TRANSITION METAL DOPED CERIUM OXIDE

FOR SPINTRONICS APPLICATIONS

by

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ABSTRACT

This thesis describes the synthesis, structural characterization, magnetic characterization, and structure-property correlation of Ce$_{1-x}$Cu$_x$O$_{2-\delta}$, Ce$_{1-x}$Mn$_x$O$_{2-\delta}$, Ce$_{1-x}$Co$_x$O$_{2-\delta}$, and Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ thin films grown on LaAlO$_3$ substrates. The films were prepared by pulsed laser deposition and were characterized using state-of-the-art characterization techniques. Two concentrations of dopants were used in this study: a low concentration ($x=0.03$) and a high concentration ($x=0.15$). Magnetization measurements showed that in the case of Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ the $x=0.03$ film exhibited room temperature ferromagnetism with a saturated magnetization of $\sim 1.0\mu_B$/Cu atom. When additional copper ions were introduced into the system ($x=0.15$), superparamagnetic behavior was observed. In the Ce$_{1-x}$Mn$_x$O$_{2-\delta}$ films, ferromagnetic behavior was observed in both the $x=0.03$ and the $x=0.15$ samples. However, in the Ce$_{1-x}$Mn$_x$O$_{2-\delta}$ $x=0.15$ film, evidence of phase separation was observed. The Ce$_{1-x}$Co$_x$O$_{2-\delta}$ sample showed ferromagnetic behavior, while the Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ and undoped films showed a diamagnetic response. An in-depth analysis was performed to understand the observed magnetic behavior of the systems. The discovery of ferromagnetism in two new transition metal doped CeO$_2$ systems represents a step forward in the field of spintronic materials.
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CHAPTER 1

INTRODUCTION AND BACKGROUND

In the field of semiconductor electronics the degree of progress over the past 50 years cannot be overstated. Since the invention of the transistor in 1947 there has been unprecedented scientific and industrial progress in this field. Miniaturization is one of the most amazing aspects of this progress because it yields better performance, at reduced cost, and reduced power consumption. However, there is a general consensus that the continued miniaturization of electronics and data storage elements will slow to a crawl without a shift in the paradigm of device design and function.

The miniaturization of electronic and magnetic devices is becoming increasingly challenging because the physical properties of the materials have become the limiting factors in device fabrication. These difficulties and challenges stem from the operational physics of these devices. When the gate length of transistors decreases the probability of electron tunneling increases. Thus, there are very real physical barriers to the scaling of CMOS technology to the atomic level. The reality is that simply making the devices smaller cannot be used as the primary method of performance improvement and new methods will need to be developed.

One of the possible new approaches to device design is based on the
utilization of both the charge and spin of electrons (and holes) as degrees of freedom in device design. This area of research is broadly defined as spintronics [1-4]. The synthesis of charge and spin degree of freedom in spintronics is shown in Figure 1.1 (a). Advances in this field are dependant on the development of new magnetic semiconductor and dielectric materials, specifically materials that are intrinsically ferromagnetic at and above room temperature. This thesis details the background and synthesis of several new dilute magnetic dielectric materials systems that may prove useful in the development of spintronic technology.

There is the potential in the field of spintronics for devices that can simultaneously store and process information, greatly enhancing the functionality of a single device. The possible advantages of spintronic devices over conventional charge based semiconductor devices for logic and memory include higher data processing speed, lower power consumption, lower data volatility, higher data process density, and higher data storage density [3]. The potential in this field is illustrated tremendous success of the first, and only thus far, commercial solid-state spintronic devices. These spintronic devices are gigantic magneto resistive (GMR) sensors used as read heads in magnetic data storage applications and magnetic random access memories (MRAM). GMR read heads are by far the more prevalent of the two devices and were quickly ushered into production a mere 10 years after the discovery of the gigantic magneto resistance effect [5-9].

Because GMR devices are primarily used as sensors or storage cells they are passive devices and logical elements based on conventional electronics are needed to interpret the signals generated by these devices. The development of new active
Figure 1.1: The diagrams in this figure illustrate the basic relationships in spintronics (a) conceptual diagram showing the enhanced functionally of a spintronic device (b) three different methods for achieving spin injection (c) three types of electron transport are illustrated; (i) spin randomized conduction, (ii) spin polarized transport, and (iii) spin polarized injection into a nonmagnetic semiconductor and spin relaxation.
spintronic devices is crucially dependent on the ability to inject, detect, and transport spin polarized carriers across material interfaces [10]. A persistent and critical difficulty in the field is the efficient injection of spin-polarized carriers into non-magnetic semiconductors. This is especially important given both the dominance of these materials in the semiconductor industry and the relatively long spin coherence times in Si, GaAs, other elemental and compound semiconductors [1]. Early attempts at spin injection into semiconductors using ferromagnetic metals such as Fe, Co and Ni [11,12] were unable to produce greater than 1% spin polarized carrier injection. This is theorized to be due to the large difference in electrical conductivity at the ferromagnet-semiconductor interface [13] that causes scattering of spin alignment.

There are three proposed and tested techniques to overcome this obstacle and achieve efficient spin injection. The first method is exercising control over the conductivity of dilute ferromagnetic semiconductors to better match the conductivity of the nonmagnetic transport medium and improve injection efficiency [14]. A second method involves tunneling electrons from a ferromagnetic metal through a dielectric barrier [15, 16]. The third method uses a dilute magnetic insulator to act as a spin selective filter for tunneling electrons [17]. Figure 1.1 (c) illustrates the basic configuration of these three types of spin injection. Each of the three techniques has been tested and researched by several groups in different applications. However, it is the first and the third method where the greatest strides have been made towards the ultimate goals of materials research on this topic—completely spin polarized carrier injection and the realization of functioning room temperature devices.
1.1 Review of Ferromagnetic Semiconductors and Dielectrics

The discovery of ferromagnetism in EuO 1961 by Matthias et al. [18] was a shocking realization of ferromagnetism present in a highly insulating material. This discovery and the subsequent discovery of ferromagnetism in the europium chalcogenides EuX (X:O, S, Se) has opened up new areas of research and understanding. The discovery of ferromagnetic behavior in the europium chalcogenides was shortly followed the discovery of ferromagnetism in the Cr-chalcogenide spinels CdCr$_2$X$_4$ (X: S, Se)[19-21].

Both systems were studied extensively however extremely low Curie temperatures and difficult synthesis limited widespread use of these materials particularly the Cr-chalcogenide spinels. However, research on the europium chalcogenides is still active and proof of concept devices have been fabricated demonstrating spin dependent tunneling, or spin filtering, in insulating EuS barriers [22]. There have been many other novel devices fabricated using this material family including direct integration of EuO with both Si and GaN [23].

The early discoveries in the chalcogenides were followed studies aiming to induce ferromagnetism in nonmagnetic semiconductor systems through the dilute incorporation of magnetic ions such as Mn, Co, and Fe. The hope was that replacing some of the atoms in the crystal would induce ferromagnetism in the matrix this research led to the term dilute magnetic semiconductor (DMS). These early studies of nonmagnetic semiconductors focused on the II-VI semiconductors (Zn,Mn)Se and (Zn,Mn)Te [24, 25]. It was found that concentrations of Mn greater than 60% in (Zn,Mn)Se showed antiferromagnetic compensation between the Mn ions. [26] For
intermediate concentrations a spin-glass is observed and for concentrations of Mn lower than 30% uncorrelated Mn spins show a paramagnetic behavior [26, 27]. Although, ferromagnetism was only realized in these materials at extremely low temperatures ($T_C \sim 2K$) much later in 1997 by Haury et al. [28] it was discovered that their optical properties were modulated by magnetic fields. This effect is explained by an sp-d exchange interaction between the s and p orbitals on the II-VI atoms and the d orbitals of the Mn ions [27]. The progress made in studies of early II-VI systems were surpassed greatly by the progress to be made in III-V based DMS.

The extensive research on III-V DMS started with the development of a non-equilibrium molecular beam epitaxy technique to grow single-phase films of (In,Mn)As on GaAs substrates by Munekata et al. in 1989 [29]. Once the technique to deposit these films was understood it was a short time before ferromagnetic ordering was observed in both (Ga,Mn)As and (In,Mn)As films with $T_C$ of 110K and 7.5K respectively [30,31]. Work on spintronic III-V materials has led to the development of low temperature Spin-LED and Spin-Laser devices [32]. The field of III-V DMS is very active and many advances have been made both in understanding the mechanism of ferromagnetic mediation and materials processing. However, the low curie temperature of these materials will limit possible usefulness.

A major shift in experimental efforts towards realizing room temperature ferromagnetic semiconductors came with the theoretical prediction of high temperature ferromagnetism in p-type Mn doped ZnO and GaN by Dietl et al. in 2000 [33]. Experimental results for Mn and other transition metal dopants in ZnO are somewhat controversial because controlling the formation of secondary phases is
difficult. There is, however, compelling evidence in the case of specific concentrations of Mn, Cu and Co doping for intrinsic ferromagnetism [35-37]. This field is still a hot topic for research and many advances have been made.

The prediction of high temperature ferromagnetism in ZnO led researchers to explore other wide band gap semiconductors. In 2001 Matsumoto et al. reported that titanium (IV) oxides anatase thin films doped with cobalt and deposited on LaAlO$_3$(100) and SrTiO$_3$ exhibited room temperature ferromagnetic behavior [38]. TiO$_2$ is an optically transparent material in the visible and near infrared with a high dielectric constant and refractive index. Later the same group reported ferromagnetism in the rutile phase of Ti$_{1-x}$Co$_x$O$_{2-\delta}$ [39]. The discovery of room temperature ferromagnetism in Ti$_{1-x}$Co$_x$O$_{2-\delta}$ anatase system was confirmed by Chambers et al. in 2001 and later by several other groups [40-43]

Griffin et al rigorously investigated the mechanism of ferromagnetism in anatase Ti$_{1-x}$Co$_x$O$_{2-\delta}$. [44]. From this study it was determined that free carriers were not necessary for the material to be ferromagnetic. By systematically varying their processing parameters Griffin et al. were able to create highly insulating single-phase ferromagnetic material. These observations disagree with earlier reports on the same system [40-43] where ferromagnetic characteristics were correlated with the carrier concentration. Zhao et al. [45] demonstrated a reversible external electric field induced modulation of room temperature magnetic moment and coercive field in anatase Co:TiO$_2$ insulating films. The ability to modulate magnetic moment and coercive field using an electric field are considered among the most important factors
for the realization of useful spintronic devices. Also, this test is considered hard
evidence for intrinsic ferromagnetism [46].

In 2003 Ogale et al. reported that Sn\textsubscript{0.95}Co\textsubscript{0.05}O\textsubscript{2-δ} films grown on R-plane sapphire show high temperature ferromagnetism with a curie temperature of 650 K [47]. Another interesting observation about this high dielectric oxide system is that the films possess a giant magnetic moment of approximately 7.5 μ\textsubscript{B}/Co atom [47]. SnO\textsubscript{2} was later shown to be ferromagnetic when doped with Mn and Fe in addition to Co [48].

Starting in 2004 with the report of ferromagnetism in undoped HfO\textsubscript{2} by Venkatesan et al. research interest shifted towards developing rare earth dilute magnetic dielectric systems. In 2006 Tiwari et al. observed high temperature ferromagnetism in another high-k dielectric oxide system, CeO\textsubscript{2} doped with Co [49] the CeO\textsubscript{2}:Co system is discussed in detail in Section 1.3.1. Very recently Co doped La\textsubscript{2}O\textsubscript{3} was shown to exhibit room temperature ferromagnetism [50].

1.2 Background of Cerium Oxide

Cerium (IV) Oxide has a long history in materials science. Cerium oxide is an insulating high-k dielectric material (k~26) that is transparent over the visible and infrared. Bulk CeO\textsubscript{2} has a cubic fluorite with an experimentally determined lattice constant of 0.5411 nm at 300 K [51]. In the fluorite structure each unit cell contains 4 cerium atoms and 8 oxygen atoms shown in Figure 1.2 (a). A notable feature of this crystal structure is that both interstitial and cation substitutional sites have eight fold cubic coordination by oxygen only differing in their radii. The unique redox
properties of cerium oxide have led to many different applications including use in
the anodes of solid oxide fuel cells [52], catalysis [51,53], and oxygen sensors [54].
Yttrium and Gadolinium doping in cerium oxide has been shown to increase oxygen
conductivity [52,55, 56] for use as an electrolyte in solid oxide fuel cells.

Both the high oxygen conductivity and high catalysis activity can be ascribed
to the inherent ability of cerium oxide to be reversibly reduced from Ce\(^{4+}\) to Ce\(^{3+}\)
through the creation of an oxygen vacancy. This is described in the following
reversible reaction written using Kroger-Vink notation in equation 1.1,

\[
O^\text{\textsubscript{O}}_\text{\textsubscript{0}} + 2Ce^\text{\textsubscript{Ce}}^{\text{\textsubscript{4+}}} \Leftrightarrow V^\text{\textsubscript{O}} + 2Ce^\text{\textsubscript{Ce}}^{\text{\textsubscript{3+}}} + \frac{1}{2}O_2
\] (1.1)

where \(O^\text{\textsubscript{O}}_\text{\textsubscript{0}}\) is a neutral oxygen on an oxygen lattice site and \(Ce^\text{\textsubscript{Ce}}^{\text{\textsubscript{4+}}}\) is a neutral cerium on
a neutral cerium site, \(V^\text{\textsubscript{O}}\) is a +2 oxygen vacancy and \(Ce^\text{\textsubscript{Ce}}^{\text{\textsubscript{3+}}}\) is a Ce\(^{3+}\) atom in a Ce\(^{4+}\)
site giving it a net negative charge of -1. In The Ce\(^{3+}\) state an electron goes into the
previously empty 4f state giving an electronic configuration of Ce \(4f^1\). The reaction
is reversible and is the process that allows cerium oxide to incorporate or release
oxygen, a process central to the industrial use of cerium oxide [51]. The proper
formula for oxygen deficient cerium oxide is written CeO\(_2\)\(_\delta\) where \(0 \leq \delta < 0.5\). The cubic
phase is stable over this range of oxygen deficiency [51].

Due to the many applications for Cerium oxide extensive experimental and
theoretical research has been performed to better understand the complex
electrochemical behavior of this rare earth oxide [51-60]. An exceptionally important
aspect of study has been to understand the behavior of point defects in bulk CeO\(_2\) and
surface states in nanoscale CeO\(_2\) [57,58]. There are many types of point defects in
bulk Cerium oxide depending on the partial pressure of oxygen and the temperature
including: oxygen vacancies $V_O$, cerium antisites $Ce_O$, cerium interstitials $Ce_i$, impurities on the lattice $D_{O,Ce}$, interstitial impurities $D_i$, and others. These possible defects are shown schematically in Figure 1.2 (b) [51,57]. The primary defects of concern at room temperature and pressure are oxygen vacancies and polarons (electrons localized on cerium III cations). Density functional theory (DFT) calculations and local density approximations (LDA) have shown that in other thermodynamic regimes additional point defects become active and important electrochemically [57,58].

The electronic band structure in cerium oxide is derived primarily from the full oxygen 2p states that form the valence band and from the empty cerium 5d states that form the conduction band. The Ce 4f band lies between these two bands. In defect free material the Ce 4f band is completely empty because all Ce are in the 4+ state [59]. The approximate energy gap band diagram of $CeO_{2-\delta}$ is shown in Figure 1.2 (c) and shows the shift of the Ce 4f$^4$ state due to defects or core excitation. In oxygen deficient cerium oxide the empty Ce 4f band becomes partially filled and a polaron forms, localized on the additional electron. A polaron is a quasiparticle formed by a charged particle and the resulting lattice polarization phonon field. It has been shown that the thermally activated n-type electrical conductivity of cerium oxide fits well to the “small polaron” model of Holstein et al. [61,62]. In the small polaron model the radius of the polaron is on order of a few lattice spacings and is centered on a Ce$^{3+}$ with an occupied 4f$^4$ state. An adjacent oxygen vacancy will bind two such polarons and become a distorted $V_O^{0+}$ site in the absence of applied electric field or doping [57].
Figure 1.2: The schematic crystal structure of CeO$_2$ is shown in (a) [structure data from 51, image made with Crystal Maker™ Software]. Possible point defects in CeO$_2$ shown in (b) [adapted from 51,57]. A schematic band structure of CeO$_2$ showing approximate energy levels is shown in (c), the Ce 4f$^1$ level varies with population [adapted from 57].
Theoretical modeling of neutral distorted oxygen vacancies using a LDA+U, where U is an energy correction factor, indicates an antiferromagnetic alignment of the localized electrons [57].

1.3 Magnetism in Cerium Oxide

Cerium oxide has shown ferromagnetic behavior both as doped and undoped nanoparticles and as thin films doped with small amounts of cobalt [49,63,64]. The mechanism of ferromagnetism in metal oxides is far from fully understood. However, the fact that pure nanoparticles of Al₂O₃, SnO₂, In₂O₃, and ZnO in addition to CeO₂ have exhibited ferromagnetism indicates that it is related to the oxygen deficiencies [63]. Oxide nanoparticles are known to be inherently oxygen deficient and have a correspondingly larger lattice parameter [65]. It was shown that after sintering all of the above-mentioned nanoparticles to 1400°C diamagnetic behavior is observed as is observed in the bulk materials [63]. Oxygen annealing of the cobalt doped cerium oxide nanoparticles also reduces the observed ferromagnetic moment, however, it does not eliminate it. Section 1.3 is separated into two subsections. In section 1.3.1 the discovery and study of ferromagnetism in the CeO₂:Co system is discussed. Section 1.3.2 describes the possible origins of ferromagnetism in doped CeO₂.

1.3.1 Cobalt Doped Cerium Oxide

In 2005 Tiwari et al. reported ferromagnetism in Ce₁₋ₓCoₓO₂₋₅ deposited by PLD on LaAIO₃ (001) substrates at and above room temperature [49]. Careful
microstructural analysis including high-resolution transmission electron microscopy
and X-ray photoelectron spectroscopy showed no evidence of cobalt clustering. If
clusters were too small to be resolved magnetic characterization would have shown
superparamagnetic behavior with a low blocking temperature. Thus, the
ferromagnetism was demonstrated to be an intrinsic property of the material. It was
found that at elevated temperatures the measured magnetic moment could not be
explained solely by the magnetization of the Co ions and that the cerium oxide matrix
itself was contributing to the measured magnetic moment. The following calculations
from reference 49 rationalize the contribution of the CeO$_2$ matrix. Both Co$^{2+}$ and
Co$^{3+}$ can exist in high or low spin states. In the low spin state the maximum moment
per Co$^{2+}$ ion is $M \approx 1.7 \mu_B$ \[ M=g \mu_B \sqrt{S(S+1)}; \ g=2 \ S=1/2 \] \[66\]. In the high spin state $S$
can have the maximum value of 2 if all of the dopant ions are in the $3^+$ state. Having
$S=2$ will result in a spontaneous moment of $M \approx 4.9 \mu_B$ both of these values are smaller
than the values observed. In the unlikely case that the orbital moments are
unquenched then the maximum net angular momentum is $J=L+S=4$ and the maximum
moment $M \approx 6.7 \mu_B$ \[ M=g \mu_B \sqrt{J(J+1)}; \ g=3/2, \ J=4 \] \[66\]. While $M \approx 6.7$ is near what
was observed at low temperature it is still about 22% lower than the maximum
observed moment, thus magnetization of the matrix is required to explain the
observed magnetic moment.

Following the first report a flurry of activity on the material ensued with other
groups reporting high temperature ferromagnetism. The nature and the origin of the
ferromagnetism has not been conclusively demonstrated, however, all of the reports
thus far confirm the presence of ferromagnetic behavior at and above room
temperature. Vodungbo et al. grew Co doped thin films on SrTiO$_3$ (STO) and Si substrates by pulsed laser deposition [67]. Films grown on Si showed a textured (111) orientation when grown in vacuum and a textured (001) orientation when grown in an oxygen rich ambient. Low temperature (below 200 K) magnetic measurements on these Si films showed slight shape anisotropy. For the films grown on STO significant shape anisotropy was observed and was attributed to a 2% epitaxial strain on the film that resulted in a uniaxial magnetization. The films grown in an oxygen ambient showed a lower moment than those grown in vacuum indicating that oxygen vacancies play a role in the ferromagnetic behavior.

In another study of cobalt doped cerium oxide deposited on Si by PLD Song et al. it was demonstrated that highly oriented $\text{Ce}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ had a maximum magnetic moment with 3 at% cobalt doping and decreased until phase separation occurred in the 12.5 at% sample [68]. The results of Song et al. contrast the observations of Bi et al. where cobalt doped CeO$_2$ was deposited on MgO substrates and phase separation was not observed even up to 25 atomic % cobalt [69]. Bi et al. observed textured thin films with domains from 40-100 nm. Magnetization versus temperature of films grown on Si, and MgO do not show an increase in magnetic moment at high temperatures and report $T_C$ ranging from over 1000 K [69] to 750 K [68].

1.3.2 Origin of Ferromagnetism in Cerium Oxide

A complete understanding of the origin of ferromagnetism in undoped and transition metal doped oxides does not yet exist. There are several predominant theories each with their own limitations and new experiments are constantly
challenging theoretical descriptions. The most basic explanation of ferromagnetic behavior in a material is that the angular momentums of unpaired electrons become aligned over a long range. The ordering of spin occurs because alignment is a lower energy condition for the system. Once ordering is created it is persistent in the absence of an external magnetic field up to the Curie temperature ($T_C$) when entropic disorder becomes dominant over the electronic order in the material. In contrast, a paramagnetic material has unpaired electron spins but in the absence of an applied magnetic field the alignment of the individual electron spins is random. The mechanism by which electrons in a material assume long range ordering varies with the material and is described depending on the material by a wide range of theoretical descriptions.

Several sorts of contradictory observations challenge researchers attempting to understand the observed ferromagnetic phenomena in oxide semiconductors and insulators. Most notable of these is that ferromagnetism has been observed in oxide systems over wide ranges of electrical conductivity through the range from insulating to metallic. Certainly it is understood that the charge carriers must be mediating long-range order; however, it does not appear that free carriers are required to mediate long-range order. Another confounding factor is the observation of magnetic precipitates in some studies but not others, indicating sensitivity to processing conditions. Additionally, because of the diluteness of the transition metal ions the double exchange nearest neighbor mechanism of ferromagnetism cannot be used to describe the observed ferromagnetic response.
The most commonly used description of ferromagnetic mediation in DMS is the impurity-band exchange model [70,71]. In the impurity-band exchange model a localized electron from a donor defect forms a hydrogenic orbital with radius ($r_H$). The hydrogenic orbital overlaps with the level of a transition metal cation to create a delocalized impurity band. For insulating systems $r_H = \varepsilon (m^*/m) a_0$ where $\varepsilon$ is the low frequency dielectric constant, $m^*/m$ is the ratio of effective electron mass over free electron mass, and $a_0$ is the Bohr radius (0.53Å). If the donor concentration is large enough and interacts with the magnetic cations the 3d orbitals can interact to form bound magnetic polarons, which can lead to long-range spin mediation and ferromagnetism [68,69].

The number of magnetic ions within a hydrogenic sphere can range from less than ten to 100 depending on $r_H$ and the concentration of magnetic ions. The probability of two magnetic polarons overlapping depends on the electron carrier concentration ($n_c$) and $r_H$. Because there are two factors, there can be two unique cases where long-range ferromagnetic exchange can occur in the impurity band exchange model, these are high $n_c$ or large $r_H$. Degenerately doped semiconductors can fulfill the high $n_c$ case where $n_c$ is greater than $10^{19}$ cm$^{-3}$ and strongly localized insulators have large $r_H$.

A closely related model is the bound magnetic polaron model and in this model the origin of ferromagnetic mediation is based on F-center exchange. An F-center is formed when a lower valent cation replaces a higher valent site thereby creating oxygen vacancies to account for the local charge balance [72]. In principle three types of oxygen vacancies are possible and these stem from the number of
electrons that the vacancy has localized (0, 1, or 2) [71]. A polaron that has localized only one electron is located deep in the gap and this is the primary difference between the impurity band exchange model and the bound magnetic polaron model [70-73]. In CeO$_{2-\delta}$ the diameter of the resulting polaron formed from an oxygen vacancy localizing one electron is between 1 and 2 lattice spacings or about 1 nm [57]. If an unpaired electron in the d orbital of a magnetic dopant overlaps with such a polaron then long range ordering can be mediated throughout the material, even though no direct energy overlap occurs in the band structure of the material [71].
1.4 References


CHAPTER 2

EXPERIMENTAL PROCEDURES: THIN FILM PROCESSING, CHARACTERIZATION, AND STRUCTURE-PROPERTY CORRELATION

The observation of ferromagnetic behavior in Co doped ceria as described in the introduction and background provokes the explorations of other dopant species. The series of experiments made for this study systematically explored the magnetic properties of thin films of CeO$_2$ doped with Cu, Mn, Zn, and Co. The effect of adding 3 and 15 atomic percent of each dopant ion was explored. The magnetic properties of CeO$_2$ thin films doped with Cu, Mn, and Zn have yet to be reported to this point.

Materials were synthesized by a citrate sol-gel technique. Thin film samples were deposited using pulsed-laser deposition (PLD). The quality and physical properties of these materials were characterized using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and atomic force microscopy (AFM). Information about the chemical oxidation state of elements in the film was obtained using X-ray photoelectron spectroscopy (XPS). The magnetic properties of the thin films were studied using a
superconducting quantum interference device (SQUID).

Because there is uncertainty about the origin of ferromagnetism in many oxide systems there is an extreme need for laboratory cleanliness [1]. Contamination at any of the processing steps by very common magnetic materials or ions would cast doubt on the prepared materials. Thus, extreme care and caution was exercised at every step of the materials processing section of this experiment. These precautionary steps included the selection of a low thermal budget sol-gel synthesis technique, use of extreme caution in materials handling, cleaning green target compresses of surface material, use polymer tweezers in sample handling, and many other precautionary measures. A systematic approach was taken; all parameters were kept as similar as possible while only varying the dopant element and concentration.

The sections of this chapter discuss both the background and the actual parameters used to conduct various experiments. The three primary sample preparation steps are described in the subsections of 2.1 and the characterization techniques used are described in the subsections of 2.2.

2.1 Sample Preparation

To study the magnetic properties thin films of the various doped ceria materials the desired compositions must first be synthesized in bulk to form a deposition target. Because the desired compositions are not available commercially and only a small amount of bulk material is needed for PLD the deposition targets were fabricated as a part of this experiment. An added benefit is confidence in the purity of the targets. To fabricate the bulk PLD target pellets a powder of the desired
stoichiometry needed first. This could be achieved by a solid-state technique; however, because this method requires large amounts of time, multiple milling steps, and high temperatures for these reasons a solution based method was chosen. The sol-gel method has numerous advantages that will be discussed in section 2.2.1.

2.1.1 Sol-gel Processing

Solution based processing of ceramic materials is a very important synthesis route and has been used in many materials systems to achieve a variety of fabrication goals. The goal of this experiment was to fabricate pure physical vapor deposition targets with a homogeneous dispersion of dopant material. In sol-gel material synthesis technique the starting point is a chemical solution (or sol) that acts as a precursor to the formation of an integrated network (or gel). The solution typically consists of dissolved metal ions or metal alkoxides. The gel can consist of discrete particles or network polymers [2].

Because of a long history as a catalyst material there are several well-developed methods to synthesis cerium oxide nanopowders [3-5]. The method chosen for this project involved the use of 99.99% pure cerium (IV) nitrate hexahydrate and citric acid as a chelating agent. The are several advantages to this synthesis route, though, perhaps the most important is that because it is a low temperature technique, high purity can be maintained while synthesizing a high temperature phase.

All of the required glassware used in the powder synthesis was cleaned first by a nitric acid rinse and then by ultrasonication. The stoichiometry was calculated
by following the mol percent of the desired metal ions [6,7]. Stoichiometric amounts of the material to be synthesized were weighed using a Mettler-Toledo AL104 analytical balance. The precursor nitrates and oxides were then dissolved in water or acid depending on their solubility. Table 2.1 gives the masses of each precursor material added for the various sols. Table 2.2 gives the various chemicals used, their manufacturer, and their purity. In the Mn samples the source material used is Manganese nitrate hydrate. Because this compound can incorporate a variable amount of water determining the proper amount to add was addressed by contacting the supplier, Alpha Aesar, and requesting a mass balance. Alpha Aesar stated that by weight the lot of Mn(NO$_3$)$_2$ X·H$_2$O contained 21% Mn. Care was taken during weighing and mixing these materials to avoid contact with possible sources of contamination including using only plastic or porcelain spatulas for measuring precursors and discarding material that may have been contaminated.

Citric acid was added as a chelating agent at a 1:1 ratio to the Ce ions [6]. The solutions were then diluted to 800 mL and refluxed for at 24 hours at constant volume using a water jacket condenser. The solutions were transferred to a clean 1L beaker in a fume hood and the volume was slowly evaporated over a 3-hour period until the solution began to gel. The solution was transferred to a clean Coors tech crucible. The gel was heated until the citric acid began to decompose and form a high surface area reaction front. Some powder was ejected from the crucible in this highly energetic reaction. The powder ejected from the crucible was not used to fabricate deposition targets as it was potentially contaminated.

The gel combustion reaction resulted in the formation of a mixed color
### Table 2.1 Masses of Precursors Used

<table>
<thead>
<tr>
<th>Composition</th>
<th>Dopant</th>
<th>Dopant Mass (g)</th>
<th>CeNH (g)</th>
<th>Citric acid (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>-</td>
<td>-</td>
<td>14.9044</td>
<td>6.798</td>
</tr>
<tr>
<td>Cu 3%</td>
<td>CuO</td>
<td>0.0789</td>
<td>13.9211</td>
<td>6.245</td>
</tr>
<tr>
<td>Cu 15%</td>
<td>CuO</td>
<td>0.4456</td>
<td>13.7866</td>
<td>7.176</td>
</tr>
<tr>
<td>Mn 3%</td>
<td>Mn(NO$_3$)$_2$·H$_2$O</td>
<td>0.1899</td>
<td>14.9043</td>
<td>6.798</td>
</tr>
<tr>
<td>Mn 15%</td>
<td>Mn(NO$_3$)$_2$·H$_2$O</td>
<td>1.0107</td>
<td>13.8983</td>
<td>7.235</td>
</tr>
<tr>
<td>Zn 3%</td>
<td>ZnO</td>
<td>0.0863</td>
<td>14.8768</td>
<td>6.87</td>
</tr>
<tr>
<td>Zn 15%</td>
<td>ZnO</td>
<td>0.4553</td>
<td>13.7626</td>
<td>7.164</td>
</tr>
<tr>
<td>Co 15%</td>
<td>Co(NO$_3$)$_2$·6·H$_2$O</td>
<td>1.6377</td>
<td>13.8463</td>
<td>7.207</td>
</tr>
</tbody>
</table>

### Table 2.2 Chemicals Used

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Manufacturer</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium (III) Nitrate Hexahydrate</td>
<td>Ce(NO$_3$)$_4$·6·H$_2$O</td>
<td>Alpha Asear</td>
<td>99.99%</td>
</tr>
<tr>
<td>Copper(II) Oxide</td>
<td>CuO</td>
<td>Alpha Asear</td>
<td>99.999%</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>ZnO</td>
<td>Alpha Asear</td>
<td>99.999%</td>
</tr>
<tr>
<td>Cobalt(II) Nitrate</td>
<td>Co(NO$_3$)$_2$·6·H$_2$O</td>
<td>Alpha Asear</td>
<td>99.99%</td>
</tr>
<tr>
<td>Manganese Nitrate Hydrate</td>
<td>Mn(NO$_3$)$_2$·X·H$_2$O</td>
<td>Alpha Asear</td>
<td>99.99%</td>
</tr>
<tr>
<td>Cerium(IV) Oxide</td>
<td>CeO$_2$</td>
<td>Alpha Asear</td>
<td>99.99%</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH</td>
<td>Fisher Scientific</td>
<td>95%</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>C$_6$H$_8$O$_7$</td>
<td>Alpha Asear</td>
<td>95%</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>HNO$_3$</td>
<td>Malincrodt</td>
<td>15 M</td>
</tr>
</tbody>
</table>
powder. The resulting powder was heated to 500°C for 12 hours in a covered crucible to combust the remaining gel and oxidized remaining carbon compounds. Following this step the powders were uniformly white indicating that a majority of the carbon had been removed. Figure 2.1 illustrates the steps in the sol-gel synthesis. EDS and SEM were used to evaluate and characterize the microstructure and purity of the prepared powder materials. Solid-state diffusion powder processing often results in a multiphase material that must be further sintered to create phase homogeneity. However, using the sol-gel technique no additional phases were observed in the powder materials.

2.1.2 Preparation of Bulk Targets for Laser Ablation

Deposition targets were formed from the powders as prepared. Special measures were taken to minimize the possibility of contamination in this critical step. The powders were gently compacted in the calcining crucible. Weighing papers [Fisher Scientific] were cut into disks on a clean surface to the same diameter as the die. The pressing die was first polished, it was then cleaned ultrasonically, and then it was lubricated with a small amount of Oleic acid [Fisher Scientific, 95%]. The powders were then carefully loaded into a 2.54 cm cylindrical die between weighing paper disks both to prevent contamination and to allow easy pellet release from the die. This arrangement is shown in Figure 2.2.

The powders were then pressed at 33 MPa for 5 min to form a pellet. The green body was pressed out of the die. The edges of the pellet were then removed by gently rubbing them with a paper tissue. This was done to prevent contamination
Figure 2.1: The processing steps for producing powders via the sol-gel technique.
Figure 2.2: Schematic of the die used to compress powders into pellets showing arrangement of paper and powder.
from the die being diffused into the pellet. The pellets were placed on Coors Tech porcelain plates in a thick bed of fine mesh CeO$_2$ powder [Alpha Aesar 99.99% REO] and heated to 1000°C, for 12 hours ramping at 100°C per hour up and down. This processing step resulted in ceramic pellets with ~80% of theoretical density. The pellets were then evaluated using SEM, EDS, and XRD. Archimedes density was measured using a pellet fragment. Characterization of these target pellets showed that they were free from observable contamination.

2.1.3 Pulsed Laser Deposition

Pulsed Laser Deposition (PLD) technique is an efficient and versatile technique for the deposition of thin films of a wide variety of materials. Metals, polymers, ceramics, and biological thin film samples have all been prepared using PLD [8]. There are many advantages of PLD over other thin film deposition techniques including a small number of process control parameters, low substrate temperatures for crystal growth, low sensitivity to differences in boiling points and vapor pressures of target materials, and good control of film stoichiometry [9]. For these and other reasons PLD is an excellent technique for growing novel thin-films and super lattice structures for research purposes.

The process of pulsed laser deposition involves a high power pulsed laser beam being focused onto a target material inside a vacuum chamber. Due to the extremely high energy densities obtained from the focused laser pulse, target material is vaporized from the target and deposited as a thin film on a substrate material such as silicon, sapphire, or other crystals facing the target. This process can occur in ultra
high vacuum or in the presence of a background gas, such as oxygen, commonly used when depositing oxides to fully oxygenate the deposited films. Figure 2.3 shows schematically the arrangement of the PLD system used in this study; this layout is typical of other PLD systems. To prevent the target from decomposing, melting, or shattering, all of which can result in nonstoichiometry of the film, a rotating target carousel is used.

Although the deposition set up is simple relative to other methods of thin film deposition, the processes that govern laser absorption, material transport, and film growth are quite complex. The pulse energy is first converted into electronic excitation when the laser pulse is absorbed by the target and then into thermal, chemical and mechanical energy resulting in evaporation, ablation, plasma formation and even exfoliation of the target [10]. The excited and ejected species expand into the surrounding vacuum in a plume containing many energetic species including atoms, ions, electrons, molecules, clusters, particulates and sometimes-molten globules, before depositing on the typically heated substrate. The characteristics of the plume are functions of the chamber pressure and the laser pulse energy.

An important consideration in the PLD process is laser safety. Safety is very important because the ultraviolet KrF exiplex laser light is quite dangerous, especially to the eyes, but also to the skin. It is extremely important to wear eye protection that can absorb the high intensity ultraviolet radiation emitted by the laser. UV opaque clothing should be worn during deposition. It is also important to develop robust laser safety practices including enclosing the laser beam and notifying people outside the lab that the laser is in operation [11]. Another safety consideration regarding the
Figure 2.3: Schematic of a Pulsed Laser Deposition system. A turbo-molecular pump backed by a rotary vane pump evacuates the chamber. The focused pulsed laser ablates the rotating target and the computer controls how many pulses are received by each target and what order the targets are ablated in the case of a multilayer deposition [12].
laser is the toxic gas required to produce the laser pulse.

The experimental setup of a pulsed laser deposition system requires understanding of a wide variety of electronic, mechanical, and chemical systems. However, PLD has a relatively simple setup in contrast to the systems required for multicomponent chemical vapor deposition or molecular beam epitaxy. The deposition chamber itself can be assembled using off the shelf vacuum components. In this experiment an Excel Instruments PLD-STD-12 chamber specifically designed for pulsed laser deposition was used. However, this system required assembly upon arrival. There are many methods to achieve the vacuum level needed for PLD, however, one of the most economical methods is to use a turbo molecular pump backed by a simple rotary vacuum pump as was used for this experiment. Figure 2.4 shows photographs of the PLD system used in this study.

Pulsed laser radiation with a wavelength of 248 nm (~5eV) and pulse duration of 25 ns was produced by a Lambda Physics Complex Pro KrF eximer laser with adjustable pulse energy set to 250 mJ and a pulse frequency of 10 Hz. This radiation was focused by a fused silica lens and then entered into the PLD vacuum chamber through a fused silica window and was incident to the target at a 45° angle. The incident pulse locally heated the target transforming the materials into a forward directional plasma. This plasma expanded and was deposited on a heated substrate across from the target material. To prevent decomposition, which can result in a non-stoichiometry of the material, or melting of the target in areas surrounding the laser spot, a rotating target carousel is used. By varying the incident pulse energy and ablation time film thickness can be precisely controlled. The LaAlO$_3$ (001) substrates
Figure 2.4: Photographs of the PLD system used in this research with major components labeled (a) side view (b) top view.
[MTI corporation] were first cleaned ultrasonically in acetone to remove any oils or wax that could interfere with thin film growth. The substrates were then cleaned in methanol to remove any acetone or water that remained on the surface. The targets were lightly sanded by diamond paper to remove surface contaminants. The substrate was attached to the holder using a tiny amount of silver paint [SPI Silver Paint Plus].

The target materials and the substrates were loaded into the PLD system and the chamber was sealed and evacuated. The target to substrate distance was 4.5 cm. The chamber was evacuated to a pressure of $10^{-6}$ mbar. The focusing lens for the laser was adjusted by firing a few test pulses to ensure that the beam was correctly aligned with the substrate and focused on the target in to a $\sim 1$ mm$^2$ area. The targets were then cleaned by the laser for 200 pulses with the substrate covered by a shutter. The substrate was heated to 600°C at 10°C/min in the case of Co, Mn, and Zn doped deposition. It was found that the deposition of Cu samples at 600°C led to the formation of a separate copper oxide phase, however, Cu doped depositions made at 450°C showed no evidence of phase separation when observed by x-ray diffraction.

The thickness of the film is directly proportional to the number of pulse fired by the laser. However, the deposition rate does depend on the material being ablated. Similar materials have a deposition rate of 0.5 Å/pulse at an energy density of 3 J/cm$^2$ [12]. These parameters were used to estimate the required number of pulses for a film $\sim 300$ nm thick. Films were deposited using 6000 pulses for each material. Following the deposition the films were immediately cooled at 10°C/min to room temperature in vacuum. The chamber was vented and allowed to return to ambient
pressure. The substrate was removed from the heater and transferred to a clean plastic sample holder using plastic forceps.

2.2 Materials Characterization

2.2.1 X-Ray Diffraction

All of the samples investigated in the study were thoroughly characterized using X-ray diffraction (XRD). XRD is a non-destructive quantitative technique that is used to determine the crystallographic structure and chemical composition of materials. There are a variety of techniques that stem from the basic principle that can give a wealth of information about a sample. William L. Bragg and his father, Sir William H. Bragg, were awarded the Nobel Prize in physics in 1915 for their mathematical description of x-ray diffraction and for their determination of crystal several structures beginning with NaCl, ZnS, and diamond [14,15].

A crystal lattice is a regular three-dimensional spatial distribution (cubic, hexagonal, etc.) of atoms in space. The atoms in a crystal are arranged such that symmetries form over very large areas resulting in a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. These planes and the distances between them are different and specific for each phase present in the material. Optical diffraction occurs when a monochromatic X-ray beam constructively interferes with the lattice. X-ray wavelengths are comparable with inter-atomic distances and are excellent probes for the atomic length scale. Bragg's Law, given in equation 2.1, relates this diffraction condition to the wavelength (\(\lambda\)) of the incident radiation, the spacing between the
various crystallographic planes \( (d_{hkl}) \), and the relative angle of the incident radiation \( (\theta) \).

\[
n\lambda = 2d_{hkl} \sin(\theta) \tag{2.1}
\]

By varying the angle theta, the Bragg's Law conditions are satisfied by different d-spacings in polycrystalline and single crystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffraction pattern is formed by addition of the individual patterns [15]. For a single crystal various diffraction conditions can be met by rotating the crystal through an alternate axis while maintaining the other angular coordinates. Multiaxis XRD can give very important information, in the case of thin films samples, about the relative crystalline orientation of the film to the substrate in addition to information about the quality of the film.

XRD patterns of powders, targets, and films were obtained using a Philips X’Pert PW3040 θ-2θ X-Ray Diffractometer using a Cu-K\(_{\alpha}\) source. The beam was energized at 45kV and 40mA. The incident optics were set to 1° and 1 cm slits. The antiscatter slit was set to 1/2° and the receiving slit was set to 1/4°. The solar slits are fixed at 0.04 rad. XRD scans were collected by first running a broad angle scan and from 5-130° 2θ at a high rate and then using the maximum intensity peak to determine the optimum scan rate for a 20-80° 2θ. Powder samples were placed in powder trays, thin film samples were leveled using a standard shim, and pellet samples were leveled on a jack stand and placed in the beam path.
A Bruker AXS HRXRD system was used for high resolution and pole figure multiaxis X-ray diffraction studies. The Cu-Kα source was energized to 40kV and 40mA variable antiscatter and divergence slits were used to optimize the beam optics as a function of theta. Data were collected at 0.04° 2θ increments for 0.5s. Φ-Scans were obtained by tilting the Chi angle to 11.25° to align with a symmetric plain and then scanning 360° around the (111) line for ceria at a 2θ of 28.55° [16].

2.2.2 Atomic Force Microscopy

Surface roughness of the prepared films was determined using an atomic force microscope (AFM). Images of the surface structure of the prepared films were also obtained using an AFM. Binning, Quate, and Gerber developed the AFM in 1986, as an extension to the scanning tunneling microscope (STM) for which the Nobel Prize was awarded to Gerd Binnig and Heinrich Rohrer in 1986 [17]. The AFM is among the most important modern tools for measuring, manipulating, and imaging matter at the atomic scale. The main advantage of the AFM over the STM is that the AFM can image a much wider variety of samples than the STM that requires a conductive sample. With a resolution approximately three orders of magnitude higher than the optical diffraction limit the AFM is used in many different situations to understand and manipulate matter.

The AFM forms an image by scanning a cantilever with an atomically sharp mechanical tip over the surface of a sample while measuring deflection of the tip. The tip, usually made from Si or Si₃N₄, is precisely scanned over very small areas using electronically controlled piezoelectric elements. The deflection of the
cantilever is measured using a laser spot shown on the cantilever and reflected into a 2 dimensional photodetector. There are other ways to measure the force including capacitance change, optical interferometry, and microstrain gauges.

The actual force on the tip may arise from a number of different physical effects such as simple mechanical contact, Van der Waals forces, electrostatic forces, chemical bonding, and many others. An AFM image is a reconstruction of the measured force or the measured deflection. Typically the AFM tip is not in actual mechanical contact with the surface because changes in topography of the sample could result in breaking the tip. Thus, another piezoelectric block is connected to a feedback control and this maintains a constant force between the tip and the sample.

There are several different methods to achieve constant force feedback including three-axis control of the tip or x-y control of the tip and a separate z control for the sample. Piezoelectric elements controlled in three dimensions give lower distortion in addition to a better representation of the topography of the sample. The mode of interaction of the tip with the sample can be static (contact mode) or dynamic (tapping mode) depending on the application. Typically for surface roughness measurements the contact mode is used.

AFM images were taken using an Agilent Technologies Inc. AFM with Picoview 1.4 software. A Si$_3$N$_4$ cantilever tip with a spring constant of 0.06 N/m was used in contact mode. Scans were made over 100, 10, 5, and 1 µm.
2.2.3 Scanning Electron Microscopy

Further characterization of the prepared films was performed using scanning electron microscopy (SEM). The SEM is an essential tool in modern materials research. This microscope operates by raster scanning a magnetically focused beam of electrons over the sample. The electrons have a precisely known energy and position before they interact with the sample. Many processes occur simultaneously in the SEM however it is secondary electrons and backscattered electrons that are primarily used to create images. The image is produced by coordination between the beam and the detector. Because the position of the interacting beam is known the detector can tell how many electrons it received when the beam was in that position over the sample. Because electrons interact with different features differently contrast between different areas is obtained in a modern SEM a computer assembles an image from the data.

SEM images were obtained using a Hitachi 2003-NSEM. Imaging used various accelerating voltages, beam currents, working distances, and aperture settings to obtain the highest resolution possible. Powder samples were packed on carbon tape, bulk samples were placed on aluminum stages, and thin film samples were lightly attached using carbon tape to an aluminum stage.

2.2.4 Optical Transmittance

Optical transmission measurements were made on the thin films prepared in this study. Optical Transmission is the physical process of light passing through a material. The optical transmittance is the fractional portion of light that is transmitted
through a sample at a given wavelength. In this measurement monochromated light of known intensity \( I_0 \) is incident on the sample and the intensity of the transmitted light \( I \) is measured. The transmittance \( T \) is defined by \( I/I_0 \). The optical absorbance \( \alpha \) is calculated from \( T \) and is defined as in equation 2.2.

\[
\alpha = -\log(T) \quad (2.2)
\]

Information about the nature and depth of the band gap can be obtained by fitting to equation 2.3. Where \( K \) is a constant, \( h\nu \) is the photon energy, \( E_g \) is the band gap, and \( n \) is 1 for indirect material and \( \frac{1}{2} \) for direct band gap material [18].

\[
\alpha = K(h\nu - E_g)^n \quad (2.3)
\]

Optical Transmission measurements were made using DU 730 Ultraviolet/Visible scanning spectrophotometer. Measurements were made from 180 nm to 1200 nm in wavelength scanning mode. The substrate contribution was subtracted by scanning a raw substrate and always facing the film side towards the light source.

2.2.5 Energy Dispersive Spectroscopy

Energy dispersive X-Ray spectroscopy (EDS) was used to identify the elemental composition of the materials prepared in this study and to check for contamination of the prepared films. EDS works by detecting X-Rays that are produced by a sample placed in an electron beam. The electron beam excites and ejects electrons in inner shells of the sample atoms. Low energy electrons of an atom in the sample are removed by interaction with the incident electron beam, higher energy electrons in the atom are able to transition to and fill the newly created low energy vacancies through the emission of X-Ray photons. The energies of the X-
Rays are characteristic of the atoms that produce them. X-Rays of different energies are detected simultaneously in EDS. The detected intensity of the X-Rays emitted from the sample are recorded simultaneously for each energy. This data can then be compared to known values for each element using a computer database or commonly available tables. EDS is a good technique to qualitatively determine the elements present in a sample [19].

EDS spectra were collected using an EDAX S13 Spectrometer attached to the Hitachi 2003-NSEM with 10 eV per channel and 100 ms dwell time. Scans were collected with the detector 5.5 cm from centerline at a working distance of 15 mm. The accelerating voltage was 25 keV with the beam current at 70. Samples were powders, sintered pellets, and thin films.

2.2.6 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the elements in each film. XPS is also known as electron spectroscopy for chemical analysis (ESCA) is a quantitative spectroscopic technique used to measure the electronic state, chemical state, empirical formula, and elemental composition of the elements that are present in the first 1-10 nm of a materials surface. Spectra are obtained by bombarding a specimen, held in ultra high vacuum (UHV), by a beam of Mg or Al Kα X-rays while simultaneously measuring the number of electrons emitted over specific kinetic energies. The kinetic energy is the difference between the incident photon energy and the work function plus the binding energy. Because the binding energy is dependent on the chemical environment, shifts in the observed
kinetic energy give information about oxidation state. Depth profiling of can be achieved using an argon ion etching system. The physical process behind XPS requires three electrons and this limits the technique to elements heavier than Li. Typical Detection limits are in the parts per thousand; however with sensitive equipment and extended collection times, parts per million is achievable [20].

A Kratos Axis UltraDLD XPS system with monochromatic Al K\textsubscript{\alpha 1} X-ray radiation was used for collection of XPS data. Surface charging was compensated with an applied voltage of 3.35V. Survey scans were collected over 0-1400 eV kinetic energies. The sample was then etched by an argon ion beam for 60 seconds and surveys were repeated. Detailed scans were then performed to determine the oxidation state of the constituent elements. Etching was then repeated for 480 s and detailed scans were also repeated.

2.2.7 Superconducting Quantum Interference Device

The superconducting quantum interference device (SQUID) is the most sensitive device available at present for measuring magnetic fields. The maximum resolution of a SQUID is around 5x10\textsuperscript{-15} T [21]. For comparison the average magnetic field of the Earth is 3.1x10\textsuperscript{-5} T [22]. At the heart of the SQUID is a Josephson junction consisting of two superconducting loops separated by a very thin electrical insulator.

The SQUID in the simplest sense is a highly linear current to voltage converter In a SQUID magnetic property measurement system (MPMS) the magnetic fields present in a sample indirectly by moving the sample through a series of
superconducting detection coils in the center of a high field superconducting magnet. The superconducting detection coils are inductively coupled by superconducting wires to the quantum interference device outside of the magnetic field. The SQUID is kept at an extremely constant magnetic field inside a superconducting shield.

During a measurement the sample moves through the detection coils and a change in magnetic flux is caused by the magnetic moment of the sample. This change in flux induces a current in the detection coils. The detection coils, connecting wires, and the input for the SQUID from a closed superconducting circuit. Therefore, any change in the magnetic flux will cause a directly proportional change in the persistent current of this circuit. This proportional change can be precisely calibrated using a material of known mass and susceptibility [23].

A SQUID magnetometer (Quantum Design, Model: MPMS-5S) was employed for magnetic property measurements over the temperature range of 10-300K. The sections of the films were cleaved, measured, weighed, cleaned, and shipped to collaborators at NCNT.
2.3 References


CHAPTER 3

OBSERVATION OF ROOM TEMPERATURE FERROMAGNETISM IN Ce$_{1-x}$TM$_x$O$_{2-\delta}$ (TM: Cu, Mn, Co) AND NO FERROMAGNETISM IN Ce$_{1-x}$TM$_x$O$_{2-\delta}$ (TM: Zn) FILMS

3.1 Introduction

There is a pressing need in the field of spintronics for efficient spin injection materials. The volumes of research on diluted magnetic semiconductors (DMS) confirm this need. To date extensive research on DMS has been done, however, there has been far less research on diluted magnetic dielectric materials (DMD). Until recently, most insulating magnetic systems showed ferromagnetism far below room temperature. To realize practical spintronic devices, it is essential that the material display ferromagnetism at room temperature. Dilute magnetic dielectric materials are very promising for realizing high temperature spin polarized electron injection. The extensive studies of the europium calcogenides (EuX, X: O, S, Se) have demonstrated the reality of spin dependent tunneling through magnetically polarized barriers [1-3].

If a room temperature intrinsically ferromagnetic dielectric material can be realized then this will open up new possibilities for realizing a high degree of spin
polarized injection. Until quite recently most of the research on spin electronics has emphasized creating a highly spin polarized density of states in a metal or semiconductor as a source of spin polarization. Spin injection can also be achieved by creating a spin dependent transmission factor in a tunnel barrier.

Spin filtering can be realized by using a magnetic dielectric material as a tunnel barrier. Figure 3.1 shows a schematic of a tunnel barrier. The barrier height $\phi_{\text{avg}}$ at temperatures above the $T_C$ for the magnetic barrier is shown by the dotted line. Below $T_C$ there is an exchange splitting $(2\Delta_{\text{ex}})$ of the conduction band leading to different barrier heights for the spin directions. The difference in barrier heights leads to a different transmission factor each spin. Given the exponential dependence of the tunnel current on the barrier height a high degree of polarization can be achieved in this manner. Equation 3.1 gives the tunneling current for a junction with an average barrier height of $\phi$ following the method of Simmons [4]. The model described in Equation 3.1 has been used by Moodera et al. to describe spin dependent tunneling in EuS [2], $(\phi)$ is the average barrier height, $(S)$ is the barrier thickness, and $(m)$ is the effective mass of an electron in the conduction band of the contact material.

\[
\begin{align*}
J &= J_0(\phi - \frac{1}{2} eV) \exp[-A(\phi - \frac{1}{2} eV)^{1/2}] - J_0(\phi + \frac{1}{2} eV) \exp[-A(\phi + \frac{1}{2} eV)^{1/2}] \\
A &= \left(\frac{4\pi S}{h}\right)(2m)^{1/2} \\
J_0 &= \left(\frac{e}{2\pi h}\right)S^{-2}
\end{align*}
\] (3.1)

Equation 3.1 shows that for slightly different barrier heights there is an exponentially large change in the current tunneled through the barrier. Thus even a small exchange
Figure 3.1: Energy diagram of a tunneling spin filter. Below $T_C$ of the ferromagnetic tunnel barrier, the barrier height for electron tunneling depends on the spin orientation of the electrons. In the spin valve shown here spin up electrons tunnel more easily than spin down resulting in a highly spin polarized current. [Adapted from 2,4]
splitting of the conduction band edge due to an internal magnetic field in the tunnel barrier can give rise to a highly spin polarized current.

If spin tunnel junctions are ever to move from the laboratory into use in future spintronic devices room temperature ferromagnetic insulator materials are needed. The discovery of high temperature ferromagnetism and extensive research on diluted magnetic oxide semiconductors, such as ZnO, has shown that transition metals not normally associated with ferromagnetism can induce ferromagnetic behavior in a host matrix. Notably among the transition metals used is copper. Copper alloys and compounds are not ferromagnetic; however, when copper is doped into ZnO the resulting material is ferromagnetic! Manganese was also chosen for investigation based on its extensive history as a magnetically diverse atom that is a component of many magnetic materials.

It may seem unusual for copper to be selected as a candidate material for magnetically doping CeO$_2$; however, a major advantage of using this dopant material is that even in the case of phase separation the resulting precipitates are not expected to be ferromagnetic. Thus, in the absence of contamination, any observed ferromagnetism can safely be assumed to be an intrinsic property of the material. Intrinsic ferromagnetism is very important to the goal of developing spin filter materials because if the magnetism is due to magnetic clusters the materials as a whole will not experience exchange splitting. Also if magnetic precipitates are the cause of ferromagnetism it will be very difficult to produce devices that behave in a predictable manor because these precipitates will not form in exactly the same way for every device.
Producing homogeneously doped magnetic films is extremely important. Because little is known about the equilibrium solubility of most transition metals in CeO$_2$ a high and a low concentration of dopant ion were studied. In addition to studding a high and low concentration a highly non-equilibrium deposition technique, pulsed laser deposition, was used. Because PLD is a highly non-equilibrium technique thin films with concentrations of dopants higher than the equilibrium solubility limit can be produced. Pulsed laser deposition has also been shown to produce a very homogeneous dispersion of dopants into host materials.

This chapter reports a study of the magnetic behavior of Ce$_{1-x}$Cu$_x$O$_{2-\delta}$, Ce$_{1-x}$Mn$_x$O$_{2-\delta}$, Ce$_{1-x}$Co$_x$O$_{2-\delta}$, and Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ films grown on LaAlO$_3$ substrates as candidate materials for further spintronic materials research. The films were prepared by pulsed laser deposition and were thoroughly characterized using state-of-the-art characterization techniques. Each of the thin film samples will be discussed in the following sections.

3.2 Structural and Magnetic Properties of Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ Thin Films

X-ray diffraction patterns of the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films grown on LaAlO$_3$ substrates are shown in Figure 3.2. Diffraction patterns of the substrate are also shown. Major peaks belonging to the (001) family of cubic cerium oxide were observed indicating the film is highly oriented in relation to the substrate [5]. No secondary phases were observed in the films. Because the detection limit for XRD is around 1% this does not completely rule out secondary phases. 0-20 XRD patterns for
Figure 3.2: X-ray diffraction patterns for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films and substrate.
the films were collected on the Philips X’Pert system described in Chapter 2 and φ-angle diffraction patterns for the films were collected on the Bruker AXS system. Previous studies of cerium oxide grown on LaAlO$_3$ using transmission electron microscopy showed that the films grew by domain matching epitaxy (DME) [5]. In this growth mechanism the [220] plane of CeO$_2$ aligns parallel to the [020] plane of the LaAlO$_3$ substrate. The c-axis of the substrate and the film are parallel in this growth mechanism and there is a $45^\circ$ rotation of the film relative to the substrate. Figure 3.3 shows the four-circle high-resolution x-ray Φ-scan for the Ce$_{0.97}$Cu$_{0.03}$O$_2$ film for the (111) plane showing the cubic symmetry of the fluorite structure. The peaks spaced at $90^\circ$ intervals reveal the cubic symmetry and a highly oriented film.

Figure 3.4 shows energy dispersive spectroscopy results for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films peaks corresponding to Ce, Al, La, Cu, and O are observed. Some carbon contamination was observed using EDS but no other contaminants were observed. The average film thickness was measured to be ~300 nm from observation in cross sectional SEM. A typical film cross section is shown in Figure 3.5 (a). Surface roughness and morphology of the films were studied using AFM. Figure 3.5 (b) and (c) show AFM images obtained for the $x=0.03$ and $x=0.15$ Cu doped films respectively. The RMS surface roughness was calculated from topological data and found to be 2.1 nm in the case of the $x=0.03$ sample and 0.8 nm for the $x=0.15$ sample. There is also visible qualitative evidence that the $x=0.03$ sample is heavily defected. Figure 3.6 shows optical transmission data for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films. As shown in the figure the absorption edge decreased in energy with increasing Cu concentration. In the inset of Figure 3.6 $\alpha^2$ versus $hv$ is plotted. By extrapolation of
Figure 3.3: X-ray Φ-scan of the Ce$_{0.97}$Cu$_{0.03}$O$_{2.6}$ film about the (111) plane.
Figure 3.4: Energy dispersive x-ray spectra for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films.
Figure 3.5: Micrographs of the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films (a) Cross sectional scanning electron microscope image of the Ce$_{0.97}$Cu$_{0.03}$O$_{2-\delta}$ film (b) AFM image of the Ce$_{0.97}$Cu$_{0.03}$O$_{2-\delta}$ film. (c) AFM image of the Ce$_{0.85}$Cu$_{0.15}$O$_{2-\delta}$ film.
Figure 3.6: Optical transmission measurements for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films. Inset absorbance squared for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films.
the linear section of these curves to zero the band gap of the samples has been estimated for the x=0, x=0.03, and x=0.15 films as 3.45 eV, 3.43 eV, and 3.39 eV respectively. The decreasing direct band gap of the materials indicates that the copper is being incorporated into the CeO$_2$ matrix. The drastic change in the transmittance of the x=0.15 film also indicates that a large number of optically active defect centers have been created in the film. The sharp decrease in transmittance for the x=0.15 film beginning at ~800nm (1.55 eV) could also be due to a copper oxide phase.

Figure 3.7 and 3.8 show x-ray photoelectron (XPS) spectra for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films. Understanding the valence state of the copper ions in the cerium oxide matrix will give insight as to the origins of the films’ magnetic properties. Figure 3.7 (a) shows XPS data for the Ce$_{0.97}$Cu$_{0.03}$O$_{2-\delta}$ film for the Cu 2p lines. XPS peaks corresponding to the Cu 2p$_{3/2}$ and 2p$_{1/2}$ emissions were centered about 953.4 eV and 933.0 eV respectively. The energy separation of these peaks is 20.4 eV. The three possibilities for the oxidation state of copper in the film are Cu metal, Cu$^{1+}$, and Cu$^{2+}$. Each of these possible oxidation states will have a different photoelectron energy position and separation. In the case of copper metal peaks would be present at 932.6 eV and 951.0 eV [6]. In the case of Cu$^{1+}$ peaks would be present at 932.4 eV and 952.5 eV [7]. Copper in the 2+ state has photoelectron peaks at 933.5 eV and 953.7 eV [7]. The observed binding energy and energy separation of Cu 2p photoelectron peaks in the x=0.03 film are consistent with Cu in the 2+ state [6]. However, because of the low intensity of photoelectron emission due to low copper
Figure 3.7: X-ray photoelectron spectroscopy for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films Cu 2p lines for the (a) x=0.03 and (b) x=0.15 films.
Figure 3.8: X-ray photoelectron spectroscopy for the Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ films O 2s lines for the (a) x=0.03 and (b) x=0.15 films.
concentration in this sample additional oxidation states could be present and unobserved.

Figure 3.7 (b) shows XPS data for the Ce$_{0.85}$Cu$_{0.15}$O$_{2-\delta}$ film, the Cu 2p XPS data showed peaks at 950.5 eV and 930.5 eV that correspond to the 2p$_{3/2}$ and 2p$_{1/2}$ states respectively. The peaks are separated in energy by 19.9 eV. The energy separation and binding energy of the peaks are consistent with the majority of the Cu in the 1+ state [7].

In both of the copper doped films the oxidation state of the cerium atoms was found to be mixed between 3+ and 4+ with the majority of the cerium in the Ce$^{4+}$ state. The observation of the Ce oxidation state was indirect and was made by evaluating the O 2s peaks. The two primary oxidation states of Ce will have different energies for the O 2s electrons; therefore, the splitting of the O 2s peak can be used to quantify the oxidation state of the Ce ions. By integrating the area under the split O 2s peaks and taking the ratio of these areas as shown in Figure 3.8 (a) and (b) it was determined that in the x=0.03 film 85% of the Ce are in the 4+ state and 15% are in the 3+ state. For the x=0.15 film 79% of the Ce are in the 4+ state and 21% are in the 3+ state. Because there are so few oxygen to copper bonds a separate peak was not observed. The ratios are only qualitatively consistent with the fact that introducing a Cu ion into the Ce$^{4+}$ lattice will create 2 oxygen vacancies.

In order to understand the observed magnetic behavior of the films all of the possible electronic configurations of Cu ions in the material must be considered. Cu atoms in unionized state have an outer shell electronic configuration of 3d$^{10}$4s$^{1}$, thus, Cu$^{+}$ and Cu$^{2+}$ ions are expected to have 3d$^{10}$ and 3d$^{9}$ configurations respectively. In
the 3d\textsuperscript{10} configuration, all of the d electrons are paired; therefore, a Cu\textsuperscript{+} ion does not have a magnetic moment. In the case of Cu\textsuperscript{2+} ions with a 3d\textsuperscript{9} configuration, one unpaired electron is available. This gives a spin angular momentum of 1/2 which can result in a net magnetic moment of \( M \sim 1.73\mu_B \) \( [M = g\mu_B\sqrt{S(S + 1)}; \; g = 2, \; S = 1 / 2] \) \[8\]. CuO has a partially occupied anti-fluorite crystal structure. CuO has no net magnetic moment because the unpaired spins of adjacent copper atoms couple in an anti-ferromagnetic manor below the Néel temperature.

Magnetic characterization of the films showed two different types of behavior. In the low concentration \( x=0.03 \) sample a ferromagnetic response was observed with a saturated magnetic moment of \( \sim 1 \mu_B/\text{Cu atom} \) as shown in Figure 3.9. The value of the saturated moment is of the same order of magnitude as the value calculated above. The coercivity of the sample was found to be \( \sim 70 \) Gauss and the remnant polarization was approximately 0.2 \( \mu_B/\text{Cu} \). If the copper ions were all in the 2+ state then a moment of 1.73 \( \mu_B/\text{Cu atom} \) should be observed. However, if all of the copper ions were in the 1+ state no magnetic moment should be observed. Thus, to explain the magnetic moment approximately 68% of the copper ions in the film should be in the 2+ state. Because extreme care was taken to prevent contamination and because all possible secondary phases are nonferromagnetic the observed magnetic properties are an intrinsic property of the material.

A very different magnetic behavior was observed in the \( x=0.15 \) film as can be seen in Figure 3.10. The saturated magnetic moment is approximately 0.2 \( \mu_B/\text{Cu} \) atom approximately 10% of the Cu in the film must be in the 2+ state to explain this moment. There is no observed coercivity for the \( x=0.15 \) film and the saturated
Figure 3.9: SQUID magnetic data for the Ce$_{0.97}$Cu$_{0.03}$O$_{2-\delta}$ film at (a) 10 K and (b) 300K. Insets show full range of data.
Figure 3.9: Continued.
Figure 3.10: SQUID magnetic data for the Ce$_{0.85}$Cu$_{0.97}$O$_{2-\delta}$ film at (a) 10 K and (b) 300K.
moment is approximately an order of magnitude lower than in the x=0.03 film. This type of behavior is symptomatic of a superparamagnetic response.

A superparamagnetic material is composed of small ferromagnetic particles that are small enough that thermal fluctuations cause randomization of polarization direction. Resulting in a material that as a whole is not internally magnetized except by an externally applied magnetic field. Superparamagnetism is similar to paramagnetism in that respect. Superparamagnetic materials exhibit behavior similar to paramagnetism at temperatures below the Curie or the Néel temperature. Because this is a small length-scale phenomenon the energy required to change the direction of the magnetic moment of a particle is of the same magnitude as the ambient thermal energy. Thus, the rate at which superparamagnetic particles will randomly reverse direction is high enough that the material will not retain a net internal magnetic polarization.

3.3 Structural and Magnetic Properties of Ce\(_{1-x}\)Mn\(_x\)O\(_{2-\delta}\) Thin Films

X-ray diffraction patterns of the Ce\(_{1-x}\)Mn\(_x\)O\(_{2-\delta}\) films are shown in Figure 3.11. Only planes belonging to the (001) family of cubic cerium oxide were observed in the x=0.00 and 0.03 films indicating the films are highly oriented [5]. In the XRD scan of the Ce\(_{0.85}\)Mn\(_{0.15}\)O\(_{2-\delta}\) film peaks corresponding to the (100) and (110) planes of hexagonal MnO\(_2\) were observed [9]. The 15% Mn film also showed a cerium (222) peak indicating that the film may have multiple crystal growth directions.

Phase separation observed in XRD in the Ce\(_{0.85}\)Mn\(_{0.15}\)O\(_{2-\delta}\) was also accompanied by extensive micro fracturing of the film. The fissures were observed
Figure 3.11: X-ray diffraction patterns for the Ce$_{1-x}$Mn$_x$O$_{2-\delta}$ films. Peaks marked with * belong to manganese oxide precipitates.
both in SEM and AFM images of the film. AFM images of the x=0.03 and x=0.15 films are shown in Figure 3.12. As can be seen in the figure the film has separated into domains between 500 nm and 1000 nm on an edge indicating that stress relaxation occurred by forming large defects in the film. Using the topography data to calculate surface roughness showed that the x=0.03 film had a RMS roughness of 2.3 nm and the x=0.15 sample had a RMS roughness of 3.5 nm.

Figure 3.13 shows energy dispersive spectroscopy results for the Ce$_{1-x}$Mn$_x$O$_{2-δ}$ films peaks corresponding to Ce, Al, La, Mn, and O are observed. Some carbon contamination was observed but no other elements were observed. The average film thickness was measured to be ~300 nm from observation in cross sectional SEM.

Optical transmission measurements of the Ce$_{1-x}$Mn$_x$O$_{2-δ}$ films shown in Figure 3.14 show that the absorption edge changed for the x=0.03 sample without significantly reducing transmission indicating that the manganese was incorporated into the lattice. For the x=0.15 sample the absorption increased in addition to a shift in the absorption edge this indicates that the material is more defected or has phase separated. In the inset of Figure 3.14 $α^2$ versus $hv$ is plotted. By extrapolation of the linear section of these curves to zero the band gap of the samples has been estimated for the x=0, x=0.03, and x=0.15 films as 3.45 eV, 3.48 eV, and 3.46 eV respectively.

Because manganese can exist in a plethora different valence states careful analysis of the x-ray photoelectron spectroscopy is essential to understand the observed magnetic properties of the thin film samples. Manganese is well known for having seven possible valence states. However, not all of these seven are observed in solid oxide phases. For instance Mn$_2$O$_7$ is a highly reactive liquid phase containing
Figure 3.12: AFM images of the Ce$_{1-x}$Mn$_x$O$_{2+\delta}$ films for (a) x = 0.03 and (b) 0.15.
Figure 3.13: Energy dispersive X-Ray spectra for the $\text{Ce}_{1-x}\text{Mn}_x\text{O}_{2-\delta}$ films for $x=0.00, 0.03, 0.15$. 
Figure 3.14: Optical transmission of Ce$_{1-x}$Mn$_x$O$_{2-\delta}$ film for x=0, 0.03, and 0.15. Inset shows absorbance squared vs. photon energy.
Mn in the +7 state. In several manganese oxide phases manganese exists in different oxidation state depending on the lattice site. Mn$_3$O$_4$ which is a ferrimagnetic material below 40 K has the spinel structure Mn$^{2+}$ occupy tetrahedral sites and Mn$^{3+}$ occupy octahedral sites [10].

Figure 3.15 (a) shows XPS data for the Ce$_{1-x}$Mn$_x$O$_{2-δ}$ films for the Mn 2p lines. Photoelectron emissions were centered about 641.4 eV, 644.0 eV and 653.2 eV the first two lines correspond to 2p$_{3/2}$ emissions the third peak to 2p$_{1/2}$ emissions. The presence of three photoelectron peaks indicates that the manganese is present in multiple valence states.

Manganese metal would show photoelectron emissions at 637.3 eV and 649.2 eV. Manganese in the 3+ state has photoelectron emissions at 641.6 eV and 653.4 eV, whereas, manganese in the 4+ state has emissions centered about 638.9 eV and 653.9 eV [11].

Manganese ions in the 2+ state have photoemission peaks centered about 643.6 eV and 653.4 eV [12]. Interpreting the observed photoelectron emissions indicates that manganese is present predominantly in the 3+, as this is the most intense emission, and that some of the manganese is also present in the 2+ state. Because the 2p$_{1/2}$ emissions for both 2+ and 3+ are so close in energy these peaks cannot be distinguished.

Figure 3.15 (b) shows XPS data for the Ce$_{0.85}$Mn$_{0.15}$O$_{2-δ}$ film with emissions for the Mn 2p core levels at 652.9 eV, 643.9 eV, and 640.9 eV that correspond to the Mn$^{3+}$ 2p$_{3/2}$, Mn$^{2+}$ 2p$_{3/2}$, and 2p$_{1/2}$ for both Mn$^{2+}$ and Mn$^{3+}$ states, respectively [11]. The small shifts in these data are likely due to over compensation of charge balance.
Figure 3.15: X-ray photoelectron spectroscopy for the Ce$_{1-x}$Mn$_x$O$_{2.5}$ films Mn 2p lines for the (a) $x=0.03$ and (b) $x=0.15$ films.
In both of the Mn doped films the oxidation state of the cerium atoms was found to be mixed between 3+ and 4+ with the majority of the cerium in the Ce$^{4+}$ state. The observation of the Ce oxidation state was indirect and was made by evaluating the O 2s peaks. By integrating the area under the split O 2s peaks as shown in Figure 3.16 (a) and (b) it was determined that in the x=0.03 film 86% of the Ce are in the 4+ state and 14% are in the 3+ state. For the x=0.15 film 79% of the Ce are in the 4+ state and 21% are in the 3+ state. Because there are far fewer Mn-O bonds than Ce-O bonds a separate peak for the different binding energy of the Mn-O bond was not observed.

In order to understand the observed magnetic behavior of the films the possible electronic configurations of Mn ions in the material must be considered. Mn atoms in unionized metallic state have an outer cell electronic configuration of 3d$^5$4s$^2$. Manganese metal follows Hund’s rules and all of the electrons occupy separate 3d orbitals with parallel spins. However, Mn metal is an antiferromagnetic material because the exchange interaction energy for adjacent Mn 3d orbitals with all spin pointing in the same direction is higher than if the spins align anti-parallel. The situation is similar for MnO$_2$ except that electrons in the anti-bonding oxygen levels in between the Mn$^{4+}$ ions exchange the anti-parallel alignment of spin. Manganese ions are able to have a very wide variety of oxidation states ranging from +1 to +7.

Figure 3.17 shows Squid magnetic data for the Ce$_{0.97}$Mn$_{0.03}$O$_{2-\delta}$ film 10K and 300K. The film exhibits a saturated magnetic moment of 0.025 $\mu_B$/Mn and a coercive field of ~450 Gauss at 10K. At 300 K the coercive field changes to 140 Gauss, however, the saturated magnetic moment only decreases to 0.021 $\mu_B$/Mn.
Figure 3.16: X-ray photoelectron spectroscopy for the Ce$_{1-x}$Mn$_x$O$_{2-δ}$ films O 2s lines for the (a) x=0.03 and (b) x=0.15 films.
Figure 3.17: SQUID magnetic measurements for Ce$_{0.97}$Mn$_{0.03}$O$_{2-\delta}$ film at (a) 10 K and (b) 300K.
Figure 3.18 shows SQUID magnetic data for the Ce$_{0.85}$Mn$_{0.85}$O$_{2-\delta}$ at 10K and 300K. The saturated magnetic moment and coercivity are much larger than for the x=0.03 sample. At 10K the saturated magnetic moment of the film is 0.11 $\mu_B$/Mn emu/cm$^3$ with a coercivity of 300 Gauss. At 300K the film has a saturated magnetic moment of 0.9 $\mu_B$/Mn and a coercive field of 150 Gauss.

3.4 Structural and Magnetic Properties of the Ce$_{0.85}$Co$_{0.15}$O$_{2-\delta}$ Thin Film

X-ray diffraction patterns of the Ce$_{1-x}$Co$_x$O$_{2-\delta}$ (x=0, 0.15) films are shown in Figure 3.19. Only planes belonging to the (001) family of cubic cerium oxide were observed indicating the films are highly oriented in relation to the substrate. No secondary phases were observed in XRD measurements. Figure 3.20 shows energy dispersive spectroscopy results for the Ce$_{1-x}$Co$_x$O$_{2-\delta}$ films peaks corresponding to Ce, Al, La, Co, and O are observed. Some carbon contamination was observed but no other elements were observed. The average film thickness was measured to be ~300 nm from observation in cross sectional SEM.

Optical transmission measurements of the Ce$_{1-x}$Co$_x$O$_{2-\delta}$ films plotted in Figure 3.21 show that the absorption increased by a very large amount for the x=0.15 sample in addition to a shift in the absorption edge from the pure sample this indicates that the material is may have an extreme number of defects. In the inset of Figure 3.21 $\alpha^2$ versus $h\nu$ is plotted. By extrapolation of the linear section of these curves to zero the band gap of the samples has been estimated for the x=0 and x=0.15 films as 3.45 eV and 3.36 eV respectively.
Figure 3.18: SQUID magnetic measurements for Ce$_{0.85}$Mn$_{0.15}$O$_{2-\delta}$ film at (a) 10 K and (b) 300K.
Figure 3.19: X-Ray diffraction pattern of the $\text{Ce}_{0.85}\text{Co}_{0.15}\text{O}_{2-\delta}$ and $\text{CeO}_{2-\delta}$ films on $\text{LaAlO}_3$. 
Figure 3.20: Energy dispersive spectroscopy results for $\text{Ce}_{0.85}\text{Co}_{0.15}\text{O}_{2-\delta}$ and $\text{CeO}_{2-\delta}$ films.
Figure 3.21: Optical transmission plotted vs. wavelength for Ce$_{1-x}$Co$_x$O$_{2-\delta}$ for $x=0$ and 0.15. Inset shows absorbance squared vs. energy.
Figure 3.22 shows XPS data for the Ce$_{0.85}$Co$_{0.15}$O$_{2-\delta}$ film. In Figure 3.22 (a) the oxygen 2s emission is shown. By integrating the area under each peak the percentage of Ce$^{3+}$ and Ce$^{4+}$ can be calculated. From this data it was found that 78% of the cerium are in the +4 state and 22% were in the +3 state. Figure 3.22 (b) shows the cobalt 2p level emissions. Core peaks were observed at 780.4 eV and 796.7 eV corresponding to the Co 2p$_{3/2}$ and 2p$_{1/2}$ levels respectively. These features are characteristic of cobalt in the 3+ state and indicate that cobalt clustering has not occurred [13]. However, shakeup peaks observed at slightly higher binding energies than the core levels indicate that the cobalt ions may be present in the 2+ state as well.

Figure 3.23 shows SQUID magnetic data collected for the Ce$_{0.85}$Co$_{0.15}$O$_{2-\delta}$ film. As can be seen in the figure the saturated magnetic moment of this sample is an order of magnitude higher than any of the other thin film sample at both 10K and 300K. At 10K the film has a saturated magnetic moment of 0.8 $\mu_B$/Co with a coercive field of 850 Gauss. At 300K the film has a saturated magnetic moment of 0.7 $\mu_B$/Cu with a coercivity of 100 Gauss.

3.5 Structural and Magnetic Properties of Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ Thin Films

A challenge to researchers working on magnetic semiconductors and dielectric materials has always been the possibility of magnetic contamination or phase separation resulting in false positives for ferromagnetic behavior. In this section the properties of the three films produced for this study that did not show
Figure 3.22: X-ray photoelectron spectra for Ce$_{1-x}$Co$_x$O$_{2-\delta}$ for x= 0.15, (a) Oxygen 2s and (b) Cobalt 2p.
Figure 3.23: SQUID magnetic data for the $\text{Ce}_{0.85}\text{Co}_{0.15}\text{O}_{2-\delta}$ film at (a) 10K and (b) 300K.
ferromagnetic behavior are discussed. These samples were prepared in an identical manor to the films that showed ferromagnetic behavior indicating that the results for the previously discussed films are not due to systematic contamination of the prepared materials.

Figure 3.24 shows x-ray diffraction patterns of the Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ samples in the x=0 and x=0.03 scans only reflections for the (001) family of Cubic CeO$_{2-\delta}$ and the LaAlO$_3$ substrate were observed indicating a highly oriented film. The x=0.15 film showed a minor peak belonging to the 100% intensity hexagonal ZnO (101) peak indicating that some degree of phase separation occurred in this film. A high-resolution four-circle phi-scan x-ray diffraction pattern is shown in Figure 3.25 for undoped CeO$_{2-\delta}$. The peaks spaced at 90° intervals show the cubic symmetry of the system.

The results of the magnetic characterization for the zinc-doped films are shown in Figure 3.26. As can be seen in this figure a strictly diamagnetic response was observed in these films. This can be understood by the fact that the zinc ions were found to be in the 2$^+$ state using XPS and Zn$^{2+}$ ions have no unpaired electrons and thus has no net magnetic moment.

3.6 Conclusion

3.6.1 Summary

The field of spintronics is a possible new paradigm for the next generation of multifunctional devices. Realization of active spintronic devices such as spin LEDs
Figure 3.24: X-ray diffraction patterns for the Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ films. The peak marked with * belongs to ZnO (101).
Figure 3.25: Phi-scan of the CeO$_{2.8}$ film.
Figure 3.26: SQUID magnetic data for the Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ (a) $x=0.03$ and (b) $x=0.15$ films.
and Spin-transistors has been hampered many technological difficulties including a lack of suitable materials. In this study room temperature ferromagnetism has been observed in two new rare earth oxide systems (Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ and Ce$_{1-x}$Mn$_x$O$_{2-\delta}$). In a third system ferromagnetism was ruled out (Ce$_{1-x}$Zn$_x$O$_{2-\delta}$). The Ce$_{1-x}$Co$_x$O$_{2-\delta}$ system had previously been shown to be ferromagnetic and this was confirmed in the present study. The bulk materials of each material system were prepared by state of the art materials processing techniques and thin films were grown by pulsed laser deposition technique on LaAlO$_3$ (001) substrates. The observation of high temperature ferromagnetism in two new lightly doped high-k dielectric materials represents a step forward in the field of spintronics and will provide future researchers with additional materials systems to explore.

Two concentrations of dopants were used in this study a low concentration (x=0.03) and a high concentration (x=0.15). The properties of the thin films were found to vary with dopant concentration. The films with a low concentration were found to be highly transparent over the visible range and no evidence of phase separation was found. The films with a high dopant concentration were found to be far less transparent and observable phase separation occurred in the case of the zinc and manganese doped films.

Magnetization measurements showed that in the case of Ce$_{1-x}$Cu$_x$O$_{2-\delta}$ the x=0.03 film exhibited room temperature ferromagnetism with a saturated magnetization of $\sim$1.0µ$_B$/Cu atom. XPS measurements on the same film showed that copper was in the 2+ state. When additional copper ions were introduced into the system (x=0.15) superparamagnetic behavior was observed. XPS measurements
showed a majority of the copper ions were in the 1+ state. The observation of ferromagnetism the Cu doped system indicates that ferromagnetism is an intrinsic property of the material. This is because even if unobserved phase separation occurred none of the possible secondary phases are ferromagnetic.

In the Ce$_{1-x}$Mn$_x$O$_{2-\delta}$ films ferromagnetic behavior was observed in both the x=0.03 and the x=0.15 samples. Evidence of phase separation was found using XRD for the Ce$_{1-x}$Mn$_x$O$_{2-\delta}$ x=0.15 film. AFM imaging showed that the x=0.15 Mn film was visibly textured. The Ce$_{1-x}$Co$_x$O$_{2-\delta}$ sample showed ferromagnetic behavior, while the Ce$_{1-x}$Zn$_x$O$_{2-\delta}$ and undoped CeO$_{2-\delta}$ films showed a strictly diamagnetic response.

The present work has shown that copper and manganese doped cerium oxide are promising candidates for future work developing high temperature spintronic devices. Further research is needed to see if the novel materials prepared in this study can function as spin filter materials. Much additional work is needed to characterize and correlate the structural and magnetic properties to determine the precise nature and origin of their ferromagnetic behavior.

3.6.2 Future Work

This section recommends additional experiments and characterization techniques that would extend the information obtained in the present study. Thin film samples with dopant concentrations slightly higher and lower than 3 atomic % should be fabricated in parallel with investigation of post annealing effects on observed ferromagnetism. The effects of oxygen partial pressure during deposition should also be studied. Another very useful study would be to attempt to deposit very smooth
and very thin films by varying the deposition rate and substrate temperature while also studying growth on conductive substrates. This would allow for characterization of magnetic field dependent electrical properties.

High resolution transmission electron microscopy (HRTEM) should be performed on cross sectional samples of all of the prepared films to observe the growth mechanism of the films and to investigate the presence of phase separation in the x=0.15 Mn sample. TEM could also be used to search for possible magnetic clusters in the films. TEM will also allow determination of crystalline orientation to the substrate.

Neutron diffraction is another characterization technique that would provide more information about the crystal structures relation to the thin film samples magnetic properties. Neutron diffraction is able to observe the magnetic properties of materials because neutrons have a magnetic moment and are thus scattered by the magnetic moments of electrons. This makes neutron diffraction more for determining the magnetic structure of materials than x-ray diffraction where x-rays are scattered only by electron density in materials and are not sensitive to the magnetic ordering. Also because the intensity of diffracted neutrons varies irregularly with atomic number thus, neutron diffraction can distinguish between adjacent atoms on the periodic table and is able to determine fine structure of observed samples.

AC magnetic susceptibility measurements should be used to study the Cu x=0.15 films superparamagnetic behavior. When an external magnetic field is applied to a superparamagnetic sample for a long time and then removed the randomization of the magnetic ordering does not occur immediately. A
superparamagnetic system will show frequency dependence in AC magnetic fields. When the AC magnetic frequency is much higher than the inverse of the randomization time scale, there will be a much different magnetic response than when the frequency is lower than this relaxation time. The precise frequency dependence can be calculated from the Néel-Arrhenius equation, assuming that the superparamagnetic domains have independent behavior.

X-ray magnetic circular dichroism (XMCD) is an advanced technique that could be used to study the magnetization of each element present in the samples. In XMCD the absorption of a beam of circularly polarized x-rays from a synchrotron source incident on the sample is measured both with and without an applied magnetic filed. By carefully analyzing differences in the absorption spectra information about the overall magnetization of each element present can be obtained.
3.7 References


