DEFECTS AND FERROMAGNETISM IN TRANSITION METAL DOPED ZINC OXIDE

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ABSTRACT

Farida Selim, Advisor

Transition metal doped zinc oxide has been studied recently due to its potential application in spintronic devices. The magnetic semiconductor, often called Diluted Magnetic Semiconductors (DMS), has the ability to incorporate both charge and spin into a single formalism. Despite a large number of studies on ferromagnetism in ZnO based DMS and the realization of its room temperature ferromagnetism, there is still a debate about the origin of the ferromagnetism.

In this work, the synthesis and characterization of transition metal doped zinc oxide have been carried out. The sol-gel method was used to synthesize thin films, and they were subsequently annealed in air. Characterization of doped zinc oxide films was carried out using the UV-visible range spectrometer, scanning electron microscopy, superconducting quantum interference device (SQUID), x-ray diffraction(XRD) and positron annihilation spectroscopy.

Hysteresis loops were obtained for copper and manganese doped zinc oxide, but a reversed hysteresis loop was observed for 2% Al 3% Co doped zinc oxide. The reversed hysteresis loop has been explained using a two-layer model.
For the Thapa Family and Friends
ACKNOWLEDGMENTS

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<td>4.10</td>
<td>31</td>
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<td>4.14</td>
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CHAPTER 1: INTRODUCTION

In this chapter, the ferromagnetism and research applications of zinc oxide are discussed. This chapter also discusses the basic properties of zinc oxide and its structure. The ferromagnetism of zinc oxide includes the current work done on ZnO nanoparticles, thin films, and other forms of ZnO. This chapter also focuses on the diluted magnetic semiconductor and mechanism of ferromagnetism in diluted magnetic semiconductors (DMS) in materials.

1.1 Crystal Structure of Zinc Oxide

Zinc oxide has recently attracted great interest due to its prospective applications in optoelectronic devices and white light emitting devices [1]. Zinc oxide is a wide band gap semiconductor with 3.3 eV of band gap and 60 meV exciton binding energy at room temperature. The wide band and high exciton binding energy make zinc oxide a potential candidate for applications in optoelectronics [2].

Figure 1.1 Wurtzite structure for ZnO crystal. The oxygen (grey) anion is surrounded by four zinc (yellow) cations [3].
Crystalline ZnO shows three forms—hexagonal wurtzite, cubic zinc blende and rocksalt, but the wurtzite structure is most stable in ambient conditions [1]. The native defects in ZnO can impact the structure, thus influencing the optical and electrical properties of ZnO [2]. The structural defects are formed during the growth method and the post-synthesis method, such as thermal treatment.

1.2 Diluted Magnetic Semiconductor (DMS)

The study for diluted magnetic semiconductors (DMS) of II-VI type have been going on for the last two decades [4]. They are semiconductors consisting of a small percentage of magnetic elements, mostly transition metals (TM) (shown in Figure 1.2), and are expected to have spin-polarized as well as electronic charge properties.

![Figure 1.2 Schematic showing magnetic, non-magnetic and diluted magnetic semiconductor. (A) magnetic semiconductor, (B) non-magnetic semiconductor, and (C) diluted magnetic semiconductor [5]. The magnetic ion is shown by blue circles.](image)

There has been a search for materials which shows ferromagnetism at higher T_C (Curie temperature) and also for the carrier contributing to the ferromagnetism. The oxide based DMS is predicted to be an important application for spintronic devices [6]. In addition, all oxide based DMS’s have band gaps greater than 3 eV, which contributes to the optoelectronic properties of
the spintronic devices. Table 1.1 shows the \( T_c \) values and magnetic moments for oxide based DMS thin films.

**Table 1.1** Oxide based DMS materials with their reported high value of \( T_c \) [7].

<table>
<thead>
<tr>
<th>Material</th>
<th>Doping(x)</th>
<th>Moment(( \mu_B/3d ) ion)</th>
<th>( T_c ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>Co:1-2%</td>
<td>0.3</td>
<td>&gt;300</td>
</tr>
<tr>
<td></td>
<td>Co:7%</td>
<td>1.4</td>
<td>650-700</td>
</tr>
<tr>
<td></td>
<td>V:5%</td>
<td>4.2</td>
<td>&gt;400</td>
</tr>
<tr>
<td></td>
<td>Fe:2%</td>
<td>2.4</td>
<td>&gt;300</td>
</tr>
<tr>
<td>ZnO</td>
<td>Co:10%</td>
<td>2.0</td>
<td>280-300</td>
</tr>
<tr>
<td></td>
<td>V:15%</td>
<td>0.5</td>
<td>&gt;350</td>
</tr>
<tr>
<td></td>
<td>Mn:2.2%</td>
<td>0.16</td>
<td>&gt;300</td>
</tr>
<tr>
<td></td>
<td>Fe:5%,Cu:1%</td>
<td>0.75</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>Ni:0.9%</td>
<td>0.06</td>
<td>&gt;300</td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>Co:5%</td>
<td>7.5</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>Fe:5%</td>
<td>1.8</td>
<td>610</td>
</tr>
<tr>
<td>Cu(_2)O</td>
<td>Co:5%,Al:0.5%</td>
<td>0.2</td>
<td>&gt;300</td>
</tr>
<tr>
<td>In(<em>{1.8})Sn(</em>{0.2})O(_3)</td>
<td>Mn:5%</td>
<td>0.8</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

1.3 Mechanism of Ferromagnetism in DMS Materials

Two mechanisms to explain the magnetic properties of DMS have been proposed. Mean-field theory, which originated from Zener model, is the first approach [8]. This model conjectures the interaction between the local moments of the atoms (as in Mn atoms) is moderated by free holes in the materials. Approximation of the mean field is also facilitated by assuming spin-spin coupling as a long range interaction [9-11]. The estimation of \( T_c \) for materials (Ga, Mn) As and (In, Mn)As is given by mean-field theory, and it also predicts that (Ga, Mn) As has a value of \( T_c \) above room temperature [9].
Defect-based bound magnetic polaron (BMP) is the second mechanism to explain intrinsic magnetic ordering. Defects such as V\textsubscript{O} (oxygen vacancies) and Zn\textsubscript{i} (zinc interstitials) are accountable for RTFM (room temperature ferromagnetism) in transition metal doped zinc oxide. There is a possibility of structural defects in the doped film that are located throughout the lattice at arbitrary distances with respect to the transition metal ions. These defects usually arise due to the highly non-equilibrium process of the thin film deposition technique\cite{12}. Polaron is produced when there is a charge-compensating electron for every V\textsubscript{O}. Superexchange between V\textsubscript{O} and magnetic impurities gives rise to ferromagnetic ordering. This exchange mechanism does not require free carriers as the percolation threshold for magnetic ordering is determined by the radius of the vacancy levels \cite{13}. This superexchange is possible due to the overlapping of hydrogenic orbitals. These hydrogenic orbitals spread out to overlap with a large number of bound magnetic polarons (BMP). The isolated polarons cannot be covered, thus they do not achieve ferromagnetic ordering\cite{14}.

The growth condition makes it difficult to verify the mechanism accountable for the observed ferromagnetism. The samples produced might be from a single-phase to nanoclusters, or even precipitates and a secondary phase formation. Also, the level of diluted magnetic atoms makes it difficult to establish the origin of ferromagnetism. Understanding the mechanism involved in the ferromagnetism requires careful observation. This can be done by connecting the magnetic properties measured with material examination method that can detect phases or precipitates \cite{15}.

1.4 Ferromagnetism in Zinc Oxide (ZnO)  

Ferromagnetism in doped ZnO has been studied, and T\textsubscript{C} for Mn-doped ZnO has been predicted by Dietl’s theory \cite{9}. Mn-doped ZnO thin films synthesized by pulsed-laser deposition
have maintained wurtzite structure [16]. The origin of ferromagnetism has been correlated with grain boundaries, strain, crystalline quality, and non-equilibrium point defects (oxygen vacancies, zinc vacancies, and zinc interstitials). Research has shown the relation between grain boundaries and magnetization in Mn-doped and undoped ZnO [17]. Moreover, a study done by Tietz et al [18] proposed that oxygen defects were responsible for the observed magnetism.

A recent study in the ferromagnetism of zinc oxide showed that both undoped and Co doped ZnO films displayed a diamagnetic behavior when annealed in oxygen. The same study also suggested that the defects near the surface are responsible for magnetism [19]. Similarly, another study proposes that defects accountable for room temperature ferromagnetism (RTFM) in undoped materials and insulated oxide films are located near the film-substrate interface because of the strain [20].

Irradiation of ZnO films with $^{107}$Ag ions altered the magnetic, optical and electrical properties maintaining the original crystal structure. The relation between RTFM and defects induced by radiation shows some degree of ferromagnetic ordering. Magnetic moments arise due to zinc vacancies, and bound magnetic polarons (BMP) associated with oxygen vacancies couple with magnetic moments to give rise to long-range ferromagnetism [21]. RTFM in undoped ZnO powder carried out by laser irradiation has been done without a change in the Wurtzite crystal structure. This method shows ferromagnetism in undoped ZnO without transition metal dopants. The RTFM can be reversed by annealing in an oxygen-rich environment, and RFTM can be produced by laser irradiation [22].

For instance, Mn doped zinc oxide synthesized by a wet chemical method on glass substrates showed room temperature ferromagnetism. The same study also found the Curie temperature ($T_c$) to be above room temperature. However, ferromagnetic properties of pure ZnO
nanorods were not observed. This study concludes that the presence of Mn$^{2+}$ in the ZnO lattice was responsible for the magnetic moment at room temperature in the thin films [23].

ZnO quantum dots doped with transition metal have been synthesized using a colloidal method. This method hosts a new class of magnetic semiconductors which have huge potential in nanotechnology [24]. Room-tempperture ferromagnetism has been observed in Co$^{2+}$ ZnO quantum dots prepared using a paramagnetic colloid. This study also suggests that high-Tc ferromagnetism comes from intrinsic property [25].

1.5 References


<http://whatiszincoxide.weebly.com/structure.html>


CHAPTER 2: ZINC OXIDE THIN FILMS SYNTHESIZED BY THE SOL-GEL METHOD

The synthesis of transparent oxide thin films has been done using the sol-gel method. The thin film grown using this method is inexpensive, and the organic impurities can be removed from the thin film by annealing at high temperature [26-27]. Electrical and optical properties of zinc oxide thin films can be modified by implementing different drying conditions and heating treatment. The resistivity and optical transmittance were seen to improve with the heating treatment [28-29]. The level of crystal orientation depends upon the thickness of the film, thus indicating there is an essential thickness showing highly oriented crystal growth [30]. This chapter focuses on the thin film synthesis method and the post treatment method.

2.1 Preparation of a Transition Metal Doped Solution

Before making ZnO thin films, a precursor solution must be made. These solutions are usually obtained by mixing solvents such as methanol, and ethanol into zinc acetate dihydrate/tetrahydrate. A stabilizer, usually ethanolamine is added to the resultant solution. This mixture is stirred at constant heat until a homogenous solution is formed. Transition metals such as cobalt and manganese can be doped to tune the ferromagnetic properties [31].

2.2 Thin Film Deposition by Spin Coating

Spin coating is used to achieve a uniform thin film and to control thickness of the thin film. This technology produces cheap thin films, which are easy to fabricate.
Figure 2.1 Schematic of spin coating device. The substrate is placed on a platform and is subjected to a vacuum suction. The spin coating begins once the lid is closed, and the solution is dispensed using a syringe [32].

ZnO solution covers the substrate which is usually quartz or sapphire. Once the solution is dispensed, the sample is placed in an oven so that the solution can evaporate leaving only the zinc oxide on the substrate. The thickness of the thin film depends on the spin coating procedure and the steps involved in solvent evaporation [33].

2.3 Annealing the ZnO Thin Films Using a Furnace

Annealing the ZnO thin films in a furnace affects the surface morphology. The annealed films have been shown to be direction dependent depending upon the annealing temperature. The preheating temperature was found to be the most important aspect for acquiring ZnO films which are oriented in a specific direction. However, studies have shown that the preferred orientation
also depends on the annealing temperature when the preheating temperature is kept constant [34].

Studies have shown that annealing the Co doped ZnO thin films in air, Ar, and Ar/H\(_2\) can change the saturation magnetization. The saturation magnetization (\(M_s\)) was found to be 0.2, 0.9, and 1.5 \(\mu_B\) (Bohr magneton) for air, Ar, and Ar/H\(_2\) respectively. The change in magnetization was associated with the increase or decrease of oxygen vacancies. Co doped ZnO thin films annealed in an Ar/H\(_2\) atmosphere were found to have oxygen vacancy density of about \(1 \times 10^{21}\) cm\(^{-3}\), using a simulation model [35].

2.4 References


CHAPTER 3: FERROMAGNETISM IN TRANSITION METAL DOPED ZINC OXIDE THIN FILMS

Diluted magnetic semiconductors have recently received attention as a relatively new field of electronics recognized as spintronics [36]. Recent research on ZnO based DMS has indicated ferromagnetism at room temperature [37]. This chapter discusses some research done on transition metal doped zinc oxide.

3.1 Cobalt Doped Zinc Oxide Thin Films

The films grown with Co doped ZnO show wurtzite structure and ferromagnetism at room temperature. The presence of ferromagnetism for pure ZnO was a surprising result [38]. The ferromagnetism decreases rapidly with the high-temperature process as seen by the VSM (vibrating sample magnetometer). The ionic radii of Co$^{2+}$ and Zn$^{2+}$(0.060 and 0.066 nm) differ only by 10 %, and Co$^{2+}$ is soluble in ZnO. This means that Co can be doped in ZnO thin films easily [39]. The concentration of Co ions and carriers plays a huge role in the magnetic properties of Co doped ZnO thin films. Apart from that, the origin of ferromagnetism in Co doped ZnO comes from the double exchange mechanism, as in III-V semiconductors. The possible origins of ferromagnetism due to weak ferromagnetism of CoO and micro Co clusters have been overlooked. The magnitude of magnetization is too large to be assigned to the weak ferromagnetism of CoO, and the XRD pattern does not reveal the CoO phase. Also, the examination of XRD patterns has ruled out the possibility of origin of ferromagnetism due to Co phase [40-41].

There have been studies, which reveal the existence of Co-metal clusters when the doping concentration is greater than 12 % of Co doping, but for Co doping less than 12%, Zn atoms are substituted for some Co atoms without the formation of Co-metal clusters or Co-oxide...
precipitates [42]. Other studies show that coexistence of Co metal clusters, and Co(II) oxide aggregates with surplus Co or coexistence of CoO aggregates with Co substituting for Zn in ZnO wurtzite lattice cannot be shown definitively [43].

3.2 Manganese Doped Zinc Oxide Thin Films

The magnetic force microscopy analysis showed the existence of rectangular shaped numerous domains for poor crystalline ZnMnO. The ferromagnetism hysteresis loop at 300 K indicated the possibility of high Curie temperature for Mn doped ZnO thin films [44]. The ionic radius of Mn$^{2+}$ is similar to Zn$^{2+}$ which means that Mn$^{2+}$ ion can be substituted for the Zn$^{2+}$ ion [45]. The examination of XRD patterns showed the presence of a single phase and the substitution of Zn site by Mn ion without a change in the structure [46]. The Mn doped ZnO thin films grown at 500 °C temperature showed ferromagnetism at room temperature but for temperatures greater than 500 °C the crystallinity of the films increases with a decrease in the magnetization due to the formation of Mn clusters [47].

A study found that undoped ZnO showed a diamagnetic behavior while the M-H (magnetization vs magnetic Field) curve for Mn doped ZnO show ferromagnetic behavior. This indicates that the ferromagnetism for Mn doped ZnO comes from the presence of Mn ions in the ZnO host matrix. This study also showed that the increased concentration of Mn (10 %) will produce antiferromagnetic behavior, which comes from the super exchange of the Mn-Mn interaction [48].

3.3 Inverted Hysteresis Loop in Co Doped Thin Films

Inverted hysteresis loops have been observed in Co-O/Cu and Co-O/Al based multilayers. These inverted hysteresis loops depend on the pure Co and Co-O phase, and absence of these phases means that inverted hysteresis loops are not seen. This kind of behavior is observed in a
two-phase model which includes interface exchange [49]. The magnetization becomes negative when the applied field is positive, and the magnetization becomes positive when the applied field is negative. The existence of a comparatively soft material (Co) and a hard material (Co-O) is the crucial feature. A theory based on a demagnetizing field states the surface charges at the ends of the films generate a field, which points in the opposite direction of the applied field. The net resultant of applied field and the demagnetizing field result in a field which acts on the soft materials, and this resultant field can be negative for a positive applied field [50]. The requirement for the observation of an inverse hysteresis loop is to apply the field direction along the hard axis. When the field is applied along the hard axis, \( M_Z \) will be larger than \( M_X \) (\( M_X \) and \( M_Z \) are the parallel and normal magnetization vector to the field direction) and the contribution of \( M_Z \) becomes large enough to generate an inverse hysteresis loop [51].

Observations of reversed hysteresis loops have been seen for CoFeAlO magnetic thin films [52]. This study shows that the coercive force is negative for a positive applied field along the hard magnetization direction. The occurrence of this phenomenon has been described using a two-layer model. The magnetically soft layer affects the demagnetizing field of the magnetically hard layer. This condition produces the reversed hysteresis loop [52-53]. In spite of a number of studies [49, 50, 53], our understanding of reversed hysteresis loops remains uncertain due to the complex nature of the problem.

3.4 References


CHAPTER 4: EXPERIMENT AND RESULTS

The chapter discusses the sol-gel method to fabricate transition metal doped zinc oxide thin films. It explains the synthesis method to obtain thin films of transition metal doped zinc oxide. In addition to obtaining thin films, this chapter also discusses the characterization carried out on the ZnO thin films; scanning electron microscopy (SEM), superconducting quantum interference device (SQUID), visible range absorbance, and positron annihilation spectroscopy.

4.1 Synthesis of Thin Films Using the Sol-Gel Method

Zinc acetate dihydrate was used as the solvent to prepare the ZnO solution. We used cobalt (II) acetate tetrahydrate as the dopant. The concentration of Co was varied from 1% to 5% with respect to Zn. We also added 2-Methoxyethanol as a solvent and ethanolamine as a stabilizer. The solution was stirred for 2 hours with a magnetic stirrer at a constant temperature of 60 °C. After the solution was prepared it was kept outside so that it would reach the room temperature.

The films were deposited on a quartz substrate using the sol-gel (spin coating) method. The solution was dispensed on a quartz substrate which was rotating at 500 rpm. After dispensing the solution, the quartz substrate rotates at 3000 rpm in order to distribute the solution evenly on the substrate. Once a zinc layer is grown on the substrate, the thin film is placed in an oven at 120 °C for 10 minutes to remove the resultant solvent and form the zinc oxide layer. This process is continued for 16 layers so that we have better coverage of the film. These films are annealed in ambient air at 700 °C for 1 hour to increase the structural properties.

Similarly, when we prepared 2% Al 3% Co doped ZnO we used aluminum nitrate, cobalt (II) acetate tetrahydrate, and zinc acetate dihydrate. We also added 2-Methoxyethanol as a solvent and ethanolamine as a stabilizer. The solution was stirred at 60 °C for 2 hours on a hot plate. The
films were deposited on a quartz substrate using above method to grow 16 layers. Also, the annealing process was done in ambient air for 2 hours at 500 °C.

The preparation of 3% Mn doped ZnO was done using manganese acetate tetrahydrate and zinc acetate dihydrate. We used 2-Methoxyethanol as a solvent and ethanolamine as a stabilizer to prepare the precursor solution. The preparation of the solution was similar to the above method. After each layer was deposited it was placed in an oven at 120 °C for 10 minutes and the films were grown to 16 layers. The annealing was done in ambient air at 700 °C for 2 hours to enhance the structural properties.

In a similar manner, the preparation of 1% Cu doped ZnO was done using copper acetate and zinc acetate. The solvent used was 2-Methoxyethanol and the stabilizer used was ethanolamine. The solution preparation method and the layer deposition method were similar to the method described above. We deposited 16 layers of zinc oxide layer on a quartz substrate and the annealing was done at 700 °C for 1 hour.

When handling the quartz substrate on all of the above methods, we used plastic tweezers instead of steel or metallic tweezers. The reason for using plastic tweezer was to avoid any contamination as we are working with transition metal doped zinc oxide thin films.
Figure 4.1 Flowchart showing the synthesis method for Co doped zinc oxide thin films. All other thin films are grown with this method and there are some changes in the annealing process and the number of layers of zinc oxide grown.
Table 4.1 Synthesized thin films with their respective dopants.

<table>
<thead>
<tr>
<th>Dopants</th>
<th>Concentration</th>
<th>Sample synthesized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese acetate tetrahydrate</td>
<td>3%</td>
<td>3% Mn doped zinc oxide</td>
</tr>
<tr>
<td>Cobalt(II) acetate tetrahydrate</td>
<td>1% and 5%</td>
<td>1% and 5% Co doped zinc oxide</td>
</tr>
<tr>
<td>Aluminum nitrate</td>
<td>2%</td>
<td>2% Al 3% Co doped zinc oxide</td>
</tr>
<tr>
<td>Cobalt (II Acetate)</td>
<td>3%</td>
<td></td>
</tr>
<tr>
<td>Copper acetate</td>
<td>1%</td>
<td>1% Cu doped zinc oxide</td>
</tr>
</tbody>
</table>

4.2 SEM Characterization

The surface of the thin film has been characterized using SEM. The SEM focuses an electron beam on the thin film. The electron beam will interact with the thin film giving off signals which may be detected. The detector records the signals and a computer compiles the signal into an image [54].
Figure 4.2 Schematic for the scanning electron microscope. The scanning electron microscope shows the condenser lens and detector [54].
Figure 4.3 SEM image of 1% Co doped ZnO thin film on quartz substrate. This thin films was deposited on a quartz substrate and annealed in air at 700 °C for 1 hour. Although the film was layered 16 times, we can see some defects in the film. The thin film has uniformity and consistency around the middle portion as shown in Figure 4.3 (a).
Figure 4.4 SEM image of 5\% Co doped ZnO thin film on quartz substrate. This thin films was deposited on the quartz substrate and annealed at 700 °C for 1 hour. The consistency and the uniformity of the thin film cannot be identified properly from the SEM images that we obtained. The edges as seen in figure (b) do not have better coverage of thin film since the solution did not spread. We did not get a better resolved SEM images for 5\% Co doped ZnO thin films.
Figure 4.5 SEM image of 2% Al 3% Co doped ZnO thin film on quartz substrate. This thin film was deposited on a quartz substrate and annealed at 500 °C for 2 hours. As we can see from the SEM image, the film has better coverage but the uniformity of the film cannot be determined as we did not get a resolved SEM image for this thin film. When we grew the film we could see by naked eye that the film was transparent and had better coverage.
Figure 4.6 SEM image of 3% Mn doped ZnO thin film on quartz substrate. This thin film was deposited on a quartz substrate and annealed at 700 °C for 1 hours. Here, figure (a) is the zoomed image and figure (b) shows the edge portion of the thin film. This thin film has better coverage, structured growth and uniformity. We can see in figure (b) that the film has some inconsistencies near the edge. The edge usually has some defects and inconsistencies as the film does not cover the substrate entirely. This may also occur depending upon with the handling of substrate.
Figure 4.7 SEM image of 1% Cu doped ZnO thin film on quartz substrate. The films were deposited on a quartz substrate and annealed at 700 °C for 1 hour. The thin film has some defects and inconsistencies.

4.3 Magnetic Measurement

A superconducting quantum interference device (SQUID) was used to measure the magnetic moments of the thin films. This device can measure a subtle magnetic moment and has a broad temperature range from 1.9 K to 500K. The magnetic fields range from -7 Tesla to +7 Tesla and the magnetic moment that can be measured is as low as $1.0 \times 10^{-8}$ emu (electromagnetic unit).
Figure 4.8 Schematic for a SQUID magnetometer [55].
Figure 4.9 Magnetic moment vs field for 3% Mn doped zinc oxide thin film. The measurement was done at 10K. The diamagnetic contribution was subtracted from the quartz substrate. After the subtraction, the curve shows a clear hysteresis loop. However, whether the observed ferromagnetic behavior comes from the intrinsic or a secondary phase (ferromagnetic clusters) is not clear. The origin of ferromagnetism in Mn doped ZnO is still unclear but a part of it can be clarified by the analyzing the X-ray diffraction (XRD) pattern.
Figure 4.10 Magnetic moment vs field for 2% Al 3% Co doped zinc oxide thin film. The thin film was grown on a quartz substrate. The measurement was done out of the plane at 10 K and we can see a hysteresis loop. As we can see from the figure, the hysteresis loop is reversed. The reason for this is unclear as there is less evidence for this kind of behavior. In a magnetically coupled layered thin film system, the reversed hysteresis loop materializes as an effect of the magnetically hard layer on the magnetically soft layer [56].
Figure 4.11 Schematic for two-layer model expanding reverse hysteresis loop for 2% Al 3 % Co doped zinc oxide thin film.

Here, the system can be viewed as a two-layer model. The bottom layer has a smaller magnetic moment ($M_1$) but a greater coercivity ($H_1$). The upper layer has a magnetic moment ($M_2$) and a smaller coercivity ($H_2$). The internal magnetic field $H_{2\text{int}}$ is the sum of external magnetic field ($H_{\text{ext}}$) and the demagnetizing field of the bottom layer $H_{21}$. The field $H_{2\text{int}}$ affects the magnetic moment of the upper layer $M_2$. As we can see from the figure, the demagnetizing field $H_{21}$ is in opposite direction to the external magnetic field. Similarly, the magnetic moment of the bottom layer depends on the $H_{1\text{int}}$, which is equal to $H_{\text{ext}}$ added to $H_{12}$ (demagnetizing field of upper layer). Within the scenario of Figure 4.11, $M_{2\text{int}}$ is negative because $H_{\text{ext}}$ (positive) is smaller than $H_{21}$ (negative). The magnetic moment of bottom layer is smaller than that of upper
layer, the external magnetic field and the total magnetic moment of the sample are in opposite directions [57].

Figure 4.12 Magnetic moment vs field for 1% Co doped zinc oxide thin film. The thin film was grown on a quartz substrate. The measurement was done at 300 K, which is at room temperature. The figure does not show a hysteresis loop. The straight line means that the thin film shows diamagnetic behavior.
Figure 4.13 Magnetic moment vs field for 5% Co doped zinc oxide thin film. The thin film was grown on a quartz substrate. The measurement was done at 300 K which is at room temperature. Even though the doping concentration is increased, there is no ferromagnetic behavior. The straight line means that the thin film shows diamagnetic behavior.
Figure 4.14 Magnetic moment vs field for 1% Cu doped zinc oxide thin film. The SQUID measurement was done at 10 K instead of 300 K. After the subtraction of the diamagnetic field that originated from the substrate, we can clearly see the hysteresis loop. Copper is a transition metal and not a magnetic material. The observance of a hysteresis loop for Cu doped ZnO casts doubt on the origin of ferromagnetism for transition metal doped zinc oxide.
4.4 Optical Characterization

Optical absorbance was measured to study the band gap of the thin films grown in our lab. We used Perkin Elmer Lambda 35 spectrometer to observe the optical absorbance for different thin films.

Figure 4.15 Diagram for Perkin Elmer spectrometer [58].
Figure 4.16 Absorbance spectrum for 1% Co, 2% Al 3% Co, and 5% Co doped zinc oxide thin film on a quartz substrate. As we can see that the thin film shows transmittance for wavelengths greater than 400 nm and absorbance for small wavelengths.

We can see from Figure 4.16 that the graph for each thin film is different. If we examine 1% and 5% Co doped ZnO thin films, we can clearly determine that 1% Co doped ZnO thin film has absorption edge with higher wavelength than 5% Co doped ZnO thin film. It clearly means that the optical band gap of these two thin films are different. The optical band gap of 5% Co doped ZnO is greater than that of 1% Co doped ZnO. Also, if we see 2% Al, 3% Co ZnO we can see that it has an absorption edge lower than that of 5% Co ZnO. So, 2% Al 3% Co ZnO has a wider optical band gap than 5% Co ZnO [59-60].
Table 4.2 show the band gap energy associated with the thin films. The wavelength at which the absorption drops was taken to calculate the band gap energy. The band gap energy is calculated in terms of an electron volt (eV).

**Table 4.2** Band gap energy for transition metal doped zinc oxide thin films.

<table>
<thead>
<tr>
<th>Thin Films</th>
<th>Wavelength associated with band gap edge (nm)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Co doped ZnO</td>
<td>368</td>
<td>3.37</td>
</tr>
<tr>
<td>2% Al 3% Co doped ZnO</td>
<td>355</td>
<td>3.49</td>
</tr>
<tr>
<td>5% Co doped ZnO</td>
<td>362</td>
<td>3.42</td>
</tr>
<tr>
<td>3% Mn doped ZnO</td>
<td>363</td>
<td>3.42</td>
</tr>
<tr>
<td>1% Cu doped ZnO</td>
<td>365</td>
<td>3.40</td>
</tr>
</tbody>
</table>
Figure 4.17 Absorbance spectrum for 3 % Mn doped zinc oxide thin film on a quartz substrate.

The absorbance spectrum in Figure 4.17 shows that 3% Mn doped zinc oxide thin film is transparent in the visible region. For wavelengths greater than 400 nm the transmittance is high, whereas absorbance is high for wavelengths less than 400 nm.
Figure 4.18 Absorbance spectrum for 1% Cu doped zinc oxide thin film on a quartz substrate.

Similarly, Figure 4.18 shows absorbance for 1% Cu doped ZnO and we can see that the thin film shows transmittance for wavelengths greater than 400 nm and absorbance for shorter wavelengths. This shows that the thin film is a transparent thin film.

4.4.1 Direct and Indirect Energy Gap

The optical energy gap can be determined by computing the absorption coefficient ($\alpha$), which relies on the film thickness and the absorbance intensity shown in the following equation:

$$\alpha = 2.303 \left( \frac{A}{d} \right)$$  \hspace{1cm} (1)
where $A$ is the absorbance intensity, and $d$ is the thickness of the thin film. Estimation of the energy gap ($E_g$) was done by assuming an indirect and direct allowed transition between a valence and a conduction bands by means of Tauc equation [61]:

$$\alpha h\nu = B(h\nu - E_g)^r$$  

where $B$ is constant, $h\nu$ is the incident photon energy, $\alpha$ is the absorption coefficient, and $r$ is constant of indirect transitions $r$ equals 2 and for direct transitions $r$ equals $1/2$ [62]. The energy band gap is determined by selecting the straight line portion of the spectrum and extrapolating that selected portion of the line to $\alpha h\nu = 0$.

**Figure 4.19** Direct allowed transition energy gap for a 1% Co doped zinc oxide thin film grown on a quartz substrate. The band gap associated with this thin film is 3.25 eV.
Figure 4.20 Indirect allowed transition energy gap for a 1% Co doped zinc oxide thin film grown on a quartz substrate. The band gap associated with this thin film is 3.08 eV.
Figure 4.21 Direct allowed transition energy gap for a 5% Co doped zinc oxide thin film grown on a quartz substrate. The band gap associated with this thin film is 3.13 eV.
Figure 4.22 Indirect allowed transition energy gap for a 5% Co doped zinc oxide thin film grown on a quartz substrate. The band gap associated with this thin film is 2.85 eV.
Figure 4.23 Direct allowed transition energy gap for a 2% Al 3% Co doped zinc oxide thin film grown on a quartz substrate. The direct band gap associated with this thin film is 3.15 eV. This direct band gap energy is slightly higher than the direct band gap energy for a 5% Co doped zinc oxide thin film.
Figure 4.24 Indirect allowed transition energy gap for a 2% Al 3% Co doped zinc oxide thin film grown on a quartz substrate. The indirect band gap associated with this thin film is 2.86 eV. This indirect band gap energy is slightly higher than the indirect band gap energy for a 5% Co doped zinc oxide thin film.
Figure 4.25 Direct allowed transition energy gap for a 3% Mn doped zinc oxide thin film on a quartz substrate. The band gap associated with this thin film is 3.18 eV.
Figure 4.26 Indirect allowed transition energy gap for a 3% Mn doped zinc oxide thin film on a quartz substrate. The band gap associated with this thin film is 2.93 eV.
Figure 4.27 Direct allowed transition energy gap for a 1% Cu doped zinc oxide thin film grown on a quartz substrate. The band gap associated with this thin film is 3.25 eV.
Figure 4.28 Indirect allowed transition energy gap for a 1% Cu doped zinc oxide thin film grown on a quartz substrate. The band gap associated with this thin film is 3.12 eV.
Table 4.3 Direct and indirect allowed transition energy gaps for zinc oxide thin films.

<table>
<thead>
<tr>
<th>Thin films</th>
<th>Direct allowed transition energy gap (eV)</th>
<th>Indirect allowed transition energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Co doped ZnO</td>
<td>3.25</td>
<td>3.08</td>
</tr>
<tr>
<td>2% Al 3% Co doped ZnO</td>
<td>3.15</td>
<td>2.86</td>
</tr>
<tr>
<td>5% Co doped ZnO</td>
<td>3.13</td>
<td>2.85</td>
</tr>
<tr>
<td>3% Mn doped ZnO</td>
<td>3.18</td>
<td>2.93</td>
</tr>
<tr>
<td>1% Cu doped ZnO</td>
<td>3.25</td>
<td>3.12</td>
</tr>
</tbody>
</table>

4.5 X-Ray Diffraction

X-ray diffraction (XRD) was used to identify the crystal phase for the transition metal doped zinc oxide thin films synthesized by the sol-gel method. Substrates coated with thin film were placed on a stage and struck by x-rays to obtain 2θ diffraction angles.
Figure 4.29 X-ray diffraction of 2% Al 3% Co doped zinc oxide thin film on a quartz substrate.

Figure 4.29 and Figure 4.30 shows XRD with multiple peaks at different position. (100), (002), (101), (102), (110), (103), and (112) appear at $2\theta = 31.78^\circ$, 32.37$^\circ$, 36.18$^\circ$, 47.33$^\circ$, 56.57$^\circ$, 62.12$^\circ$, and 68.06$^\circ$ respectively. These observed diffraction peaks match the hexagonal wurtzite ZnO structure. The peak at $2\theta = 45.28^\circ$ corresponds to the AlO phase and the peak at 50.96$^\circ$ corresponds to the AlCo phase. Even though we see the AlO and AlCo phases in the thin film, these phases are not responsible for the ferromagnetism in 2% Al, 3% Co doped ZnO thin films. In addition, the absence of Cobalt oxides and Co clusters in the XRD means the ferromagnetism
is not coming from the secondary phases.

**Figure 4.30** X-ray diffraction for 2% Al 3%Co doped zinc oxide thin film on a quartz substrate magnified around 25°-58°.

4.6 Positron Annihilation Spectroscopy

Positron annihilation spectroscopy has been carried out to study the effect a substrate has on the transition metal doped zinc oxide thin films.
4.6 References


CHAPTER 5: CONCLUSIONS AND FUTURE WORK

It is clear that we can observe ferromagnetism for Mn and Cu doped zinc oxide thin films. Even though Cu is not a magnetic material, observance of ferromagnetism for a Cu doped thin film suggests that the origin of magnetic moment in transition metal doped zinc oxide is not solely dependent upon the dopants.

In addition, the observance of reversed hysteresis loop for 2% Al 3% Co doped zinc oxide opens many research possibilities. Though this phenomenon is new for zinc oxide thin films, research has shown observance of reversed hysteresis loop for other materials. This phenomenon has been explained by a two-layer model for thin film materials which are layered. In contrast, Co doped zinc oxide thin film has shown diamagnetic behavior.

The selection of substrate also affects the defects in transition metal doped zinc oxide thin films. The substrate will also have an effect on the ferromagnetic behavior of the thin film. So, it creates doubt in the observed ferromagnetic behavior of transition metal doped zinc oxide.

Study of transition metal doped zinc oxide nanopowders will reveal much more about the observed ferromagnetic properties and the defects in it. The detection of any secondary phases that we can observe from the X-ray diffraction measurement will give more insight towards the origin of ferromagnetism.