MODIFICATION OF ELECTRICAL PROPERTIES VIA INTERFACIAL MANIPULATION IN NOVEL OXIDE HETEROSTRUCTURES

by

Stefan Nikodemski
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Golden, Colorado

Date ______________________

Signed: _________________________

Stefan Nikodemski

Signed: _________________________

Dr. Ryan O’Hayre
Thesis Advisor

Signed: _________________________

Dr. David Ginley
Thesis Advisor

Golden, Colorado

Date ______________________

Signed: _________________________

Dr. Ryan Richards
Professor and Head
Department of Materials Science
ABSTRACT

Recent advancement in the fabrication of materials with critical dimensions on the nanoscale has resulted in the emergence of new multiphase solid composites (aptly named nanocomposites). Nanocomposites based on oxide, metal, polymer, and hybrid (cermet, organic-inorganic) constituents have been recognized as a potential strategy to join the properties of different materials with the possibility of greatly enhanced properties due in part to the high interfacial area exhibited by nanomaterials. In this thesis, the effects of processing, microstructure, and interfacial design on the electrical properties of novel ionic and electronically conducting nanocomposites is established. Two classes of materials still in their infancy (proton conducting oxides and transparent conducting oxides) served as the composite constituents for the bulk of this work. Physical vapor deposition processes such as sputtering and pulsed laser deposition proved to be instrumental in the ability to fabricate well-defined heterostructures with layers/particles of nanometer thickness. For proton conducting heterostructures (based on the prototypical proton conductor BaCe$_{0.6}$Zr$_{0.3}$Y$_{0.1}$O$_{3-\delta}$ - BCZY), order of magnitude enhancement and depletion were observed in BCZY/oxide and BCZY/metal heterostructures, respectively. This abnormal modification in electrical properties was found to coincide with a high spatial density of junctions between the two composite constituents. Multilayer compositing was also used to drastically improve the crystal structure quality and by extension the electrical properties of doped titania thin films on glass. The impact of an ultra-thin interfacial seed layer was clarified, and showed that high oxygen pressure during deposition resulted in the preferential formation of the high electron mobility anatase phase upon annealing. We show that interfaces, when introduced on the nanoscale, have a profound impact on the
macroscopic transport characteristics of the composite systems and open the doorway towards new and exciting possibilities.
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CHAPTER 1
INTRODUCTION

This first chapter serves as a general introduction to composite materials and provides motivation for the work presented herein. Finally, the organization of the dissertation will be outlined.

1.1 Composite Materials Introduction

A composite material is generated when two or more individual materials, known as constituents, are combined. Based on this combination of distinct constituent materials, the composite can display macroscopic properties (e.g. mechanical, electrical, magnetic, optical properties) that are superior to that of the parent components, or the composite properties may be entirely unique (not possessed by either of the parent components) [1-4]. Perhaps one of the most heavily utilized (and most well known) composite materials is concrete, which combines cement with a particle aggregate to form a structure with enhanced mechanical properties. Recent advancement in the fabrication of materials with critical dimensions on the nanoscale has resulted in the emergence of new multiphase solid composites (aptly named nanocomposites). Nanocomposites based on oxide, metal, polymer, and hybrid (cermet, organic-inorganic) constituents have been recognized as a potential strategy to join the properties of different materials with the possibility of greatly enhanced properties due in part to the high interfacial area exhibited by nanomaterials.

1.1.1 Morphology

The macroscopic properties of nanocomposites depend on the properties of their constituents, but they also are greatly affected by the spatial arrangements of the individual components. Therefore, fabricating ideal nanocomposite morphology between the discrete
phases is critical in tailoring the properties of a given nanocomposite. Figure 1.1 shows common sample morphologies of various nanocomposites using a schematic diagram [5]. As indicated in Figure 1.1, the connectivity of each phase in the composite can be in 0, 1, 2, or 3-dimensions. Some of the more commonly employed composite microstructures are the 0-3 type structure (nanoparticles are dispersed in a matrix) and the 2-2 type structure (multilayers/superlattices). The drastic improvement of electrical properties in some oxide materials has been successfully achieved via the 2-2 composite strategy by leading to the preferential growth crystal phases with high electron mobility [6]. An example of a 1-3 type nanocomposite is the combination of single-wall carbon nanotubes within a nanocrystalline alumina (Al$_2$O$_3$) matrix, which displayed fracture toughness nearly three times greater than that of pure nanocrystalline alumina [7]. The effective bonding between the ropes of single-wall carbon nanotubes and the ceramic matrix played a central role in this superior toughening.

![Diagram](image)

**Figure 1.1:** Common connectivity patterns for a two-phase solid. Each phase has 0, 1, 2, or 3-dimensional connectivity to itself.

### 1.1.2 Interfaces

Interfacial interactions and quantum effects in nanocomposites can also have a big impact on the macroscale properties that are not displayed by a similar combination of bulk-like materials. Depending on the details of the interfacial region (e.g. inter-diffusion/chemical
reactions, doping, strain induced from lattice mismatch, grain boundaries/defects), the spatial distribution of this region can extend from several nm down to only a few angstroms. As this region is quite small, macroscopic effects are most strongly manifested in systems with high interfacial area such as superlattices in which the periodicity is also on the nanometer length scale.

Figure 1.2: Schematic illustrating the potential charge transfer interaction between two materials in the 2-2 and 0-3 type composite systems. These effects may be magnified when the interfacial domain and the layer/nanoparticle spacing are of the same length scale.

Enhanced carrier transport due to interfacial effects in nanocomposites has been the subject of several recent reports [4,8,9]. In order to explain this novel behavior, it was proposed that a space charge region develops at the interface between the constituent materials (see Figure 1.2) [4,9]. Consequently the local concentrations of charged defects were believed to deviate significantly from their bulk values, which resulted in increased carrier concentration in an area near to the interfaces. It has also been proposed that strain enhanced diffusion could justify some of these observations [8]. Coherent interfaces between materials with small lattice parameter mismatch result in the build-up of elastic strain, with the strain concentration highest at the boundary. As a consequence, the mobility of charge carrying species (typically ionic) can be affected.
1.2 Our Novel Conducting Nanocomposites

Here we gather an in-depth understanding of the links between processing and microstructure on the electrical properties of novel ionic and electronically conducting nanocomposites. In this thesis, we focus on nanocomposites based on the so-called 0-3 and 2-2 types. Novel composites of ionic/ionic, electronic/electronic, and mixed conductivity systems will be addressed. These composites are primarily comprised of two classes of materials that are still in their infancy, namely proton conducting perovskite oxides and transparent conducting oxides. Physical vapor deposition processes such as pulsed laser deposition and sputtering will be used to tune the nanostructure morphology, thereby facilitating investigation of the relationship between film structure and transport properties. Proton conducting oxide heterostructures (based on the prototypical proton conductor $\text{BaCe}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_{3-\delta}$) comprised of materials of varying thickness/morphology (from microns to nm) and nanocomposites with varying particles densities will be investigated. For transparent conducting oxides, the modification of structural and electrical properties of doped titania thin films will be studied by altering the details of the film/substrate interface through the insertion of ultra thin seed layers.

1.3 Thesis Organization

This thesis will be divided into several chapters. The second chapter will discuss the relevant background information on the individual materials used to create our novel nanocomposite systems. Chapter 3 will elaborate on the multitude of deposition techniques used to fabricate our nanocomposites. Special emphasis will be spent on the physical vapor deposition methods since they were utilized most heavily. Chapter 4 expands on the characterization techniques used to examine and analyze our nanocomposites. Chapter 5 will discuss the work on the intriguing electrical properties exhibited by novel multilayer oxide
heterostructures based on ionic/ionic and ionic/electronic conducting composites. Chapter 6 will present similar findings in metal/oxide based nanocomposites. Chapter 7 will examine the structural and electrical properties of transparent conducting oxide heterostructures deposited on amorphous glass substrates. Chapter 8 ends the thesis with concluding remarks about the implications of the findings in this thesis and also discusses some avenues for future work. References will be cited at the end of each chapter.

1.4 References


CHAPTER 2
MATERIALS FUNDAMENTALS

In this second chapter, the fundamental transport properties of the various materials utilized in this work will be discussed. An extensive literature review was performed in order to generate this summary.

2.1 Proton Conducting Perovskite Oxides

Materials crystallizing in the perovskite structure have recently garnered an explosion in notoriety due to the advent of high efficiency hybrid organic/inorganic lead halide materials for photovoltaics [1-3]. However, the initial discovery of perovskites (CaTiO$_3$) [4] and their subsequent application in many areas of materials science has been conducted since the mid 1800’s. Perovskites have a general stoichiometry of ABX$_3$, where the A and B-sites are typically occupied by +2 and +4 cation species, respectively. The A-site cation (having a generally larger ionic radius than the B cation) has a coordination number of 12, whereas the B-site cation forms a six-fold coordination octahedral structure with neighboring oxygen ions (with the cation located in the center). The X-site is generally occupied by anion species of charge state -2. The cubic form of the perovskite structure has been included in Figure 2.1 for reference.

The perovskite structure is highly flexible and thus supports a vast number of elements (both metals and non-metals) on the periodic table. This variety in atomic composition leads to numerous unique properties, many of which have been exploited in the fields of superconductors [5-7], dielectrics [8-9], magnetism [10], catalysis [11-12], and ion conducting membranes [13-18]. The extent of this flexibility of a perovskites structure from the ideal cubic structure is captured by the Goldschmidt tolerance factor ($t$):

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}$$  \hspace{1cm} (2.1)
where $R_A$ and $R_B$ are the ionic radii of the cations occupying the A and B sites, respectively, and $R_O$ is the oxygen ionic radius. Stable perovskite structures are possible when the tolerance factor is between 0.75 - 1.0. The cubic symmetry has been observed in the range $0.95 < t < 1.04$, while compounds having a tolerance factor outside this range tend to have orthorhombic symmetry [19].

Figure 2.1: Perovskite crystal structure ($ABX_3$), where the green spheres are the A-site cations, the teal sphere is the B-site cation, and the red spheres are the X-site anions. The lattice constant is specific for our case study material $\text{BaCe}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_{3-\delta}$.

Since our interest lies in conductive materials, this requires us to consider perovskites whose structure deviates from stoichiometric conditions typically achieved via doping. Doping of the perovskite structure typically begins by replacing some of the B-site elements with aliovalent ions of lower oxidation state (typically +3). In order for charge neutrality to be maintained in the crystal, electrically compensating defects are formed. The wide band-gap results in the energetically favorable formation of oxide-ion vacancies rather than electronic defects as the compensation mechanism when the dopant concentration is low [20-21]. In the following thesis, a modified Kröger-Vink notation [22] will be used as a short notation for the description of lattice position and charge state of point defects. The general format is $X_S^{c}$, where
X corresponds to the species i.e. either an atom or vacancy (V). The subscripted index, S, indicate the position in which the atom/vacancy in question is located (lattice site or interstitial – i) while the superscripted index, C, denotes the charge state of the point defect. An example of this oxygen-ion vacancy creation method (in the aforementioned Kröger-Vink notation) is shown in Equation 2.2 (where D represents a dopant ion).

\[
D_2O_3^{2ABX_3} \rightarrow 2D'_B + V_o^- + 2O_o^{x} + \frac{1}{2}O_2
\]

(2.2)

In some cases, the defect chemistry of doped ABO_3 perovskite structures can be quite complicated and can become convoluted when there is partial substitution of the dopant cation into the A-site (rather than the B-site) or if the amount of dopant becomes too large. Consequently, oxygen vacancies are consumed instead of being created [20,23] and there is the possibility of electronic carrier compensation as well as the formation of secondary phases. Several experimental measurements and theoretical simulations indicated that A-site substitution occurs preferentially using dopant cations having a relatively large ionic radius (Hume-Rothery argument) [24-26]. Furthermore, an A-site deficient structure, resulting from experimental processing conditions (i.e. non-stoichiometric A-site cation content in the original composition or A-site vaporization after severe processing procedures) also promotes dopant substitution into the A-site [23]. All of these factors imply that the choice of dopant cations with large ionic radius and/or high dopant concentrations can in general have a strong impact on the electrical performance [27].

Protonic defects can be introduced into the perovskite structure in one of two ways. First, consider the process of proton uptake in wet atmospheres. A water molecule reacts with the surface and dissociates into a hydroxide ion and a proton. The hydroxide species then relaxes
onto a vacant oxygen lattice site (generated through the doping process detailed previously), and the bare proton forms a covalent bond with another oxygen ion:

\[ V_{O^-} + H_2O + O_o^x \rightarrow 2O_{H_o}^\cdot \]  

(2.3)

In dry atmospheres containing hydrogen, the formation of hydroxide defects can occur via the following reaction:

\[ H_2 + 2O_o^x \rightarrow 2O_{H_o}^\cdot + 2e' \]  

(2.4)

While these two mechanisms are possible, proton uptake through the dissociative adsorption of water has been found to be most relevant [28-30]. Thus the formation of protonic defect in these doped perovskites has been addressed. A detailed mechanism of proton transport has been studied using quantum mechanical simulations based on density functional theory [31,32]. The transport of protons across the material is handled exclusively by the oxygen sub-lattice (Grötthuss-type diffusion) [30]. The motion of protons is divided into two categories (see Figure 2.2). The first is the rapid rotation of the proton about the oxygen ion with which it is bonded. At some later time, the proton reorients itself with another nearby oxygen ion and is transferred through coulombic attraction. In addition, most simulations suggest that the proton transfer between oxygen ions is phonon assisted. These phonons result in a reduction of the distance between the neighboring oxygen ions that consequently lowers the energy barrier for proton transfer.

2.1.1 Proton Transport Properties – Yttrium doped Barium Cerate Zirconate

Proton transport has been characterized for a variety of perovskite based oxide materials (see Figure 2.3) [33]. The origin of the boomerang shape in the Arrhenius curve is related to desorption of protons at higher temperatures. Since water adsorption is an exothermic reaction, the oxides are be dominated by proton transport only in the low temperature regime [34] and
start to lose protons around 500-900°C (material dependent). At higher temperatures, oxygen vacancies become more energetically favorable so that oxygen permeation may become dominating at these temperatures.

Figure 2.2: Simplified sketch of the proton transfer between two oscillating oxygen ions in the perovskite structure. The rotation of the proton defect about one of the oxygen ions is also indicated.

The yttrium doped barium cerate and barium zirconate (BCY and BZY, respectively) class of perovskites show some of the highest proton conductivity relative to other materials in this temperature range.

The doped barium cerates have higher total proton conductivity (based on less resistive grain boundaries) [35-38], but are not stable in carbon containing environments [39-40], which severely hinders their potential use. Another advantage is the relative ease of processing BCY compared to BZY [33]. The strong zirconium bonds in BZY result in a refractory material with excellent chemical stability (difficult for “corrosive” atmospheres to break these bonds), but as a consequence BZY requires extreme sintering temperatures to produce fully dense compacts with
large grain size [33,41]. BZY grain boundaries are highly resistive, leading typically to lower total proton conductivity due to high density of the grain boundaries. In fact, careful analysis of impedance spectroscopy data revealed that BZY has large proton conductivity for transport through the bulk crystal [42].

![Figure 2.3: Proton conductivities of various oxides with a perovskite or fluorite-type structure as calculated from data on proton concentrations and mobilities [33].](image)

The formation of a solid solution between these two structures has a synergistic effect whereby an increase in stability is accompanied with high proton conductivity [43-49]. Indeed, it was found that the ionic conductivity for compositions containing 60% Ce and 30% Zr was nearly equivalent to the pure doped barium cerates. Furthermore, this material also shows higher chemical stability than the zirconium-free compounds. Still, the grain boundary resistance of these solid solution materials is not so low, and there is room for continued improvement.

Based on the proton blocking nature of the grain boundaries in BZY/BCY, it is clear that
the synthesis of large grain size/single crystal proton conducting oxides is highly desirable. Various strategies have been developed to address this issue (sintering aids, reduction in starting particle size), and recently, high proton conductivities have been realized in BZY/BCY thin films deposited by physical vapor deposition techniques on single crystal substrates [50-55]. Most studies regarding BZY thin films involve PLD as the physical vapor deposition method of choice. Sputtering is, as of yet, a tool utilized less often in the growth of these materials [51]. Many researchers have attempted to grow large grain size BZY films on high quality single crystal substrates such as MgO, Al$_2$O$_3$ (sapphire) and, SrTiO$_3$ in an attempt to reduce the grain boundary density [50-55]. One of the most prominent studies achieved epitaxial growth of BZY on MgO at 600$^\circ$C, which resulted in vastly improved proton conductivity (several orders of magnitude enhancement) [55]. Even their depositions on sapphire substrates (which have a poor lattice match with BZY) resulted in a marked improvement. Several other groups have attempted to reproduce these results, and many have found that the temperatures required to achieve epitaxial growth on MgO substrates can vary substantially. Low temperature depositions lead to polycrystalline growth (or in the extreme case amorphous growth) and thus poorer electrical performance is always observed [54]. Thus a clear trend is formed of higher conductivity with increased crystallinity (less grain boundaries and larger grain separation distances). There also exists a relationship between the thickness of the film and the measured crystallinity. Thin films with thickness less than several hundred nanometers grow preferentially in one particular orientation (depending on the substrate). If the thickness of the film became too great, the material begins to develop grains and grain boundaries (strain relaxation). Due to this morphological change, there exists a conductivity-thickness relationship [54]. Enhanced conductivity was identified in thin samples mostly oriented in (100) direction while thick
Polycrystalline films showed conductivities converging to a lower value.

The effect of ambient oxygen pressure on BZY thin films produced through PLD has also been studied [50]. The formation of conical microstructural defects was observed for samples deposited in extremely high $\text{PO}_2$‘s. It was proposed that these defects caused substantially lower electrical properties. XRF measurements of films deposited in high oxygen concentration led to a large degree of A-site nonstoichiometry. It has been shown previously that highly Ba deficient bulk samples are far less conductive than their stoichiometric counterparts [56]. The total conductivities of the samples deposited in lower $\text{PO}_2$ were determined to be similar to the conductivity of the suitable reference samples. Another crucial investigation revealed the effects of film aging. Highly textured BZY/BCY/BZY heterostructures grown by PLD on MgO substrates were held in wet 5\%$\text{H}_2$ in Ar at elevated temperatures over several days [57]. The aging of these samples caused a microstructural change from epitaxial to polycrystalline. The morphology variation led to the occurrence of grain boundaries, which negatively affected the overall conductance.

Proton conducting oxide film growth through sputtering techniques has also been achieved [51,58]. Various sputtering procedures have been examined including reactive co-sputtering, 2-step techniques, and conventional deposition from single-phase targets. The conclusion from studies involving complex fabrication procedures (reactive sputtering from multiple targets) is that the long-term stability of sputtered films is compromised. The decomposition of BZY into two phases occurs in many cases in only a few hours. Stability of BZY films produced from single phases targets is improved, but its properties are still inferior to those films produced by PLD. The other drawback of sputtering is the difficulty in maintaining proper stoichiometry, which is another possible explanation for poor film performance.
2.1.2 Proton Transport Properties – Strontium Titanate

The general structural and conduction properties of strontium titanate (SrTiO$_3$/STO) will be briefly discussed. Strontium titanate (like BCZY) crystallizes in the perovskite structure where Sr$^{2+}$ represents the A-site cation, Ti$^{4+}$ ions occupy the B-sites, and O$^{2-}$ is the counter charge anion. The presence of both intrinsic defects (vacancies) and extrinsic defects (dopants) lead to modifications of the electronic structure and consequently the electronic conductivity of STO [59]. Simulations show that the highest concentration intrinsic defects are O and Sr vacancies, and in the extrinsic case that the charge compensation mechanism can change based on the nature of the foreign species [60]. Most studies confirm that STO shows a typical intrinsic response, whereby heavily reducing atmospheres lead to an outgassing of oxygen creating charge compensating oxygen vacancies and n-type electronic carriers [59]. In our experiments, intrinsic STO is subjected to moist atmospheres (wet 5%H$_2$ and wet UHP Ar) at elevated temperatures (400-150$^\circ$C). The number of studies conducted at these conditions is very small. Fortunately, they confirm the presence of proton conductivity in this particular set of operating conditions [61-63]. The proton transport number increases with decreasing temperature, and the proton conductivity seems to dominate the total conductivity at temperatures below ~500$^\circ$C in wet, reducing atmospheres.

2.2 Proton Transport Properties – Palladium (Pd)

Hydrogen permeation through metals occurs via the solution-diffusion mechanism [63-67]. For Pd, the magnitude of the diffusion coefficient for hydrogen varies between roughly $10^{-8}$-$10^{-10}$ m$^2$/s between 450-150$^\circ$C [65]. Pd membranes must be operated above 150$^\circ$C due to the formation of Pd hydrides at low temperatures [68-70]. Below this critical temperature, the solubility of hydrogen in Pd increases greatly and causes the material to act as a proton sponge.
On the other hand the self-diffusion of Pd atoms is \( \sim 10^{-30} \text{ m}^2/\text{s} \) at 300°C [71] and a general observation is that diffusion of substitution impurities is within several orders of magnitude (±100×) of self-diffusion in the metal [72]. Being extremely small in both mass and size, the diffusion of hydrogen atoms in Pd drastically exceeds nearly all other solid solution diffusion, and this diffusion coefficient is more closely matched by diffusion in liquids. The anomalously high mobility of hydrogen in Pd is one of the primary reasons this material was chosen as a good counterpart material to our proton conducting oxide BCZY. In addition to good chemical stability, it has been found that Pd has the possibility to form a solid solution with the BCZY perovskite structure via incorporation into the B-site of the host matrix [73-75].

2.3 Transparent conducting oxides

Materials classified as transparent conducting oxides (TCOs) must meet several criteria. The first requirement is that they are transparent to light in the visible portion of the electromagnetic spectrum, which is only possible for materials with a large intrinsic band-gap (>2.5eV). The second condition is that they must have high densities (> \( \sim 10^{18} \text{ n/cm}^3 \)) of mobile charge carriers that result in excellent electrical characteristics. These charge carriers can be introduced in one of two ways, either by generating intrinsic defects (such as atomic vacancies) or by doping the host matrix with heterovalent anion or cation species. Lastly, it is highly desirable (but not necessary) that a TCO material has a high electron/hole mobility based on the dispersion relationship of the electronic band structure around either the conduction band minimum (n-type) or valence band maximum (p-type) depending on the nature of the charge carrier. Several binary oxides fitting these TCO descriptors have been discovered, and the materials that have traditionally received the most attention are ZnO, SnO\(_2\), and In\(_2\)O\(_3\) [76-78]. The structural, optical, and electronic properties of these TCOs have been extensively
characterized in the intervening decades. Generally poor doping efficiency, defect compensation, and low mobility has hindered the development of p-type TCOs [76]. Thus in this work, we focus on the n-type doping of the recently discovered TCO material TiO$_2$ [79].

2.3.1 Optical, structural, and electronic properties of TiO$_2$

The intrinsic band gap ($E_g$) of a semiconducting or insulating material is given by the following equation:

$$E_g = E_{CB} - E_{VB}$$

where $E_{CB}$ and $E_{VB}$ represent the conduction band minimum and valence band maximum, respectively. The material is transparent for all photons with energy less than $E_g$, while strong absorption occurs for higher photon energies. Perfectly stoichiometric TiO$_2$ at low temperatures (thermal energy not sufficient to excite electrons across the band-gap – $E_g > k_B T$) is insulating due to an absence of charge carriers. Titania as a conventional transparent conducting oxide (TCO) material can be made electrically conducting by manipulating the details of either the intrinsic or extrinsic defects.

In undoped TiO$_2$, intrinsic defects are commonly expressed in terms of oxygen deficiency. Increasing this non-stoichiometry value results in a higher the number of electronic carriers, culminating in an increase in conductivity. The following defect reaction applies:

$$Null \rightarrow V_{O}^- + 2e' + \frac{1}{2}O_2$$

where a pure crystal loses oxygen to the surrounding environment and the intrinsic charged defects that remain are oxygen vacancies and electrons. The position of this defect energy level ($E_D$) with respect to the edge of the conduction band is of great importance and has a large influence on the intrinsic electrical properties of TiO$_2$. If the difference between the defect level and the conduction band edge ($\Delta E = E_{CB} - E_D$) is on the same order of magnitude as the
available thermal energy ($k_B T$), then these shallow defects will become ionized. Consequently they will release electrons into the conduction band resulting in a temperature dependent electrical conductivity in TiO$_2$. In addition to the outgassing of these oxygen ions in heavily reducing atmospheres, these defects can be artificially introduced in a non-equilibrium deposition process. Fortunately, advances in physical vapor deposition techniques permit the careful monitoring and manipulation of the oxygen content in a vacuum chamber during material deposition so as to adjust the titanium to oxygen ratio in TiO$_2$ thin films.

The use of heterovalent dopants is another strategy to improve the electrical properties of titania. Upon doping TiO$_2$ with a small amount of niobium/tantalum, a massive increase in conductivity is observed, which is associated with an enhancement in the carrier density [81,82]. Niobium, a group V element, substitutes onto a lattice site normally occupied by a titanium $+4$ ion. The niobium donates an additional electron represented by the following defect equation:

$$Nb_2O_5 \rightarrow 2Nb_{Ti} + 2e' + 4O_0^{x} + \frac{1}{2}O_2 \quad (2.7)$$

First principles calculations have shown that Nb raises the Fermi level into the conduction band resulting in metallic-like behavior (see Figure 2.4) [82].

Figure 2.4: Density of states calculation for A) undoped TiO$_2$ showing intrinsic behavior where the Fermi level, $E_F$, is in the middle of the band-gap B) Nb doping into TiO$_2$ causing a shift of the Fermi level into the conduction band. This doped TiO$_2$ is now degenerate and exhibits metallic-like conductivity. [82]
The absence of defect states in the middle of the band-gap also produces films with high optical transparency. The optimum doping necessary to achieve the most conductive TiO$_2$ films lies in the 3-6 at.% range [83]. Above this value the ionization of the niobium ions becomes more difficult. Moreover, additional niobium atoms only serve to hinder an electron’s progress through the lattice by providing extra sources of scattering.

Another subtle method of improving the electrical performance is related to the crystal structure of TiO$_2$. The three most abundant TiO$_2$ polymorphs are anatase, rutile, and brookite (see Figure 2.5).

![Crystal Structures](image)

**Figure 2.5: Crystal structure (AX$_2$), where the grey spheres are the Ti cations and the red spheres are the O anions. These three structures (corresponding to anatase, rutile, and brookite) are the most common crystalline phases of TiO$_2$.**

Since the thermally exited electrons populate the bottom of the conduction band their effective mass ($m_o^*$) is determined by the dispersion relationship at the conduction band minimum:

$$m_o^* = \hbar^2 \left( \frac{d^2\epsilon(k)}{dk^2} \right)^{-1}$$  \hspace{1cm} (2.8)

The electron effective mass in anatase TiO$_2$ is anisotropic and depends on the transport direction. This corresponds to $m_o^* = 0.2m_e$ when electron transport occurs perpendicular to the c-axis while it is roughly three times higher for transport parallel to the c-axis [84]. Additionally,
excessive doping can result in an increase in the electron effective mass [86]. However, $m_o^*$ in rutile structures has been calculated to be lower than its anatase counterpart [86]. Consequently, in epitaxial c-axis oriented degenerately doped anatase thin films electron mobilities of about 25 cm$^2$ V$^{-1}$s$^{-1}$ were achieved, and are much higher than the 1 cm$^2$ V$^{-1}$s$^{-1}$ mobility achieved in epitaxial rutile TiO$_2$ thin films [87]. There is still debate as to the significant disparity in electronic properties between anatase and rutile, and some first principles calculations indicate that the low electron mobility in the rutile TiO$_2$ phase can be attributed to an increased effective mass resulting from strong polaron coupling [88,89]. Thus for many TCO applications, the anatase structure is the most important as it possesses the highest electron mobility and consequently the highest conductivity (all else being equal).

### 2.3.2 Electrical Characteristics of Doped TiO$_2$ Thin Films

TiO$_2$ has gained significant attention as a next generation TCO material upon Furubayashi’s recent discovery that cationic Nb and Ta doping of epitaxial anatase TiO$_2$ thin films results in excellent conduction and optical properties [80,81]. Subsequently, the crystalline, transmission, and conduction properties of doped TiO$_2$ (TNO) films grown on single crystal substrates (Si, sapphire, LaAlO$_3$, and SrTiO$_3$) by physical vapor deposition processes such as pulsed laser deposition and sputtering were examined [90,91]. TNO films grown on these high quality substrates (with subsequent annealing in reducing atmospheres) result in both high conductivity (in some cases >1000 S/cm) and high transparency [91]. However, large-scale production of TCO films on crystalline substrates is costly and thus alternative substrate choices (such as glass) are more attractive for industrial applications. Unfortunately, anneals at extreme temperatures in very reducing atmospheres (pure H$_2$) is required to produce high quality TiO$_2$ films on glass [92]. Growth of large crystalline domains is made difficult by the amorphous
nature of the substrate. Discontinuities in the crystal lattice structure between grains in polycrystalline TiO$_2$ contain a high density of defects, which lead to electronic states within band gap that can trap charge carriers. As a result, the trap defects become charged forming a potential barrier of that impedes further charge transport across grain boundaries. Thus there is a necessity to generate large grain size TiO$_2$ materials on amorphous substrates. One strategy to improve the crystal growth of oxides is to use seed/buffer layers to act as an intermediary phase between the film and amorphous substrate surface. Several studies have employed this strategy in order to examine the effect of seed layers on the growth orientation of pure and doped TiO$_2$ on glass [93-97]. Yang et. al. showed that a bilayer SrTiO$_3$/TiN template grown by physical vapor deposition on glass substrates produces anatase thin films with uniaxial c-axis orientation [96]. Hoang et al. reported some promising results, whereby low temperature sputter deposition of an initially amorphous oxygen-rich Nb-TiO$_x$ film followed by a thicker oxygen-deficient Nb-doped TiO$_x$ film with a subsequent rapid thermal treatment produced structures with high conductivities [93]. While this approach has achieved conductivities close to ~1000 S/cm, this method has yet to rival the epitaxially grown materials. In addition, it is still unclear what the impact of doping concentration in the TiO$_2$ layer has on the phase stability. Shibata et al. [94], Yamada et. al. [97], and Taira et. al. [95] have conducted a significant amount of research utilizing Ca$_2$Nb$_3$O$_{10}$ nanosheets with a 2D perovskite structure to template the growth of high quality, (001) oriented anatase films, which in some cases (when combined with PVD deposited Nb-doped TiO$_2$ films) have succeeded in significantly enhancing the carrier transport properties.

2.4 References


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CHAPTER 3

EXPERIMENTAL METHODS I: HETEROSTRUCTURE DEVELOPMENT

Physical and electrical properties of thin film oxides are highly dependent on deposition techniques due in part to the large degree of flexibility in the material growth parameters. In this chapter we will discuss the deposition techniques employed to grow our metal oxide films/heterostructures.

3.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a physical vapor deposition technique used to transfer material from a target onto a nearby substrate inside a vacuum chamber. The PLD process begins by directing a focused high power laser beam at a source material inside a vacuum chamber. Our PLD system utilizes a Kr:F excimer laser ($\lambda = 248$ nm) as the photon source. These high energy photons transfer their energy to the target material, which is subsequently ablated. The material travels through the vacuum chamber in the form of a plasma and finally condenses onto the chosen substrate. Figure 3.1 is a schematic illustration of our PLD system and the film growth process. Several factors control film growth dynamics: the mean free path of the ions, the number of ions arriving at the substrate (and their associated energy), and the ability for ions to diffuse on the surface of film during growth (provided by the thermal energy of the substrate heater). Since this technique is frequently applied in our studies, we will discuss film growth in further detail.

Changing just one of the multitude of deposition variables available to researchers can modify the dynamics of thin film growth in the PLD process. The most frequently controlled parameters are laser pulse count/firing frequency/energy, deposition atmosphere (both total and partial pressures of $O_2$, $Ar$, $N_2$, etc...), distance from the substrate to the target, choice of
Figure 3.1: Schematic of a pulsed laser deposition system including a vacuum chamber capable of being filled with a low pressure gas. The laser beam is focused onto the target surface and the target atoms are ejected and travel towards the substrate, where they condense to form a thin film.
substrate, temperature of substrate, and target composition. This list is by no means exhaustive and new systems are continuously in development with additional features. One key advantage of PLD is its ability to retain similar cation stoichiometry as the target material; thus the film composition is directly affected by the source material. Therefore, using high quality PLD targets is critical. For our experiments, some target materials were purchased commercially (99.9% pure TiO$_2$ and SrTiO$_3$ - verified with XRF) while one was synthesized in-house to ensure high quality. For a detailed explanation of the BaCe$_{0.6}$Zr$_{0.3}$Y$_{0.1}$O$_{3-\delta}$ target synthesis, see Chapter 5 – experimental section. Another important note regarding PLD targets is the surface uniformity. The production of fine particulates is enhanced when the target surface becomes rough. Thus, we frequently polish our targets to ensure homogeneity. In addition, the target is also rotated to reduce uneven ablation during deposition.

The laser fluence impinging on the target surface is effectively controlled by two factors. The first consideration is the voltage setting of the laser. Calibrations of the actual laser energy and the laser voltage show a linear dependency. The output energy per pulse (indicated on the laser control panel) was found to be lower than the actual value due to losses from the optics. If left unchecked, another set of transparency losses could come from material depositing on the laser port window. Thus, we always cover this port with a sacrificial circular quartz slide. This slide is transparent to the light generated by the laser (248nm), and is replaced after every deposition. Dilute hydrochloric acid is used to etch these windows thereby removing deposition material in order to maintain a high transparency. The second factor is related to the spot size of the laser light. Small changes in the focusing optics can adjust the illuminated area on the target surface resulting in an increase or decrease in energy density. Generally, these optics are left unaltered, and thus the laser energy density is primarily manipulated through set voltages of the
laser unit. External control over the laser fluence coupled with computer control of pulse frequency and count leads to the ability to grow thin films of precise thickness. In our own experiments, we found that ceramic targets (BCZY) have a much higher deposition rate than metal targets (Pd) due in part to the high thermal conductivity of the metals. Typically, calibration samples are fabricated in order to determine growth rates at particular conditions. For thick films, FESEM cross-sectional imaging is sufficient to gauge the height of the film. For our thinner films, spectroscopic ellipsometry is utilized.

Once the laser radiation has been generated at the desired energy and subsequently focused onto the target surface, the light is absorbed in the surface region of the target material and this electromagnetic energy is immediately converted into electronic excitation in the form of plasmons, excitons, and unbound electrons. The response depends greatly on the electronic band structure. For very short pulse durations ($t \sim 10$ ps) and very high energy densities, the laser pulse itself may have an electric field amplitude that exceeds the threshold electric field strength for dielectric breakdown. Above ($t \sim 20$ ps), ablation occurs via conventional heat deposition. Since our PLD system has a pulse duration in the ns regime ($\sim 50$ ns), the material removal is controlled by the rate of thermal conduction through the target lattice. The excited electrons transfer their energy to the lattice within a few picoseconds and heating begins within the optical absorption depth of the material $1/\alpha$, where $\alpha$ is the optical absorption coefficient. For ablation of metals with a ns pulse, the situation is complicated by ionization of the erosion cloud before the laser pulse is over. Transfer of energy from the electrons to the lattice occurs within a few picoseconds, and heating of the absorption layer will begin. Thereafter, the bulk material under the plasma is largely screened from the remainder of the laser pulse, which is efficiently absorbed by the plasma as it becomes increasingly ionized. This process is known as laser
supported absorption and this process generates the hottest ejected species but the lowest ablation yields.

Oxygen pressure (which effectively controls the particle mean free length) is another critical factor to consider during film growth. Mass flow controllers attached to high purity process lines provide gas to the chamber. The PO$_2$ is monitored with the help of two separate gauges inside our PLD system. The first is a Pirani gauge, which is used when the chamber pressure resides in the mTorr range, and the second is an ion gauge that is only employed for high vacuum situations. Typical base pressures lie between $3.0-6.5\times10^{-6}$ Torr and can be lower if the system is left to pump overnight. The energetic particles ejected from the PLD target are subject to scattering by the process gas, which causes them to lose energy and also influences their final distribution on the substrate surface. The mean free path of an ejected species is dependent on the number of process gas molecules in the chamber as well as the elastic scattering cross-section (related to gas size). Therefore, a large increase in the total pressure results in increased scattering and thus reduced growth rates (ejected target atoms are scattered away from the substrate) but the thickness of the film will be more uniform over a larger area.

Substrates are mounted on the heater block with either Ag paste or Kapton tape. Ag paste is commonly used for high temperature depositions due to potential degradation of the Kapton tape (that could negatively impact the film properties). The heater has degrees of freedom in the X, Y, and Z directions; however, the heater position (in X and Y) has been previously optimized such that the plume is centered on the samples, and therefore it is moved very infrequently. The heater temperature has a maximum value of 900°C, is left idling at room temperature when not in use, and is monitored with the help of a K-type thermocouple. We are not concerned with lower temperature edge effects in the heater due to our small sample size.
(typically 1cm×1 cm).

Once the ejected species travels across the vacuum chamber and arrives at the substrate, the development of the thin films microstructure begins to occur. A common illustration utilized to facilitate the understanding of the evolution of a film microstructure is called a structure zone diagram (SZD) (see Figure 3.2). SZDs classify films into different regions according to their microstructure. The microstructure is heavily influenced by the mobility of the deposited atoms, which is related to both the substrate temperature and the thermal energy of the ejected species arriving at the substrate.

![Figure 3.2: Illustration of a thin film microstructure and its dependence on surface temperature][201].

At very low temperatures the surface atom mobility is too small to overcome diffusion barriers and consequently the atoms remain in place. This results in the “Zone I” structure that contains a column-like microstructure separated by voids that form due to shadowing effects. A further rise in the substrate temperature increases the surface diffusion resulting in “Zone T” structure. Nucleation and growth of randomly oriented grains occurs by condensation of the ejected species from the PLD target. The Zone-T stable shape is directly related to the crystal faces having the lowest growth rate (fastest growing crystal faces grow themselves out of existence) [198]. Transfer of atoms from one grain to another cause the grain boundaries to
migrate which leads to wider columns with increasing temperature. In this way, the total energy is minimized and the “Zone II” structure (the thermodynamically most stable one) is achieved. “Zone III” structures contain polyhedral 3-D grains, and can arise from nucleation and grain growth during post-deposition annealing of amorphous or disordered layers.

3.2 Radio-Frequency Plasma Sputtering

The sputtering method (another physical vapor deposition technique) uses ion bombardment to eject species from a target in order to fabricate thin films. A schematic diagram of sputtering technique is illustrated in Figure 3.3. In our case, Ar atoms are ionized in a vacuum chamber (using RF waves at 13.56 MHz), which are subsequently accelerated towards a negatively biased anode. The target material (also placed on the anode) is then impacted by the Ar ions. Momentum transfer causes atoms/ions/clusters to discharge from the target and travel through the vacuum chamber where they collect on the substrate. Our Denton sputtering system uses angled electrodes to facilitate combinatorial studies; thus we rotate the substrate during deposition to achieve more uniform film thicknesses. Our system also employs magnetrons to aid in the formation of plasma at lower pressures by using magnetic field to confine the charged Ar particles near to the anode surface. As with our PLD system, external computer control over deposition parameters leads to the fabrication of high quality films. Some of the critical parameters that can be controlled are: deposition time (thickness), substrate temperature, RF power applied to the target, partial pressure of gas in the chamber such as O2, Ar, and N2. Our system is designed to handle circular substrates up to 6” diameter. Unfortunately, there are complications associated with uniformly heating substrates of this size. Thus we always use small samples placed directly in the center of the heater to ensure a properly calibrated substrate temperature. Historically, sputtering techniques lead to marginally inferior film quality compared
to PLD, but the films have sufficient electrical and optical properties to be suitable for a number of device application. Additionally, sputtering allows for large-scale production, and therefore it is heavily used in industrial applications.

Figure 3.3: Schematic of a magnetron sputtering source. A ring shaped magnet creates a magnetic field trapping the electrons, which collide with Ar gas to produce positive ions. Ar$^+$ ions are then accelerated onto the target and sputter target atoms, which condense on a substrate.

3.3 Atomic Layer Deposition

The atomic layer deposition (ALD) process fabricates thin films from the bottom-up by using alternating pulses of chemical precursors that first react with the substrate and finally each other. Each constituent has a so-called ‘half-reaction’ whereby the precursor is introduced into a chamber and remains until the substrate surface has been coated with a monolayer (achieved through self-limiting chemical processes). Then, the chamber is purged of any residual precursor, and this process is iterated (with other constituents) until the desired film thickness is attained. Our ALD experiments on TiO$_2$ seed layers (on glass) were performed in the low to intermediate
temperature range (100-300°C) in order to study the effect of crystallinity on the electrical properties of subsequently sputter deposited Nb doped TiO$_2$. We use the ALD technique as a platform to prepare layers with well-defined properties in order to compliment our experiments on purely sputter deposited oxide layers/heterostructures.

3.4 Evaporation

Thermal evaporation was used in order to produce high quality metal top contacts for our impedance measurements. Our metals of interest (Pd or Pt) are evaporated in vacuum and condense on the substrate as a thin layer. The thickness of the film is monitored using a quartz crystal microbalance. Typically, a thin layer of Ti is first deposited to act as an adhesion layer between our sample and the bulk contact material. Shadow masks were utilized to preferentially deposit metal in desired areas thus producing contacts of a well-defined geometry.

3.5 References


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CHAPTER 4

EXPERIMENTAL METHODS II: HETEROSTRUCTURE CHARACTERIZATION

The deposition of our materials using the large variety of fabrication methods (and tunable parameters) outlined in the previous chapter results in thin films with differing physical characteristics. Clearly, changes in these properties can drastically affect material performance, and thus careful monitoring of these changes is crucial. In this section, we will discuss the relevant analytical techniques employed to monitor some of the basic structural and electrical properties of our oxide thin films.

4.1 X-ray Diffraction

X-ray diffraction (XRD) is a widespread experimental technique primarily designed to examine the crystalline phases present in a specimen. In addition, XRD can be used to study a variety of other structural properties such as epitaxial/textured growth in films, strain, and crystallite domain size. We have utilized both 1D and 2D detectors in our studies. Generally, 2D detectors are better at assessing some features (such as film texture) at the cost of reduced resolution. The detected diffraction signal is based on the constructive interference of monochromatic (CuKα = 1.54 Å) x-rays, and the angles at which this signal summation is observed depends entirely on the symmetry of the crystal lattice. Consider two identical x-rays approaching a crystal that scatter from adjacent atomic planes separated by a distance, d. If the x-rays are approaching the sample at an incidence angle of \( \theta \), then a simple geometric argument will show that the x-ray penetrating deeper into the sample will travel an additional distance equal to \( 2dsin(\theta) \) (see Figure 4.1). For constructive interference to occur, x-rays exiting the sample must be perfectly in phase with one another. This requirement is satisfied when the extra length traversed by the second x-ray is equal to an integer multiple of the wavelength. Bragg’s
law captures the essence of this constructive interference condition,

\[ n\lambda = 2dsin(\theta) \]  

(4.1)

Several experiments we performed coupled the x-ray source and detector with a controllable substrate heater. These experiments allowed us to assess the minimum thermal energy required in order for crystallization to occur for each of our materials. Furthermore, by continuing to increase the temperature we can detect the onset of harmful inter-diffusion or secondary phases in oxide heterostructures. This enables us to determine appropriate processing windows where we are confident that measurements conducted inside this range will not result in material degradation. The degree of crystallinity was determined by measuring the integrated area beneath certain XRD peaks. This analysis must be carefully conducted, as the x-ray intensity is directly dependent on various factors in including number of diffracting crystals and orientation. Thus we typically compare samples of nominally the same thickness to ensure that these differences are minimized.

Figure 4.1: Schematic illustration of diffraction from a crystal and the constructive interference which occurs when Bragg’s law is satisfied.

4.2 Raman Spectroscopy

In a typical Raman experiment, a beam of monochromatic light (in our case 532nm) is produced and applied to the sample in question. A detector subsequently collects the radiation
generated as a result of laser light interactions with the sample. When the incident photons collide with the sample, they may gain energy, lose energy, or exit with an energy equal to the incoming light (this process is summarized in Figure 4.2). When the specimen absorbs a portion of the energy from the incident photon and transitions into an excited state, the emerging photon has a downward shift in energy (called the Stokes lines). If the sample already exists in an excited state (due to room temperature thermal energy activation), the emerging photon can exit with energy greater than the incident beam (called the anti-Stokes lines).

Figure 4.2: Schematic representation of light scattering processes collected by Raman spectroscopy.

The temporary excitation of the sample into a virtual state coupled with decay into an energy state lower than its initial position is the origin of the energy gain of the exiting photons. The component of the scattered radiation without change of frequency is called Rayleigh radiation. A complete Raman spectra is generated as a result of these inelastic scattering processes. The Rayleigh scattering of the incident radiation, is by far the most intense component of Raman spectrum but contains no relevant information. However, the Stokes lines are related to the
atomic arrangement (bonding environment) of the sample and their modes of vibration. This is similar to the information obtained with infrared spectroscopy (although with different mechanisms), and are therefore exploited to identify the compounds present in the sample.

4.3 Atomic Force Microscopy

Atomic force microscopy (AFM) was used to measure the surface morphology/topography of our oxide thin films. A microscopic probe (a tip with a small radius of curvature) fabricated on a cantilever is brought within close proximity of the sample surface. Interatomic forces between the surface of the specimen and the probe head cause the cantilever to deflect from its resting position. Careful monitoring of the tip deflection is coupled with a rastering across the sample, which ultimately allows for a topographical reconstruction of the surface.

4.4 Spectroscopic Ellipsometry

Spectroscopic ellipsometry is an analysis technique most commonly used to estimate film thickness (especially for very thin films) and index of refraction. The assessment of these film properties is accomplished by exposing the sample surface to polarized light (at various wavelengths) and measuring the corresponding shifts in intensity and polarization at the detector. This measurement is typically repeated while altering the incidence angle of the incoming light (as well as the position of the detector). Theoretical modeling of the acquired data is a crucial component in the analysis, as there are a multitude of solutions that will produce the same system response (in addition to a large amount of input parameters such as surface roughness). Thus great care is taken to ensure that the outputs of these models produce reasonable values (closely resemble previous literature reports). We have independently confirmed that the thickness values produced by our modeling matches the film thickness measured by cross-
sectional electron microscopy.

4.5 Electron Microscopy

Various experimental techniques can be used to visualize sample morphology. Since the critical dimension of our thin film samples is only a few hundred nm in size, electron microscopy techniques are utilized due to their ability to resolve small features. In the following sections, the two electron microscopy techniques used most prevalently in our study will be discussed in detail.

4.5.1 Field Emission Scanning Electron Microscopy

Morphology (both cross-sectional and surface) of our oxide thin films was studied using field emission scanning electron microscopy (FESEM). A beam of electrons is produced at a source, subsequently focused with the help of magnetic lenses, and is finally scanned across the specimen in a raster pattern. The image is generated from the collection of electrons that have scattered/otherwise interacted with the sample as a function of the probe position. This interaction between electrons and the various atomic components within the sample reveals information about the sample’s surface topography and composition (which is ultimately the source of image contrast). The advantage of a field emission system lies in its ability to generate electrons at the source with lower applied potentials. This is accomplished by fashioning a sharp tip out of the material used to generate the electrons. In this way, the electric field is concentrated at the source tip thus requiring a lower applied potential to achieve the same field strength as a conventional tip. Several of our materials are electrically insulating at room temperature. The lower electron energy reduces the charging effects that are apparent at higher source potentials. Therefore, it is unnecessary to coat our materials with a conductive layer (e.g. Au, C, etc…) in order to image the sample, and the sample retains the ability to be examined by
other analytical techniques.

4.5.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is another imaging technique that allows us to resolve very fine structural features (nm scale) within a sample. The enhanced spatial resolution is due to the small de Broglie wavelength of electrons. Similar to SEM, a beam of electrons is generated at a source (typically at much higher potentials – 200keV vs. 2keV), is focused using magnetic lensing, and is transmitted through an ultra-thin specimen. The image is formed from the interaction of the electrons passing through the thin section. Contrast in TEM imaging is a complex topic, but can be due to unequal amounts of electron scattering from thickness gradients to compositional changes (average Z value).

TEM preparation was accomplished with a FEI Helios NanoLab 600i focused ion beam (FIB) with an isotopically pure gallium source (see Figure 4.3 for a graphical illustration of the preparation process).

![Figure 4.3: Process of preparing a TEM sample with FIB. A) Pt protection cap is deposited on area of interest B) trenches are milled on either side of the Pt capping layer C+D) sample is isolated from the remainder of the sample E) Omniprobe tip is welded to the liftout, and the liftout is extracted from the sample F) liftout is attached to Cu grid G) Omniprobe weld is cut H) sample is thinned to appropriate thickness.](image-url)
The standard sample lift-out procedure with subsequent attachment onto a copper TEM grid is summarized briefly. An area of interest is first identified, and then covered with a several micron thick layer of Pt to protect against further ion damage. The section is isolated from the rest of the sample by ion milling, and welded onto an Omniprobe tip. The sample is finally transferred to a Cu TEM grid, and thinned until suitable for TEM analysis.

4.6 Atom Probe Tomography

Atom probe tomography (APT) is a relatively new analytical technique that has the capability to spatially resolve atomic scale features of a sample. Classically, APT applies a large electrical potential to a sharp needle-like specimen in order to generate electric fields sufficiently strong to overcome atomic bonding. In our case, a pulsed laser also provides additional thermal energy to assist in the controlled evaporation process. Time of flight mass spectrometry is used to categorize the mass-to-charge ratio of the ions collected after repeated application of the laser pulses. Through successive evaporation of material, layers of atoms are removed from a specimen, and thus both the surface and sub-surface regions of the sample can be probed. Computer modeling can build a three-dimensional reconstruction of the sample providing both atomic scale spatial and chemical information. APT sample preparation is similar to the procedure previously outlined for TEM samples modified from an established procedure (see Figure 4.4) [1].

Several notable differences are to be detailed. Once the lamella has been removed from the sample, small/thin sections are cut and welded onto Cu posts (generated by slicing a mesh TEM grid). These sections are thinned further using circular patterning until the radius of curvature is appropriate for APT (typically <150nm but depends on the material).
Figure 4.4: Process of preparing APT sample with FIB. All steps for APT sample prep. mirror those for TEM sample prep. up to the liftout stage. A) Schematic of APT samples that will be isolated from FIB liftout B) liftout is segmented by welding sections of the lamella onto Cu posts C) sample is thinned into cone shapes D) TEM image of oxide multilayer ready for APT analysis.

4.7 Electrical

The general approach for all electrical measurements is to apply an electrical stimulus (a well-known potential or current) to electrodes (of arbitrary shape and positioning on a sample) and observe the system response (the created current or voltage). The relationship between this electrical input and output is related to the resistivity (intrinsic property that describes the ability to impede the flow of electrical charges) of the material under examination. It can be generalized as the ratio of an applied potential gradient to the current density created by that electric field. This generalized approach to resistivity can be further simplified by employing electrical contacts of well-defined area. In this case resistivity can be described as:

\[ \rho = \frac{R \times A}{L} \]  

(4.2)

where \( \rho \) represents the intrinsic resistivity, \( R \) signifies the measured resistance, and \( A/L \) are geometric factors related to the cross-sectional area of the sample and the distance between
contacts. The resistance measured by certain impedance spectroscopy techniques is a linear combination of the contacts and bulk material. Thus, as long as the transport (electronic or ionic) through the bulk material remains the rate-limiting step, this simple definition for resistivity will suffice. However, for some of our highly conductive oxide thin films, the details of the contact materials become increasingly important (because an ever increasing fraction of the resistance results from the contacts). For these types of films, conductivity can also be calculated using the standard four-point probe measurement, which (given a few geometric requirements) removes the effects of the contacts. Then, the only parameters needed to calculate the conductivity are the sheet resistance and the thickness of the film. Typically, our four-point probe experiments are direct current (DC) measurements with no sinusoidal attenuation of the current input.

4.7.1 Hall Effect

Our Hall effect measurements were acquired using a van der Pauw configuration (contacts are located at the corners of a square shaped sample) and a current is forced between two contacts (A+B) while the voltage is measured between two different contacts (C +D). This measurement (in a similar fashion to the co-linear 4-point probe method) eliminates the effects of contact resistance to give a true resistivity. The Hall effect yields a direct measure of the majority carrier density. In the Hall measurement, a uniform magnetic field is applied normal to the direction of a current flow. The magnetic field induces a force on the moving charged particles pushing them in a direction perpendicular to both the particle flow and the magnetic field (Lorentz force). This induces a voltage at the facets where the charges collect called the “Hall voltage”. By measuring this voltage \( V_H \) and knowing the sample details (thickness - t) as well as the details of the applied magnetic field (B) and current (I) one can calculate the conductivity, carrier concentration (n), and Hall mobilities (\( \mu \)) from the following equations:
\[ \sigma = n \times \mu \times q = \frac{1}{R_s \times t} \tag{4.3} \]

\[ n = \frac{1}{q} \times \frac{l}{t} \times \frac{B}{V_H} \tag{4.4} \]

\[ \mu = \frac{|V_H|}{R_s \times l \times B} \tag{4.5} \]

where \( q \) represents the fundamental charge and \( R_s \) is the sheet resistance [2,3].

### 4.7.2 Electrochemical Impedance Spectroscopy Measurements

A variety of elementary transport processes occur throughout any electrochemical device when the sample is perturbed with an electrical input. The principle purpose of EIS is to measure these properties and determine their dependence on parameters such as temperature and gas composition. There are numerous measurement methods in EIS, but we focus our efforts on perhaps the standard/most common approach. This process measures impedance by applying an AC voltage to the electrodes and measuring the amplitude and phase shift of the resulting current. If the perturbation is small, then only a pseudo-linear portion of the samples’ overall I-V characteristics is observed. In these cases, Ohm’s law can be applied to calculate the real and imaginary components of the resistance. This measurement is subsequently repeated at various AC frequencies to access different transport processes. Our EIS system is a Gamry ref600, which has the ability to measure the impedance as a function of frequency automatically from 1 MHz down to 10 mHz. Driving the system at even lower frequencies is possible, but the measurements increase in duration with no real benefit (due to the capture of mainly electrode processes). Our test cell setup is schematically illustrated in Figure 4.5. The sample is suspended in the middle of a large alumina tube with four Pt wires (allowing for 2, 3, or 4 probe measurements). These isolated Pt wires run through a separate, smaller alumina piece and connect the sample with our ref600.
The large tube is sealed at one end with flange that has been modified to include a gas inlet/outlet and thermocouple feed-through. This contraption is then placed in the center of a tube furnace for computer control over temperatures and ramp rates. The thermocouple is positioned near to the sample to ensure that an accurate measure of the temperature is made. The gas inlet is connected to high purity gas cylinders through mass flow controllers. In addition, bubblers can be quickly added to the flow diagram to provide humidification if needed.

The measured cell response based on the experimental conditions described above can be broadly divided into two categories:

1. The material response: conductivity, mobilities of electrical charges, inter vs. intra grain transport.

2. The electrode–material interface: typically refers to charge transfer resistance and the capacitance at the heterogeneous interface.

This raw impedance data is commonly displayed as real vs. imaginary resistance and is often referred to as a Nyquist plot. For our purposes, we only consider the first category of cell response to be relevant. Fitting of this data is conventionally accomplished by matching it to an equivalent circuit model of idealized elements such as resistors, capacitors, inductors, etc... However, for the results of the data fitting to have physical meaning, one must establish a connection between the model circuit elements and real electrochemical processes. One
potential pitfall in the modeling process is that the circuit models used to approximate the data can become infinitely diverse. A large equivalent circuit with many components could easily produce a fit that matches each data point perfectly. Thus simple circuits should be used in the description of the experimental data, and added complexity must be justified.

In many of our own experiments, a combination of semicircular arcs is observed at lower temperatures (see Figure 4.6). Each arc corresponds to a diffusion process with a different relaxation time constant. Generally, impedance arcs are modeled with a parallel combination of resistors and capacitors/constant phase elements. In such a circuit, any given resistor represents a unique conduction pathway, such as the bulk conductivity of the material or the crossing of a grain boundary.

Figure 4.6: Raw impedance data with equivalent circuit model fitting for BCZY pellets measured at 150°C in two different gas atmospheres.

Capacitances generally are associated with space charge polarization regions. Ideal capacitors elements assume that the interface generating the space charge region is perfectly smooth
(charge separated by a fixed distance). However, most real systems have irregularities in material properties on a microscopic scale leading to fluctuations in the local electric field. For example, the electrode–electrolyte interface is not often smooth and uniform. It contains a large number of defects such as kinks, jags, and ledges, local charge inhomogeneities, two- and three-phase regions, adsorbed species, and variations in composition and stoichiometry. Thus, other circuit elements such as the constant-phase element (CPE) were developed to account for this non-ideality. The behavior of CPE’s approaches and ideal capacitor in the limit as the surface roughness goes to zero. The use of CPE’s in place of capacitors in our circuit modeling generally leads to lower deviation between the data and model.

4.8 References


CHAPTER 5

IONIC CONDUCTION MODIFICATION IN NANOSCALE PROTON-CONDUCTING OXIDE HETEROSTRUCTURES PREPARED BY PULSED LASER DEPOSITION

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Stefan Nikodemski¹,³, Jianhua Tong¹, Philip Parilla², David Ginley²,⁵, Joseph Berry², and Ryan O’Hayre¹,⁴,⁵

5.1 Abstract

Recently, a growing number of reports have shown orders of magnitude enhancement in ionic conductivity due to elastic strain fields and/or space charge regions originating from heterointerfaces in oxide nanocomposite and superlattice systems. Here, we explore the role of interfacial density⁶ on the electrical properties of novel, well-defined, two-phase oxide/oxide multilayer heterostructures. We show that it is possible to modulate the conductivity by several orders-of-magnitude (with both increases and decreases in conductivity demonstrated) in multilayer composites containing the prototypical proton conductor BaCe₀.₆Zr₀.₃Y₀.₁O₃₋₅ (BCZY) and second phase oxides SrTiO₃ (STO) or TiO₂. These composites are fabricated by pulsed laser deposition (PLD) on electrically conductive and insulating single crystal substrates, thereby enabling transverse and lateral impedance measurements respectively at moderate temperatures (150-400°C). For BCZY/TiO₂ multilayer heterostructures, both lateral and transverse conductivity increase with increasing interfacial density. However, even the most conductive BCZY/TiO₂ heterostructures fall below the conductivity of single-layer “bulk-like” TiO₂ films. For BCZY/STO multilayer heterostructures, lateral conductivity increases with increasing

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¹ Staff associated with the department of Metallurgical and Materials Engineering, Colorado School of Mines
² Staff associated with the National Renewable Energy Laboratory, experimental assistance
³ Graduate Student, primary researcher, and author
⁴ Corresponding author
⁵ Co-advisors of graduate student
⁶ Variations in the spacing of junctions between composite constituents
interfacial density, but transverse conductivity decreases with increasing interfacial density. Intriguingly, lateral conductivity in BCZY/STO multilayer composites greatly exceeds (by more than 50×) the conductivity of single-layer “bulk-like” BCZY and STO films. Furthermore, the conductivity enhancement is confirmed to be primarily protonic through isotope exchange experiments, thereby suggesting a significant positive nanoionic effect in this system.

5.2 Introduction

The ability to dramatically influence the electrical properties of composite materials via the careful manipulation of the interfaces between the constituents has gained significant interest in recent years [1-3]. For solid-state ion-conducting systems, these nanoscale interfacial effects, or “nanoionic” phenomena have the potential to greatly improve the performance of devices such as fuel cells, batteries, and super-capacitors. While positive nanoionic effects are generally desired, even large negative shifts in ionic conductivity resulting from interfacial effects can be useful in applications such as gas sensors and atomic switches.

At the interface between dissimilar ionic materials, the local concentrations of defects may deviate significantly from their bulk values due to space charge effects [1,2]. The spatial extent of this enhanced conductivity region is related to the Debye length and thus for most ionic materials is expected to be on the nanometer scale. As the space charge region is quite small, macroscopic effects are most strongly manifested in systems with high interfacial density such as superlattices in which the periodicity is also on the nanometer length scale. Many studies of nanoionic effects have focused on the enhancement of oxygen ion diffusion in prototypical solid oxide fuel cell (SOFC) materials such as yttria-stabilized zirconia (YSZ) [1-9]. Recently, a few studies have also examined nanoionic effects in proton conducting oxides [10-20]. Advanced bulk and thin film processing approaches have recently resulted in the improvement of these
proton-conducting materials, opening the door to a number of intriguing potential applications [21-29]. The systematic exploitation of nanoionic effects therefore offers opportunities for the development of thin film proton conducting oxide systems with even further enhanced transport characteristics.

Here we report on the development of novel ionic/ionic and ionic/electronic multilayer composites based on a proton-conducting oxide (BaCe$_{0.6}$Z$_{0.3}$Y$_{0.1}$O$_{2.95}$ = BCZY63, hereafter BCZY for short) with a second oxide (SrTiO$_3$ or TiO$_2$, respectively). SrTiO$_3$ (STO) has been shown to possess proton conductivity at intermediate temperatures in wet atmospheres [30-33] whereas TiO$_2$ is primarily an electron conductor when subjected to high temperature anneals in reducing atmosphere [34]. Pulsed laser deposition (PLD) is used to deposit multilayers with well-controlled interfacial spacing (individual layers of nanometer thickness), thereby facilitating investigation of the relationship between interfacial density and ionic transport properties. Impedance spectroscopy is used to study the resulting lateral and transverse conductivity of the BCZY/TiO$_2$ and BCZY/STO multilayer heterostructures in wet reducing conditions (5% H$_2$). These experiments suggest that introducing interfaces at a sufficient density can strongly alter the conduction properties of these oxides, and that both positive and negative effects are possible. Furthermore, the oxide heterostructures examined here can provide a versatile scientific platform for future studies regarding fundamental issues in H/H$^+$ transport, nanoionics, and oxide/oxide interfaces.

5.3 Experimental Section

The following section will discuss the various experimental details related to this study. First, the synthesis of the PLD target material and the relevant deposition parameters will be outlined. Next, the instruments utilized in the assessment of the structural properties of our thin
film samples will be discussed. Lastly, details will be provided regarding further preparation of a given specimen for electrical measurements.

5.3.1 Target and film fabrication

Powder samples of cerate–zirconate solid solutions having the nominal composition \( \text{BaCe}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_{3-\delta} \) were prepared by a modified sol–gel process. The process used \( \text{Ba(NO}_3)_2 \) (Sigma-Aldrich, 99+%), \( \text{Ce(NO}_3)_3\cdot6\text{H}_2\text{O} \) (Alfa Aesar, 99.5%), \( \text{ZrO(NO}_3)_2 \) (Sigma-Aldrich, ≥99%), and \( \text{Y(NO}_3)_3\cdot6\text{H}_2\text{O} \) (Alfa Aesar, 99.9%) as metal precursors with EDTA (ethylenediaminetetraacetic acid, Alfa Aesar, 99.4+%%) and citric acid monohydrate (Alfa Aesar, 99-102%) as complexing and polymerizing agents, respectively. Ammonium hydroxide (Alfa Aesar, \( \text{NH}_3 \) 28-30%) was added to promote the dissolution of EDTA in deionized water. After the addition of stoichiometric amounts of the barium, cerium, zirconium, and yttrium salts into a beaker of deionized water, a measured amount of EDTA, citric acid, and ammonium hydroxide were added and the final solution was stirred on a hot plate at 200 °C. Water slowly evaporated resulting in a yellow–brown gel. The dried gel was treated at 150 °C in air until a char was produced. Fine BCZY powders were obtained by calcination of the char in air for 12 h (heating rate 2°C min\(^{-1}\)) at a temperature of 900°C. The resulting powders were axially pressed in the form of cylindrical discs at 30000 psi and sintered for 12 hours in air at 1650°C. The BCZY pellet used as an impedance reference was prepared in the same manner as above. The sintered pellet was polished with increasing grit sand paper until the surface became mirror-like. Silver paste was applied to either side and cured at 800°C for 1 hr. to produce contacts for EIS measurements.

BCZY, TiO\(_2\), and STO thin films were deposited by PLD on (0001) sapphire, (001) silicon, and (001) 0.7 wt% Nb doped strontium titanate substrates using a KrF excimer laser
(Lambda Physics, 248 nm). The laser was operated at a pulse rate of 10 Hz and the number of applied laser pulses was regulated in order to produce films with desired thickness. The laser beam was focused onto a rotating target at a 45° angle of incidence. The target–substrate distance was 5 cm. Prior to placement inside the deposition chamber, the substrates were cleaned in an ultrasonic cleaner for 10 min with acetone and then isopropanol. All substrates were then blown dry with high purity nitrogen gas. The deposition chamber was initially evacuated to $6.5 \times 10^{-6}$ torr and depositions were conducted under vacuum at various temperatures to form different sample morphologies. The substrates were attached to the heater with cured silver paste.

### 5.3.2 Film structural characterization

X-ray diffraction (XRD) was conducted on a Bruker Discovery 08 with a large area detector, and on a Scintag X-1 using Cu-Kα radiation. XRD annealing experiments were conducted using a hot stage attachment to the Bruker system. An important experimental choice was the selection of single crystal Si substrates (with native oxide layer) to act as an excellent thermal junction between the heater and surface of the thin films. In addition, these substrates do not have the strong reflections present in our region of interest unlike other commonly employed single crystal substrates such as sapphire. The microstructure and morphology of the layered structures were characterized by observing fractured cross sections using field-emission scanning electron microscopy (FE-SEM, JEOL 7000, Peabody, MA) and transmission electron microscopy (TEM, CM200). Our TEM specimens were prepared using a lift-out technique in a focused ion beam/scanning electron microscope (FIB/SEM) (Helios 600i, FEI, Hillsboro, OR).

### 5.3.3 Film electrical characterization

Platinum thin-film electrodes (with a chromium adhesion layer) were deposited on the back of the niobium doped strontium titanate substrates in order to form an ohmic contact for
electrochemical impedance spectroscopy measurements. Palladium and Platinum films were deposited on the surface of the heterostructure as rectangular-shaped electrodes for perpendicular conductivity measurements. For the parallel conductivity measurements, films/heterostructures were deposited on insulating SrTiO$_3$ single crystal substrates to reduce electronic contributions from the substrate and to provide a template layer that has been previously reported to be an excellent lattice match for BZY. Platinum electrodes were deposited on top of the film/stack by electron-beam evaporation and mounted in a temperature controlled tube furnace. More precise Pt bars deposited with focused ion beam (FIB) were placed at a distance 10’s of microns apart (several orders of magnitude greater than the film thickness) to ensure a minimization of surface diffusion (see Figure 5.1). Conductivities were extracted from AC impedance spectra measured from 1 to $10^6$ Hz at a range of temperatures from ~100-400$^\circ$C.

![Figure 5.1: Schematic illustration of A) lateral and B) transverse conductivity measurement schemes.](image)

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5.4 Results and Discussion

The following section will discuss the results of the various experiments conducted in this study. The first subsection will present the structural characterization information. A bulk of the discussion will be focused on the electrical characterization performed on various samples under several testing conditions.

5.4.1 Oxide Multilayer Structural Characterization

This section on specimen structural characterization will be sub-divided into two categories. First, the electron microscopy results will be presented (representative images of our specimens fabricated by PLD). Finally, crystal structure characterization will be presented.

5.4.1.1 Transmission Electron Microscopy results

Multilayer heterostructures consisting of alternating layers of $\text{BaCe}_{0.6} \text{Zr}_{0.3} \text{Y}_{0.1} \text{O}_{2.95}$ (BCZY) and either SrTiO$_3$ (BCZY/STO) or TiO$_2$ (BCZY/TiO$_2$) were prepared by PLD as described in further detail in the experimental section. In all cases, the total thickness of the multilayer heterostructure “stacks” was held constant at 75-80 nm with one notable exception. The exception involved the BCZY/STO multilayer stack used for transverse measurements, which was deliberately synthesized with a stack thickness around 200nm in order to ensure the measured heterostructure resistance was large enough to be distinguishable from the wire resistance at high temperatures. The total number of layers in the majority of the stacks was varied from 3 to 31 by changing the thickness of each individual BCZY and STO/TiO$_2$ layer, thereby introducing between 2 and 30 interfaces. Due to the greater total thickness of the BCZY/STO stacks used for perpendicular measurements, these stack had a few additional layers (up to 41 layers). The finest heterostructures gave an interfacial spacing of 2.5 nm, which is expected to be on the same order as the Debye length in this system. The coarsest
heterostructures gave an interfacial spacing of 50 nm, approximately one order of magnitude larger than the Debye length in this system.

Deposition rates for each oxide depended strongly on temperature and chamber pressure; STO and BCZY were measured to have comparable deposition rates (0.1 Å/shot) at our typical processing conditions (400°C) while the TiO₂ deposition rate was found to be about 3 times lower. By tuning the PLD shot rate accordingly, we were therefore able to deposit multilayer heterostructures with an even volume fraction (50/50) and layer thickness for each material (see Figure 5.2). Total stack thickness was maintained constant while individual layer thickness was varied, thereby enabling direct comparison of impedance measurements between samples with nominally the same total thickness but varying interfacial density.

Figure 5.2: A) BCZY/STO multilayers fabricated at 400°C deposition temperatures to prevent interdiffusion. B) BCZY/TiO₂ multilayers fabricated at 400°C C) Cross-sectional FESEM image of a BCZY/STO heterostructure film deposited at 700°C.
Figure 5.2a,b shows typical bright field transmission electron microscopy (TEM) images for BCZY/STO and BCZY/TiO$_2$ multilayer heterostructures, respectively. These samples, which were deposited at relatively low temperature (400°C) resulted in continuous and well-defined dyads of the two materials. TEM investigations, combined with microstructure analysis via cross-sectional field emission scanning electron microscopy (not shown), demonstrated that the long-range order (smoothness and thickness) of the BCZY/oxide multilayers could be nicely preserved so long as the total stack height was maintained below a critical thickness value (several hundred nm). Variations in the interfacial density at greater stack thicknesses were likely the result of SAC window contamination during the PLD process. Depositions at higher temperature (700°C) produced samples with reacted interfaces and significant interdiffusion as shown by the TEM inset in Figure 5.2c.

5.4.1.2 Heterostructure development - XRD and In-situ annealing

Reports on the growth of other oxide/oxide heterostructure systems have typically utilized high substrate temperatures (700°C) during the deposition process in order to produce epitaxial multilayers [1,3,9,10]. However, when these high temperatures are employed in the growth of our oxide materials we find that there is a significant amount of interdiffusion present in the XRD patterns that is especially intensified when the dyad periodicity is on the order of a few nanometers (Figure 5.3c compare the blue curves). For our specific materials system, we hypothesize that the addition of cerium into the perovskite structure causes the material to be less chemically stable at higher temperatures, resulting in oxide interdiffusion at the interface. To minimize interdiffusion, PLD should therefore be carried out at temperatures significantly lower than 700°C. Unfortunately, deposition at room temperature leads to amorphous oxide/oxide heterolayer structures, which poses a different stability problem due to crystallization during
impedance measurement at higher temperatures. Additionally, amorphous multilayers undergo a self-destruction process if they remain in air for any extended period of time (~days). The small particle size produced from the PLD process may allow for the ingress of ambient moisture along the particle boundaries, which causes the materials to swell resulting in mechanical failure.

In order to further probe the temperature stability of our heterostructure systems, a series of initially amorphous heterolayer samples prepared via room-temperature PLD were studied by \textit{in-situ} XRD during a post-deposition annealing treatment (Figure 5.3a). Standard x-ray patterns for BCZY63, STO, and anatase TiO$_2$ are included below the experimentally acquired patterns for reference. Upon annealing, both the BCZY/STO and BCZY/TiO$_2$ multilayer stacks transform from amorphous to crystalline films between 250-330°C. One clear distinction between the two samples is the exact temperature at which the onset of crystallization occurs. As shown in Figure 5.3b, which plots the average integrated intensity of peaks for each material as a function of temperature, crystallization of the BCZY/STO film occurs at ~260-270°C, while crystallization of the BCZY/TiO$_2$ sample occurs at higher temperatures (~300°C-325°C). The origin of this crystallization suppression in the BCZY/TiO$_2$ case is unclear but it may have some basis in increased nucleation energy barriers between the two materials that are non-lattice matched. Correspondingly, BCZY/STO heterostructures crystallize at lower temperatures due to lattice matching (reduced nucleation energy barrier). Upon crystallization, the XRD peak widths (as measured by full-width at half maximum, FWHM) maintains a constant value of approximately 0.2-0.3 degrees, and does not decrease within the time scales investigated in this study (~2 hrs.). Once crystallization begins, the peak intensity achieves a maximum value within 5-6 integration frames for BCZY/STO multilayers and twice that for BCZY/TiO$_2$ samples, corresponding to
Figure 5.3: A) *In-situ* XRD annealing patterns for BCZY-STO and BCZY-TiO$_2$ multilayers annealed to 400°C in air. B) Averaged integrated intensity for each peak relative to each sample. C) XRD patterns of BCZY/STO heterostructures deposited at various temperatures. The integrated intensity for the TiO$_2$ peak in B) is plotted on a separate axis due to the low relative intensity of this peak in the XRD pattern. This reduced intensity is simply the result of the smaller TiO$_2$ layer thickness derived from its low deposition rate compared to BCZY and STO.
annealing times of 25-30 minutes and 1 hour, respectively. Once either sample reaches 400°C and is allowed to dwell, no further structural changes are observed by XRD. Based on this study, we selected 400°C as the optimal deposition temperature for our multilayer heterostructures, as it is high enough to ensure the formation of stable, crystalline films, but low enough that interdiffusion is minimized.

It may be possible to drive the heterostructures into a state with higher crystal quality in the temperature range between 400°C and 700°C. Certainly, the FWHM for samples deposited at 700°C were less than those deposited at 400°C. However, the in-situ annealing suggests that 400°C is a temperature at which crystallization of the heterostructures is guaranteed but the reaction between the two materials is mitigated. This result is corroborated by our XRD on a BCZY/STO sample that was deposited at 400°C (Figure 5.3c-black curve), which shows no peak shift or satellite peaks associated with undesirable phases. Since one of the objectives in this study is to make careful examinations of the stack electrical properties, it is most desirable to conduct impedance measurements on samples with pristine interfaces thereby removing any potential influence of layer interdiffusion. This justifies the choice of focusing on the fabrication of heterostructures deposited at 400°C.

5.4.2 Electrical Measurements

A series of BCZY-STO and BCZY-TiO₂ heterostructures were fabricated on electrically insulating (001) STO and electrically conductive (001) 0.7 wt.% Nb:STO single crystal substrates to enable the measurement of electrical properties both parallel and perpendicular to the oxide interfaces. The initial and terminating layer in each multilayer was the electrically insulating BCZY oxide, thereby providing proton-selective contacts. Single layer thin films of
BCZY, STO, and TiO$_2$ were also grown on these substrates to serve as internal references for evaluating the endpoint behavior of the individual constituents of the multilayer films.

Impedance measurements were acquired from 150-400°C in both wet UHP Ar and wet 5%H$_2$ bal. Ar. A maximum measurement temperature of 400°C was chosen to avoid potentially detrimental interdiffusion of the pristine oxide materials at higher temperatures (see Figure 5.3c). The gas environments were selected to produce conditions where protons should be the dominant charge carrier in BCZY. Typical impedance spectra at several temperatures for parallel and perpendicular measurements of both the BCZY/TiO$_2$ and BCZY/STO multilayer heterostructures in wet 5% H$_2$ and wet UHP Ar are plotted in Figure 5.4 and Figure 5.5, respectively. Perpendicular (through-film) EIS measurements of both BCZY/STO and BCZY/TiO$_2$ oxide heterostructures generally produce impedance spectra with 2-4 arcs (Figure 5.4a,c). We associate the first two (highest frequency) arcs with proton transport through the solid-state electrolyte. This assignment is reinforced by the fact the magnitude of the capacitance, as well as the absolute magnitude and temperature dependence (i.e., activation energy) of the conductivity extracted from these arcs are consistent with proton conduction. Therefore, the sum of the resistances extracted from the first two arcs was used to calculate the total proton conductivity for the multilayer films in the perpendicular measurement mode. We associate the lower frequency arcs with electrode response (capacitance and charge transfer resistance at the solid electrolyte-electrode interface). Perpendicular measurements used asymmetric contacts, as the bottom surface of the conductive Nb:STO substrate was coated with a layer of Pt, while the top contact was a Pd thin film deposited by PLD. The Pd contact was found to oxidize at higher temperatures during EIS measurements in UHP Ar, resulting in a fundamental change of the top contact from a BCZY/Pd interface to BCZY/PdO interface. For an illustration of this change in
the electrode-material interface see Figure 5.6, which shows a drastic increase in the low frequency arc when switching from 5%H₂ to UHP Ar.

Parallel transport EIS measurements of both BCZY/STO and BCZY/TiO₂ oxide heterostructures yield a single semicircular high-frequency arc, which we attribute to a “lumped” total film/heterostructure resistance (Figure 5.4b,d). This arc represents a combination of all resistance factors including grain bulk and grain boundary transport of the two materials. This blending of impedances has been previously observed in parallel impedance measurements of other ion conducting multilayers [7,17,37]. The total in-plane (lateral) conductivity of the multilayer structure can be extracted by equivalent circuit modeling of this impedance response as a parallel combination of a resistor (R) and constant phase element (CPE). Typical “n” values for our CPEs range between 0.9-1.0, which indicates that the CPE response approaches that of a perfect capacitor. This high “n” value provides some qualitative information about our multilayer structure and suggests that the interfaces are smooth and well preserved. A small electrode interface polarization is present as a partial arc in the low-frequency region due to the ion blocking effect of the electrode-material interface. Although this response is captured in our equivalent circuit model via a second parallel R/CPE element, we do not analyze it further. Figure 5.7 provides Arrhenius plots of total heterostructure conductivity vs. reciprocal temperature calculated from the impedance spectra for all the multilayer samples measured in wet 5%H₂. Values for single-layer BCZY, STO, and TiO₂ “reference” thin films grown individually on STO substrates are also included. All films were grown at a deposition temperature of 400°C. For comparison, Figure 5.7 also includes the conductivity values for a bulk BCZY pellet (fabricated using sol-gel synthesis) measured in our laboratory using the same set-up (temperature profiles, gas atmospheres). The BCZY pellet was fabricated utilizing the
Figure 5.4: Typical Nyquist impedance plots of both BCZY/STO and BCZY/TiO₂ multilayer film as a function of temperature with included circuit model fits in 5%H₂. A) BCZY/STO measured perpendicular to interfaces (10nm dyad period), B) BCZY/STO impedance measured parallel to interfaces (10nm dyad period) C) BCZY/TiO₂ impedance measured perpendicular to interfaces (50nm dyad period) D) BCZY/TiO₂ impedance measured parallel to interfaces (5nm dyad period)
Figure 5.5: Typical Nyquist impedance plots of both BCZY/STO and BCZY/TiO$_2$ multilayer film as a function of temperature with included circuit model fits in UHP Ar. A) BCZY/STO measured perpendicular to interfaces (for enhanced image see Figure 5.6), B) BCZY/STO impedance measured parallel to interfaces C) BCZY/TiO$_2$ impedance measured perpendicular to interfaces D) BCZY/TiO$_2$ impedance measured parallel to interfaces
Figure 5.6: Comparison between impedance measurements for BCZY/STO multilayer sample in two different gas atmospheres.
Figure 5.7: A) Arrhenius plot for BCZY/STO perpendicular measurements plotting conductivity of each multilayer sample vs. reciprocal temperature. B) Arrhenius plot for BCZY/TiO$_2$ perpendicular measurements. C) Arrhenius plot for BCZY/STO parallel measurements. D) Arrhenius plot for BCZY/TiO$_2$ parallel measurements. Conductivity as a function of dyad spacing is included beneath each Arrhenius plot for the appropriate samples.
same processing conditions as our BCZY PLD target (sintering temperature, dwell time, stoichiometry, etc…)—see experimental section 5.3 for further details.

5.4.2.1 Impedance spectroscopy of control films and conductivity modeling

As a first observation, the activation energy of the BCZY control film is very similar to that of the BCZY pellet, at around 0.5eV. This activation energy is also consistent with other literature reports of BCZY [23,41]. The offset in the absolute conductivity values between these two data sets is related to the finer grain size of the BCZY thin film compared to the bulk pellet (see Figure 5.8).

![FESEM cross-sectional image of BCZY film deposited on STO at 400°C with fine grain size.](image)

Proton-blocking grain boundaries are present in the film at a higher density than the pellet, which leads to the reduction in conductivity. The absolute conductivity of our STO control film falls into the expected range for STO under reducing conditions at these temperatures [41]. At around 0.7 eV, the activation energy of our STO control film is slightly higher than expected, but is still in an appropriate range for proton conduction in oxides. The small grain size in our films is the most likely explanation for this increase in the activation barrier compared to other reports
Finally, the TiO$_2$ control sample shows minimal temperature dependence in wet 5%H$_2$, suggesting strong, intrinsic, n-type conduction. PLD growth of TiO$_2$ at moderately high temperatures in low oxygen partial pressures is known to produce films with high levels of oxygen non-stoichiometry [34]. This leads to the formation of compensating electronic defects and thus degenerate n-type conductivity. Indeed, values above 1 S/cm with shallow temperature dependence are typical for the electron conduction in non-stoichiometric (reduced) TiO$_2$ deposited on single crystal substrates [34].

Using the reference conductivities of the single-layer “control” films of BCZY, STO, and TiO$_2$ as inputs, simple composite conduction models can be used as a starting point to isolate the effect of interfacial interaction in the more complex oxide/oxide multilayer systems. In the limit of no interaction between layers, the multilayer heterostructures can be modeled as simple two-layer (binary) composites. The equation for parallel conduction through a bilayer composite is given by [38]:

$$\sigma_{total} = \nu\sigma_A + (1 - \nu)\sigma_B = \frac{1}{2}(\sigma_A + \sigma_B) \quad (5.1)$$

where $\sigma_A$ and $\sigma_B$ are the conductivities of the two phases and $\nu$ represents the volume fraction of each phase. For perpendicular conduction through a bilayer composite, the following mixing rule equation applies [40]:

$$\frac{1}{\sigma_{total}} = \frac{\nu}{\sigma_A} + \frac{(1-\nu)}{\sigma_B} = \frac{1}{2(\sigma_A + \sigma_B)} \quad (5.2)$$

In our heterostructures, the volume fraction of each phase is 50% ($\nu = 0.5$) and we can take the endpoint conductivities for each phase from the single-layer thin film reference samples. The resulting model predictions are included in Figure 3 as dashed lines.
5.4.2.2 Impedance spectroscopy perpendicular measurements

The experimentally measured perpendicular transport behavior of the BCZY/TiO$_2$ heterostructures is presented in Figure 5.7a. Both heterostructures (50 nm period and 10 nm period) have a lower total conductivity than either of the control single-layer control thin films. Classically, the conductivity of layered structures measured perpendicular to the interfaces is limited by the most resistive component (which in this case would be the BCZY). The fact that the conductivity of both multilayer structures falls below the conductivity of even the BCZY film suggests that the BCZY/TiO$_2$ interfaces introduce an additional resistive or “blocking” effect on perpendicular transport. In addition, the activation energies of both multilayer samples are substantially higher than the activation energies of the single-layer TiO$_2$ and BCZY thin films. We extrapolate activation energies of approximately 0.76 eV and 1.0 eV (abnormally high) for the 10 nm period and 50 nm period multilayer samples respectively, vs. ~0.0 and ~0.53 eV for the TiO$_2$ and BCZY control samples (which match literature values) [34,41]. Conductivity data for the multilayer heterostructures sectioned with respect to the interfacial density is presented in Figure 5.7 below each corresponding Arrhenius curve. Contrary to our hypothesis that BCZY/TiO$_2$ interfaces introduce a blocking effect on perpendicular transport, we note that heterostructure conductivity increases with increasing interfacial density. The reason for this seeming contradiction is unknown, although we do note that the total conductivity of the most conductive multilayer sample is still more than an order of magnitude below that of the BCZY thin film and is 6-8 orders of magnitude below that of the TiO$_2$ thin film. The experimentally measured perpendicular transport behavior of the BCZY/STO heterostructures is presented in Figure 5.7b. As with the BCZY/TiO$_2$ multilayer heterostructures, the BCZY/STO multilayer heterostructures also have a lower total conductivity than either of the constituent single-layer
thin films under perpendicular measurement mode. In this case, however, total conductivity also
decreases with increasing interfacial density (i.e., decreasing dyad spacing), fully consistent with
a resistive interfacial blocking effect. The activation energy for all of the BCZY/STO multilayer
samples is ~0.7eV, which is closer to the STO control film (0.74eV) than the BCZY film
(0.53eV). The conclusion here is that the core region of the BCZY/STO interfaces are classically
blocking to proton transport, consequently leading to a drop in conductivity with increasing
interfacial density.

5.4.2.3 Impedance spectroscopy parallel measurements

The experimentally measured parallel conductivity behavior of the BCZY/TiO$_2$
 heterostructures (Figure 5.7c) is bound by the conductivities of the BCZY and TiO$_2$ control
samples but falls below the simplified bilayer model. For heterostructures with thicker layers
(fewer interfaces), the conductivity values flatten as a function of temperature indicating a
decrease in the activation energy. We suspect that this activation energy behavior is indicative of
a total conductivity response that can be characterized by a superposition of both electrical and
ionic components, with the ionic component becoming more prominent at higher temperatures
and thinner dyad spacing. The film with the thinnest layers approaches the bilayer model
prediction at high temperatures. We hypothesize that electron transport in the TiO$_2$ layers
coupled with enhanced proton conductivity in progressively thinner BCZY layers leads to
heterostructures that have a higher total conductivity when the distance traversed by each charge
carrier is small. As mentioned previously, however, the total conductivity of these
heterostructures falls below (or at best, begins to approach) the idealized composite model,
which suggests that these interfaces do not result in an enhancement effect where the composites
exceed the expected “standard” behavior.
In contrast, the experimentally measured parallel conductivity behavior of the BCZY/STO heterostructures (Figure 5.7d) shows conductivity values for all samples that lie above the predictive bilayer composite model for this system. Furthermore, as shown in Figure 5.7d, conductivity increases with decreasing dyad spacing (i.e., increasing interfacial density) down to 10 nm, where the total heterostructure conductivity is three orders of magnitude higher than the idealized composite model. At the finest dyad spacing of 5 nm, the conductivity begins to decrease again. The significant increase in the conductivity with decreasing dyad spacing from 100 nm to 10 nm is strong evidence for a positive nanoscale transport effect in this system. Furthermore, the fact that a maximum in conductivity is observed for the 10nm dyad spacing (5nm thick BCZY layer) is consistent with the estimated Debye length of $\lambda \sim 2$nm for the related compound BZY10, which was calculated using a Mott-Schottky space charge model [40]. We hypothesize that a reduction of the multilayer dyad period below 10 nm likely yields a decrease in the conductivity due to increased core-core interactions at higher interfacial densities [41]. Another possibility is that the layers are no longer continuous at these small thickness over the distance probed by the contacts leading to additional scattering of the protons.

5.4.2.4. Deuterium isotope exchange measurements

The observation of a significant positive nanoionic effect for lateral conduction through BCZY/STO multilayers, as well as the remarkable absolute value of conductivity observed in this multilayer system (~0.05 S/cm at 400°C) raises the question of whether the measured transport is primarily electronic or ionic in nature. Deuteron exchange experiments (Figure 5.9) were therefore performed in order to gain further (qualitative) insight into the relative contribution of proton transport to the measured conduction response of this system. The deuteron exchange was completed immediately subsequent to the measurements in 5%H$_2$ to
guarantee that the sample positioning and contacting was not altered from one experiment to the next. The results of the deuteron exchange experiment indicate that proton transport appreciably contributes to the total conductivity of films. Classical hopping models suggest that the conductivity ratio between pure hydrogen and deuterium is expected to be $\sqrt{2}$, related to the difference in the effective mass of the charge carriers. Our measurements resulted in a ratio slightly lower than classical modeling (~1.25) would predict. However, deuterium exchange experiments performed on other proton conducting oxides show a wide array of ratio values that do not necessarily match the classical case [36]. Furthermore, total parallel conductivity of the BCZY/STO multilayers in wet UHP Ar decreases by ~5X compared to wet 5% H$_2$ (see Figure 5.9).

![Figure 5.9: Temperature dependence of parallel electrical conductivity of BCZY/STO heterostructure film with 10 nm periodicity measured in H$_2$O and D$_2$/H$_2$O atmosphere. Inset) D$_2$ exchange effects as function of temperature](image)

This behavior is expected if the conductivity is dominated by protonic transport. If the
conductivity was dominated by electron holes instead (the minority carrier in BCZY), total conductivity would be expected to increase in UHP Ar. Based on these results; we suggest that the measured lateral conduction behavior of the BCZY/STO multilayer system likely involves a significant (i.e., greater than 50%) contribution from protons.

5.4.2.5 BCZY/STO Impedance spectroscopy parallel/perpendicular measurements in UHP Ar

In UHP Ar, the trends in perpendicular conductivity with dyad periodicity in the BCZY/STO system are generally consistent with the trends in 5% H$_2$, although less clear (Figure 5.10).

![Figure 5.10: A) Arrhenius plot for BCZY/STO perpendicular measurements plotting conductivity of each multilayer sample vs. inverse temperature in UHP Ar B) Arrhenius plot for BCZY/STO parallel measurements](image)

Figure 5.10: A) Arrhenius plot for BCZY/STO perpendicular measurements plotting conductivity of each multilayer sample vs. inverse temperature in UHP Ar B) Arrhenius plot for BCZY/STO parallel measurements
BCZY/STO samples with a fewer number of layers (thicker layers) have a temperature dependence which highly resembles the STO control sample in UHP Ar. However, the BCZY/STO sample with the bilayer periodicity around 10 nm has behavior more closely associated with the BCZY control. In fact, this sample trended above the idealized model conductivity prediction for temperatures less than 250°C. Thus this sample may have some form of enhancement in the conductivity due to a positive nanoionic interfacial effect. We note that this effect appears for the same interfacial density, which produced the maximum conduction enhancement in the parallel mode measurements. UHP Ar conductivity measurements on BCZY/STO multilayers measured parallel to the interfaces mirror the response seen in 5%H₂, although the absolute values of conductivity are lower in UHP Ar (consistent with behavior expected for proton-dominated transport).

5.4.2.6. Potential conductivity modification mechanism

Both undoped STO and TiO₂ targets were used in the fabrication of our oxide heterostructures. These materials have a similar band gap (~3.2-3.3eV) and both materials reduce in oxygen poor environments. This reduction likely introduces defect levels into the band gap (near the conduction band edge) that are easily ionized resulting in n-type conductivity. Intrinsic STO thin films in reducing atmospheres were measured and modeled to have a decrease in oxygen vacancy concentration and subsequent increase in electronic carriers in a region near the interface [30]. In our humidified atmospheres at moderate temperatures, these oxygen vacancies are likely compensated by protonic defects [30-33]. A buildup of negative charge carriers on the STO side of the interface could result in the electrostatic attraction of positive ions and thus an accumulation of protons on the BCZY side of the interface can result (see Figure 5.11). As the layers become increasingly thin, these regions of enhanced proton concentration may overlap.
This higher in carrier concentration has the potential to create a “superprotonic” highway in a region near to the interface thereby increasing conductivity (since conductivity is proportional to the carrier concentration).

Figure 5.11: Schematic illustration of proposed spatial defect distribution that results in conductivity modification in BCZY/STO and BCZY/TiO$_2$ multilayer samples.

Heterostructure composites of BCZY/TiO$_2$ have a more complex response depending on the interfacial density. One potential explanation of the observed behavior shall be discussed. TiO$_2$ has gained attention recently as an excellent model system for the study of memristive switching devices [42]. For these applications, an electric field is used to control the spatial distribution of oxygen vacancies in titania films. The electrical properties of titania are highly dependent on both their intrinsic and extrinsic defect level as discussed in Chapter 2. A similar situation may be occurring in our oxide heterostructures. The high number of electronic carriers may have masked the contribution of oxygen vacancy diffusion to the total conductivity in our
bulk TiO\textsubscript{2} thin film. In addition, our control film was relatively thick compared to the multilayer samples (~1 micron vs. ~100 nm, respectively). Thus the electric fields experienced by the two samples vary by an order of magnitude. The extent of this field effect on the vacancy transport is currently unclear. If this field effect is causing oxygen vacancies to accumulate at the TiO\textsubscript{2} side of the interface, then there may be a corresponding depletion of protonic defects on the BCZY side (see Figure 5.11). This is one hypothesis to the origin of the unexpected trends in the conductivity behavior for the BCZY/TiO\textsubscript{2} composites. Analysis of the conductivity enhancement reveals a maximum increase of ~50X (Figure 5.12) for the 10nm dyad spacing sample compared to bulk proton conduction values for BCZY.

![Figure 5.12: Apparent enhancement in conductivity of multilayer BCZY/STO samples in wet 5%H\textsubscript{2} compared to conductivity of proton diffusion through bulk BCZY. Lines represent exponential fits to the enhancement data as a function of dyad spacing at different temperatures.](image)

For bulk BCZY, if the yttrium dopant (10 mol\%) on the perovskite B-site was entirely compensated by oxygen vacancies that are subsequently hydrated, approximately one out of every thirty oxygen ions will have an associated protonic defect. For the maximum conductivity
enhancement (of 50X) to be purely ionic, each oxygen ion would have more than one associated proton on average. This model seems physically unlikely; therefore, by combining the isotope exchange results with the conductivity enhancement analysis, we suggest that the measured lateral conduction behavior of the BCZY/STO multilayer system involves a significant (i.e., greater than 50%) contribution from protons, but is likely influenced by additional electronic carriers as well.

5.5 Conclusions

We have shown nearly a three order of magnitude enhancement in the total conductivity (likely partly ionic and partly electronic) parallel to BCZY/STO interfaces in heterostructures where the layer thickness approaches the space charge width for this class of materials. This large increase in electrical performance at intermediate-to-low temperatures suggests that expanded research on proton conducting perovskite oxide composites is warranted. With the continuing improvement of both physical vapor deposition systems as well as traditional wet chemical synthesis methods, it may be possible to tailor the microstructure of these perovskite oxide nanocomposites in order to enable their use in practical applications such as micro fuel cells.

5.6 References


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CHAPTER 6

PROTON TRANSPORT IN BaCe$_{0.6}$Zr$_{0.3}$Y$_{0.1}$O$_{3-\delta}$ (BCZY) / Pd NANOCOMPOSITE HETEROSTRUCTURES FABRICATED VIA PULSED LASER DEPOSITION

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Stefan Nikodemski$^{1,3}$, Jianhua Tong$^1$, Adam Stokes$^6$, Philip Parilla$^2$, David Ginley$^{2,5}$, Joseph Berry$^2$, and Ryan O’Hayre$^{1,4,5}$

6.1 Abstract

We report on the fabrication and electrical properties of BaCe$_{0.6}$Zr$_{0.3}$Y$_{0.1}$O$_{3-\delta}$ (BCZY) / Pd nanoparticle proton-conducting oxide composite films synthesized by pulsed laser deposition (PLD). The addition of 20-70 volume percent of Pd nanoparticles reduces the conductivity of the BCZY film by approximately one order of magnitude in wet 5% H$_2$. Upon switching to wet UHP Ar, the conductivity of the BCZY/Pd nanocomposite further decreases roughly two orders of magnitude compared to a pure BCZY thin film. These observations lead us to postulate the existence of a thin PdO insulating interfacial layer between the particles and the bulk material, which increases in thickness upon switching from reducing to oxidizing atmospheres. Atom probe tomography was used to probe the composites directly and confirmed the presence of a thin atomically mixed region at the particle/bulk interface. A high density BCZY/Pd nanocomposite film showed a maximum shift of ~400X change in conductivity upon switching from wet 5%H$_2$ to UHP Ar compared to a pure BCZY film, thereby achieving a sensitivity that compares favorably with other PO$_2$ sensors and suggesting potential use for this system in gas sensor applications. The reversibility and response/recovery times are still unknown for these

$^1$ Staff associated with the department of Metallurgical and Materials Engineering, Colorado School of Mines
$^2$ Staff associated with the National Renewable Energy Laboratory, experimental assistance
$^3$ Graduate Student, primary researcher, and author
$^4$ Corresponding author
$^5$ Co-advisors of graduate student
$^6$ Assistance with atom probe tomography
6.2 Introduction

Recent advances in the fabrication of large grain size proton-conducting oxide thin films based on yttrium doped barium zirconate/cerate (BZY/BCY) perovskites have opened the door to their application in next generation electrochemical devices such as solid oxide fuel cells (SOFCs) and gas sensors (especially in the intermediate temperature range) [1-3]. Furthermore, the fabrication of ultra thin BZY films that are also continuous by physical vapor deposition (PVD) methods has enabled the development of novel micro fuel cell and sensor architectures with enhanced response times that can be operated at progressively lower temperatures [1]. Despite these considerations, the performance (power density) for most state-of-the-art proton-conducting fuel cells (PCFCs) still lags behind that of oxygen ion-conducting SOFCs [4]. Thus, the fabrication of thin film materials with further improved proton permeability is highly desirable. It has been previously reported that the introduction of a well-dispersed second phase (mostly metals) in BCY/BZY bulk pellets can significantly alter the macroscopic ionic transport properties of the material [5-10]. Generally, an internal reduction mechanism is used to create these two-phase composites by first incorporating the second-phase metal in its oxide form during material synthesis and then converting to the metal during a post-fabrication reduction anneal [6].

In this paper, we demonstrate that pulsed laser deposition (PLD) can be employed to controllably fabricate similar nanocomposite functionalities. The nanocomposite heterostructures are realized by sequentially depositing $\text{BaCe}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCZY) and palladium (Pd) from individual targets in the same vacuum chamber above 500°C. Pd is chosen due to its well established transparency to hydrogen (it is commonly used for...
hydrogen sensing and separation membranes) in the intermediate temperature range of 150-400°C [10-13], while BCZY also possess excellent proton conductivity in this temperature range in humidified atmospheres [14-16]. PLD is used as it provides a route to controllably tune the density of Pd nanoparticles in the nanocomposite, thereby enabling a study of the relationship between film structure and the resulting ionic transport properties. Surprisingly, the BCZY/Pd nanocomposite heterostructures show dramatically reduced electrical conductivity compared to a single-phase BCZY thin film deposited by PLD under the same conditions. Since hydrogen diffusion through Pd is exceptionally fast, the classical expectation is that the nanocomposite should have superior properties to the single-phase bulk BCZY material [17]. However, even in reducing atmospheres, heterostructure conductivity is at least an order of magnitude lower than the thin-film BCZY control sample. Under wet UHP argon, high-density heterostructures have conductivity two orders of magnitude lower than the BCZY control film. Similar declines in conductivity were observed in the SZY/Pt nanocomposite system with increasing volume fraction of Pt [5]. Based on observations from atom probe tomography (APT) the anomalous conduction behavior of the nanocomposite heterostructures is attributed to the formation of an insulating phase (likely PdO) at the interfaces between the Pd nanoparticles and the BCZY matrix. While not likely useful for fuel cell architectures, the large shift in the conductivity of the composite (up to 400X) upon switching from wet 5%H₂ to UHP Ar compares favorably with other PO₂ sensors and therefore suggests potential use for this system in gas sensor applications.
6.3 Experimental

The following section will discuss the various experimental details related to this study. First, the synthesis of the PLD target material and the relevant deposition parameters will be outlined. Next, the instruments utilized in the assessment of the structural properties of our thin film samples will be discussed. Then, details will be provided regarding further preparation of a given specimen for electrical measurements. Finally, we will reveal the settings used in the fabrication of our atom probe tomography sample.

6.3.1 Target and Film fabrication

Powder samples of cerate–zirconate solid solutions having the nominal composition \( \text{BaCe}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_{3-\delta} \) were prepared by a sol–gel modified process. The starting materials were \( \text{Ba(NO}_3\text{)}_2 \) (Sigma-Aldrich, 99+%), \( \text{Ce(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) (Alfa Aesar, 99.5%), \( \text{ZrO(NO}_3\text{)}_2 \) (Sigma-Aldrich, ≥99%), and \( \text{Y(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) (Alfa Aesar, 99.9%) as metal precursors and EDTA (ethylenediaminetetraacetic acid, Alfa Aesar, 99.9%) and citric acid monohydrate (Alfa Aesar, 99-102%) as complexing and polymerizing agents. Ammonium hydroxide (Alfa Aesar, NH\(_3\) 28-30%) was added to promote the dissolution of EDTA in deionized water. After the addition of stoichiometric amounts of the barium, cerium, zirconium, and yttrium salts into a beaker of deionized water, a measured amount of EDTA, citric acid, and ammonium hydroxide were added and the final solution was stirred on a hot plate at 200 °C. Water slowly evaporated resulting in a yellow–brown gel. The dried gel was treated at 150 °C in air until a charcoal was produced. Fine BCZY powders were obtained by calcination in air for 12 h (heating rate 2°C min\(^{-1}\)) at a temperature of 900°C. The resulting powders were axially pressed in the form of cylindrical discs at 30000 psi and sintered for 12 hours in air at 1650°C.

BCZY/Pd nanocomposite thin films were deposited on (0001) sapphire, and (001) 0.7
wt% Nb doped strontium titanate substrates using a KrF excimer laser (Lambda Physics, 248 nm). The laser was operated at a pulse rate of 10 Hz and the number of applied laser pulses changed in order to produce films with varying thickness and nanoparticle density. The laser beam was focused onto a rotating target at a 45° angle of incidence. The target–substrate distance was 5 cm. Prior to introduction inside the deposition chamber, the substrates were cleaned in an ultrasonic cleaner for 10 min with acetone and then isopropanol. All substrates were then blown dry with high purity nitrogen gas. The deposition chamber was initially evacuated to $6.5 \times 10^{-6}$ torr and depositions were conducted under oxygen flow at various temperatures (500-600°C) to form the film/nanoparticle sample morphology. The substrates were attached to the heater with cured silver paste.

6.3.2 Film structural characterization

X-ray diffraction (XRD) patterns were measured on a Bruker Discovery 08 with a large area detector, and on a Scintag X-1 using Cu-Kα radiation. The microstructure and morphology of the layered structures were characterized by observing fractured cross sections using field-emission scanning electron microscopy (FE-SEM, JEOL 7000, Peabody, MA).

6.3.3 Film electrical characterization

Platinum layers (with a chromium sticking layer) were deposited on the back of the niobium doped strontium titanate substrates in order to form an ohmic contact for electrochemical impedance spectroscopy measurements. Palladium and platinum films were deposited on the surface of the heterostructure as rectangular-shaped electrodes for perpendicular conductivity measurements (see Figure 6.1). This geometry ensures that the conductance perpendicular to the film interfaces was measured. Platinum electrodes were deposited on top of the film/stack by electron-beam evaporation and mounted in a temperature controlled tube furnace. Conductivities were extracted from impedance spectra, obtained by a.c. impedance
measurements from 1 to $10^6$ Hz at different temperatures over the range $\sim$100-400°C. The atmospheres tested were wet 5%H$_2$ balance Ar and wet UHP Ar.

### 6.3.4 Atom Probe Tomography (APT) sample preparation

An APT specimen was prepared from a cycled nanocomposite sample using the lift-out technique in a focused ion beam/scanning electron microscope (FIB/SEM) (Helios 600i, FEI, Hillsboro, OR) [21]. A final 2 kV ion-clean with the Ga beam was performed in order to reduce the amount of damage to the material. The specimen was imaged in a TEM (CM200, Philips Electron Optics, Eindhoven, Netherlands) before the APT experiment to assist in the reconstruction of the APT data. APT (LEAP 4000X Si, Cameca, Inc., Gennevilliers, France) was performed using a base temperatures of 30–40 K. Previous literature has determined that an optimized laser pulse energy of 30 pJ is suitable for measuring accurate composition information in the barium zirconate/cerate system [22]. The laser pulse frequency was set to 625 kHz. The data were reconstructed and analyzed using Cameca’s IVASTM 3.6.4 software (Cameca, Inc., Gennevilliers, France).
6.4 Results and Discussion

The following section will discuss the results of the various experiments conducted in this study. The first subsection will present the structural characterization information. Next the discussion will focus on the electrical characterization performed under several testing conditions. Lastly, the results of the atom probe tomography experiment will be discussed and linked with the structural and electrical results.

6.4.1 Nanocomposite morphology and phase

Electron microscopy (Figure 6.2) was utilized to inspect the BCZY/Pd nanocomposite sample morphology after deposition. Figure 6.2a is a top-view secondary electron image that was acquired after a single BCZY/Pd deposition iteration (sapphire substrate). Pd nanoparticles form a well dispersed and non-continuous layer on top of the continuous BCZY layer. The formation of Pd nanoparticles, rather than a continuous Pd film, occurs only at high (500-600°C) deposition temperatures. Pd deposition at lower temperatures results in the formation of continuous films, which retain their structure upon annealing (see Figure 6.3). The Pd nanoparticles appear to be well dispersed across the sample surface and manifest a variety of shapes including circular, triangular, and rod-like. A majority of the Pd particles have diameters in the 20-30 nm range, although the rod-like particles can have a much longer length due to their distorted aspect ratio. The particle coverage in Figure 6.2a is estimated to be ~20%; by changing the number of laser shots applied to the Pd target material during deposition, the particle density can be modified (see Figure 6.2b).

Figure 6.2c presents a backscatter cross-sectional scanning electron microscopy image of a composite film where multiple (in this case three) BCZY/Pd depositions have been performed. By alternating between BCZY and Pd deposition over several cycles, higher order structures
consisting of layers of Pd nanoparticles sandwiched between layers of the proton conducting oxide can be formed. Figure 6.2b was acquired using a backscatter detector, which highlights the compositional differences between the two materials, and confirms that the long-range structure of each “bilayer” is well preserved.

Another important observation is that the layer structure contains no porosity. Thus each BCZY layer deposition fully encapsulates the Pd particles, resulting in a continuous interface between the two constituents.
It should be noted that all composite heterostructures start and end with a BCZY layer, thereby ensuring proton-selective top and bottom contacts to the heterostructure. In order to probe the phase stability of the heterostructures, “post-mortem” XRD was performed on composite samples after heat treatment in both reducing and inert atmospheres using a similar temperature profile to what was used for our impedance measurements (400°C for 1-hr). Since these composites were deposited at temperatures too low to induce epitaxial growth (550°C) the x-ray patterns revealed reflections from multiple crystal planes of various orientations.

Figure 6.4: XRD patterns for BCZY/Pd nanocomposite sample post-annealed in the reducing and “oxidizing” atmospheres used for EIS measurements. The tube furnace temperature was increased to 400°C and allowed to dwell for 1 hr before ramp-down. The sample was subjected to a continuous flow of wet reducing (5%H₂) gas and wet “oxidizing” gas (UHP Ar) throughout the entire ramp profile.

Under reducing conditions (dashed line) both the BCZY and Pd appear to maintain their phase purity (no ternary phase satellite peaks in the examined 2θ range). In contrast, under “oxidizing” conditions (solid line-- UHP argon), the formation of PdO is clearly observed. At the same time,
however, the peak associated with Pd does not disappear, suggesting that the nanoparticles form a shell and core structure under these conditions. Therefore, it is possible that the un-oxidized Pd remains in the particle interior, while the PdO resides on the surface. As we will discuss later, this PdO (a non-proton conducting material) shell formation is likely contributing to the greatly reduced conductivity of the BCZY/Pd nanocomposites in UHP argon atmosphere.

6.4.2 Composite electrical conductivity

Impedance data was measured perpendicular to the “layer” structure for two BCZY/Pd samples hereafter referred to as the “low” density sample and the “high” density sample. The low-density sample has the same coverage as the specimen presented in Figure 6.2a (~20%) whereas the high-density sample has a much larger coverage (~70%). Arrhenius plots were generated from the impedance data (see Figure 6.5) acquired in both humidified 5%H\textsubscript{2} and UHP Ar and are presented in Figure 6.6. Both composite samples show an order of magnitude lower conductivity than the polycrystalline BCZY reference film. Furthermore, conductivity in the wet "oxidizing" UHP Ar atmosphere is drastically lowered an additional ~2 orders of magnitude compared to the BCZY control film at the same conditions (see Figure 6.6). Finally, the conductivity of the “low density” nanocomposite is generally lower than the conductivity of the “high density” nanocomposite, particularly in reducing conditions. Despite the decreased absolute conductivity of the nanocomposite samples compared to the BCZY thin film reference sample, the activation energies calculated for all samples are comparable at ~0.6eV, within the typical range for this class of proton conductors in wet reducing atmospheres (generally 0.5-0.7eV) \cite{20}. The resistance sensitivity of composites, defined as the maximum change (in resistance or resistivity) from the initial state to the final state is
~70X for the high density composite, whereas the low-density sample has a greater average sensitivity ~170X (made greater by the deviation in the UHP Ar data at lower temperatures). This change in conductivity between the two atmospheres is comprised of two effects. The first is a fundamental change in the conductivity of the BCZY matrix material. This 5X average conductivity decrease, exhibited by the BCZY film when switched from 5%H₂ to UHP Ar, is the result of a drop in the number of protonic carriers introduced into the structure by the inert gas [9]. The second (and more pronounced decrease 14-32X) is the result of the PdO formation in the “oxidizing” atmosphere. The reversibility and response/recovery times are still unknown for these composites, but the sensitivity is comparable to other metal oxides in this intermediate temperature range [19]. The recovery/response speed of the BCZY/Pd nanocomposite to changes in the atmosphere between wet UHP Ar and 5% H₂ at 360 °C is slow compared to other technologies (see Figure 6.7). The absolute difference in conductivity between the two atmospheres when alternated on a 30 minute time scale is less than the two orders of magnitude difference when the specimen is completely stabilized in the various atmospheres. This smaller conductivity delta is probably a combination of the inherent changes in the BCZY material and the onset of oxidization of the Pd particles. The multiple order of magnitude difference in conductivity can only be achieved if the stabilization time is drastically increased.

The decreased conductivity of the BCZY/Pd nanocomposites compared to pure BCZY in reducing atmospheres is surprising given that hydrogen transport through Pd is very high [11]. Classical composite modeling would suggest that the two-phase system should have a much greater total ionic conductivity than the unmodified control and that conductivity should increase
Figure 6.5: Typical Nyquist plot for A) BCZY single-film B) BCZY/Pd nanocomposites with included circuit model fit in 5%H₂ C) BCZY/Pd nanocomposites with included circuit model fit in UHP Ar
Figure 6.6: Conductivity vs. reciprocal temperature for BCZY/Pd composites of differing Pd nanoparticle density. Also included is an idealized model for the (20 vol. fraction) nanocomposite sample assuming that spherical particles and that the Pd phase is infinitely conducting compared to the BCZY host matrix.

with increasing Pd loading [17]. An idealized conductivity model involving spherically shaped particles distributed randomly in a host matrix is given by the following [17]:

\[
\sigma_{\text{comp}} = \sigma_{\text{matrix}} \left( \frac{1}{1-3f} \right)
\]

(6.1)

where \( f \) represents the volume fraction of the particles. This model is plotted in Figure 6.6 as a dashed line (for 20% vol. fraction Pd). This model makes several generalizations. The most important is that the particles are assumed to be perfect conductors. In reality the diffusion coefficient for hydrogen through pure Pd is only 2 orders of magnitude greater than proton
diffusion through BCZY in our temperature range [11,18]. Nevertheless, this model provides an upper bound on the expected behavior of our low density composites.

Figure 6.7: Response of the nanocomposite upon switching the atmosphere from humidified UHP Ar to 5%H₂ at 360°C.

Our measured composite behavior falls significantly below the model prediction. In contrast, previous studies of bulk BCZY/Pd composites have all found positive enhancements in conductivity and/or fuel cell performance [6,7]. There could be several reasons for this apparent conflict. The solubility of hydrogen in Pd is large (much higher than BCZY) at low temperatures, but there is a sharp decrease in its solubility occurring at temperatures near 150°C coinciding with the decomposition of the metal-hydride system [11]. Thus, for the conductivity measurement temperatures investigated here (150-400°C) the equilibrium hydrogen atom concentration in the Pd particles is relatively low. The true H/Pd ratio at our conditions has not been established, but the small pressure exerted by the hydrogen molecules in our gas stream (5%H₂ in Ar) is not sufficient to force any appreciable uptake. The low conductivity of the BCZY/Pd nanocomposites could therefore at least partially be associated with reduced solubility
of the protons in the Pd nanoparticles compared to the BCZY matrix. Perhaps the most likely explanation for the nanocomposite behavior, however, is the development of a high resistance to proton transfer across the Pd/BCZY interface. PdO formation is clearly observed in the nanocomposite samples under oxidizing conditions (solid-line XRD pattern in Figure 6.3). Despite the absence of this secondary phases under reducing conditions (dashed line XRD pattern in Figure 6.3), Pd is known to incorporate into the perovskite B-site under reducing conditions [6-9], and therefore we cannot rule out the possibility of atomic level intermixing between the particles and the host matrix and/or the formation of a thin second phase between the Pd and BCZY that is below the limits of XRD detection even under reducing conditions.

6.4.3 Atom probe tomography of BCZY/Pd nanocomposites

The possibility that a thin non-conducting/undesirable phase develops between the Pd nanoparticles and the BCZY bulk (even under reducing conditions) as a result of the high substrate temperatures present during the PLD process was examined via atom probe tomography (APT). The low-density nanocomposite sample was selected for APT analysis. APT analysis was conducted on the specimen after it had been subjected to impedance measurement in both oxidizing and reducing conditions (reducing step last). APT generates a high electric field applied between a needle-like specimen (fashioned with a focused ion beam –FIB) [21] and a local electrode to deconstruct the sample atom-by-atom and generate a 3-dimensional atomic level reconstruction of the sample. For most complex oxide materials, the laser pulse energy used for APT measurement has a significant effect on the apparent stoichiometry. Previous work on BCZY has shown that laser energies in the range of 20-30 pJ ensure optimal stoichiometric quantification in this material [22]. We therefore employed these previously optimized conditions in this study as well.
The total mass spectrum collected for our low-density sample is shown in Figure 6.8. In general, the peaks are isolated from one-another and have been labeled to identify the collected species. The subplots of Figure 6.8 are integrations of the mass spectrum in regions of interest (specifically in areas where the two phases are spatially isolated from each other). The insets of these subplots indicates that the total mass spectrum has a small amount of peak overlap between the Pd$^{2+}$ and the YO$^+/ZrO^+$ peaks in the ~100-120 m/z range. Fortunately, additional YO and ZrO peaks at lower m/z values allows for the deconvolution of the peak overlap and permits accurate measurements of sample composition Figure 6.9 includes a bright field transmission electron microscopy (TEM) image of the low-density BCZY/Pd sample prepared for atom probe analysis. As with the cross-sectional FESEM results, the TEM image clearly shows the presence of Pd nanoparticles sandwiched between the proton conducting oxide layers. The reconstruction of the BCZY/Pd tip is also included in Figure 6.9 adjacent to the TEM image, and the reconstruction is rotated such that the two images are of the same orientation. For clarity, only three signals are overlaid to create this reconstruction image. The barium and oxygen signals are represented by the blue pixels, and the yellow spheroids are palladium iso-surfaces at a concentration of 85%. The top view image of the reconstruction reveals additional Pd nanoparticles in the same plane but hidden behind the particles in the forefront (not resolved in the TEM micrograph). The arrows in the top view image indicate the distance over which analysis of the chemical composition of the particles and adjacent region was performed. The average Ba/(Zr+Ce+Y) ratio across the bulk of the BCZY layer (where no Pd is present) was calculated to be 98.8%, which indicates that the cation stoichiometry was well preserved between the PLD target and the thin film (within the error bars of APT). The one major discrepancy is the low measured oxygen signal (~45 at% oxygen) compared to stoichiometric
Figure 6.8: Total mass spectrum measured by atom probe tomography. This total spectrum is a linear combination of the bulk BCZY and Pd particle mass spectrums as indicated by region of interest integrations. The insets in each region of interest mass spectrum highlight peak overlap in the 100-120 m/z range.
Figure 6.9: TEM image of BCZY/Pd tip fashioned with FIB prior to APT analysis and corresponding APT reconstruction. Concentration profile across the region indicated with arrows in the top view reconstruction and a magnified inset of the transition region between the Pd particle and the BCZY bulk.
BCZY (60 at% oxygen). Since these films were deposited by PLD in a vacuum chamber (with only a small O\textsubscript{2} flow rate), some decrease in the oxygen content is expected, although the large apparent decrease measured here is surprising. Accurately reproducing oxygen stoichiometry in complex metal oxides via APT is extremely challenging and it therefore likely that much of this apparent stoichiometric discrepancy is due to non-optimal APT calibration. Within the Pd nanoparticles, the Pd fraction is high (>95 at% for most particles), but some particles manifest appreciable oxygen content (~10 at% oxygen in some cases). Thus, even though the sample was subjected to impedance testing under reducing conditions (5% H\textsubscript{2}) immediately prior to APT analysis, this result indicates that some of the nanoparticles are at least partially oxidized. The inset in Figure 6.9 provides a magnification of the compositional profile at the transition between the Pd particle and the BCZY bulk. From this profile, it is clear that there is a region approximately 10nm thick where the Pd and the BCZY signals significantly overlap. This interfacial region, which is thin enough that it is not detected by XRD, is thick enough to cause high interfacial proton transport resistance in the BCZY/Pd nanocomposite samples. However, additional data is required to prove that this interfacial layer indeed exists and is not simply an artifact of the atom probe data acquisition.

6.5 Conclusions

Atom probe tomography discovered the possibility of atomic scale intermixing in BCZY/Pd nanocomposites at the particle/bulk interface (despite the acquisition of pure phase XRD patterns). This thin region of interdiffusion is a likely cause of the poor electrical performance of our nanocomposite samples (in wet reducing atmospheres) compared to single-phase thin films (especially since our particle coverage was very high). The sensitivity of these nanocomposites after switching between reducing and oxidizing atmospheres is between 70-
170X on average depending on the particle loading. This change in resistance originates from two processes. The first is the fundamental change (~5X) in the BCZY conductivity when switched to an atmosphere with a lower number of carriers. The second is related to the formation of PdO upon annealing in wet UHP Ar atmospheres created a blocking phase resulting in a large decrease in proton conductivity (~14-32X). Additional experiments must be conducted to ensure that this process is reversible, and with sufficiently fast response times to be suitable for gas sensing applications.

6.6 References


CHAPTER 7
THE ROLE OF NANOSCALE SEED LAYERS ON THE ENHANCED PERFORMANCE OF NIOBIUM DOPED TiO$_2$ THIN FILMS ON GLASS

Modified from a paper to be submitted to Scientific Reports

Stefan Nikodemski$^{1,3}$, Arrelaine A. Dameron$^2$, John D. Perkins$^2$, Thomas Gennett$^2$, Ryan P. O’Hayre$^{1,5}$, David S. Ginley$^{2,5}$, and Joseph J. Berry$^{2,4}$

7.1 Abstract

Transparent conducting oxide (TCO) coatings with decreased cost and greater process or performance versatility are needed for a variety of optoelectronic applications. Among potential new TCO candidates, doped titanium dioxide is receiving particular interest. In this study, niobium-doped titania bilayer structures consisting of a nanoscale seed layer (deposited by atomic layer deposition or RF magnetron sputtering) followed by a thick bulk-like layer were grown directly on glass in order to examine the effects of the seed layer processing on the subsequent crystallization and electrical properties of these heterostructures. We show that creating an oxygen-rich crystalline seed layer on glass is critical to the development of high conductivity (>1000 S/cm) anatase-TiO$_2$ films produced by successive deposition of the bulk-like layer in a low oxygen partial pressure environment with subsequent annealing. Observations from Raman spectroscopy suggest that the higher oxygen content in the seed layer suppresses the formation of detrimental titania polymorph phases, found in films produced by annealing directly after synthesis without any exposure to oxygen. Our results indicate that the generation of excellent Nb:TiO$_2$ conductors on glass (without breaking vacuum) only occurs within a narrow processing range and that the sequential deposition of oxygen-poor layers on oxygen-rich layers

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1 Staff associated with the department of Metallurgical and Materials Engineering, Colorado School of Mines
2 Staff associated with the National Renewable Energy Laboratory, experimental assistance
3 Graduate Student, primary researcher, and author
4 Corresponding author
5 Co-advisors of graduate student
is a critical step towards achieving films with low resistivity.

7.2 Introduction

New high-performance yet low-cost transparent conducting oxide (TCO) contacts are needed for high-efficiency optoelectronic applications. Many of these applications rely on indium-based TCOs, most commonly indium tin oxide, or ITO. There are, however, concerns regarding the abundance of indium and resulting material reserves as it relates to future ITO availability and costs [1-5]. Anatase titania (TiO$_2$) has been shown to be a viable candidate for TCO applications [8-10]. Upon doping with niobium (optimally between 3-6 at.%) [8-10], titania shifts from non-metal to metallic-like properties resulting in both high electrical conductivity and high optical transmittance. For anatase TiO$_2$ thin films with Nb doping in this ideal range deposited on single crystal substrates, the resistivity is comparable to that of conventional ITO films [8-11].

Presently, the best Nb-doped TiO$_2$ (TNO) films have been achieved by physical vapor deposition on epitaxially-matched single crystal substrates such as LaAlO$_3$ and SrTiO$_3$ [8-11]. Generally, studies involving TNO films grown on these high quality substrates (with subsequent high temperature anneals in reducing atmospheres) result in both high conductivity (in some cases ~3000 S/cm) and moderate transparency (60-80% for films ~200nm thick) [8]. For films on these substrates, the epitaxial relationship between the substrate and the doped titania stabilizes the high mobility anatase phase while excluding the lower mobility rutile phase [6-9]. However, large-scale production of TCO films on crystalline substrates is costly and technologically limiting, thus alternative substrate choices (such as glass) are more attractive for a broader range of industrial applications. Recently, significant efforts have been undertaken to translate these results from crystalline substrates to non-epitaxial systems [9]. Studies of TNO
films deposited directly on glass have concluded that the most crucial growth parameters influencing the final crystalline phase are deposition/annealing temperature and gas pressure/composition [12,13]. However, only samples subjected to harsh annealing conditions (high temperatures of ~600°C in pure H₂) produce the most conductive and transparent films. This high temperature reducing anneal is required to produce larger crystalline domains (thus reducing grain boundary scattering), which is made difficult by the amorphous nature of the substrate. One method to improve the crystal growth of oxides is to use seed/buffer layers to act as an intermediary phase between the film and the amorphous substrate surface [14]. Recently, several studies investigating the effect of nanoscale seed layers on the growth orientation of pure and doped TiO₂ on glass have been conducted [15-20]. Yang et al. showed that a bilayer SrTiO₃/TiN template grown by physical vapor deposition on glass substrates produces anatase thin films with uniaxial c-axis orientation [15]. Hoang et al. reported some promising results, whereby low temperature sputter deposition of an initially amorphous oxygen-rich Nb-TiOₓ film followed by a thicker oxygen-deficient Nb-doped TiOₓ film with a subsequent rapid thermal treatment produced structures with high conductivities (~1000 S/cm) [16]. While this approach has achieved conductivities close to ~1000 S/cm, this method has yet to rival the epitaxially grown materials. In addition, it is still unclear what the impact of doping concentration in the TiO₂ layer has on the phase stability. Shibata et al. [17,18], Yamada et. al. [19], and Taira et. al. [20] have conducted a significant amount of research utilizing Ca₂Nb₃O₁₀ nanosheets with a 2D perovskite structure to template the growth of high quality, (001) oriented anatase films, which in some cases (when combined with PVD deposited Nb-doped TiO₂ films) have succeeded in significantly enhancing the carrier transport properties.

In this study, a design-of-experiments matrix based on a survey of reported results was
developed to gain insight regarding the key deposition parameters along with resulting physical properties of the seed and bulk layers (structural phase, dopant concentration, crystallinity, oxygen content, and annealing time) ability to control desirable TNO film properties leading to desirable electronic properties (high carrier concentration and mobility) leading to high electrical conductivity. The seed layers were fabricated using both atomic layer deposition (ALD) and RF magnetron sputtering. ALD TiO$_2$ seed layers were deposited at low and high temperature with various thicknesses using two different titanium precursors (TiCl$_4$, Ti[OCH(CH$_3$)$_2$]$_4$) and two different oxygen sources (H$_2$O, H$_2$O$_2$). Sputtered TNO seed layers of varying thickness and oxygen content were deposited immediately prior to the deposition of the bulk TNO film in the same chamber without breaking vacuum. The bulk layer film had a constant thickness of ~140nm. After deposition, the seed+bulk layer films were annealed at various temperatures under reducing atmospheres (both *in-situ* and *ex-situ*), to clarify the effect of post deposition oxygen exposure and annealing temperature on film properties. For specific procedural conditions see Table 7.1 in the experimental section.

It is believed that the stabilization of the anatase phase in the seed layer (which subsequently acts as a nucleation center for the bulk film crystallization during annealing) is critical to achieve high conductivity films. We confirm this by demonstrating that both ALD and sputter seed layers can form stable anatase seeds on glass that enables subsequent crystallization of the overlying layer at around 300 °C. Further heating causes the activation of the niobium dopant, releasing additional electronic carriers into the conduction band. This seed layer + overlying layer strategy results in films with vastly superior electrical properties compared to monolithic films deposited directly on glass (i.e., without a seed layer) under equivalent conditions (~2-3 fold improvement). Furthermore, our results suggest a key guiding principle to
achieve films possessing high phase purity and high electrical conductivity is related to the oxygen content in the underlying seed layer. Only by depositing sputtered seed layers in oxygen rich environments can the formation of detrimental titania polymorph phases be suppressed.

7.3 Experimental

Corning Eagle\textsuperscript{2000} (E2K) glass slides were prepared by ultrasonic cleaning while soaking in acetone and isopropyl alcohol solvents (10 minutes each). The films studied in this work were deposited using the ALD and sputtering methods. To deposit the films, the substrates were alternately exposed to the Ti precursor and oxygen precursor In order to ensure layer-by-layer growth, the reaction zone was purged after each precursor pulse. The substrate temperatures used for deposition ranged from 100 to 300\degree C.

Our sputtering targets were all 2-inch diameter disks with composition of $\text{Ti}_{0.90}\text{Nb}_{0.10}\text{O}_2$, $\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_2$, and undoped $\text{TiO}_2$ (99.9\% purity). The base pressure achieved prior to each deposition was $5\times10^{-6}$ Pa. A mixture of Ar and O\textsubscript{2} at various flow rate ratios maintaining a total system pressure of 1.0 Pa was utilized during deposition. The RF power applied to the target was kept constant at 75W. Preceding each deposition, the target surface was first sputter-cleaned in pure Ar for several minutes and subsequently pre-sputtered for 10 min using the same gas flow ratio and total pressure as for the bulk film. The as-deposited films (when amorphous), were crystallized by annealing in the deposition chamber under vacuum (no gas flow). The substrate temperature during deposition/annealing was confirmed using a thermocouple under the same pressures achieved during post treatment processes.

We first deposited a variety of seed layers directly on E2K glass by sputtering and atomic layer deposition (ALD) and subsequently grew thick TNO layers (also by sputtering) with varying oxygen content (typically $O_2$ deficient). Samples based entirely on sputtering were
performed in the same chamber, thus eliminating the need to break vacuum. For the sputtered seed layers, we elected to vary a number of parameters including seed thickness (5-30 nm), doping concentration (undoped, 5% Nb, and 10% Nb), and oxygen content (5%-50% flow rate O₂). Pure TiO₂ ALD seeds were grown incorporating several additional factors (precursor chemistry, crystallinity, and annealing duration).

<table>
<thead>
<tr>
<th>Deposition variables</th>
<th>ALD seed layers</th>
<th>Sputtered seed layers</th>
<th>Bulk TNO layers on seed layers</th>
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<tbody>
<tr>
<td>Ti precursor</td>
<td>TiCl₄, Ti[OCH(CH₃)₂]₄</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>H₂O, H₂O₂</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dep. temp (°C)</td>
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<td>RT</td>
<td>RT, 550</td>
</tr>
<tr>
<td>Anneal temp (°C)</td>
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<td>550</td>
<td>200 - 550</td>
</tr>
<tr>
<td>Anneal time (hrs.)</td>
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<td>2</td>
<td>2-18</td>
</tr>
<tr>
<td>Oxygen flow rate ratio (%)</td>
<td>-</td>
<td>0 - 50</td>
<td>0 - 30</td>
</tr>
<tr>
<td>Thickness (nm)</td>
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<td>140</td>
</tr>
<tr>
<td>Niobium content (at. %)</td>
<td>0</td>
<td>5, 10</td>
<td>5, 10</td>
</tr>
</tbody>
</table>

The figures of merit were represented by electrical conductivity and anatase signal intensity from Raman spectroscopy. Note, due to fluctuations in the anatase signal at high magnifications (100×), we opted to reduce the magnification power to 20× in order to sample a larger portion of the film surface. This way, the microscopic variations in the signal intensity are averaged out in a single spot scan. Typically, correlation factors range from +1 to -1, and values...
near these endpoints indicate strong correlations (positive and negative, respectively) between the growth parameter and the figure of merit. Values approaching zero imply little/no association. In this situation, we have calculated and plotted the absolute value of these correlation factors, and are only interested in growth parameters that result in a large interdependence with the figures of merit.

For the x-ray annealing experiments, all samples were heated at 1°C/min to a maximum temperature of 500°C in flowing N\textsubscript{2} while simultaneously acquiring diffraction data. N\textsubscript{2} was used in order to decrease the oxygen partial pressure during the experiment in order to more accurately represent the annealing conditions in the sputter system vacuum chamber. The samples dwelled at the highest temperature for several hours (~8) to measure changes in the crystal phases present at longer annealing times.

Conductivity measurements were conducted using a standard 4-point probe setup. Crystallographic structure and orientation were characterized by X-ray diffraction (XRD) measurements using a two-dimensional detector (Bruker, D8 Discover with GADDS) and Raman spectroscopy. Film smoothness and long-range characteristics were examined by field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). Film thickness was determined using spectroscopic ellipsometry and independently confirmed with FESEM. In order to determine the crystallization temperatures as a function of seed layer, we conducted XRD hot-stage experiments under N\textsubscript{2} flow.

7.4 Results and Discussion

The following section will discuss the results of the various experiments conducted in this study. The first portion will present the structural characterization information (including X-
ray diffraction and Raman mapping results). Finally, the relationship between the measured structural information and electrical characterization will be discussed.

7.4.1 In-situ XRD annealing

To understand the influence of the seed layer on the crystallization of the Nb doped TiO$_2$ film we performed a series of in situ XRD annealing experiments. Figure 7.1 plots the x-ray intensity (in the 25.5° anatase peak region) as a function of both 2θ and substrate temperature for 140 nm thick TNO films deposited on optimized 30 nm thick ALD and sputtered TNO seed layers as well as a control sample consisting of an 140 nm thick TNO film deposited directly on the glass substrate without a seed layer. For complete scan information with standard x-ray reference patterns for both anatase and rutile phases, see Figure 7.2. The fluctuations in the x-ray intensity (observed most prominently in the 20-35° range) are the result of background subtraction. The Anton Paar DHS 900 dome used to encapsulate the samples (and trap the N$_2$ purge gas) has a very intense x-ray signature, and the associated peaks are difficult to completely eliminate. Nevertheless, diffraction patterns were recorded as Debye ring patterns in a two-dimensional detector image, and the XRD results after background corrections clearly indicate that randomly-oriented polycrystalline TiO$_2$ films were obtained. All samples (including the control) were found to be anatase phase for our set of annealing conditions (see Figure 7.2). One clear distinction between the seed-based samples and the control sample is the temperature at which the onset of crystallization occurs (Figure 7.1a). In order to better visualize the temperature onset of crystallization, the integrated intensity of all anatase peaks was calculated, averaged, and plotted as a function of temperature in Figure 7.1b. TiO$_2$ crystallization for all samples, regardless of seed properties, occurred in the temperature range of 260-320°C and is concluded within a short time span (30 minutes). The presence of crystalline ALD seed layers
and oxygen rich sputtered seed layers produced films that crystallized at the low end of this temperature range (260°C) while the absence of a seed layer in the control sample delayed crystallization to the upper end of this temperature range (330°C). The negligible difference in the crystallization temperature of a thicker TNO layer with an underlying oxygen rich sputtered seed layer (crystalline or amorphous) may indicate that a high oxygen content in the seed layer leads to the reduction of the nucleation energy barrier.

Figure 7.1: A) Magnification of the 25.5° anatase x-ray peak for Nb:TiO₂ films deposited on seed layers as well as directly on glass. B) Temperature dependence of Nb:TiO₂ film phase formation (produced from the average integrated intensity of all anatase x-ray peaks).
On the other hand, initially amorphous ALD seed layers (deposited at low temperatures ~100°C) clearly do not lead to a reduction in this energy barrier for film crystallization, as these films have a similar crystallization onset as the control sample. Another key observation from these experiments is the variation in the average integrated x-ray intensity despite all films being the same thickness. For samples with sputtered seeds (whether crystalline or amorphous), the average integrated intensity is relatively similar, and it was found that the electrical properties of the sputtered samples were also comparable. This suggests that the final crystallite sizes are
approximately equal and lead to near identical rates of electron scattering. However, TNO films deposited on crystalline versus amorphous ALD seed layers resulted in markedly different behavior. Compared to their amorphous ALD counterparts, TNO films deposited on crystalline ALD seed layers exhibited a much higher average integrated intensity upon annealing (see Figure 7.1b) and growth oriented along particular crystal planes (see Figure 7.2 – compare “crystalline ALD seed” with “no seed”). The PVD deposited samples also showed preferred orientation compared to the control sample, particularly the lower relative intensity of the (004), (105), and (211) planes in favor of more intense (101) and (200) crystal planes.

7.4.2 Raman mapping

Due to the low spatial resolution of our 2D x-ray detector, Raman spectroscopy using a confocal microscope (100x objective) and a Nd\(^{3+}\):YAG laser with an operational wavelength of 532 nm was additionally used to spatially resolve the crystal phases of the annealed heterostructures. Additionally, Raman spectroscopy is also very sensitive to minor impurity phases present in our films that otherwise might go undetected by XRD. Spatial maps of the films measuring 10 microns \(\times\) 10 microns were constructed by combining sequential line scans across the sample. In our case, only XY information (resolution \(\sim\)250 nm) is available and the measured phase at a given position represents an average through the entire film thickness. Both anatase and brookite polymorphs are observed in our films by Raman spectroscopy. The observation of brookite in our films is surprising since rutile is the more commonly observed and thermodynamically stable TiO\(_2\) polymorph. Nevertheless, the presence of the brookite polymorph in our films is strongly reinforced by direct comparison to Raman measurements of single crystal brookite mineral samples using the same system (Figure 7.3). The relative intensity of the anatase and brookite signals can be deconvoluted (see Figure 7.3) by modeling each spot
scan with a linear combination of pure phase spectra (with different weighting factors). By taking a ratio of the two signals, we can estimate the anatase to brookite fraction. These values are plotted in Figure 7.4.

Because of the small percentage of brookite in the films, each graph is plotted on a log scale to better resolve contrast between regions with “high” to “low” brookite content. Thus, a value of 0.0 would represent a 50/50 mixture between the brookite and anatase phases; a value of 1.0 would be a 10:1 ratio of anatase to brookite and so on. Each sample was annealed in vacuum to a maximum temperature of 540°C for 2 hrs immediately following deposition and subsequently mapped. A histogram of the intensity ratios was generated for each sample and is included beside each corresponding Raman map.

Figure 7.3: Raman spectra for various TiO$_2$ polymorph samples. The highlighted regions provide an example of the integrated peak intensity used to calculate the impurity ratios for bulk films. Note, these spectra are presented to highlight the regions of interest and have not been subjected to any background subtraction (which is required for the calculation of the anatase/impurity ratio).
The control sample (TNO deposited directly on glass) has mixed phase behavior where the ratio of the weighting factors (between the anatase and brookite phases) in the Raman spectra deconvolution ranges from 10-100:1 (closer to 30:1 given the histogram peak value of \( \sim 1.5 \)). TNO films deposited on thinner (~5 nm) ALD seed layers show very similar post-anneal structure to the control sample. However, the anatase-to-brookite ratio has a slightly higher average value (50-60:1) in this case, which is indicated by a shift in the histogram peak to greater values. TNO films deposited on thick (30 nm) ALD seed layers as well as on oxygen-rich sputtered seed layers achieve the greatest degree of anatase fraction. In these cases, the brookite fraction is extremely low and is only just above the background signal. The majority of the film

Figure 7.4: Raman mapping results for Nb:TiO\(_2\) films. Maps are plotted on a log scale. Histogram of anatase fraction values for a variety of seed layer samples and the control.
has an anatase to brookite ratio on the order of 100-1000:1 (with some regions achieving even higher fractions). The thickness of the sputtered seeds has little impact on the anatase-to-impurity ratio as observed by Raman mapping. The more important deposition parameter affecting this ratio is the oxygen content of the seed. We found that the brookite phase is suppressed as long as the underlying seed layer has high oxygen content (see Figure 7.5). One critical difference between the Raman and XRD experiments was the exposure to the ambient environment. XRD samples were necessarily exposed to ambient air before the experiment commenced whereas Raman mapping specimens were annealed in the vacuum chamber directly following deposition. Therefore, short-term O₂ exposure could have resulted in changes to the nature of the phases present post-annealing.

Figure 7.5: Peak value and FWHM of the Raman mapping data (Gaussian fit) histograms for sputtered TNO5 samples with different oxygen flow rates for the seed layer deposition.
Atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM) were used to evaluate the smoothness and long-range morphology of the films. These observations confirm that variations in the Raman intensity were not the result of roughness fluctuations in the film and substrate (see Figure 7.6). From Figure 7.4 it is clear that the anatase/brookite domain sizes are on the micron scale for the control sample deposited directly on glass, and become substantially larger for films deposited on oxygen-rich sputtered seed layers. Once the anatase domain size has reached a critical value, the likelihood of a continuous anatase area, which extends the length of the sample, becomes very high. Thus, an increase in the domain size is likely responsible for the excellent electrical properties of the sputtered TNO heterostructures.

Figure 7.6: AFM and FESEM images showing the surface morphology/roughness after bulk Nb:TiO$_2$ deposition. A) ALD seed+bulk TNO layer after dep. B) sputtered seed+bulk TNO film after annealing C) Top view FESEM image of ALD+bulk TNO sample.
7.4.3 Ex-situ and Hall effect electrical transport measurements

An ex-situ annealing experiment was performed which measured the resistance of a TNO film (deposited on a oxygen rich seed layer) as a function of temperature under a reducing gas environment (5% H₂ by vol. bal. Ar). The aim of this experiment was to establish a complete conductivity profile as a function of the anneal temperature. The data was collected in traditional 4-point probe fashion with four collinear contacts and the results are plotted in Figure 7.7. During the initial stages of annealing, the film resistance begins to decrease around 300°C. A second, more pronounced decrease in the resistance occurs once the sample attains the anneal hold temperature of 500°C, where it dwells for 1.5 hrs. This data is directly correlated with the sample resistivity, via a geometric factor associated with the sample and contact geometry, and was used to identify annealing conditions to examine the nature of this resistance trend in more detail via Hall analysis (see Table 7.2).

![Figure 7.7: In–situ conductivity measurements plotted vs. annealing temperature and time. Temperature dependence of anatase x-ray intensity compared with film resistance.](image)

The Hall analysis addresses a potential pitfall of the ex-situ annealing experiments. While in the tube furnace, the sample is free-floating and is not in direct contact with the alumina tube.
Despite the slow ramp rate (1°C/min), the sample may not have reached a true thermal equilibrium with the annealing environment. Therefore, the annealing experiments were used to identify four temperature regions of interest that require further investigation. Hall measurements were then subsequently conducted on 140 nm thick TNO films deposited on top of sputtered-seed layers (5 nm thick). Each of these samples was annealed immediately post-deposition in the vacuum of the sputtering system to a temperature within each region of interest for 2 hrs. Based on the Hall data, the initial decrease in resistivity is likely the result of niobium dopant activation. The “hump” in the sample resistivity at around 325°C appears to be the result of a change in the mobility. The observed double minimum in the mobility around this temperature is a curious result, as the XRD for all seed layer samples shows an absence in structural changes after the initial crystallization. However, this lack of structure change could be masked by the limitations of our XRD instrument.

Table 7.2: Detailed Hall effect measurements corresponding to regions of interest in in-situ annealing

<table>
<thead>
<tr>
<th>Annealing Region</th>
<th>Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Carrier Concentration (cm⁻³)</th>
<th>Resistivity (ohm cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>1×10¹⁷</td>
<td>54</td>
</tr>
<tr>
<td>II</td>
<td>3.8</td>
<td>1.07×10²¹</td>
<td>1.5×10⁻³</td>
</tr>
<tr>
<td>III</td>
<td>2.6</td>
<td>1.28×10²¹</td>
<td>1.88×10⁻³</td>
</tr>
<tr>
<td>IV</td>
<td>4.5</td>
<td>1.39×10²¹</td>
<td>1×10⁻³</td>
</tr>
</tbody>
</table>

Bulk TNO films deposited on thinner sputtered seeds outperformed (conductivity) all other seed layer types regardless of thickness. Whilst higher temperatures produced films with better electrical properties given a constant annealing time, it is currently unknown if a sufficiently
long anneal at lower temperatures will produce films with equivalent resistivity values. As a
sanity check, the transmission/reflection characteristics of our 5% Nb doped TiO$_2$ samples were
tested and a transparency between 60-80% was obtained even for the most conductive samples
(see Figure 7.8). Hall measurements were also conducted on TNO films deposited on ALD seed
layers. In this case, the temperature was maintained at a constant 540°C and the annealing time
was varied. Optimum performance of these materials is achieved with an anneal lasting
approximately 2hrs. If the duration of this anneal is increased substantially (18 hrs.), the
performance of these samples is worsened. This dip in electrical properties is the result of a
mobility decrease at the long anneals times.

![Transmission and Reflectance](image)

Figure 7.8: Transmission data for high conductivity (>1000 S/cm) sputtered seed layer sample -
5% Nb doped TiO$_2$ composition on E2K glass.
7.4.4 Design of experiments

Correlation factors calculated from the analysis of the design of experiments are plotted in Figure 7.9. The two most important parameters in achieving films with a high degree of anatase are sputtering on thicker (30 nm) seed layers and deposition of the bulk film in a high oxygen partial pressure (PO$_2$). The major factors impacting conductivity are bulk deposition in low PO$_2$ and Nb content. 10%Nb doped TiO$_2$ films were found to be far less conductive than their 5%Nb counterparts despite being annealed at the same temperature and equivalent durations. This is likely due to the decrease in doping efficiency, increased dopant-dopant association, and increased dopant-scattering with increasing Nb content (above 6%) [9]. The doping concentration in the bulk film showed no correlation with anatase phase formation. Instead, O$_2$ pressure during the deposition of the bulk film was highly correlated and associated with the formation of the anatase phase.

![Figure 7.9: Design of experiments results plotting the film/seed deposition parameters against the figures of merit.](image)

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However, samples produced with bulk layers deposited in a high $\text{PO}_2$ tend to have relatively poor electrical properties. We speculate that low oxygen pressure during deposition results in large quantities of oxygen vacancies in the bulk lattice. In order to preserve charge neutrality, these vacancies are compensated with electronic defects. Thus oxygen-rich films essentially quench these additional electronic carriers ultimately resulting in high resistivity. Additionally, oxygen-rich conditions increase the formation enthalpy of $\text{Nb}^{+}_{\text{Ti}}$ donors, while the compensating Ti vacancies form with higher probability, and consequently the effective dopant activation is determined by the oxygen content of the as-grown material [25]. Thus, large anatase intensity is not necessarily a good indicator of a highly conductive film. Nonetheless, our results indicate that the mechanism behind the improvement in film properties is the stabilization of the anatase phase in the seed layer, which subsequently acts as a nucleation center for the bulk film crystallization during annealing. The bulk film must be oxygen deficient for high conductivities to be achieved. Additionally, these results confirm previous hypotheses regarding the role of the seed layer on the enhancement of structural and electrical properties of TNO heterostructures [16].

The key results from the Raman mapping, XRD annealing, and Hall effect experiments is summarized graphically in the Figure 7.10 illustration. It provides a roadmap schematic, which can be employed to predict the post annealing bi-layer TiO$_2$ structure and provide some insight into the electrical properties based on the seed layer deposition parameters. TNO films deposited directly on glass show a polycrystalline structure with high levels of titania polymorph impurities. This leads to poor electrical performance compared to bulk TNO films deposited on seed layers.
7.5 Conclusions

The impact of an underlying interfacial seed layer was clarified by carefully examining the dependency of bulk TNO film properties (phase purity, resistivity) on key seed/deposition parameters. This careful analysis relied on Raman spectroscopy, which allowed us to observe the structure and spatial distribution of minor impurity phases that were difficult to resolve with conventional XRD experiments. Our results suggest a key guiding principle to achieve films possessing high phase purity and high electrical conductivity is related to the oxygen content in both the seed and bulk layers. Fabrication of low resistivity TNO bilayer films on glass is realized for heterostructures consisting of an oxygen-rich base layer immediately followed by an
oxygen-deficient bulk layer. In this way, detrimental titania polymorphs phases are suppressed while dopant activation occurs at moderate temperatures.

7.6 References


CHAPTER 8
SUMMARY AND CONCLUSIONS

In this final chapter, a general summary of the work accomplished from each section of this dissertation is presented. Finally, the chapter is concluded with a few recommendations for future research.

5.1 General Discussion

In this thesis, we focused on the fabrication of nanocomposites (based on proton conducting perovskite oxides and transparent conducting oxides) with various structures and studied how changes in morphology impacted the resulting electrical properties. For proton conducting heterostructures, order of magnitude enhancement and depletion were observed in oxide/oxide and oxide/metal heterostructures, respectively. This modification in electrical properties was found to coincide with a high spatial density of junctions between the two composite constituents. It was hypothesized that ionic conductivity parallel to BCZY/STO interfaces was enhanced (in layers ~5 nm thickness) due to the accumulation of positive protonic charge carriers on the BCZY side of the interface. This has the possibility, in essence, to create a superprotonic highway that allowed protons to move quickly from one side of the heterostructure to another. Multilayer compositing was also used to drastically improve the crystal structure quality and by extension the electrical properties of doped titania thin films on glass. The impact of an underlying interfacial seed layer was clarified, and showed that high oxygen content in the seed layers caused the preferential formation of the high electron mobility anatase phase. The layered composite had the added benefit of suppressing the formation of detrimental titania polymorphs phases (rutile and brookite). The combination of these effects (coupled with the niobium dopant activation at moderate temperatures) lead to the formation of high conductivity
films. Regardless of whether the effects originate from structure related changes or space charge regions, we have shown that interfaces, when introduced on the nanoscale, have a profound impact on the macroscopic transport characteristics of the composite systems and open the doorway towards new and exciting possibilities.

5.2 Recommendations for Future Research

While compositing effects provided a unifying theme to this thesis, the research presented can be broadly divided into two categories. Our studies showed that novel proton conducting oxide heterostructures have great potential, and thus there are many avenues for expansion in this field of study. For the purely oxide based multilayers BCZY/STO, we used a qualitative approach to confirm the nature of the ionic conductivity enhancement parallel to the interfaces. If this enhancement were described in a quantitative fashion, the results would be the true “smoking gun” evidence needed to prove the so-called nanoionic enhancement effect is real for this class of materials. Transport numbers are typically established in bulk materials through concentration cell measurements, but these experiments are not for the faint of heart. If a clever cell setup were devised (with proper sealing), these transport numbers could be determined in these multilayer structures as well. Another consideration for these oxide structures is the limited number of material system we explored (only STO and TiO$_2$ were studied as second phase oxides materials in our multilayer design). There is no telling what properties (magnetic, electrical – ionic/electronic, or optical) could be present if other oxide materials are chosen. Supercapacitors are new field that will certainly benefit from new types of composites. A composite synthesized between BCZY (or perhaps BZY) and BaTiO$_3$ (a common dielectric material in capacitors with a perovskite crystal structure), may show enhanced charge storage capacity as the layers are decreased to the length scale of the space charge region. For BCZY/Pd
nanocomposites, it was proposed that the decrease of conductivity in reducing atmospheres was due to the existence of an atomically mixed region at the particle/matrix boundary. This needs further confirmation through high resolution TEM analysis or another appropriate analysis technique. This type of composite will be suitable for gas sensing applications if it can be shown that the transition between the “oxidizing” and reducing states occurs on a reasonable time scale. Also, the long-term durability of these layers needs to be established. Much like the choice of STO and TiO$_2$ for the oxide structures, the choice of Pd as the second phase metal material in our nanocomposites was based on several factors. However, the BCZY perovskite structure can tolerate the addition of many transition metals (Cu, Ni, and Co), and one of these metals may provide the ionic conductivity enhancement needed to make these structures suitable for various sections of an electrochemical device (electrolyte/electrode).

Transparent conducting oxide heterostructures are also in their infancy and also have the potential for great improvement. There are a large variety of materials suitable for seed layers and one of these may prove more useful in achieving TCO heterostructures with greater optical and electrical properties. Expanding this seed layer concept outside the realm of physical vapor deposition, to wet chemical synthesis may provide a pathway towards inexpensive and high-throughput TCO devices (if the properties can be maintained between the two fabrication approaches). An interesting twist that combines both of these sections would be to deposit an interfacial seed layer (i.e. another perovskite structured material - STO) on glass in order to template the growth of BCZY thin films/composites. If this were accomplished on flexible glass substrates, this may provide an interesting route to fabricating low temperature chemical sensors.