, the width of the depletion region on the SRO side of the junction is expected to be unmeasurably small, and therefore will not affect XPS peak shape. A similar assumption may be made about the effect of any surface states that will be covered up by a capping layer because the SRO is metallic.

The reference spectra for the epitaxial SRO film provides a similar picture as seen in Figure 34. The sample was a 60 nm film cleaved from a larger sample from the same batch. Region selection and fitting was similar. The line shape used was A(0.2,0.3,0)GL(50) and the ratio of the areas of the peaks was 2.14:1. As with the amorphous reference sample, line shape and area ratios will be used as future constraints on fitted data, but not FWHM.

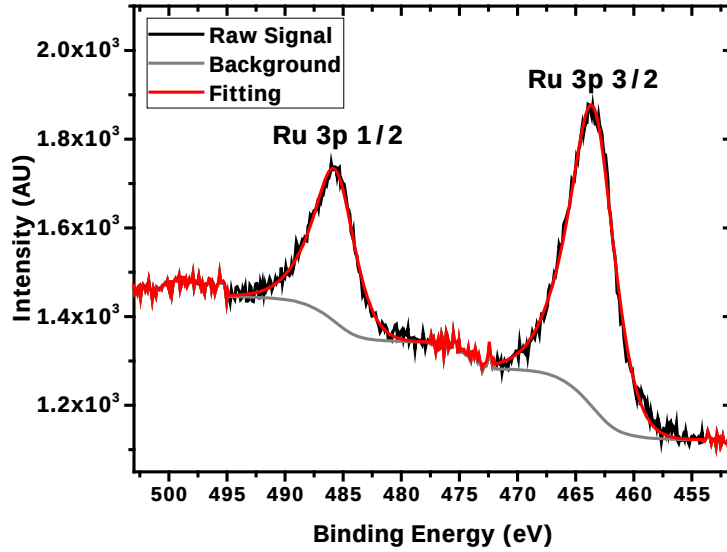


Figure 34: XPS spectra for an epitaxial SrRuO₃ reference sample.

7.3 TiO₂/SrRuO₃ Interface

In the case of the TiO₂/SRO heterojunction, the measurements to determine band bending are not so straightforward. Oxygen will have several different bonding states on the TiO₂ free surface, in the TiO₂ bulk, at the heterojunction interface, and in the SRO bulk; core shell position measurements will be difficult to accurately obtain as signals from each of the above states will produce a heavily convoluted peak. Using titanium core shell peaks require extra effort as the Ti 2p peak and Ru 3p peaks have significant overlap in position close to a binding energy of 460 eV, and will require deconvolution.

The exact thicknesses of the TiO₂ overlayers on the SRO substrates displayed in Figure 35 and Figure 36 are not known. Below a thickness of about 10 nm, the XRR data becomes too noisy and the feature size was not easily distinguishable in cross sectional SEM. In both cases, the film is expected to be less than 5 nm considering the attenuation of the Ru 3p intensity relative to Ti 2p.

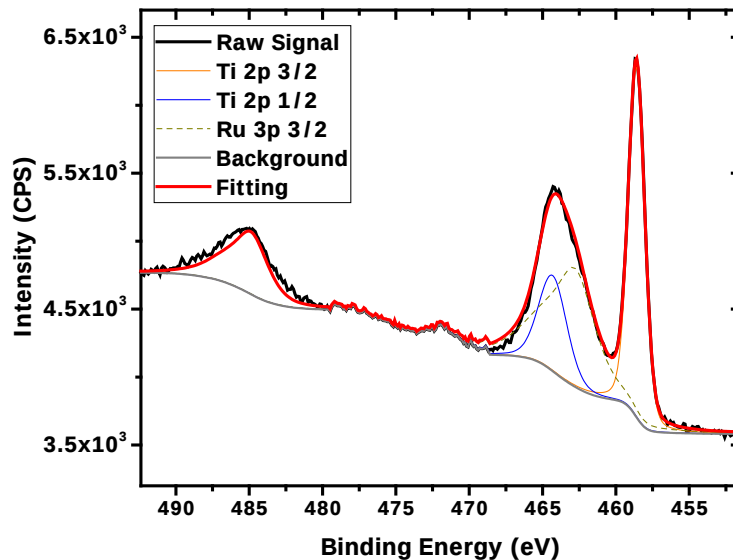


Figure 35: XPS of Amorphous TiO_2 /Amorphous SrRuO_3 .

Fitting of the data was performed using all of the constraints on the Ti peaks listed above in addition to the area ratios of Ru 3p peaks. Shirley background regions were as closely matched to those of the reference samples as possible while avoiding the Ti plasmon near 472 eV and the Ru plasmon near 500 eV. Fitted data for the Ru 3p 1/2 peak is not shown on the plots as it overlaps directly with the composite fitted curve in red. Results were similar to earlier fitting attempts which held the FWHM of the Ru 3p 3/2 peak constant with the reference sample, but ignoring the Ru 3p 1/2 peak details of which can be found in Appendix C.

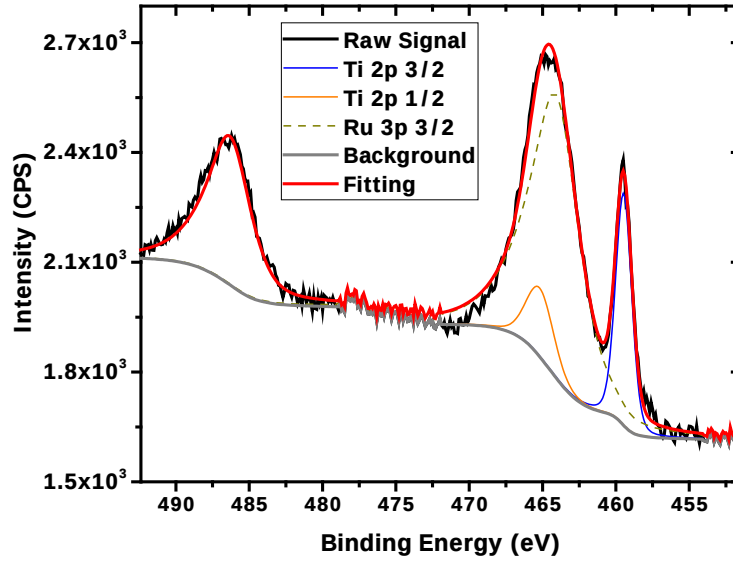


Figure 36: XPS of Amorphous TiO₂/Epitaxial SrRuO₃.

7.4 Discussion

The FWHM of Ti 2p 3/2 reference peak in Figure 32 was 1.189, the FWHM of the same peaks for the capping layers of TiO₂ in Figure 35 and Figure 36 were 1.307 and 1.294 respectively, an average broadening of 0.111 eV. As stated previously, a physical interpretation of this value is not straightforward. While peak broadening may be correlated to band bending, doing so quantitatively requires a parallel computational experiment. The best reference point may be the result in Reference [155] above. Similarly, the junction under examination is a wide bandgap semiconductor (SrTiO₃) and a metallic oxide (LaAlO₃). In Figure 31, a 0.9 eV band bending offset is shown to produce a peak broadening of about 0.4 eV. If a linear relation were to be assumed, it would suggest that the band bending in the TiO₂/SRO junction would be on the order of 0.2 eV. In reality, this would likely be an overestimate as SrTiO₃ is more insulating than TiO₂ so the need for charge compensation at the junction would be even greater for the STO/LAO.

Despite the qualitative nature of the 0.1 eV peak broadening, confidence may be taken in the validity of the measurement for several reasons. First, when alternative constraints were applied to the system as part of the effort to deconvolute the Ti 2p and Ru 3p peaks, the fitted data were all within a few

percent of the same 0.1 eV result. Second, although the FWHM of the Ru 3p peaks were not constrained the FWHM ratios of the 3/2 to 1/2 peaks were monitored. In both cases the FWHM ratios of the reference Ru 3p peaks and the sample Ru 3p peaks were very close; they were 1.16/1.20 for the amorphous SrRuO₃ reference and sample, 1.08/1.12 for the epitaxial SrRuO₃ reference and sample.

7.5 Conclusions

The evidence of slight band bending agrees with the idea of a truncation approximation where as layer thickness approaches zero, the less net charge transfer occurs²⁹. The degree to which charge is compensated through the saturation of some ‘bulk’ defect or surface state is unknown as defects and surfaces of amorphous materials cannot be easily characterized in the same manner as their crystalline counterparts.

Because of the limitations of XPS, we cannot tell to what degree this band bending changes with the thickness of TiO₂. Even if we assume that the band edges of TiO₂ will be pinned at the free surface such that the magnitude of the band bending remains constants, the strength of the resulting electric field from the interface would drop of increasing TiO₂ thickness. Given that the overall strength of band bending appears to be modest, a diffusion current to explain the results of Chapter 6 is likely more appropriate.

If the opportunity were to present itself, this experiment should be repeated using a TiO₂/SrVO₃ heterojunction system. SrVO₃ (SVO) is a correlated metallic perovskite oxide with strong visible light absorption like SRO and is similarly epitaxially matched with both anatase TiO₂ and STO⁵⁹. The difference in carrier concentrations will be of a similar order of magnitude, but SVO forms an ohmic contact with TiO₂ so the conduction band offsets will be smaller. Peak measurement and fitting will be made significantly easier by the fact the V 2p peaks are near a binding energy of 515 eV, far from the Ti 2p peaks at 460 eV.

CHAPTER 8

REFERENCES

1. Sellers, M. C. K. DEFECT ENGINEERING OF POLYCRYSTALLINE TITANIUM DIOXIDE SYNTHESIZED BY ATOMIC LAYER DEPOSITION. University of Illinois, Urbana, 2011.
2. Londos, C. A.; Sgourou, E. N.; Chroneos, A., Impact of isovalent defect engineering strategies on carbon-related clusters in silicon. *Journal of Materials Science: Materials in Electronics* **2013**, 24 (5), 1696-1701.
3. Oliviero, E.; David, M. L.; Fichtner, P. F. P.; Beaufort, M. F.; Barbot, J. F., Lithium implantation at low temperature in silicon for sharp buried amorphous layer formation and defect engineering. *Journal of Applied Physics* **2013**, 113 (8), 083515-7.
4. Ronning, C.; Borschel, C.; Geburt, S.; Niepelt, R., Ion beam doping of semiconductor nanowires. *Materials Science and Engineering: R* **2010**, 70, 30-43.
5. Yang, P.; Li, X.; Zhao, Y.; Yang, H.; Wang, S., Effect of triangular vacancy defect on thermal conductivity and thermal rectification in graphene nanoribbons. *Physics Letters A* **2013**.
6. Shotan, Z.; Jayakumar, H.; Considine, C. R.; Mackoit, M.; Fedder, H.; Wrachtrup, J.; Alkauskas, A.; Doherty, M. W.; Menon, V. M.; Meriles, C. A., Photoinduced Modification of Single-Photon Emitters in Hexagonal Boron Nitride. *ACS Photonics* **2016**, 3 (12), 2490-2496.
7. Jungwirth, N. R.; Calderon, B.; Ji, Y.; Spencer, M. G.; Flatté, M. E.; Fuchs, G. D., Temperature Dependence of Wavelength Selectable Zero-Phonon Emission from Single Defects in Hexagonal Boron Nitride. *Nano Letters* **2016**, 16 (10), 6052-6057.
8. Knowles, H. S.; Kara, D. M.; Atatüre, M., Observing bulk diamond spin coherence in high-purity nanodiamonds. *Nat Mater* **2014**, 13 (1), 21-25.
9. Dolde, F.; Jakobi, I.; Naydenov, B.; Zhao, N.; Pezzagna, S.; Trautmann, C.; Meijer, J.; Neumann, P.; Jelezko, F.; Wrachtrup, J., Room-temperature entanglement between single defect spins in diamond. *Nat Phys* **2013**, 9 (3), 139-143.
10. Lorenz, K.; Nogales, E.; Miranda, S. M. C.; Franco, N.; Méndez, B.; Alves, E.; Tourbot, G.; Daudin, B., Enhanced red emission from praseodymium-doped GaN nanowires by defect engineering. *Acta Materialia* **2013**, 61 (9), 3278-3284.
11. Kim, S.; Lee, D.; Park, J.; Jung, S.; Lee, W.; Shin, J.; Woo, J.; Choi, G.; Hyunsang, H., Defect engineering: reduction effect of hydrogen atom impurities in HfO₂-based resistive-switching memory devices. *Nanotechnology* **2012**, 23 (32), 325702.
12. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238 (5358), 37-38.
13. Hanaor, D. H.; Sorrell, C., Review of the anatase to rutile phase transformation. *Journal of Materials Science* **2011**, 46 (4), 855-874.
14. Ong, S. W. D. DESIGN OF BAND-ENGINEERED PHOTOCATALYSTS USING TITANIUM DIOXIDE. University of Illinois, Urbana, 2013.

15. Pore, V.; Kivela, T.; Ritala, M.; Leskela, M., Atomic layer deposition of photocatalytic TiO₂ thin films from TiF₄ and H₂O. *Dalton Transactions* **2008**, (45), 6467-6474.
16. O'Regan, B.; Gratzel, M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **1991**, 353 (6346), 737-740.
17. Mor, G. K.; Varghese, O. K.; Paulose, M.; Shankar, K.; Grimes, C. A., A review on highly ordered, vertically oriented TiO₂ nanotube arrays: Fabrication, material properties, and solar energy applications. *Solar Energy Materials and Solar Cells* **2006**, 90 (14), 2011-2075.
18. Lee, C.-S.; Kim, J.; Gu, G. H.; Jo, D.-H.; Park, C. G.; Choi, W.; Kim, H., Photocatalytic activities of TiO₂ thin films prepared on Galvanized Iron substrate by plasma-enhanced atomic layer deposition. *Thin Solid Films* **2010**, 518 (17), 4757-4761.
19. Methaapanon, R.; Bent, S. F., Comparative Study of Titanium Dioxide Atomic Layer Deposition on Silicon Dioxide and Hydrogen-Terminated Silicon. *The Journal of Physical Chemistry C* **2010**, 114 (23), 10498-10504.
20. Pheamhom, R.; Sunwoo, C.; Kim, D.-H. In *Characteristics of atomic layer deposited TiO₂ films and their photocatalytic activity*, THE 52ND INTERNATIONAL SYMPOSIUM OF AVS, AVS: 2006; pp 1535-1539.
21. Heikkilä, M.; Puukilainen, E.; Ritala, M.; Leskelä, M., Effect of thickness of ALD grown TiO₂ films on photoelectrocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry* **2009**, 204 (2-3), 200-208.
22. Cheng, H.-E.; Hsu, C.-M.; Chen, Y.-C., Substrate Materials and Deposition Temperature Dependent Growth Characteristics and Photocatalytic Properties of ALD TiO₂ Films. *Journal of The Electrochemical Society* **2009**, 156 (8), D275-D278.
23. Lee, S.; Apgar, B. A.; Martin, L. W., Strong Visible-Light Absorption and Hot-Carrier Injection in TiO₂/SrRuO₃ Heterostructures. *Advanced Energy Materials* **2013**, 3 (8), 1084-1090.
24. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Letters* **2011**, 11 (7), 3026-3033.
25. Yan, Y.; Han, M.; Konkin, A.; Koppe, T.; Wang, D.; Andreu, T.; Chen, G.; Vetter, U.; Morante, J. R.; Schaaf, P., Slightly hydrogenated TiO₂ with enhanced photocatalytic performance. *Journal of Materials Chemistry A* **2014**, 2 (32), 12708-12716.
26. Morrison, S. R., Surface states associated with acid sites on solids. *Surface Science* **1975**, 50 (2), 329-342.
27. Roy, P.; Fuerstenau, D. W., The effect of doping on the point of zero of charge of alumina. *Surface Science* **1972**, 30 (2), 487-490.
28. Nandakumar, N. K.; Seebauer, E. G., Relating Catalytic Activity of d⁰ Semiconducting Metal Oxides to the Fermi Level Position. *The Journal of Physical Chemistry C* **2014**, 118 (13), 6873-6881.
29. Nandakumar, N. K.; Seebauer, E. G., Manipulating Surface Potentials of Metal Oxides Using Semiconductor Heterojunctions. *The Journal of Physical Chemistry C* **2016**, 120 (10), 5486-5494.
30. Kapinus, E. I.; Viktorova, T. I., Kinetics of the photocatalytic degradation of methylene blue on titanium dioxide. *Theoretical and Experimental Chemistry* **2010**, 46 (3), 163-167.
31. Sellers, M. C. K.; Seebauer, E. G., Manipulation of polycrystalline TiO₂ carrier concentration via electrically active native defects. *Journal of Vacuum Science & Technology A* **2011**, 29, 061503.

32. Seebauer, E. G.; Kratzer, M. C., Charged point defects in semiconductors. *Materials Science and Engineering: R: Reports* **2006**, *55* (3-6), 57-149.
33. Seebauer, E. G.; Kratzer, M. C., *Charged Semiconductor Defects: Structure, Thermodynamics and Diffusion*. Springer: London, 2009.
34. Seebauer, E. G.; Noh, K. W., Trends in semiconductor defect engineering at the nanoscale. *Materials Science and Engineering: R: Reports* **2010**, *70* (3-6), 151-168.
35. Nowotny, M. K.; Sheppard, L. R.; Bak, T.; Nowotny, J., Defect Chemistry of Titanium Dioxide. Application of Defect Engineering in Processing of TiO₂-Based Photocatalysts. *The Journal of Physical Chemistry C* **2008**, *112* (14), 5275-5300.
36. Pärna, R.; Joost, U.; Nömmiste, E.; Käämbre, T.; Kikas, A.; Kuusik, I.; Hirsimäki, M.; Kink, I.; Kisand, V., Effect of cobalt doping and annealing on properties of titania thin films prepared by sol-gel process. *Applied Surface Science* **2011**, *257* (15), 6897-6907.
37. Xu, H.; Zhang, L., Controllable One-Pot Synthesis and Enhanced Visible Light Photocatalytic Activity of Tunable C-Cl-Codoped TiO₂ Nanocrystals with High Surface Area. *The Journal of Physical Chemistry C* **2009**, *114* (2), 940-946.
38. Sellers, M. C. K.; Seebauer, E. G., Structural and magnetic properties of Mn-doped anatase TiO₂ films synthesized by atomic layer deposition. *Applied Physics A* **2011**, *104* (2), 583-586.
39. van de Krol, R.; Goossens, A.; Schoonman, J., Mott-Schottky Analysis of Nanometer-Scale Thin-Film Anatase TiO₂. *Journal of The Electrochemical Society* **1997**, *144* (5), 1723-1727.
40. Ong, S. W. D.; Lin, J.; Seebauer, E. G., Control of Methylene Blue Photo-Oxidation Rate over Polycrystalline Anatase TiO₂ Thin Films via Carrier Concentration. *The Journal of Physical Chemistry C* **2015**, *119* (21), 11662-11671.
41. Chua, Y. P. G.; Gunasooriya, G. T. K. K.; Saeys, M.; Seebauer, E. G., Controlling the CO oxidation rate over Pt/TiO₂ catalysts by defect engineering of the TiO₂ support. *Journal of Catalysis* **2014**, *311*, 306-313.
42. Ong, S. W. D.; Lin, J.; Seebauer, E. G., Control of Photoactivity over Polycrystalline Anatase TiO₂ Thin Films via Surface Potential. *The Journal of Physical Chemistry C* **2015**, *119* (48), 27060-27071.
43. Yoon, M.; Seo, M.; Jeong, C.; Jang, J. H.; Jeon, K. S., Synthesis of Liposome-Templated Titania Nanodisks: Optical Properties and Photocatalytic Activities. *Chemistry of Materials* **2005**, *17* (24), 6069-6079.
44. Knorr, F. J.; Zhang, D.; McHale, J. L., Influence of TiCl₄ Treatment on Surface Defect Photoluminescence in Pure and Mixed-Phase Nanocrystalline TiO₂. *Langmuir* **2007**, *23* (17), 8686-8690.
45. Liu, G.; Wang, L.; Yang, H. G.; Cheng, H.-M.; Lu, G. Q., Titania-based photocatalysts-crystal growth, doping and heterostructuring. *Journal of Materials Chemistry* **2010**, *20* (5), 831-843.
46. Osterloh, F. E., Inorganic Materials as Catalysts for Photochemical Splitting of Water. *Chemistry of Materials* **2008**, *20* (1), 35-54.
47. Nazeeruddin, M. K.; Splivallo, R.; Liska, P.; Comte, P.; Gratzel, M., A swift dye uptake procedure for dye sensitized solar cells. *Chemical Communications* **2003**, (12), 1456-1457.
48. Kongkanand, A.; Tvrdy, K.; Takechi, K.; Kuno, M.; Kamat, P. V., Quantum Dot Solar Cells. Tuning Photoresponse through Size and Shape Control of CdSe–TiO₂ Architecture. *Journal of the American Chemical Society* **2008**, *130* (12), 4007-4015.

49. Huang, H.; Li, D.; Lin, Q.; Zhang, W.; Shao, Y.; Chen, Y.; Sun, M.; Fu, X., Efficient Degradation of Benzene over $\text{LaVO}_4/\text{TiO}_2$ Nanocrystalline Heterojunction Photocatalyst under Visible Light Irradiation. *Environmental Science & Technology* **2009**, *43* (11), 4164-4168.
50. McDaniel, M. D.; Posadas, A.; Ngo, T. Q.; Dhamdhere, A.; Smith, D. J.; Demkov, A. A.; Ekerdt, J. G., Growth of epitaxial oxides on silicon using atomic layer deposition: Crystallization and annealing of TiO_2 on SrTiO_3 -buffered $\text{Si}(001)$. *Journal of Vacuum Science & Technology B* **2012**, *30* (4), 04E111.
51. McDaniel, M. D.; Posadas, A.; Wang, T.; Demkov, A. A.; Ekerdt, J. G., Growth and characterization of epitaxial anatase $\text{TiO}_2(001)$ on SrTiO_3 -buffered $\text{Si}(001)$ using atomic layer deposition. *Thin Solid Films* **2012**, *520* (21), 6525-6530.
52. Dereń, P. J. B., A.; Goldner, P.; Guillot-Noël, O., Laser action in $\text{LaAlO}_3:\text{Nd}^{3+}$ single crystal. *Journal of Applied Physics* **2008**, *103* (4), 043102.
53. Vijatović, M. M.; Bobić, J. D.; Stojanović, B. D., History and challenges of barium titanate: Part II. *Science of Sintering* **2008**, *40* (3), 235.
54. Cheng, J.; Dong, S., Review on high temperature piezoelectric ceramics and actuators based on $\text{BiScO}_3\text{-PbTiO}_3$ solid solutions. *Journal of Advanced Dielectrics* **2014**, *04* (01), 1430002.
55. Shur, V. Y., 6 - Lithium niobate and lithium tantalate-based piezoelectric materials A2 - Uchino, Kenji. In *Advanced Piezoelectric Materials*, Woodhead Publishing: 2010; pp 204-238.
56. Grabowska, E., Selected perovskite oxides: Characterization, preparation and photocatalytic properties—A review. *Applied Catalysis B: Environmental* **2016**, *186*, 97-126.
57. Stranks, S. D.; Snaith, H. J., Metal-halide perovskites for photovoltaic and light-emitting devices. *Nat Nano* **2015**, *10* (5), 391-402.
58. Luo, J.; Im, J.-H.; Mayer, M. T.; Schreier, M.; Nazeeruddin, M. K.; Park, N.-G.; Tilley, S. D.; Fan, H. J.; Grätzel, M., Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts. *Science* **2014**, *345* (6204), 1593.
59. Apgar, B. A.; Lee, S.; Schroeder, L. E.; Martin, L. W., Enhanced Photoelectrochemical Activity in All-Oxide Heterojunction Devices Based on Correlated “Metallic” Oxides. *Advanced Materials* **2013**, *25* (43), 6201-6206.
60. Yang, H. C.; Liu, S. H.; Wang, L. M.; Horng, H. E., Longitudinal and transverse Hall resistivity of epitaxial SrRuO_3 films. *Journal of Applied Physics* **1999**, *85* (8), 5792-5794.
61. Majcher, A. M.; Rode, K.; Coey, J. M. D.; Stamenov, P., Magnetic, transport, and structural properties of SrRuO_3 thin films. *Journal of Applied Physics* **2014**, *115* (17), 17C735.
62. Verissimo-Alves, M.; García-Fernández, P.; Bilc, D. I.; Ghosez, P.; Junquera, J., Highly Confined Spin-Polarized Two-Dimensional Electron Gas in $\text{SrTiO}_3/\text{SrRuO}_3$ Superlattices. *Physical Review Letters* **2012**, *108* (10), 107003.
63. García-Fernández, P.; Verissimo-Alves, M.; Bilc, D. I.; Ghosez, P.; Junquera, J., First-principles modeling of the thermoelectric properties of $\text{SrTiO}_3/\text{SrRuO}_3$ superlattices. *Physical Review B* **2012**, *86* (8), 085305.
64. Bern, F.; Ziese, M.; Setzer, A.; Pippel, E.; Hesse, D.; Vrejoiu, I., Structural, magnetic and electrical properties of SrRuO_3 films and $\text{SrRuO}_3/\text{SrTiO}_3$ superlattices. *Journal of Physics: Condensed Matter* **2013**, *25* (49), 496003.

65. Koster, G.; Klein, L.; Siemons, W.; Rijnders, G.; Dodge, J. S.; Eom, C.-B.; Blank, D. H. A.; Beasley, M. R., Structure, physical properties, and applications of SrRuO₃ thin films. *Reviews of Modern Physics* **2012**, *84* (1), 253-298.
66. Ikeda, S. I.; Azuma, U.; Shirakawa, N.; Nishihara, Y.; Maeno, Y., Bulk single-crystal growth of strontium ruthenates by a floating-zone method. *Journal of Crystal Growth* **2002**, 237–239, Part 1, 787-791.
67. Zhao, Q. X.; Ma, J. K.; Wei, D. Y.; Wang, K. M.; Li, X. H.; Zhang, X. Y.; Liu, B. T., Epitaxial SrRuO₃/BiFeO₃/SrRuO₃ heterostructure sputtered at low temperature. *Journal of Crystal Growth* **2011**, *316* (1), 71-74.
68. Barlaz, D. E.; Seebauer, E. G., Manipulation of carrier concentration, crystallite size and density in polycrystalline anatase TiO₂ via amorphous-phase medium range atomic order. *CrystEngComm* **2015**, *17* (10), 2101-2109.
69. Duminica, F. D.; Maury, F.; Hausbrand, R., Growth of TiO₂ thin films by AP-MOCVD on stainless steel substrates for photocatalytic applications. *Surface and Coatings Technology* **2007**, *201* (22-23), 9304-9308.
70. Rahtu, A.; Ritala, M., Reaction Mechanism Studies on Titanium Isopropoxide–Water Atomic Layer Deposition Process. *Chemical Vapor Deposition* **2002**, *8* (1), 21-28.
71. Cho, S.-I.; Chung, C.-H.; Moon, S. H., Surface decomposition mechanism of Ti(OC₃H₇)₄ on a platinum surface. *Thin Solid Films* **2002**, *409* (1), 98-104.
72. Tuan, A.; Yoon, M.; Medvedev, V.; Ono, Y.; Ma, Y.; Rogers Jr, J. W., Interface control in the chemical vapor deposition of titanium dioxide on silicon(100). *Thin Solid Films* **2000**, 377-378, 766-771.
73. Aarik, J.; Aidla, A.; Uustare, T.; Ritala, M.; Leskelä, M., Titanium isopropoxide as a precursor for atomic layer deposition: characterization of titanium dioxide growth process. *Applied Surface Science* **2000**, *161* (3-4), 385-395.
74. Xie, Q.; Musschoot, J.; Deduytsche, D.; Van Meirhaeghe, R. L.; Detavernier, C.; Van den Berghe, S.; Jiang, Y.-L.; Ru, G.-P.; Li, B.-Z.; Qu, X.-P., Growth Kinetics and Crystallization Behavior of TiO₂ Films Prepared by Plasma Enhanced Atomic Layer Deposition. *Journal of The Electrochemical Society* **2008**, *155* (9), H688-H692.
75. Fictorie, C. P.; Evans, J. F.; Gladfelter, W. L., Kinetic and mechanistic study of the chemical vapor deposition of titanium dioxide thin films using tetrakis-(isopropoxo)-titanium(IV). *Journal of Vacuum Science & Technology A* **1994**, *12* (4), 1108-1113.
76. Zhang, Q.; Griffin, G. L., Gas-phase kinetics for TiO₂ CVD: hot-wall reactor results. *Thin Solid Films* **1995**, *263* (1), 65-71.
77. Bergese, P.; Bontempi, E.; Depero, L. E., A simple solution to systematic errors in density determination by X-ray reflectivity: The XRR-density evaluation (XRR-DE) method. *Applied Surface Science* **2006**, *253* (1), 28-32.
78. Holy, V.; Pietsch, U.; Baumbach, T., *High Resolution X-ray Scattering from Thin Films and Multilayers*. Springer: New York, 1999.
79. Barlaz, D. E.; Seebauer, E. G., Solid phase epitaxial regrowth of (001) anatase titanium dioxide. *Journal of Vacuum Science & Technology A* **2016**, *34* (2), 020603.
80. Sellers, M. C. K.; Seebauer, E. G., Measurement method for carrier concentration in TiO₂ via the Mott-Schottky approach. *Thin Solid Films* **2011**, *519* (7), 2103-2110.

81. Barlaz, D. E. INVESTIGATION OF DEFECT FORMATION AND CONTROL IN POLY-CRYSTALLINE ANATASE TITANIUM DIOXIDE. Masters, University of Illinois, Urbana, 2013.
82. Enache, C.; Schoonman, J.; Krol, R., The Photoresponse of Iron- and Carbon-Doped TiO₂ (Anatase) Photoelectrodes. *Journal of Electroceramics* **2004**, *13* (1-3), 177-182.
83. Pickup, D. M.; Sowrey, F. E.; Drake, K. O.; Smith, M. E.; Newport, R. J., New insights into medium-range order around titanium in sol-gel derived silica through isotope difference neutron diffraction and reverse Monte Carlo modelling. *Chemical Physics Letters* **2004**, *392*, 503-507.
84. Lee, B.-S.; Bishop, S. G.; Abelson, J. R., Fluctuation Transmission Electron Microscopy: Detecting Nanoscale Order in Disordered Structures. *ChemPhysChem* **2010**, *11* (11), 2311-2317.
85. Lee, B.-S.; Burr, G. W.; Shelby, R. M.; Raoux, S.; Rettner, C. T.; Bogle, S. N.; Darmawikarta, K.; Bishop, S. G.; Abelson, J. R., Observation of the Role of Subcritical Nuclei in Crystallization of a Glassy Solid. *Science* **2009**, *326* (5955), 980-984.
86. Kondratenko, Y. V.; Seebauer, E. G., Directed self-assembly by photostimulation of an amorphous semiconductor surface. *AIChE* **2010**, *56* (12), 3206-3211.
87. Gorai, P.; Hollister, A. G.; Pangan-Okimoto, K.; Seebauer, E. G., Kinetics of oxygen interstitial injection and lattice exchange in rutile TiO₂. *Applied Physics Letters* **2014**, *104* (19), 191602.
88. Pangan-Okimoto, K. M.; Gorai, P.; Hollister, A. G.; Seebauer, E. G., Model for Oxygen Interstitial Injection from the Rutile TiO₂(110) Surface into the Bulk. *The Journal of Physical Chemistry C* **2015**, *119* (18), 9955-9965.
89. Li, M.; Seebauer, E. G., Surface-Based Control of Oxygen Interstitial Injection into ZnO via Submonolayer Sulfur Adsorption. *The Journal of Physical Chemistry C* **2016**, *120* (41), 23675-23682.
90. Gorai, P.; Seebauer, E. G.; Ertekin, E., Mechanism and energetics of O and O₂ adsorption on polar and non-polar ZnO surfaces. *The Journal of Chemical Physics* **2016**, *144* (18), 184708.
91. Diebold, U., The surface science of titanium dioxide. *Surface Science Reports* **2003**, *48*, 53-229.
92. Knauth, P.; Tuller, H. L., Electrical and defect thermodynamic properties of nanocrystalline titanium dioxide. *Journal of Applied Physics* **1999**, *85* (2), 897-902.
93. Vogtenhuber, D.; Podloucky, R.; Redinger, J.; Hebenstreit, E. L. D.; Hebenstreit, W.; Diebold, U., *Ab initio* and experimental studies of chlorine adsorption on the rutile TiO₂ (110) surface. *Physical Review B* **2002**, *65* (12), 125411.
94. Hebenstreit, E. L. D.; Hebenstreit, W.; Geisler, H.; Ventrice, C. A.; Hite, D. A.; Sprunger, P. T.; Diebold, U., The adsorption of chlorine on TiO₂(110) studied with scanning tunneling microscopy and photoemission spectroscopy. *Surface Science* **2002**, *505*, 336-348.
95. Diebold, U., Understanding Metal Oxide Surfaces at the Atomic Scale: STM Investigations of Bulk-defect Dependent Surface Processes. *MRS Proceedings* **2001**, 654.
96. Mollwo, E., Die Wirkung von Wasserstoff auf die Leitfähigkeit und Lumineszenz von Zinkoxydkristallen. *Zeitschrift für Physik* **1954**, *138* (3), 478-488.
97. Thomas, D. G.; Lander, J. J., Hydrogen as a Donor in Zinc Oxide. *Journal of Chemical Physics* **1956**, *25* (6), 1136-1142.
98. Oh, B.-Y.; Jeong, M.-C.; Kim, D.-S.; Lee, W.; Myoung, J.-M., Post-annealing of Al-doped ZnO films in hydrogen atmosphere. *Journal of Crystal Growth* **2005**, *281* (2-4), 475-480.

99. Ip, K.; Overberg, M. E.; Heo, Y. W.; Norton, D. P.; Pearton, S. J.; Stutz, C. E.; Luo, B.; Ren, F.; Look, D. C.; Zavada, J. M., Hydrogen incorporation and diffusivity in plasma-exposed bulk ZnO. *Applied Physics Letters* **2003**, 82 (3), 385-387.
100. Henrich, V. E.; Kurtz, R. L., Surface electronic structure of TiO₂: Atomic geometry, ligand coordination, and the effect of adsorbed hydrogen. *Physical Review B* **1981**, 23 (12), 6280-6287.
101. Pan, J. M.; Maschhoff, B. L.; Diebold, U.; Madey, T. E., Interaction of water, oxygen, and hydrogen with TiO₂(110) surfaces having different defect densities. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **1992**, 10 (4), 2470-2476.
102. Göpel, W.; Rocker, G.; Feierabend, R., Intrinsic defects of TiO₂(110): Interaction with chemisorbed O₂, H₂, CO, and CO₂. *Physical Review B* **1983**, 28 (6), 3427-3438.
103. Fujino, T.; Katayama, M.; Inudzuka, K.; Okuno, T.; Oura, K.; Hirao, T., Surface hydroxyl formation on vacuum-annealed TiO₂(110). *Applied Physics Letters* **2001**, 79 (17), 2716-2718.
104. Walsh, F. C.; Wills, R. G. A., The continuing development of Magnéli phase titanium sub-oxides and Ebonex® electrodes. *Electrochimica Acta* **2010**, 55 (22), 6342-6351.
105. Shin, J.-Y.; Joo, J. H.; Samuelis, D.; Maier, J., Oxygen-Deficient TiO_{2-δ} Nanoparticles via Hydrogen Reduction for High Rate Capability Lithium Batteries. *Chemistry of Materials* **2012**, 24 (3), 543-551.
106. Rohde, C.; Choi, B. J.; Jeong, D. S.; Choi, S.; Zhao, J.-S.; Hwang, C. S., Identification of a determining parameter for resistive switching of TiO₂ thin films. *Applied Physics Letters* **2005**, 86 (26), 262907.
107. Choi, B. J.; Jeong, D. S.; Kim, S. K.; Rohde, C.; Choi, S.; Oh, J. H.; Kim, H. J.; Hwang, C. S.; Szot, K.; Waser, R.; Reichenberg, B.; Tiedke, S., Resistive switching mechanism of TiO₂ thin films grown by atomic-layer deposition. *Journal of Applied Physics* **2005**, 98 (3), 033715.
108. Kim, K. M.; Choi, B. J.; Lee, M. H.; Kim, G. H.; Song, S. J.; Seok, J. Y.; Yoon, J. H.; Han, S.; Hwang, C. S., A detailed understanding of the electronic bipolar resistance switching behavior in Pt/TiO₂/Pt structure. *Nanotechnology* **2011**, 22 (25), 254010.
109. Kwon, D.-H.; Kim, K. M.; Jang, J. H.; Jeon, J. M.; Lee, M. H.; Kim, G. H.; Li, X.-S.; Park, G.-S.; Lee, B.; Han, S.; Kim, M.; Hwang, C. S., Atomic structure of conducting nanofilaments in TiO₂ resistive switching memory. *Nat Nanotechnology* **2010**, 5 (2), 148-153.
110. Gusev, A. A.; Avvakumov, E. G.; Vinokurova, O. B., Synthesis of Ti₄O₇ magneli phase using mechanical activation. *Science of Sintering* **2003**, 35 (3).
111. Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S., Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* **2011**, 331 (6018), 746.
112. Liu, N.; Schneider, C.; Freitag, D.; Hartmann, M.; Venkatesan, U.; Müller, J.; Spiecker, E.; Schmuki, P., Black TiO₂ Nanotubes: Cocatalyst-Free Open-Circuit Hydrogen Generation. *Nano Letters* **2014**, 14 (6), 3309-3313.
113. An, H.-R.; Park, S. Y.; Kim, H.; Lee, C. Y.; Choi, S.; Lee, S. C.; Seo, S.; Park, E. C.; Oh, Y.-K.; Song, C.-G.; Won, J.; Kim, Y. J.; Lee, J.; Lee, H. U.; Lee, Y.-C., Advanced nanoporous TiO₂ photocatalysts by hydrogen plasma for efficient solar-light photocatalytic application. *Scientific Reports* **2016**, 6, 29683.
114. Leufke, P. M.; Mishra, A. K.; Beck, A.; Wang, D.; Kübel, C.; Kruk, R.; Hahn, H., Large-distance rf- and dc-sputtering of epitaxial La_{1-x}Sr_xMnO₃ thin films. *Thin Solid Films* **2012**, 520 (17), 5521-5527.

115. Sanderson, R. J.; Hewitt, K. C., Stoichiometry control of magnetron sputtered $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($0 \leq x \leq 0.5$) thin film, composition spread libraries: Substrate bias and gas density factors. *Physica C: Superconductivity* **2005**, 425 (1–2), 52-61.
116. Alema, F.; Reinholz, A.; Pokhodnya, K., Stoichiometry and phase purity control of radio frequency magnetron sputter deposited $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ thin films for tunable devices. *Journal of Applied Physics* **2013**, 114 (17), 174104.
117. Hou, S.; Kwo, J.; Watts, R.; Cheng, J.; Fork, D., Structure and properties of epitaxial $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{SrRuO}_3/\text{ZrO}_2$ heterostructure on Si grown by off-axis sputtering. *Applied Physics Letters* **1995**, 67 (10), 1387-1389.
118. Lee, K.; Lee, M.; Jang, C.; Kim, D. In *Nucleation and growth of epitaxial SrRuO_3 thin films on vicinal (001) SrTiO_3 substrates*, 2012 12th IEEE International Conference on Nanotechnology (IEEE-NANO), 20-23 Aug. 2012; 2012; pp 1-2.
119. Belkind, A.; Orban, Z.; Vossen, J. L.; Woollam, J. A., Optical properties of RuO_2 films deposited by reactive sputtering. *Thin Solid Films* **1992**, 207 (1), 242-247.
120. Patake, V. D.; Lokhande, C. D., Chemical synthesis of nano-porous ruthenium oxide (RuO_2) thin films for supercapacitor application. *Applied Surface Science* **2008**, 254 (9), 2820-2824.
121. Gujar, T. P.; Shinde, V. R.; Lokhande, C. D.; Kim, W.-Y.; Jung, K.-D.; Joo, O.-S., Spray deposited amorphous RuO_2 for an effective use in electrochemical supercapacitor. *Electrochemistry Communications* **2007**, 9 (3), 504-510.
122. Kakkad, R.; Smith, J.; Lau, W. S.; Fonash, S. J.; Kerns, R., Crystallized Si films by low-temperature rapid thermal annealing of amorphous silicon. *Journal of Applied Physics* **1989**, 65 (5), 2069-2072.
123. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S., Solar Water Splitting Cells. *Chemical Reviews* **2010**, 110 (11), 6446-6473.
124. Currao, A., Photoelectrochemical Water Splitting. *CHIMIA International Journal for Chemistry* **2007**, 61 (12), 815-819.
125. Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C., Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. *International Journal of Hydrogen Energy* **2002**, 27 (10), 991-1022.
126. Zhang, J.; Zhou, P.; Liu, J.; Yu, J., New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO_2 . *Physical Chemistry Chemical Physics* **2014**, 16 (38), 20382-20386.
127. Nozik, A. J.; Memming, R., Physical Chemistry of Semiconductor–Liquid Interfaces. *The Journal of Physical Chemistry* **1996**, 100 (31), 13061-13078.
128. Bessekhoud, Y.; Robert, D.; Weber, J. V., $\text{Bi}_2\text{S}_3/\text{TiO}_2$ and CdS/TiO_2 heterojunctions as an available configuration for photocatalytic degradation of organic pollutant. *Journal of Photochemistry and Photobiology A: Chemistry* **2004**, 163 (3), 569-580.
129. Lee, J. S.; Lee, Y. S.; Noh, T. W.; Char, K.; Park, J.; Oh, S. J.; Park, J. H.; Eom, C. B.; Takeda, T.; Kanno, R., Optical investigation of the electronic structures of $\text{Y}_2\text{Ru}_2\text{O}_7$, CaRuO_3 , SrRuO_3 , and $\text{Bi}_2\text{Ru}_2\text{O}_7$. *Physical Review B* **2001**, 64 (24), 245107.

130. Paasche, S. M.; Toyama, T.; Okamoto, H.; Hamakawa, Y., Amorphous-SiC thin-film p-i-n light-emitting diode using amorphous-SiN hot-carrier tunneling injection layers. *IEEE Transactions on Electron Devices* **1989**, 36 (12), 2895-2902.
131. Sambur, J. B.; Novet, T.; Parkinson, B. A., Multiple Exciton Collection in a Sensitized Photovoltaic System. *Science* **2010**, 330 (6000), 63-66.
132. Cooper, G.; Turner, J. A.; Parkinson, B. A.; Nozik, A. J., Hot carrier injection of photogenerated electrons at indium phosphide-electrolyte interfaces. *Journal of Applied Physics* **1983**, 54 (11), 6463-6473.
133. Turner, J. A.; Nozik, A. J., Evidence for hot-electron injection across p-GaP/electrolyte junctions. *Applied Physics Letters* **1982**, 41 (1), 101-103.
134. Bernardi, M.; Vigil-Fowler, D.; Lischner, J.; Neaton, J. B.; Louie, S. G., *Ab Initio* Study of Hot Carriers in the First Picosecond after Sunlight Absorption in Silicon. *Physical Review Letters* **2014**, 112 (25), 257402.
135. Hirst, L. C.; Fürher, M.; Farrell, D. J.; Le Bris, A.; Guillemoles, J.-F.; Tayebjee, M. J. Y.; Clady, R.; Schmidt, T. W.; Sugiyama, M.; Wang, Y.; Fujii, H.; Ekins-Daukes, N. J. In *InGaAs/GaAsP quantum wells for hot carrier solar cells*, 2012; pp 82560X-82560X-6.
136. Chung, S.; Shrestha, S.; Wen, X.; Feng, Y.; Gupta, N.; Xia, H.; Yu, P.; Tang, J.; Conibeer, G., Hafnium nitride for hot carrier solar cells. *Solar Energy Materials and Solar Cells* **2016**, 144, 781-786.
137. König, D.; Casalenuovo, K.; Takeda, Y.; Conibeer, G.; Guillemoles, J. F.; Patterson, R.; Huang, L. M.; Green, M. A., Hot carrier solar cells: Principles, materials and design. *Physica E: Low-dimensional Systems and Nanostructures* **2010**, 42 (10), 2862-2866.
138. Shewchun, J.; Green, M. A.; King, F. D., Minority carrier MIS tunnel diodes and their application to electron- and photo-voltaic energy conversion—II. Experiment. *Solid-State Electronics* **1974**, 17 (6), 563-572.
139. Liu, M.; Nam, C.-Y.; Black, C. T.; Kamcev, J.; Zhang, L., Enhancing Water Splitting Activity and Chemical Stability of Zinc Oxide Nanowire Photoanodes with Ultrathin Titania Shells. *The Journal of Physical Chemistry C* **2013**, 117 (26), 13396-13402.
140. Campet, G.; Puprichitkun, C.; Sun, Z. W., Protection of photoanodes against photocorrosion by surface deposition of oxide films. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1989**, 269 (2), 435-445.
141. Himpsel, F. J.; McFeely, F. R.; Taleb-Ibrahimi, A.; Yarmoff, J. A.; Hollinger, G., Microscopic structure of the SiO₂/Si interface. *Physical Review B* **1988**, 38 (9), 6084-6096.
142. Kim, H. J.; Kearney, K. L.; Le, L. H.; Haber, Z. J.; Rockett, A. A.; Rose, M. J., Charge-Transfer through Ultrathin Film TiO₂ on n-Si(111) Photoelectrodes: Experimental and Theoretical Investigation of Electric Field-Enhanced Transport with a Nonaqueous Redox Couple. *The Journal of Physical Chemistry C* **2016**, 120 (45), 25697-25708.
143. Hu, S.; Richter, M. H.; Lichterman, M. F.; Beardslee, J.; Mayer, T.; Brunschwig, B. S.; Lewis, N. S., Electrical, Photoelectrochemical, and Photoelectron Spectroscopic Investigation of the Interfacial Transport and Energetics of Amorphous TiO₂/Si Heterojunctions. *The Journal of Physical Chemistry C* **2016**, 120 (6), 3117-3129.

144. Kasinski, J. J.; Gomez-Jahn, L. A.; Faran, K. J.; Gracewski, S. M.; Miller, R. J. D., Picosecond dynamics of surface electron transfer processes: Surface restricted transient grating studies of the n-TiO₂/H₂O interface. *The Journal of Chemical Physics* **1989**, *90* (2), 1253-1269.
145. Ditchfield, R.; Llera-Rodríguez, D.; Seebauer, E. G., Semiconductor surface diffusion: Nonthermal effects of photon illumination. *Physical Review B* **2000**, *61* (20), 13710-13720.
146. Matthews, R. W., Photocatalytic oxidation and adsorption of methylene blue on thin films of near-ultraviolet-illuminated TiO₂. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1989**, *85* (6), 1291-1302.
147. Houas, A.; Lachheb, H.; Ksibi, M.; Elaloui, E.; Guillard, C.; Herrmann, J.-M., Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B: Environmental* **2001**, *31* (2), 145-157.
148. Zhang, T.; Oyama, T.; Aoshima, A.; Hidaka, H.; Zhao, J.; Serpone, N., Photooxidative N-demethylation of methylene blue in aqueous TiO₂ dispersions under UV irradiation. *Journal of Photochemistry and Photobiology A: Chemistry* **2001**, *140* (2), 163-172.
149. Pouretedal, H. R.; Kadkhodaie, A., Synthetic CeO₂ Nanoparticle Catalysis of Methylene Blue Photodegradation: Kinetics and Mechanism. *Chinese Journal of Catalysis* **2010**, *31* (11), 1328-1334.
150. Xia, S.; Zhang, L.; Pan, G.; Qian, P.; Ni, Z., Photocatalytic degradation of methylene blue with a nanocomposite system: synthesis, photocatalysis and degradation pathways. *Physical Chemistry Chemical Physics* **2015**, *17* (7), 5345-5351.
151. Shirafuji, T.; Hieda, J.; Takai, O.; Saito, N.; Morita, T.; Sakai, O.; Tachibana, K. In *FTIR study of methylene blue plasma degradation products through plasma treatment on water*, TENCON 2010 - 2010 IEEE Region 10 Conference, 21-24 Nov. 2010; 2010; pp 1938-1942.
152. Butler, E. C.; Davis, A. P., Photocatalytic oxidation in aqueous titanium dioxide suspensions: the influence of dissolved transition metals. *Journal of Photochemistry and Photobiology A: Chemistry* **1993**, *70* (3), 273-283.
153. Mills, A.; McFarlane, M., Current and possible future methods of assessing the activities of photocatalyst films. *Catalysis Today* **2007**, *129* (1-2), 22-28.
154. Ohno, T.; Sarukawa, K.; Matsumura, M., Crystal faces of rutile and anatase TiO₂ particles and their roles in photocatalytic reactions. *New Journal of Chemistry* **2002**, *26* (9), 1167-1170.
155. Qiao, L.; Droubay, T. C.; Kaspar, T. C.; Sushko, P. V.; Chambers, S. A., Cation mixing, band offsets and electric fields at LaAlO₃/SrTiO₃(001) heterojunctions with variable La:Al atom ratio. *Surface Science* **2011**, *605* (15-16), 1381-1387.
156. Chambers, S. A.; Droubay, T.; Kaspar, T. C.; Gutowski, M., Experimental determination of valence band maxima for SrTiO₃, TiO₂, and SrO and the associated valence band offsets with Si(001). *Journal of Vacuum Science & Technology B* **2004**, *22* (4), 2205-2215.

APPENDIX A: LIQUID PHOTOCATALYSIS REACTION CELL

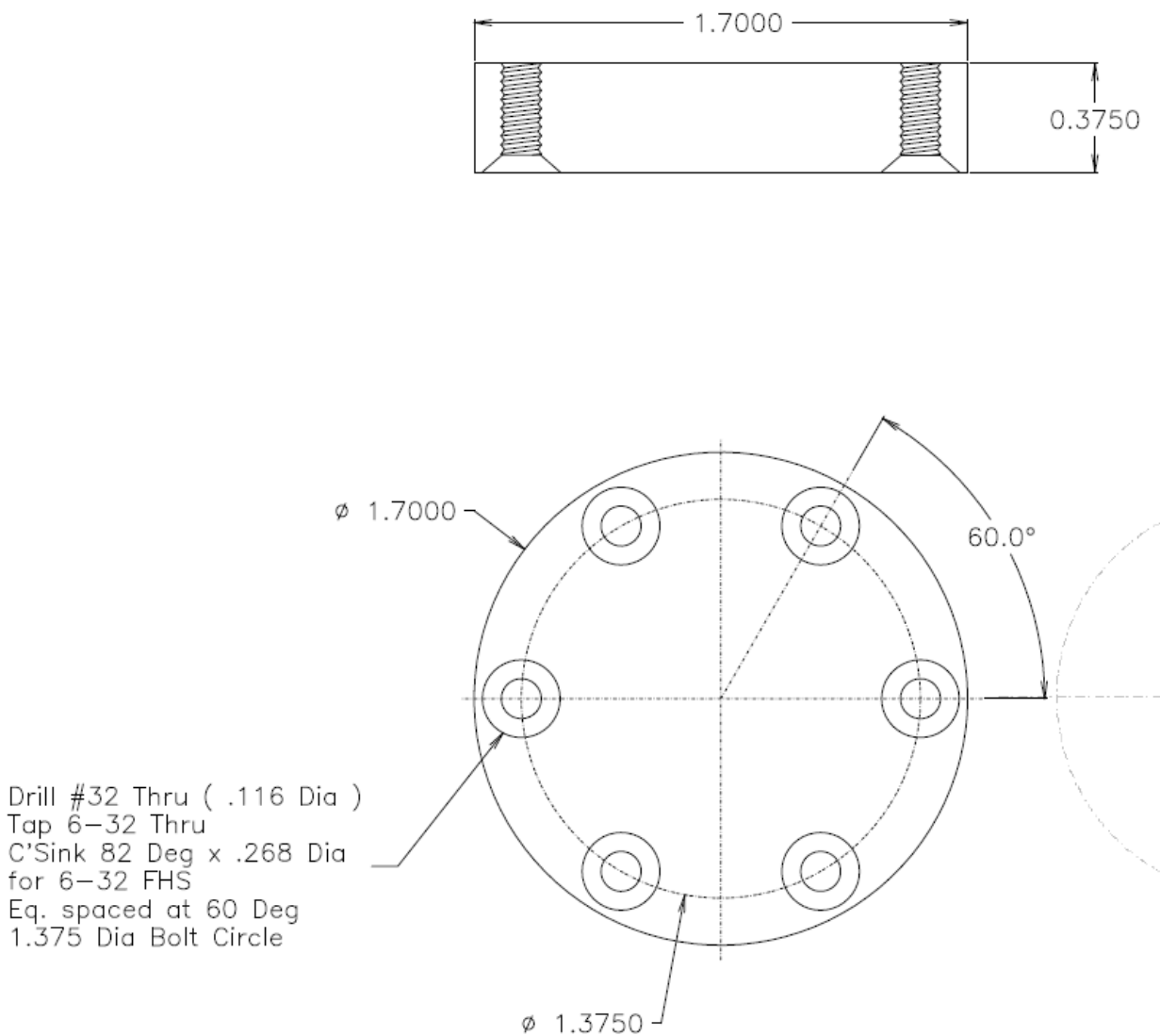


Figure 37: Stainless steel base with six machine screws extending vertically.

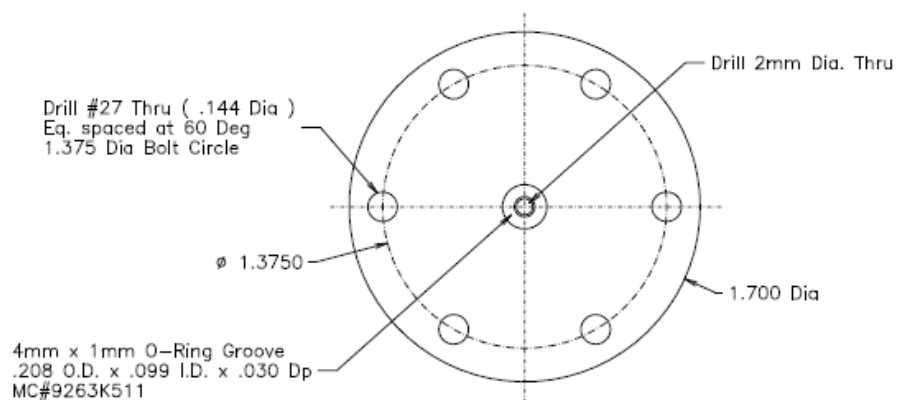
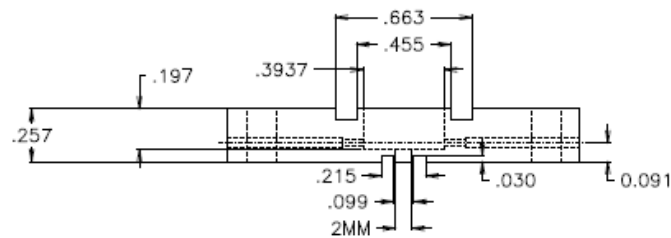
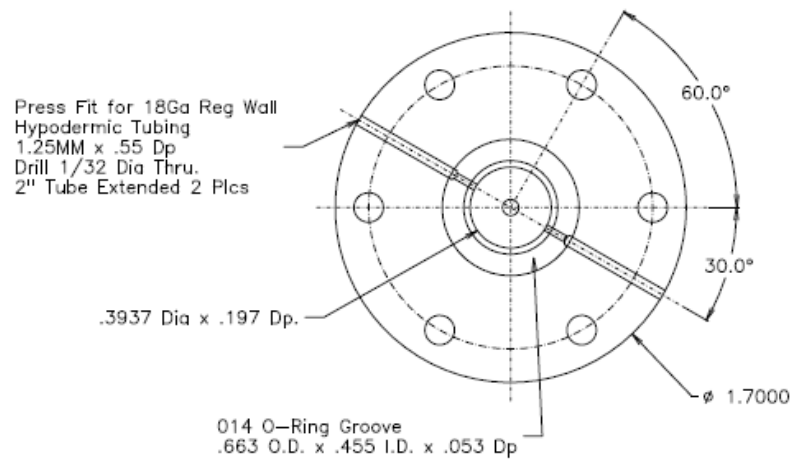


Figure 38: Teflon liquid cell body with liquid ports, top and bottom O-ring grooves, and light through hole above sample.

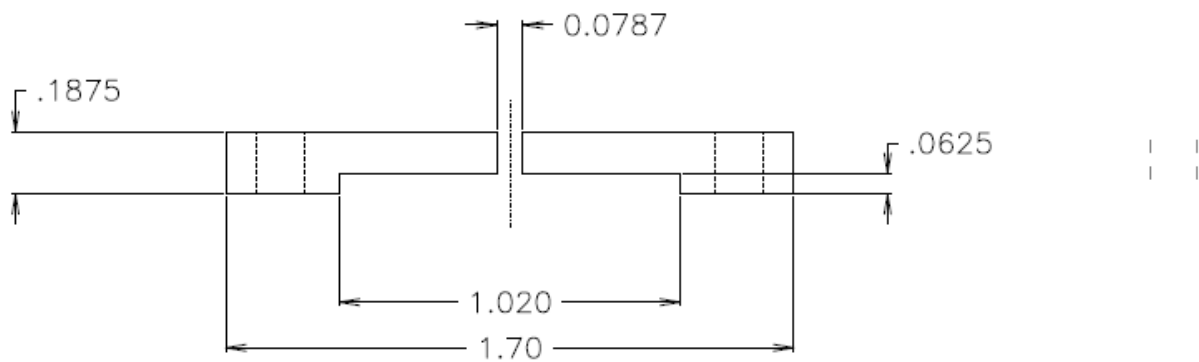
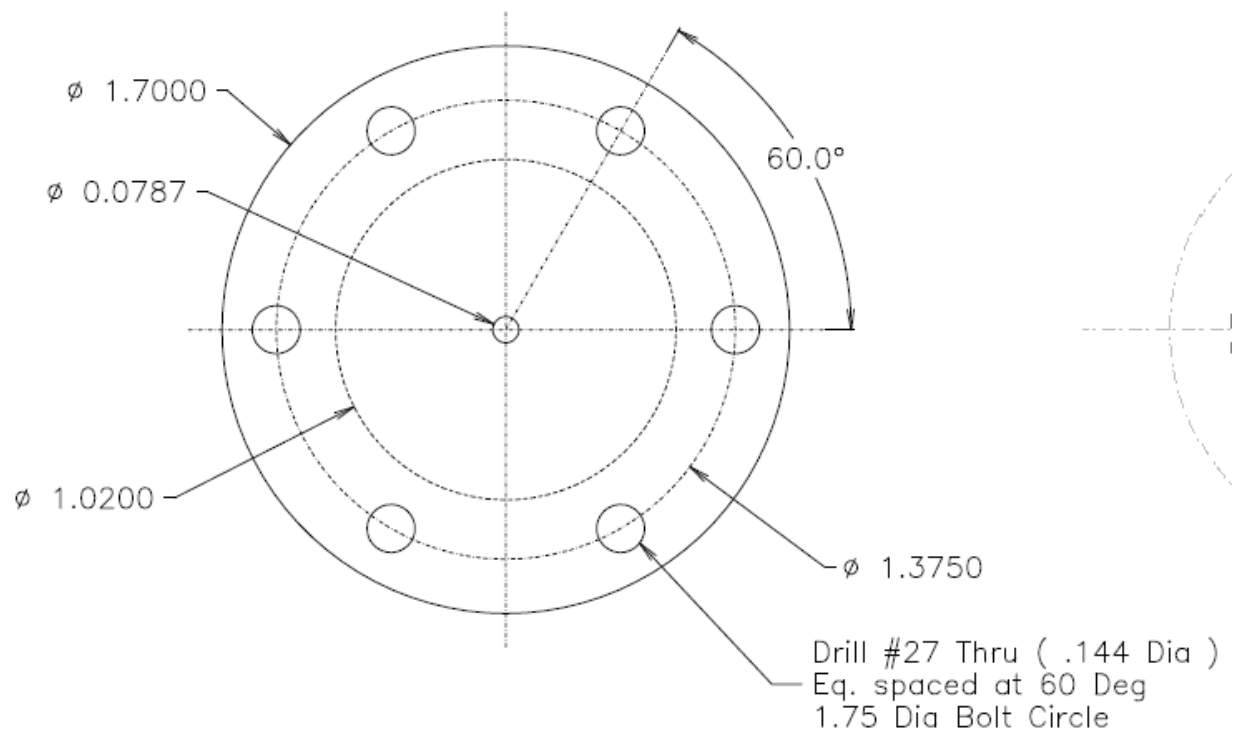


Figure 39: Aluminum top clamp with light through hole centered above sample, and groove cut for quartz window.

APPENDIX B: SOLAR SIMULATOR OPERATION INSTRUCTIONS

- 1) Turn on the Ocean Optics spectrometer light source. It should be left for a minimum of 30 minutes to warm up before any experimental work may begin.
- 2) Connect the pump outlet to the z-cell inlet. Load a reservoir with DI water. Begin flowing DI water through the system, peristaltic pump setting = 4.0, ensure flow is in the direction shown in Figure 25. If significant dye remains in the system from the previous user, flush for as long as needed changing DI water every 15-30 minutes.
- 3) Connect the Ocean Optics spectrometer to the computer by USB cable, Open the Spectrasuite software on the PC. Detailed information can be found in help files or the software manual. This procedure will only cover the changes necessary to complete an absorbance measurement.
- 4) Adjust the integration time (~2,500 ms) so that the intensity of the peak of the spectrum is between 55,000 and 60,000. Saturation of the detector occurs at ~70,000 counts.
- 5) To begin an absorbance measurement, click File => New => Absorbance Measurement. Click next.
Input the previously determined integration time. Click next.
Click on the button to save the light reference. Continue to click the button until the spectra shown in the window does not change. Click next.
Block the light source by inserting a piece of metal into the slit on the light source. Click the button until the spectrum shown does not change. Click next. Click Finish. Remove metal from slit.
- 6) If not already done, mount the sample in the Teflon cell and assemble the cell. Use a new small O-ring with each sample. The large O-ring will need to be replaced ~ 20 sessions, if it is sticky or shows any residue, replace immediately.
- 7) Fill a reservoir with a measured amount of methylene blue of known concentration.
- 8) Empty the system by reversing the flow of the peristaltic pump (reverse).
Mount the Teflon liquid cell in front of the condenser lens. Connect liquid tubing and turn on the peristaltic pump (forward) with the MB reservoir connected.
Check the system for any leaks.
- 9) The data is not saved automatically, and can be set up using File => Save Spectrum. To save the absorbance data, select the second line in the "Spectrum Source" box.
- 10) If only the absorbance peak of methylene blue is required, a Strip Chart can be used to monitor the intensity of a single wavelength over time.
 - a. Select the icon
 - b. Select the second source listed
 - c. The field for update is only for visual purposes on screen. The save interval is set later. 1 – 10 seconds is usually sufficient for this field
 - d. For "Range Selection," select "One Wavelength" and type 665.03 into the box
 - e. Select the "Auto-Save" tab
 - f. Check the box to enable Auto-Save
 - g. Enter the directory, filename and save interval

- h. Click Accept
- 11) Allow the system to run for two hours without the solar simulator to allow the methylene blue to equilibrate.
 - 12) Turn on the power supply for the solar simulator.
 - 13) Turn on the output power for the solar simulator.
If the through hole is not entirely covered by the elliptical light source, move the liquid cell by the base until the hole is completely exposed.
Let run for the desired time.
 - 14) After the experiment is over, stop data acquisition on the computer by closing the strip chart and absorbance spectrum. If finished, close the Spectrasuite program.
Turn off the output power to the solar simulator. Do not turn off the power supply until the cooling fan has turned off on the light source.
 - 15) Reverse flow to remove MB solution, remove the liquid cell. Connect pump outlet to z-flow as before. Flush with DI water for 30 minutes to ensure any absorbed dye has been removed. Disassemble and clean liquid cell components with DI water.
 - 16) Ensure that the power supply has been turned off. Turn off Ocean Optics power supply if not done so already.

APPENDIX C: XPS CONSTRAINTS

TiO2 amorphous reference				
Background Range	451.5		468.6	
	Ti2p 3/2	Ti2p 1/2		
Curve Shape:	SGL(20)	SGL(20)		
	Area	25992.3	12226.1	Ratio:
FWHM	1.18913		2.04796	Ratio:
Position	459.1028	464.8193	Difference:	5.7165

Constraints
0.47037392
1.7222339

Amorphous SRO reference				
Background Range	451.5		471.392	
	A(0.2,0.6,0)SGL(50)	Start	End	
Peak				
Ru 3p 3/2	451.944		471.469	
Ru 3p 1/2	479.213		492.384	
FWHM				3.5391
				3.05634
Ratio:				1.15795363

Epitaxial SRO reference				
Background Range	454.091		471.969	
	A(0.2,0.4,0)SGL(50)	Start	End	
Peak				
Ru 3p 3/2	454.091		471.969	
Ru 3p 1/2	477.6		494.89	
FWHM				4.26963
				3.94409
Ratio:				1.08253868

User Fitted
Constraint developed from Reference
Field constrained
Determined Value

Thin Amorphous TiO2/a-SRO				
Background Range	451.5		468.6	
	Ti2p 3/2	Ti2p 1/2		
Curve Shape:	SGL(20)	SGL(20)		
	Area	3930.3	1848.7	3775.7
FWHM	1.30693	2.24776		3.27177
Position	458.585	464.3015		462.8212
Band Bending				0.1178

Thin Amorphous TiO2/e-SRO				
Background Range	454.091		471.969	
	Ti2p 3/2	Ti2p 1/2		
Curve Shape:	SGL(20)	SGL(20)		
	Area	941	442.6	3767.2
FWHM	1.29375	2.1804		3.70425
Position	459.4464	465.1629		463.9691
Band Bending				0.1046