Title
Transition Metal Doped ZnO as Diluted Magnetic Semiconductor

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Transition Metal Doped Zinc Oxide as Diluted Magnetic Semiconductor

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy
in
Electrical Engineering
by
Zheng Zuo

March 2013

Dissertation Committee:

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Committee Chairperson

University of California, Riverside
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ABSTRACT OF THE DISSERTATION

Transition Metal Doped Zinc Oxide as Diluted Magnetic Semiconductor

by

Zheng Zuo

Doctor of Philosophy, Graduate Program in Electrical Engineering
University of California, Riverside, March 2013
Dr. Jianlin Liu, Chairperson

Transition metal doped ZnO has been proposed to be a Diluted Magnetic Semiconductor with room temperature ferromagnetism. High quality Mn doped ZnO was grown on R-sapphire substrate. Results support intrinsic ferromagnetism, while μB/ion number was found to be larger than maximum permitted by Hund’s law. Saturation strength and coercivity field was found to be manipulated by varying Mn doping concentration. Mn/Ag co-doping was found to alter saturation strength and coercivity field as well. Ag was investigated as substitution dopant to achieve high quality p-type ZnO. With optimization of growth parameters, phase segregation was suppressed and p-type was observed. Besides being p-type, Ag doped ZnO was found to exhibit room temperature ferromagnetism. This is the first high quality demonstration of Ag doped ZnO as DMS.
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Chapter 1

Introduction: ZnO Diluted Magnetic Semiconductor

ZnO as semiconductor

ZnO has previously been used for various applications such as transparent contacts for solar cells, gas sensors, and surface acoustic wave devices \textsuperscript{[1]}. Its own properties as a semiconductor and related applications were ‘rediscovered’ in the early 1990s and triggered intense research activities. The band gap of ZnO of 3.37 eV at room temperature makes the material a promising candidate for optoelectronic devices in the blue and ultraviolet region. It appears especially favorable for such applications because of its large exciton binding energy of 60 meV \textsuperscript{[2]}, its low power threshold for optical pumping at room temperature and the availability of bulk ZnO substrates, which offers the possibility of homo-epitaxy for the fabrication of devices. Furthermore, the band gap of ZnO can be tuned in a large energy range by doping it with Cd or Mg. Also, high quality self-aligned ZnO nanowire has been demonstrated by our group for electrically pumped laser diodes.

In comparison to GaN, ZnO has further advantages in its cheaply available raw material (Zn in comparison to Ga), thus is more environmentally friendly. Wet etching of ZnO can be easily performed, in comparison to dry etching in GaN, and would offer greater convenience in device fabrications. Although still immature, ZnO is being developed for more application possibilities. Research on ZnO semiconductor has expanded to various areas of interest, and may provide solution for novel optoelectronics and spintronics applications.
The major challenge for ZnO research is to achieve high quality p-type. Various dopants have been proposed for p-type doping and investigated. Group V dopants P, As and Sb attracted much efforts [3-14] leading to controversial reports on p-type. The major problem is that these dopants rely on intrinsic point defect zinc vacancy (V$_{Zn}$) to form an acceptor level [15]. The presence of V$_{Zn}$ would fundamentally compromise ZnO lattice, and thus would pose difficulty when attempting higher quality thin film material. The most prominent demonstration to date has been N based p-type doping from Kawasaki et al [16]. The advantage of N doping in ZnO is its substitution doping mechanism. But it faces challenge in proper incorporation of nitrogen atom into ZnO lattice. Furthermore, the mechanism of N doping in ZnO remains controversial and is still under debate [17-18]. Group IB elements (Ag and Au) have been proposed to be substitution dopants [19]. But only limited methods were able to utilize such dopants, and results had mostly been unfavorable [20-22]. Sodium (Na) has also been proposed as possible substitution dopant [23], but deployment method is further restrained than group IB elements. Great efforts are still needed to develop robust p-type doping of ZnO.

Diluted Magnetic Semiconductors

Diluted Magnetic Semiconductors (DMS), or sometimes referred to as semi-magnetic semiconductors, are semiconducting materials in which a fraction of the host atoms can be substituted by magnetic ions or rare earths ions. Much of the attention on DMS materials is due to its potential application in spintronics devices, which exploit spin
in magnetic materials along with charges of electrons in semiconductors. Transition metals that have partially filled $d$ states (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) and rare earth elements that have partially filled $f$ states (e.g. Eu, Gd, Er) have been used as magnetic atoms in DMS. The partially filled $d$ states or $f$ states contain unpaired electrons, which would contribute spin to the system, and if appropriate ordering was achieved the semiconductor would show ferromagnetic property while retaining majority of its semiconductor nature and thus be applicable for spintronics applications. Or, from the energy band representation, in DMS materials the delocalized conduction band electrons and valence band holes interact with the localized magnetic moments associated with the magnetic atoms. When $3d$ transition metal ions are substituted into the hosting semiconductor, the resultant electronic structure is influenced by strong hybridization of the $3d$ orbital of the magnetic ion and mainly the $p$ orbital of the neighboring host anions. This hybridization gives rise to the strong magnetic interaction between the localized $3d$ spins and the carriers in the host valence band $^{[24]}$. This is refered to as $p$-$d$ Zener theory model and had been widely cited by researchers within the field. However, experimental results had shown vastly different behaviors than originally predicted. $p$-$d$ Zener model requires carrier mediated mechanism, thus relies heavily on the energy level alignment of $d$ orbit within the host system. The original prediction of room temperature ferromagnetic DMS was based on some extremely high carrier concentration $^{[25]}$. In many cases such requirements cannot be met. To explain how a semi-insulating material or material with limited amount of carrier exhibits room temperature ferromagnetism, Coey et al. proposed Bound Magnetic Polarons (BMP) as a possible mechanism providing indirect coupling
between magnetic ions \cite{26,27}. Wang et al. proposed F center \cite{28} model to explain ferromagnetism when no evident magnetic dopant is present. As addressed by Dietl \cite{29}, the original p-d model fits well with the well-established Mn:GaAs DMS system, but fails to explain for several other systems. As such, fundamental understanding of DMS remains to be further developed.

**ZnO based DMS**

DMS is believed to be the solution for future spintronic devices. However, one of the major obstacles for DMS is its curie temperature. For instance, Mn:GaAs had been a well-developed DMS in the 1990s. It had repeatable magnetic property and prototype devices were demonstrated \cite{30}. However, it suffered greatly for its low curie temperature (lower than 110K), which makes descent commercial application not applicable. It was T. Dietl’s prediction of room temperature ferromagnetism of ZnO and GaN in 2000\cite{24} that sparked the interest in DMS again. Much efforts have been made on both theoretical and experimental research on achieving room temperature DMS.

In the original prediction, T.Dietl et al predicted necessity of p-type conduction for the realization of many DMS. They specifically appointed GaN and ZnO to be possible candidate for room temperature DMS \cite{24}. K. Sato et al utilized ab initio simulation to investigate various factors that may affect the realization of room temperature ferromagnetism \cite{25}. They did simulation on the doping concentration of various TM dopants in ZnO and the results suggested that while for most cases ferromagnetism would
tend to stabilize with higher doping concentration, in the case of Mn higher doping would lead to spin-glass state. Their research on the effect of carrier type also suggested that p-type conduction should be necessary to realize room temperature ferromagnetism.

However, it was soon reported after the original prediction, that ferromagnetism was observed on TM doped n-type ZnO, especially from Mn doping, which was considered only possible under p-doping. Also various magnetism ordering were reported from different groups, sometimes even for same material prepared by same method. Debate is still on-going whether the magnetism ordering observed was intrinsic or extrinsic due to secondary phases or even metal clusters. Some recent reports even suggested that undoped ZnO can be ferromagnetic \[31\]. For specific doping scenario, like Co and Mn doping, detailed work have been performed trying to identify secondary phases and their magnetism prosperities. In the Co doping case, Co itself is strongly ferromagnetic with a very high curie temperature, thus being the major origin of extrinsic ferromagnetism in Co doped ZnO films. Some recent work suggested that Co clusters with amount beyond detection capability of typical XRD can provide enough ferromagnetism signals to confuse with the reported weak ferromagnetism cases \[32\]. So, painful work is needed to verify the origin of ferromagnetism in Co doped ZnO system, as like in our group’s previous work \[33\]. In Mn doped ZnO system, such controversies are slightly less complicated, since most of Mn-rich secondary phases are either antiferromagnetic \[34,35\] (including Mn itself), ferrimagnetic \[36-38\], or ferromagnetic with a low curie temperature \[35\]. Research on this system is mainly compromised by experimental methods. Non equilibrium growth methods would usually give out results with evident secondary phases, thus leading to
complicated discussions and reports with conflicting phenomenon from different groups. Equilibrium growth methods, like MBE and MOCVD are vitally important for development of ZnO DMS.

**Molecular Beam Epitaxy of ZnO DMS**

Various growth techniques have been utilized to grow ZnO, such as chemical reactions\[^{34}\], sintering\[^{39}\], ion implantations\[^{33,40-42}\], sputtering\[^{43}\], pulse laser deposition\[^{44}\], metal-organic chemical vapor deposition\[^{45}\] and radio-frequency (RF) plasma-assisted molecular-beam epitaxy (MBE)\[^{46}\] and most of them have also been utilized to grow ZnO DMS, by doping transition metal. MBE has been a method supposedly to provide better quality film. In ultra-high vacuum, only free drifting atoms reach the substrate surface, and aggregates formed on the path would be pumped away instead of participating growth. Due to its equilibrium growth nature, it was easier to minimize the emergence of secondary TM-rich phases or clusters. Many substrates are used for ZnO growth, including Si (100), Si (111), C-Sapphire, R-Sapphire, M-Sapphire and ZnO substrate\[^{47}\]. However, substrates with low lattice mismatch, high availability and low cost remains to be found. Most commonly used substrates are Si and sapphire substrates. Si substrate has obvious advantage of low cost, but the lattice mismatch between Si and ZnO can be as high as 40%, making high quality growth very challenging, if not impossible. In the case of sapphire substrate, two kinds of substrate need to be noted. Growth on the C-plane sapphire is straightforward. The C-axis of ZnO will be aligned with C-axis of the substrate. The crystal
structure is similar and a possible in-plane rotation would reduce mismatch to ~18.4%. In the case of R-plane sapphire, the lattice mismatch can be reduced to ~2% along the sapphire [0-111] direction. The preferential growth direction would be ZnO [0001] along Sapphire [0-111] direction, which is in the plane of substrate. High quality films have been reported by growing ZnO on R-sapphire. However, there are other concerns that affect the potential of R-sapphire. Various buffer techniques are being developed to grow higher quality ZnO on Si or C-sapphire. The application of MgO buffer before ZnO growth is suggested to reduce lattice mismatch to ~9.6%, and restrain much of the threading dislocations within buffer layer [48]. Also low temperature buffer technique is being applied to improve ZnO film quality. ZnO substrate is an obvious choice to eliminate the lattice mismatch problem, but high price and difficulty in characterization limit its use in research.

Conclusion

ZnO is a wide band gap semiconductor with great potential in optoelectronics and spintronics applications. It has been predicted as a room temperature ferromagnetic DMS, with Curie temperature well beyond room temperature. Transition metals have been proposed as magnetic dopants for ZnO DMS. However, experimental results conflict with the original prediction and new models are still controversial. As a high quality equilibrium growth method, MBE will provide accurate control of growths and thus contribute significantly for the development to ZnO DMS.
Reference


Chapter 2

Epitaxial growth of Mn doped ZnO Diluted Magnetic Semiconductor


Introduction

ZnO based diluted magnetic semiconductor (DMS) materials have been widely studied in recent years [1-2], because of the theoretically predicted above-room-temperature Curie temperature [3-4]. In the past decade, ZnO DMS materials have been investigated in various preparation methods, such as chemical reactions [5], sintering [6], ion implantations [7-10], sputtering [11], pulse laser deposition [12], metal-organic chemical vapor deposition [13] and radio-frequency (RF) plasma-assisted molecular-beam epitaxy (MBE) [14]. However, epitaxial ZnO DMS thin films grown with precisely controllable techniques, such as MBE, have not been widely reported yet. Our group had previously worked on hybrid MBE-implantation prepared ZnO DMS thin films [15-17], and demonstrated intrinsic room temperature ferromagnetism. To fully utilize MBE for multilayer device applications, entirely epitaxial growth is necessary.

Instrumentation

The MnZnO thin films were grown using plasma-assisted MBE. Knudsen effusion cells filled with elemental Zn (6N) and Mn (5.5N) were used as sources. An electron
cyclotron resonance plasma tube supplied with O$_2$ (5N) was used as the oxygen source. Two different substrates were investigated for MnZnO growth, namely Si (100) and c-plane sapphire. Different Zn cell temperature was utilized to accommodate different substrate. During growth, while all other parameter remained the same for each group of samples, the amount of Mn concentration in MnZnO was controlled by varying the Mn effusion cell temperature. In both cases Mn cell temperature within the range of 600°C ~800°C was investigated.

X-ray photoelectron spectroscopy (XPS) was used to identify elements and estimate the Mn concentration in the samples. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance x-ray diffractometer. The resolution of XRD system is ~0.1°. Reflection high-energy electron diffraction (RHEED) measurements were performed in situ on the as-grown samples in the MBE system. Scanning electron microscopy (SEM) images were taken using a Philips XL 30 FEG SEM system. Atomic force microscopy (AFM) experiments were performed to investigate the surface roughness of the samples using a Veeco Dimension 5000 AFM system. Magnetic properties were measured with a Quantum Design MPMS-XL SQUID magnetometer. Photoluminescence (PL) measurements were carried out using a home-built system with temperature control over a range of 8.5 K to 300 K in a Janis cryostat. A 325-nm wavelength Kimmon He-Cd laser was used as an excitation source and a photomultiplier tube was used to detect the PL signals. Field-dependent Hall Effect and Magneto Resistance (MR) measurements were performed using a Quantum Design PPMS system with magnetic fields up to 10 T.
Results and discussions

MnZnO films were firstly grown on Si (100) substrates to explore epitaxial doping of Mn. The Si substrates were cleaned by a modified Piranha-HF method. Firstly, the substrates were dipped in the piranha solution (H₂SO₄: H₂O₂ = 5: 3) solutions for 1 minute to remove the organic contaminations and then rinsed by de-ionized (DI) water. Subsequently, the substrates were dipped into diluted HF solution for 1 minute to remove oxide layer and then rinsed by DI water. These two steps were repeated alternatively for 3 times and samples were dried by nitrogen gun before transferred into the MBE load-lock chamber. Growth on Si were performed at room temperature, with a subsequent rapid thermo annealing process performed at at 900ºC for 5 minutes in N₂ environment. For these growths, Zn cell temperature and O₂ flow rate were kept at 370ºC and 18 sccm, respectively.

Table 2.1 and Figure 2.1 show the growth rates as a function of Mn effusion cell temperature, with constant Zn cell temperature at 370ºC and O₂ flow rate of 18 sccm. A smooth trend of growth speed is visible

<table>
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<th>Mn Cell Temp (°C)</th>
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<tr>
<td>u</td>
<td>N/A</td>
<td>4.8</td>
</tr>
<tr>
<td>a</td>
<td>600</td>
<td>5.8</td>
</tr>
<tr>
<td>b</td>
<td>650</td>
<td>6.3</td>
</tr>
<tr>
<td>c</td>
<td>700</td>
<td>6.5</td>
</tr>
<tr>
<td>d</td>
<td>750</td>
<td>6.7</td>
</tr>
<tr>
<td>e</td>
<td>800</td>
<td>7.1</td>
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Figure 2.1 MnZnO growth rate
based on varying Mn cell temperature (Figure 2.1). Undoped reference sample (u) had a growth speed of 4.8 nm/min, and growth speed of Mn doped samples (a~e) increased from 5.8 nm/min to 7.1 nm/min when increasing Mn cell temperature from 600ºC to 800ºC. The correlation between Mn parameter and growth rate may indicate that a large amount of Mn was incorporated into these ZnO films.

Figure 2.2 shows XRD spectra of some of the samples. Samples all showed evident ZnO (0002) peak, indicating C-direction growth. Mn-rich sub phases related XRD peaks have been observed in samples prepared by other methods and ferromagnetism of those samples was largely attributed to Mn-rich sub phases \cite{7, 15}. However, no Mn-rich secondary phases related peaks were evidently visible in our samples. Most doped samples did show visible ZnO (101) peak, which indicates that the films are generally polycrystalline. In the case of heavy doping (Figure 2.2d), other ZnO peaks are also visible, indicating decrease of crystal quality due to doping.
Figure 2.3 shows field dependence of magnetization of Mn doped ZnO DMS samples being measured at room temperature, with Figures a~e correspond to samples a~e. As shown in the figure, when Mn cell was at 600°C, diamagnetic behavior dominates. When Mn cell was increased to 700°C, ferromagnetic behavior dominates and hysteresis loop was observed (insert, Figure 2.3c). However, further increase of Mn cell temperature
led to decrease of saturation magnetization. As can be seen in Figure 2.3e, diamagnetic behavior dominates over ferromagnetism again when Mn cell reached 800ºC.

While room temperature ferromagnetism was observed on epitaxial MnZnO grown on Si, their poly crystalline nature limits their potential for applications. To improve the MnZnO thin film, further growths were performed on c-plane sapphire substrates. The sapphire substrates were chemically cleaned with hot (~150ºC) aqua regia (HNO₃:HCl = 1:3) solutions for 20 minutes, rinsed with de-ionized water, and dried with a nitrogen gun. Table 2.2 shows the growth parameters of MnZnO grown on sapphire substrate. For sapphire growths the substrate temperature was kept at ~300ºC during the growth, while the Zn cell temperature was increased to 390ºC. Mn concentrations were acquired from XPS measurements and shown in Table 2.2 as well.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$T_{\text{growth}}$ (ºC)</th>
<th>$T_{\text{Zn}}$ (ºC)</th>
<th>$T_{\text{Mn}}$ (ºC)</th>
<th>Mn Concentration x (%)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>~300</td>
<td>390</td>
<td>620</td>
<td>~1.8</td>
<td>Mn$<em>{0.02}$Zn$</em>{0.98}$O</td>
</tr>
<tr>
<td>B</td>
<td>~300</td>
<td>390</td>
<td>660</td>
<td>~4.3</td>
<td>Mn$<em>{0.04}$Zn$</em>{0.96}$O</td>
</tr>
<tr>
<td>C</td>
<td>~300</td>
<td>390</td>
<td>700</td>
<td>~7.7</td>
<td>Mn$<em>{0.08}$Zn$</em>{0.92}$O</td>
</tr>
<tr>
<td>D</td>
<td>~300</td>
<td>390</td>
<td>740</td>
<td>~9.3</td>
<td>Mn$<em>{0.09}$Zn$</em>{0.91}$O</td>
</tr>
<tr>
<td>E</td>
<td>~300</td>
<td>390</td>
<td>780</td>
<td>~12.6</td>
<td>Mn$<em>{0.15}$Zn$</em>{0.85}$O</td>
</tr>
</tbody>
</table>

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Figure 2.4 shows the Arrhenius plot of the relation between the Mn concentrations (vertical-axis in percentage unit) and reciprocal of the Mn effusion cell temperatures
(horizontal-axis). A reasonably well fitting of experimental data is achieved. The error bars of Mn concentrations arise from the calculation uncertainties of the XPS peak integrated intensities.

Figure 2.5 shows the XRD pattern of the MnZnO epitaxial thin film sample C. Only MnZnO (0002) and (0004) peaks are observed at 34.8° and 73.0°, respectively, indicating that the film is well aligned along the c-direction. This is an improvement from the heavily poly crystalline growth on Si. Besides the MnZnO peaks, a sapphire (0006) peak is also observed at 42.0° from the substrate. The XRD peak position and FWHM of the MnZnO (0002) peaks from all the five samples are at 34.8° and ~0.30°, respectively.

Neither Mn-related impurity phase peaks, nor evident Mn concentration dependence of the MnZnO (0002) peak positions and full-width-at-half-maximums (FWHMs) were observed within the detection and resolution limits of the XRD system. The latter is due to the relatively small Mn concentrations (2%~13%) in the samples.

According to reference [12], the c-lattice constant of MnZnO only changes slightly
from 0.521 nm to 0.523 nm, when Mn concentration in MnZnO increases from 0% to 10%. Hence, it is not too surprising that these tiny changes within 0.002 nm were not detected among these five MnZnO samples. A higher resolution XRD system may help clarify this issue in the future.

The inset in Fig. 2.5 shows the RHEED pattern of the MnZnO epitaxial thin film sample C. The spotty pattern indicates a rough surface of the MnZnO thin film. Surface roughness of all the five MnZnO samples was characterized using AFM. Figure 2.6 shows the AFM image of the MnZnO sample C within a 1μm × 1μm area. The root-mean-square (RMS) surface roughness of MnZnO samples A-E are 19.7, 20.9, 23.3, 25.4, and 30.6 nm, respectively. Such large RMS numbers are in close agreement with the observed spotty RHEED pattern. The textured morphology and relatively larger surface roughness of the MnZnO samples are mainly due to the relative low growth temperature (~300°C) and Mn incorporation.

Figure 2.6 AFM image of sample C surface. Reprinted with permission from Elsevier.*
Figures 2.7 a–e show the magnetic field dependence of the 300K magnetizations of MnZnO epitaxial thin film samples A–E. Samples A–E are grown with the same growth parameters except for the different Mn effusion cell temperatures $T_{\text{Mn}}$, which ranges from 620°C to 780°C with a step of 40°C (Table 2.2). Figure 2.7f shows the plot of the saturated magnetization versus Mn effusion cell temperature for the five MnZnO samples, showing the dependence of the magnetic properties of the MnZnO samples on $T_{\text{Mn}}$. With increasing
$T_{\text{Mn}}$, which corresponds to increased Mn incorporation, the saturated magnetization ($M_s$) of the MnZnO increases from $\sim7$ emu cm$^{-3}$ when $T_{\text{Mn}} = 620^\circ$C to $\sim13$ emu cm$^{-3}$ when $T_{\text{Mn}} = 660^\circ$C, and finally to $\sim22$ emu cm$^{-3}$ in $T_{\text{Mn}} = 700^\circ$C. However, when $T_{\text{Mn}}$ is further increased from 700 to 740$^\circ$C, the $M_s$ slightly decreases to $\sim19$ emu cm$^{-3}$. At or beyond 780$^\circ$C, the magnetism is dominated by the diamagnetic behavior from the contribution of the sapphire substrate. This reduction in ferromagnetic character may suggest that the primary magnetic coupling mechanism between Mn ions in the MnZnO thin films changes gradually from a pure carrier-mediated one to a coexistence involving of both carrier mediation among Mn ions and direct exchange when a large amount of Mn is incorporated.

Figure 2.8a shows the temperature dependence of the magnetization measured at 2.0 kOe for the MnZnO sample C. The magnetization only drops slightly with increasing temperature from 2 K to 300 K, indicating a Curie temperature well above room temperature. Figure 2.8b shows the magnetic anisotropy of MnZnO sample C. The black and red curves show the magnetic field dependence of the magnetization with

\[ \text{Figure 2.8} \] Fielded cooling and magnetic anisotropy of sample C. Reprinted with permission from Elsevier.*
out-of-plane (magnetic field perpendicular to the film plan) and in-plane (magnetic field parallel to the film plane) geometries, respectively. The coercivity in the in-plane geometry is ~50 Oe, while the out-of-plane magnetization has a slightly larger coercivity. Generally clustering phases show isotropic magnetism; so the magnetic anisotropy is a sign of intrinsic ferromagnetism.

In magnetic materials, the Hall resistance is contributed by both the ordinary and anomalous Hall effects (AHEs) and is expressed as:

$$R_{\text{Hall}} = \frac{R_0}{d} (\mu_0 H) + \frac{R_S}{d} (\mu_0 M),$$

where $R_0$ and $R_S$ are the ordinary and anomalous Hall coefficients, $d$ is the thickness of the film, $H$ and $M$ are the magnetic field and magnetization perpendicular to the film plane, respectively, and $\mu_0$ is the free space permeability. The anomalous Hall coefficient $R_S$ can be extracted by extrapolation of the linear fit to the high field Hall resistance to zero field, as discussed in detail previously. \[10\]. Figure 2.9a shows

Figure 2.9 Anomalous Hall Effect coefficient and quadratic term fitting. Reprinted with permission from Elsevier. *
temperature dependence of the anomalous Hall coefficient of the MnZnO thin film with
the inset showing the temperature dependence of the resistivity $\rho_x$. By examining the
relation between $R_S$ and $\rho_x$, the (scattering) mechanisms for charge carriers in the MnZnO
thin film can be determined $^{[10]}$. $R_S$ has both linear and quadratic dependence on $\rho_x$, and it
can be expressed as $R_s = a_{sk} \rho_s + b_{sj} \rho^2_s$. The linear term is interpreted as the skew
scattering and the quadratic term is associated with side-jump scattering or intrinsic
mechanisms. Figure 2.9b) shows a plot of $R_s/\rho_s$ versus $\rho_s$. The square symbols with error
bar are the experimental data and the dashed line is a linear fit. The linear fit represents the
dominance of the quadratic dependence. From the fitting, the parameters are
$a_{sk} = (-3.3 \pm 0.7) \times 10^{-7} \text{G}^{-1}$ and $b_{sj} = (2.0 \pm 0.4) \times 10^{-6} \text{G}^{-1} \Omega^{-1} \text{cm}^{-1}$, respectively. Based
on parameter $a_{sk}$, the skew scattering angle is estimated to be $-0.4 \sim -0.3 \text{mRad}$. Early
studies tended to assume the existence of the quadratic term is a possible indication of
intrinsic carrier-mediation ferromagnetism $^{[18,19]}$.

Figure 2.10a and b show the Magneto Resistance (MR) for the MnZnO thin film at
2, 5, 10, 20, 50, 100, and 100 K with magnetic fields up to 10 T in the out-of-plane and in-
plane geometries, respectively. The MR is defined as $\text{MR} = [R(H) - R(0)]/R(0)$. The out-of-
plane and in-plane MR curves show similar shape, indicating the same scattering
mechanism, but slightly different magnitudes are observed due to the anisotropic
magnetism in the MnZnO thin film. At 2 K, the MR is dominated by a positive contribution,
and as the temperature is increased the competition from a negative component increases
and is very apparent at 5 K. Above 5 K, the MR is clearly negative. The positive MR is attributed to a giant spin-splitting of band states caused by a $sp$-$d$ exchange interaction in DMSs while the negative MR could be from either weak localization or bound magnetic polarons $^{[10]}$. These discussions are consistent with the MR studied in MnZnO:Al (with electron carrier concentration of $\sim 10^{20}$ cm$^{-3}$) $^{[20]}$, in which the positive and negative MR of MnZnO were also attributed to giant spin-splitting of the conduction band and formation of bound magnetic polarons.

The main point of this chapter is the experimental demonstration of a growth window for MBE-grown MnZnO epitaxial thin films, within which the MnZnO samples show room temperature ferromagnetism. The experimental results discussed pave the way to the investigation of Mn concentration dependence of the magnetic properties in MnZnO. Tremendous efforts are still required to further clarify the real origins and mechanisms of the ferromagnetism in ZnO-based DMS materials. The observed behaviors do not necessarily support intrinsic ferromagnetism. For instance, early studies tended to assume the existence of the quadratic terms is a possible indication of intrinsic carrier-mediation.
ferromagnetism \cite{18,19}. However, recent AHE studies \cite{21} classify both screw-scattering and side jump terms as extrinsic mechanisms to AHE, while a contribution which only depends on bands structure but is independent of scattering process is defined as intrinsic mechanism. On the other hand, the observed smooth fielded cooling measurement shown in Figure 2.8a is a good indication that a magnetically singular phase is observed, and no other phases with Curie temperature within the range of 4~300K was present in the current MnZnO DMS being discussed.

More reliable platform for ZnO DMS studies will be forming, if the properties of hosting ZnO materials (before magnetic doping), such as background donor impurity species and density, mobility, and crystallinity, do not show significant difference among different research groups in ZnO DMS community. The current status is still far away from that. For example, the background electron concentration and mobility of undoped ZnO show several orders of magnitude difference from groups to groups. Starting from a quite distinct platform, it is evidently not surprising that ZnO DMS show different properties after being magnetically doped. Further comparisons among these results are more likely to lead to controversies rather than clarifications. This is also somehow true for GaN-based DMS \cite{1} and other oxide-based DMS \cite{2} materials, unlike the classic semiconductors such as GaAs, for which many different groups and companies can obtain same crystallinity samples with almost identical intrinsic carrier concentration and mobility. Further improvement of ZnO as host material is crucial for the advancement of ZnO DMS research.
Conclusion

MnZnO DMS thin films were epitaxially grown on Si and sapphire substrates using MBE. With improved growth based on sapphire substrate, the MnZnO DMS thin films are well aligned along c-direction according to XRD, although their surfaces are rough and textured. No impurity phase segregation was observed in the XRD patterns within the system detection limit. Effusion cell temperature of Mn between 600 °C and 800°C was explored with the largest saturated magnetization shown at a cell temperature of 700°C. The ferromagnetism in the MnZnO DMS thin films shows an above-room-temperature Curie temperature and a weak anisotropy. Positive and negative MR were observed below and above 5 K, respectively. Anomalous Hall effects were observed in the MnZnO DMS thin films, with a quadratic dependence of the anomalous Hall coefficient on the longitudinal resistivity observed.

Acknowledgement

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Reference


Chapter 3

Single-crystalline Mn doped ZnO Diluted Magnetic Semiconductor


Introduction

Diluted magnetic semiconductor has been proposed for more than two decades and has attracted much attention for its potential in spintronic applications [1], such as logic process, memory storage, communication and quantum computation [2-5]. Extensive work has been performed on transition metal (TM) doped ZnO synthesized using various methods, including chemical reaction [6,7], sintering [8,9], ion implantation [10-12], sputtering [13], pulsed laser deposition [14], metal-organic chemical vapor deposition [15] and molecular beam epitaxy (MBE) [16,17]. However, for device applications in reality, only high quality thins films are real candidates. Poly crystalline ZnO DMS presents great difficulty in clarifying the origin of the observed ferromagnetism. One major problem concerning TM doped ZnO DMS is whether the ferromagnetism is associated with clusters of the TM dopant. Further possible candidates to contribute extrinsic magnetism signals include surface states and grain boundaries. Thus it is crucial to develop high quality TM doped ZnO to clarify the mechanism. Here we report MBE growth of high-quality single
crystalline Mn-doped ZnO with very low Mn concentration and their magnetic properties. Strong above room-temperature intrinsic ferromagnetism is demonstrated. The results may be explained by singular ion induced intrinsic ferromagnetism mechanism.

**Instrumentation**

The Mn-doped ZnO thin films were grown using electron cyclotron resonance (ECR)-MBE. Radical Knudsen effusion cells filled with elemental Zn (6N) and Mn (5.5N) metals were used as Zn and Mn sources. The Zn and Mn fluxes were controlled by the effusion cell temperatures. An ECR plasma tube supplied with O\textsubscript{2} (5N) gas was used as the oxygen source, and the oxygen flow rate was precisely tuned by a mass flow controller. The films were grown on r-sapphire substrates (Rubicon). The substrates were cleaned in boiling aqua regia solution for 50 minutes before DI water rinsing and blown dry by nitrogen. Samples were then annealed in vacuum at 800 ºC for 30 minutes. A low temperature ZnO buffer was grown at 450 ºC. The buffer growth lasted 5 minutes with an estimated thickness of 1~2 nm. During the growth, the Zn cell temperature and O\textsubscript{2} flow rate were kept at 430 ºC and 14 sccm, respectively. For Mn doped samples the Mn cell temperature was set at 750 ºC. The substrate temperature was 650 ºC, and the growths lasted 2 hours. An annealing at 800 ºC for 30 minutes was performed after growth in vacuum. A reference sample was grown with the same growth procedure without Mn flux. The thickness of the films was measured using a Dektak 8 Surface Profilometer. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance X-ray diffractometer. The photoluminescence
(PL) study was carried out using a home-built PL system with a Janis cryostat, with a 325-nm He-Cd laser for the excitation source and a photomultiplier tube for the PL detection. Polarization-dependent PL measurement was performed with a homemade PL setup. A Glan-Tyler type laser polarizer was inserted in the final stage of laser to provide polarized laser light. The polarizer was mounted on a rotational mount to change polarization angle. Energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) were done using an Oxford/INCA SEM system. Atomic force microscopy (AFM) and magnetic force microscopy (MFM) measurement was done with a Veeco/Bruker AFM with a Co coated MFM tip in tapping mode. Cross-sectional TEM specimens were prepared in a FEI Quanta 3D FEG dual-beam FIB and diffraction contrast TEM imaging and selected area electron diffraction (SAED) were carried out in a FEI/Philips CM-20 TEM at the materials characterization facility (LEXI) in UC Irvine. High-resolution TEM and Z-contrast STEM work was performed in a JEOL JEM ARM200F TEM at the Florida State University. The magnetic properties of the samples were characterized using a Quantum Design MPMS SQUID magnetometer with the magnetic field parallel to the film plane. Samples were cut into rectangles with dimensions of 6 mm × 8 mm and mounted in a non-magnetic straw during the measurement.
Results and discussion

Both un-doped and doped ZnO samples have similar thicknesses of ~35 nm, measured with a profilometer. This number was also confirmed by secondary ion mass spectrometry (SIMS) and TEM results. Figures 3.1a and 3.1b show reflective high energy electron diffraction (RHEED) patterns acquired in the MBE system at room temperature after the growth. The un-doped sample shows a streaky pattern indicating a smooth surface, while Mn-doped sample shows slightly widened streaks, indicating deviation from flat surface. SEM images were acquired for both samples, and the surfaces are smooth and featureless, as shown in Figure 3.1e and 3.1f. The AFM image of a Mn-doped ZnO sample (Figure 3.1c) shows long stripes with ~0.5 μm spacing, which is

Figure 3.1 RHEED pattern, MFM and SEM Images of ZnO and MnZnO. Reprinted with permission, Copyright 2012, American Institute of Physics.*
similar to the pattern of single crystal ZnO surface after thermal treatment, as reported by Meyer et al \[18\]. Similar stripe pattern has been reported on annealed sapphire substrate \[19\], so there is a possibility that these patterns may be inherited from the atomic steps on the wafer surface as a result of thermal treatment, considering that the ZnO film is very thin. The roughness (rms) is 0.7 nm within a 10 \( \mu \text{m} \times 10 \mu \text{m} \) scan range. Figure 3.1d shows a phase image of a MFM measurement, obtained with a lift distance of 80 nm during the AFM measurement. The image shows no evident signal of perpendicular magnetic moment. Since Mn-rich clusters would tend to randomly align, lack of perpendicular moment indicates no evident clustering.

To further confirm that there are no Mn-rich clusters in the Mn-doped...
sample, cross-sectional TEM experiments were carried out. Figures 3.2a and 3.2b show bright-field and weak-beam images of the Mn-doped ZnO film grown on sapphire substrate. These images display line defects (dislocations) in the film, but no Mn-rich clusters were observed. Figure 3.2c is a typical SAED pattern from both the film and substrate, where the substrate was tilted to its zone axis and the film was slightly away from its zone axis. There are only two sets of the diffraction spots present, highlighted by solid lines and by dash lines, corresponding to the substrate and the film, respectively. The pattern indicates that the film is single crystal and the (1120) plane of the film is parallel to the (1102) plane of the substrate, which fits the epitaxial relationship of ZnO grown on r-sapphire [20]. Figure 3.2c also indicates that there are no other phases including Mn-rich clusters in the film. Figures 3.2d and 3.2e are typical high-resolution TEM and Z-contrast STEM images, respectively, with the ZnO film tilted exactly along its zone axis, and the substrate is 4.4° off its zone axis. The individual brighter dots in the Z-contrast STEM image (Figure 3.2e) are the Zn atomic columns of the film and the lower intensity lines are the Al atomic columns of the substrate. It shows that the single crystalline ZnO film has an epitaxy growth on the substrate. The film/substrate interface is flat and abrupt at atomic scale.

Figures 3.3a and 3.3b show XRD spectra of Mn-doped ZnO and MnZnO and reference samples. Reprinted with permission, Copyright 2012, American Institute of Physics.*
un-doped ZnO, respectively. The θ-2θ scan shows peaks for r-sapphire (1102) as well as A-plane (1120) ZnO. None of the other ZnO directions are observed due to the high-quality epitaxial growth by MBE. No peak shift is observed between the doped and un-doped ZnO samples. No Mn-rich secondary phases are detected within detection limit.

Various methods were implemented to assess the Mn concentration of the thin film. Both EDX (Figure 3.4a) and XPS (Figure 3.4b) results showed no trace of Mn, which would appear if there was a significant amount of clustered Mn. STEM with nanometer electron probe was also used to detect elements from different areas of the film and no Mn signal was detected, indicating that the Mn signal was below the detection limit and no Mn-related clusters were developed in the

Figure 3.4 (a) EDX, (b) XPS and (c) SIMS of MnZnO sample. Reprinted with permission, Copyright 2012, American Institute of Physics.*
film. Figure 3.4c shows SIMS spectrum, in which a $\sim 2 \times 10^{19}$ cm$^{-3}$ Mn concentration is acquired. This leads to a number of $\sim 0.04\%$ at Mn content.

Figures 3.5a and 3.5b show temperature-dependent PL spectra of un-doped and Mn-doped ZnO. At 15 K both samples show a dominant peak at $\sim 3.362$ eV with a broad mixture of luminescence in the 3.3-3.2 eV region. As the temperature increases, the high energy peak blue-shifts to $\sim 3.384$ eV, evident at around 60 K. Further increase of temperature induces a typical red shift due to temperature-induced band-gap shrinkage.

Figure 3.6a shows polarization-dependent PL spectra of the Mn-doped ZnO. Coexistence of two peaks (3.362 eV and 3.384 eV) at 15 K and a clear polarization dependence of the two peaks are evident, as predicted for a perpendicular incident beam against the c-axis$^{[21]}$. The two peaks show up at different excitation polarization that is $\sim 90^\circ$ apart, while the general
behavior evolves at a period of 180°. This behavior fits the symmetry model as predicted by Reynalds et al [22]. Figure 3.6b is intensity plot of the polarization dependent PL data. The high energy edge shift is evident, while the broad luminescence around 3.25eV shifts along with the high energy edge, indicating related origin. The observation of this fine structure split upon different polarization confirms an A-plane epitaxial growth of single crystalline ZnO wurtzite structure. For the exciton related peaks there are no qualitative difference between the doped and un-doped samples, supporting the very low doping concentration claim and the doped film remains close to its intrinsic semiconductor nature. It is reasonable to believe that the 3.362eV and 3.384eV peaks are of the same donor bound origin. Assume the sample is still following the polarization selection rule under unstrained situation, 3.362eV can be assigned to A/B band donor bound exciton and 3.384eV to C band. This means ~22meV energy difference between A/B and C band, which is much
different from reported value ~45meV \cite{20}. Under normal unstrained circumstances, the energy split between A/B band and C band is attributed to crystal field while the energy split between A and B band is due to spin-orbit coupling. It is predicted that under anisotropic strain in c-plane, the exciton bands will bend, deform and cross-over, especially evident with the A and B bands \cite{22}. Thus the larger energy change may indicate a larger spin-orbit term, which will affect magnetic property of the thin film. The exact assignment of the observed peaks requires further examination and analysis.

The magnetic moment as a function of the applied magnetic field was acquired at different temperatures for both doped and un-doped samples. Figure 3.7a shows the measurement for the un-doped ZnO sample. No ferromagnetic behavior was observed within the measurement temperature range (10 K-300 K). The data shows diamagnetic behavior, which can come from several sources. No ‘unintentionally doped’ ZnO ferromagnetism was observed, and our sample preparation process before measurement...
did not result in ferromagnetism. The Mn doped sample shows ferromagnetic behavior over the entire temperature range. Figure 3.7b shows M-H hysteresis loop after removal of a linear response term. The measured moment was normalized to per unit ion (i.e., µB/ion) utilizing the Mn concentration determined from the SIMS data. At room temperature, the saturation moment (M_s) is ~6 µB/ion, while the coercivity field is larger than 200 Oe. The saturation moment does not vary much as the temperature is reduced, while the coercivity field does increase at lower temperatures. At 10 K the coercivity field is larger than 500 Oe. It should be noted that the sample has a much higher remnant moment at zero field (M_r). The M_r/M_s ratio reaches ~70% at 300 K, much larger than our previously reported MnZnO samples[^8], which makes the M-H loop more of a square shape like those of hard magnets. Hard hysteresis loops are rarely observed in Mn doped ZnO, and this is desirable for applications involving the storage of information. We also performed temperature scans on the Mn doped ZnO sample. Due to

![Figure 3.8 Cooling measurements of MnZnO. Reprinted with permission, Copyright 2012, American Institute of Physics.*](image-url)
the diamagnetic background, field cooling (FC) measurements were performed at two fields, 1000 Oe and 2000 Oe. Both measurements were done with a history field of 6000 Oe. Zero field cooling (ZFC) measurement was also carried out with the same history field of 6000 Oe. As shown in Figure 3.8a, there are no sharp maximum in the data for all three measurements between 20 K and 300 K, eliminating the possibility of several Mn-rich phases with Curie/Neel temperatures in the range from 40 K to 120 K\textsuperscript{[18]}. There seems to be a phase transition at around 20K, the origin of which remains to be clarified as no specific Mn-rich phase showing transition was reported at this temperature. Assuming a strictly linear term for the diamagnetism, $M_s$, the saturation moment at 2000 Oe, can be assessed. Figure 3.8b shows $M_s$ and $M_r$ plotted against temperature. $M_r$ is obtained directly from ZFC data. The data matches reasonably well with that from hysteresis loop measurements shown in Figure 3.7b. From the trend shown in Figure 3.8b, Mn doped ZnO has a very large Currie temperature making it applicable for room temperature devices.

Large remnant moment ratio is attributed to the single crystalline nature of the film. According to classical magnetism, for a given measurement, the measured coercivity field and remnant moment will depend on the geometric alignment of the external field against the easy axis of the object, as well as internal ‘pinning’ of domain walls. The remnant moment is maximized when the external field is aligned with internal easy axis thus making rotation and flipping of magnetic moment most difficult. For a polycrystalline thin film, the easy axis of each crystal domain will be random; some portion of the domains would always be misaligned against a given external field. Thus the $M_r/M_s$ ratio of such systems would tend to be lower. Through the advantage of single-crystal thin film growth by MBE,
the easy axis of the thin film is aligned along a single direction; therefore ratios of $M_r/M_s$ as high as $\sim 70\%$ are achieved. The saturation moment of $\sim 6 \, \mu B/\text{ion}$ at room temperature is larger but quite close to the results acquired with the ion-implantation method we reported before \cite{11}. Our assumption is that Mn would substitute Zn site in the crystal and thus have valence of $2^+$. Mn$^{2+}$ ion configuration is $3d^5$, thus five unpaired electrons are at the $3d$ orbit. Based on the classical calculation $|m| = g' \mu_B g' = 1 + \frac{J(J+1)+s(s+1)-L(L+1)}{2J(J+1)}$, for $3d^5$, the maximum moment is $5 \mu B$. So we believe our results are marginally correct for a scenario of isolated Mn ion assuming that real Mn concentration may be slightly higher than the SIMS data. With a Mn concentration of $2 \times 10^{19} \text{ cm}^{-3}$, the average ion to ion distance would be $\sim 3$ nm, which is too large to allow super-exchange or double exchange to take place. Treating Mn ions as singular isolated ion would be more feasible, thus explaining the large $\mu B/\text{ion}$ value. It is worth noting that an earlier report by Kittilstved et al. on a Mn doped ZnO with a 0.2% concentration did report a $\mu B/\text{ion}$ value larger than 1 \cite{23}. The Mn dopant concentration in the present sample is very low, therefore bound magnetic polaron model might have difficulty to apply, since it practically depends on double-exchange and there are no other dopants available to act as intermediate moment host. As recently addressed by Dietl \cite{24}, carrier mediated indirect coupling is possible based on a modified p-d Zener model to provide room temperature ferromagnetism. Such a mechanism allows larger ion-ion distances, although the actual limit of such an assumption remains unexplored. Nevertheless, considering the fact that semiconductor can have orders of magnitude large spin coherence time than metals \cite{2}, a long distance indirect coupling is not totally unwarranted.
Finally we briefly comment on the doping concentration effect on magnetic properties. Low-Mn-concentration ferromagnetism was rarely studied while high-Mn-concentration ferromagnetism is commonly reported in literature. Heavily Mn-doped ZnO thin films usually contain clustering and phase segregation due to low solubility of Mn in ZnO. It is possible that the measured ferromagnetism was offset partially by non-magnetic or paramagnetic Mn phases. The existence of such Mn phases could be substantial enough to reduce the $\mu_B$/ion value. Also, with larger Mn concentration, the Mn-ions are close enough to enable super-exchange or double exchange coupling, which would provide a smaller $\mu_B$/ion number [24]. Thus the reported behaviors can be reconciled and optimized Mn doping condition toward perfect ferromagnetic properties may be acquired at lower Mn concentration, instead of higher ones.

**Conclusion**

We have observed strong room temperature ferromagnetism with very low doping concentration of Mn ion in ZnO thin films. The Mn concentration is well below the reported solubility limit and minimizes the chances for secondary phase formation. The magnetic behavior is found to have a fairly large coercivity field of 200 Oe as well as very large remnant moment of 70%. The normalized moment of 6 $\mu_B$/ion is so large that only an isolated moment explanation is reasonable, which also matches the large mean distance between ions inferred from the low Mn concentration. The result supports intrinsic ferromagnetism of Mn doped ZnO induced by singular Mn ions.
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References:


Chapter 4

Doping controlled Strong Ferromagnetism in Mn doped ZnO DMS

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Introduction

One of the major interests in developing DMS materials is to utilize them for spintronic applications [1,2]. For device applications, especially memory devices, traditional GMR and TMR based devices would require two distinct ferromagnetic layers with different coercivity. So some ways to understand and control the mechanism of the observed room temperature ferromagnetism is necessary. From research point of view, Mn-doped ZnO is of particular interest since it lacks room-temperature ferromagnetic Mn-rich phases [3]. Original predictions based on the p-d Zender model required very high p-type doping for MnZnO to be a room temperature DMS [4], which is very challenging to fulfill. Nevertheless many different types of behavior have been reported with MnZnO, such as being non-magnetic [5], paramagnetic [6], ferromagnetic [7-9], antiferromagnetic [10], and spin-glass like [11], with no evident instance of the required heavy p-type doping. Other theories based on bound magnetic polarons (BMP) [12,13], F centers [14], etc. forgo such requirements on carrier type and concentration, although other factors are introduced. One area that remains to be fully explored is low concentration Mn doping (below 0.1 at.%). An early report on MnZnO with a Mn concentration of ~0.2 at.% showed magnetic moments larger
than $1 \mu_B$/ion $^{[15]}$. Recently, we also observed strong ferromagnetism at room temperature in MnZnO with a low Mn concentration of $2 \times 10^{19}$ cm$^{-3}$. $^{[9]}$. Here a series of high-quality single crystalline Mn-doped ZnO thin films were grown by MBE with very low Mn concentrations. Again peculiarly strong RT ferromagnetism is observed with a per ion magnetic moment larger than isolated ion based on Hund’s rules. The strength of the ferromagnetism is found to evolve with the Mn concentration.

**Instrumentation**

Mn-doped ZnO thin films were grown using electron cyclotron resonance (ECR)-MBE. Radical Knudsen effusion cells filled with elemental Zn (6N) and Mn (5.5N) metals were used as Zn and Mn sources. The Zn and Mn fluxes were controlled by the effusion cell temperatures. An ECR plasma tube supplied with O$_2$ (5N) gas was used as the oxygen source, and the oxygen flow rate was precisely tuned by a mass flow controller. The films were grown on r-sapphire substrates (Rubicon). The substrates were cleaned in boiling aqua regia solution for 50 minutes before DI water rinsing and blown dry by nitrogen. Samples were then annealed in vacuum at 800°C for 30 minutes. A low temperature ZnO buffer was grown at 450°C. The buffer growth lasted 5 minutes with an estimated thickness of 1–2 nm. During the growth, the Zn cell temperature and O$_2$ flow rate were kept at 340°C and 14 sccm, respectively. For Mn doped samples the Mn cell temperature was set at 500°C – 800°C. The substrate temperature was 650°C, and the growths lasted 2 hours. An annealing at 800°C for 30 minutes was performed after growth in vacuum. A reference
sample was grown with the same growth procedure without Mn flux. The thickness of the films was measured using a Dektak 8 Surface Profilometer. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance X-ray diffractometer. Photoluminescence (PL) study was carried out using a home-built PL system with a Janis cryostat, a 325 nm He-Cd laser for the excitation source and a photomultiplier tube for the PL detection. Cross-sectional transmission electron microscopy (TEM) specimens were prepared in a FEI Quanta 3D FEG dual-beam focused ion beam (FIB) system, and diffraction contrast TEM imaging and selected area electron diffraction (SAED) were carried out in a FEI/Philips CM-20 TEM at the materials characterization facility (LEXI) in UC Irvine. High-resolution TEM was performed in a JEOL JEM ARM200F TEM at the Florida State University. The magnetic properties of the samples were characterized using a Quantum Design MPMS SQUID magnetometer. Magneto-transport properties were investigated using a Quantum Design PPMS system.

**Results and Discussions**

Figure 4.1a and 4.1b–4.1h show reflection high energy electron diffraction (RHEED) patterns of both undoped ZnO and Mn doped ZnO films, respectively. The patterns were acquired within the MBE chamber after growth at room temperature. The streaky patterns indicate smooth surface on all samples, as befitting high quality growth by MBE, and there is no evident difference among the series of samples.
Figure 4.1 RHEED patterns of reference ZnO and MnZnO samples.
Figure 4.2a and 4.2b–4.2h show XRD patterns of both undoped ZnO and Mn doped ZnO, respectively. The θ-2θ scan shows peaks for r-sapphire (1\overline{1}02) as well as A-plane (1\overline{1}20) ZnO. The pattern indicates that the film is single crystal and the (11\overline{2}0) plane of the film is parallel to the (1\overline{1}02) plane of the substrate, which fits the epitaxial relationship of ZnO grown on r-sapphire [3]. None of the other ZnO directions are observed due to the high-quality epitaxial growth by MBE. No Mn-rich secondary phases are detected either. Finally, no peak shift is observed among the samples indicating the doping levels are so low that they neither affect the lattice parameter, nor result in alloying.

Figure 4.3a shows a bright-field cross-sectional TEM image of Mn doped ZnO grown on sapphire at the Mn cell.
temperature of 800°C. The film contains dislocations which cause contrast variations in the image. However, no Mn-rich secondary phases were observed. X-ray Energy Dispersive Spectroscopy (EDS) measurements were performed on the sample and no Mn signals show up in EDS spectra, suggesting that the Mn concentration is below EDS detection limit. The SAED pattern in Figure 4.3b clearly shows two sets of diffraction patterns, which are related to the sapphire substrate and Mn doped ZnO thin film, respectively. These patterns reveal the single-crystalline nature of the thin film and epitaxial growth. They also confirm that the film (1\(\bar{1}02\)) plane is parallel to the substrate (1\(\bar{1}02\)) plane, which is consistent with the XRD results. Figure 4.3c is a high resolution TEM image of the same sample, showing high quality single crystalline growth. Fast Fourier Transform (FFT) patterns of three
selected areas are also shown in Figure 4.3c, indicating clear distinction between Mn doped ZnO and sapphire substrate. The patterns, together with SAED pattern, and TEM images prove that single crystalline ZnO was grown.

Mn doping was controlled by varying Mn cell temperature from 500 °C to 800 °C. Various methods were attempted to assess Mn concentrations. XPS spectra were collected on all samples. Figure 4.4a and 4.4b show XPS spectra of undoped ZnO and Mn doped ZnO with a Mn cell temperature of 800°C, respectively. There is no evident difference between the two spectra at the Mn(2p) binding energy of ~640 eV, i.e. no evident Mn signal can be observed even from the most heavily doped sample. Figure 4c summarizes the Zn to O signal ratio in the XPS spectra.

Figure 4.4 XPS of (a) undoped ZnO and (b) MnZnO. (c) Zn/O signal ratio from XPS.
spectra of all samples with undoped sample marked as a Mn cell temperature of zero. The Zn to O signal ratio is similar for all samples, indicating no evident deviation from undoped ZnO growth.

Figure 4.5 shows SIMS spectra of Mn doped ZnO with various Mn cell temperatures. As indicated by the signal of Al from sapphire substrate, all thin films have similar thickness of ~25nm, which is close to the results measured by the profilometer. All figures were aligned by aligning Zn signal to an atomic concentration \(\sim 4 \times 10^{22} \text{ cm}^{-3}\). When Mn cell temperature is low at 500°C and 600°C, as in Figure 4.5a and 4.5b, the Mn signals are on the order of \(10^{18} \text{ cm}^{-3}\) and are actually close to system noise, meaning an extremely low concentration. Figure 4.5c shows SIMS spectra of the sample with Mn cell temperature 700°C in which a \(\sim 1 \times 10^{19} \text{ cm}^{-3}\) Mn

![Figure 4.5 SIMS of selected MnZnO samples.](image-url)
concentration is acquired. This leads to a number of \( \sim 0.02 \) at.% Mn content. Figure 4.5d shows SIMS spectra of the sample with Mn cell temperature 800ºC. The Mn signal has a slope in this sample, but it is reasonable to assess that the Mn concentration in this sample is less than \( 1 \times 10^{20} \) cm\(^{-3} \), or 0.2 at.%. So all doping concentrations in this series of samples are way below the reported incorporation limit \(^{[11]}\), and thus exclude the chance of Mn phase segregation.

Magnetic measurements were performed by mounting cleaved ZnO/Mn-doped ZnO samples in non-magnetic straws. Precautions were taken to prevent extrinsic signals \(^{[16]}\). Carbon-tipped tweezers were used during preparation to avoid iron based tool contamination. Samples were held in position by extra straws placed inside the mounting straw, thus excluding contamination signals from tapes or pastes. Figure 4.6a shows the magnetic moment as a function of external field for undoped ZnO, and the behavior is diamagnetic, associated with both the thin film and substrate. This result suggests that the undoped ZnO does not exhibit ferromagnetism. At a Mn cell temperature of 500ºC, a small change is seen in the magnetic response in Figure 4.6b, but the signal is still clearly diamagnetic. When the Mn cell temperature is increased beyond 500ºC, there is sudden onset of hysteretic behavior, clearly indicating the presence of ferromagnetism. Notice that for Figures 4.6c through 4.6h, the linear diamagnetic signal was subtracted from the raw data. As can be seen, room temperature ferromagnetism is evident for samples with a Mn cell temperature of 550ºC and higher. Ferromagnetic hysteresis remains similar at different measurement temperature, and the temperature dependence of the saturation
Figure 4.6 M-H response of reference ZnO and MnZnO samples.
moment is not significant for each sample. The magnetic behavior is summarized in Figure 4.7. Figure 4.7a is the saturation moments (M_s) and residue moments (M_r) for the six samples with evident ferromagnetism. The saturation moment reaches a maximum when the Mn cell temperature is 600°C. Further increases of the Mn cell temperature lead to lower saturation moments with a minimum at 750 °C, followed by a small increase at 800 °C. Figure 4.7b shows the coercivity field of Mn doped ZnO samples. At room temperature, the coercivity starts out at ~50 Oe for a Mn cell temperature of 500 °C and gradually increases to 100 Oe when cell temperature is 800 °C. The exception to this monotonic trend occurs at 750 °C where it has the exceptionally large value of ~200 Oe. In most samples the coercivity field increases as the measurement temperature decreases, as can be seen by comparing the 10 K and 300 K data. The one exception is with the Mn cell temperature of 550°C the coercivity does not change with temperature. Figure 4.7c shows the ratio of M_r and M_s, showing a general increasing trend with the increasing Mn cell temperature. The Mn 750°C sample is the anomaly with its larger M_r/M_s ratio and much larger coercivity. Similar behavior was

Figure 4.7 Saturation moment, coercivity field and residue moment of ferromagnetic MnZnO.
observed in another sample with similar growth parameters\textsuperscript{[9]}, thus we believe this behavior is intrinsic with mechanism that will be discussed later.

Magnetic anisotropy is an important characteristic of intrinsic ferromagnetism. The c-axis of ZnO epitaxially grown on r-sapphire does not align with the growth direction\textsuperscript{[3]}, thus in-plane anisotropy is expected since the thin films are single crystals. For field in-plane measurements, samples were cut into 6mm x 8mm pieces and mounted in a non-magnetic straw, as illustrated in Figure 4.8a. We have noticed an easy cleaving direction of r-sapphire, which is closely parallel to its main flat. The factory specification states that the main flat of the substrate is 45° off M on C-plane. Our samples prepared for the magnetic measurements were normally cut with their long edge aligned with the easy

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure4.8}
\caption{In-plane anisotropy of MnZnO.}
\end{figure}
cleaving direction, hereon noted as ‘cut A’. When they are cut with the short edge aligned with the easy cleaving direction, hereon noted as ‘cut B’, we observed a larger saturation moment and smaller coercivity field, as can be seen in Figure 4.8b. Figure 4.8c shows fielded cooling measurement data for the different cuts in Figure 4.8b. An alignment field of 6000 Oe was applied before the measurements were started at 2000 Oe. In both cases, the magnetic moments remain very stable without any abrupt phase change steps during the cooling process. The smooth temperature scan data further proves that no evident secondary phases are present.

Figure 4.9a illustrates how out-of-plane anisotropy was measured. The Mn doped ZnO sample was cleaved into a 4mm by 12mm stripe and then cleaved again into three 4mm by 4mm squares, thus providing the same amount of sample as was used for our in-plane measurements. The squares were then stacked together and placed vertically into a nonmagnetic straw for the measurement. As shown in Figure 4.9b, the off-plane measurement yields a larger saturation moment.

Figure 4.9 In-plane/off-plane magnetic anisotropy of MnZnO.
than the normal cut A, with a ratio similar to that of in-plane anisotropy. However, the coercivity field remains similar to in-plane reference in this case.

Figure 4.10 shows the temperature-dependent PL spectra of undoped and Mn-doped ZnO. For undoped ZnO the data in Figure 4.10a shows two well resolved peaks with a donor bound exciton (DX) at 3.362eV and an AES peak at 3.308eV \[^{[17]}\]. The broad luminescence bump at ~3.23eV should consist of multiple peaks like phonon replicas, donor acceptor pairs, etc, which are not resolved enough to be identified. There is a third peak at ~3.384eV, which is evident at 60K and presents a seemly blue-shift. From a previous polarized PL study, \[^{[9]}\] this peak was identified as a DX from a C-band exciton of MnZnO.
ZnO. Due to the A-plane ZnO growth, PL from C-band is expected \cite{18,19}, which is evidence of single-crystalline growth. For the Mn doped samples the low-temperature PL behavior is similar in nature but with a slight variance among samples. In the 500°C, 600°C and 800°C samples the dominant high energy peak remains the ~3.36eV A/B band DX, and a trace of the 3.38eV C-band DX is visible at a slightly elevated measurement temperature, thus providing the blue shift. The AES peak is no longer easily resolvable, but a trace of it can be identified in the Mn 500°C sample. The Mn 700°C sample shows stronger C-band luminescence at low temperature and thus its ‘blue-shift’ is not evident. The broad luminescence in the Mn 700°C sample is also shifted to higher energy at ~3.3eV, which is probably due to an enhanced phonon replica from the C-band DX. The exact mechanism of how the C-band signal is enhanced in the Mn 700°C sample remains to be investigated. However it is evident that no additional energy levels were introduced by incorporating Mn at these low doping concentrations.

Figure 4.11 shows the magneto resistance (MR) of both the undoped and Mn doped samples. For the undoped ZnO as shown in Figure 4.11a, a generally negative MR is present at low temperature, as reported for undoped ZnO \cite{20,21}, although there is possibly a weak positive contribution at 200K. For the Mn doped ZnO samples, while the dominant MR response is negative, a stronger positive contribution is evident, and in the anomalous case of Mn 700°C sample, the MR is dominated by a positive contribution at 200K. Figure 4.12a shows the Hall Effect data of these samples. While anomalous Hall Effect is evident
on all of these samples, Mn 800°C sample shows an exceptionally large anomalous term. Figure 4.12b shows the carrier concentrations as extracted from room temperature Hall effect measurements. All samples have very similar electron concentrations of $10^{18}$ to $10^{19}$ cm$^{-3}$, indicating no evident effect on the carrier concentration.

Magnetic anisotropy for both in-plane and out-of-plane cases and anomalous Hall Effect suggest that the observed ferromagnetism is intrinsic. However the strength of the magnetic moment becomes peculiar when quantized to per-Mn-ion moment. We had previously reported our findings of a Mn doped ZnO with a similarly low Mn concentration of $\sim 2 \times 10^{19}$ cm$^{-3}$ \cite{9}. That sample was characterized to have $\sim 6 \mu_B$/ion, which is larger than the maximum calculated moment of $\sim 4 \mu_B$/ion based on Hund’s rules. Considering the possible fluctuations in Mn concentration characterization, we attributed the situation to a

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig4-11}
\caption{Magneto Resistance of ZnO and MnZnO.}
\end{figure}
possible isolated ion scheme and the excess per-ion-moment as a consequence of error in Mn concentration estimation. However, in this extended batch of samples, we demonstrated that this anomalously large moment is a robust phenomenon. The previously measured sample is very similar to the Mn 750°C sample here, with similar saturation moment, high coercivity field and high remnant moment. Nevertheless, other presented samples exhibit even more peculiar magnetic properties. For example, with a Mn cell temperature of 700°C, using the acquired Mn concentration from SIMS, the saturation moment is quantified to be ~45 \( \mu_B \)/ion. What is more, we believe the ‘B cut’ in our samples is closer to the easy axis of the ferromagnetism than the convenient ‘A cut’. When samples in ‘B cut’ geometry were measured, saturation moments are typically three times larger than that of samples with ‘A cut’. This would in turn push the per-ion moment three times larger. XPS and SIMS measurements persistently indicate Mn concentrations smaller than 1%, or \( 4\times10^{20} \) cm\(^{-3} \). Even if we assume this maximum number

![Figure 4.12 Hall Effect data of ZnO and MnZnO.](image)
of $4 \times 10^{20}$ cm$^{-3}$ for all samples, the quantified magnetic moment is still very large. In the case of Mn 600°C sample, the saturation moment would amount to $\sim 13$ $\mu_B$/ion for the ‘B cut’, which is clearly in excess of the expected value for isolated ions.

Finally we discuss a possible mechanism for the large saturated moments in an elimination manner. Contributions from Mn related secondary phases are quite unlikely in our case. The small concentration would minimize phase segregation due to the solubility limit, as confirmed through XRD and XPS measurements. Also, secondary phases would yield smaller magnetic moments than with isolated ions. For the intrinsic mechanisms, firstly given the extremely diluted nature of Mn ions, it is unlikely they can correlate with each other directly to support double exchange [22] or super exchange mechanisms. Also the large per ion moment we observe (at 10-100 $\mu_B$/ion level) does not support such mechanisms, since they cannot provide such large moment [23]. Long distance indirectly coupled ions may be a contributing mechanism, and the measured relatively abundant carrier concentration should permit it. However, the measured moment being larger than single ion moment requires some other entities to contribute magnetic moment as well. This leads to a situation close to the BMP mechanism, where multiple species can correlate and contribute to ferromagnetism [12]. No evident ferromagnetism for undoped and very low doping samples indicates that Mn dopant still acts as a crucial factor for the RT ferromagnetism. It is possible that point defects or zinc nuclei form the BMP centered on Mn ions. However, one argues that BMP theory would not result in such large moments, i.e. magnetic moments reaching 10-100 $\mu_B$/ion as in our case. We note that types of investigations on materials with such low dopant concentrations are rarely reported. As a
result of this research, a new understanding of the mechanisms behind intrinsic ferromagnetism in a DMS system with low transition-metal ion concentrations is necessary.

Conclusion

We have observed peculiarly strong room temperature ferromagnetism in lightly Mn doped ZnO thin films. Both in-plane and out-of-plane magnetic anisotropy were observed to support intrinsic ferromagnetism. Both the saturation moment and coercivity field vary with different Mn content. The observed magnetic moment when expressed in terms of the number of \( \mu B/\text{ion} \) exceeds what calculated for isolated Mn ions. Contributions from other local entities are necessary, but the absence of ferromagnetism in undoped ZnO confirms the crucial role of the Mn dopant. The result supports intrinsic ferromagnetism of Mn doped ZnO, while raises a challenging question on the origin of room temperature ferromagnetism in DMS system with low transition-metal ion concentrations.

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The author would like to acknowledge Professor W. P. Beyermann from Department of Physics and Astronomy, UC Riverside, for allowing using PPMS and MPMS systems and helpful discussions. Dr. Jianguo Zheng from UC Irvine prepared the
TEM sample and performed the TEM analysis. High resolution TEM and STEM images were acquired by Dr. Yan Xin from National High Magnetic Field Laboratory. TEM facility at FSU is funded and supported by the Florida State University Research Foundation, National High Magnetic Field Laboratory (NSF-DMR-0654118) and the State of Florida.

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Chapter 5

Epitaxial Growth of High Quality Ag doped ZnO

Introduction

ZnO was rediscovered as functional semiconductor in the 1990s. The potential of ZnO has been widely investigated for optoelectronics and spintronics \[1\]. However, one major obstacle within the field remains to be the difficulty to achieve high quality p-type ZnO. ZnO has many naturally occurring point defects, including Zn interstitials, oxygen vacancies etc., which will behave like donors and contribute to native n-type conduction. Furthermore, other external dopants like hydrogen complexes are dormant in many fabrication methods and will provide extra donor states \[2-4\]. There have been various efforts exploring p-type doping of ZnO. Group V elements, namely P \[5-8\], As \[9-12\], Sb \[13-16\], were proposed to introduce acceptor levels into ZnO, thus p-type doping \[17\]. Our group has successfully demonstrated various materials and devices based on Group V doping for optoelectronic and memory applications \[13-16\]. However, there remains a fundamental limit in these doping scenarios, since the doping mechanism is believed to be based on a particular point defect \[17\]. It would be challenging to introduce a particular point defect in large quantity without compromising the overall crystal quality. Thus it is essential to develop non-defect based p-type doping of ZnO to further explore its applications for optoelectronics. Group IB elements (Na, Ag, Au) were proposed to be p-type dopants for
ZnO, with a mechanism based on substitution doping \[^{18,19}\]. Among them, Ag is most favorable option for MBE growth due to its solid form (in comparison to Na) and reduced melting temperature (in comparison to Au). Here Ag doped ZnO is investigated and improved high quality material is demonstrated.

**Instrumentation**

Ag-doped ZnO thin films were grown using plasma enhanced MBE system. Radical Knudsen effusion cells filled with elemental Zn (6N) and Ag (6N) metals were used as Zn and Ag sources. The Zn and Ag fluxes were controlled by the effusion cell temperatures. Both ECR and RF types of plasma were used to provide atomic oxygen beam, and growths were performed on both R and C plane sapphire substrates. The thickness of the films was measured using a Dektak 8 Surface Profilometer. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance X-ray diffractometer. Photoluminescence (PL) study was carried out using a home-built PL system with a Janis cryostat, a 325 nm He-Cd laser for the excitation source and a photomultiplier tube for the PL detection. Energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) were done using an Oxford/INCA SEM system.
Results and discussions

An ECR plasma tube supplied with O$_2$ (5N) gas was used as the oxygen source, and the oxygen flow rate was precisely tuned by a mass flow controller. The films were grown on R-sapphire substrates (Rubicon). The substrates were cleaned in boiling aqua regia solution for 50 minutes before DI water rinsing and blown dry by nitrogen. Samples were then annealed in vacuum at 800°C for 30 minutes. A low temperature ZnO buffer was grown at 450°C. The buffer growth lasted 5 minutes with an estimated thickness of 1–2 nm. During the growth, the Zn cell temperature and O$_2$ flow rate were kept at 380°C and 14 sccm, respectively.

Figure 5.1 show the SEM images of undoped and Ag doped ZnO samples grown on R-sapphire. The samples are undoped 5.1a and Ag doped ZnO with Ag cell temperature 5.1b 600°C, 5.1c 700°C and 5.1d 800°C, respectively. All other growth procedures and parameters remain the same. The insets are their RHEED patterns taken after growth at room temperature. The undoped and lightly doped samples show streaky patterns which indicate relatively smooth surface, while for the Ag 800°C sample there is barely any image intensity, indicating very rough surface. The undoped and low Ag cell temperature samples all have relatively smooth surface, corresponding to their RHEED patterns. The sample with Ag cell 800°C has severely compromised surface morphology, indicating intolerance to Ag dopant.
To verify the growth direction, XRD was performed on all samples. The $\theta$-2$\theta$ scan shows peaks for R-sapphire (1102) as well as A-plane (11$ar{2}$0) ZnO, which fits the epitaxial relationship of ZnO grown on R-sapphire \cite{1}. None of other ZnO directions are observed due to the high-quality epitaxial growth by MBE. No peak shift is observed between the doped and undoped ZnO samples. No Ag-rich secondary phases are detected within detection limit. Undoped sample and sample with Ag cell temperature 800ºC is shown here in Figure 5.2.
What is surprising is that even with its compromised surface morphology the sample remained clearly oriented in A-direction.

The growths on R-sapphire show limited tolerance to Ag doping, so growths were further explored on C-sapphire (Kyocera). An RF plasma tube supplied with O₂ (6N) gas was used as the oxygen source, and the oxygen flow rate was precisely tuned by a mass flow controller. The substrates were cleaned in boiling aqua regia solution for 50 minutes before DI water rinsing and blown dry by nitrogen. The samples were grown with a two stage buffer to accommodate the larger lattice mismatch during growths on sapphire. Firstly an MgO/MgZnO/ZnO low temperature buffer was grown at 450ºC, and then a thin ZnO was grown at 650ºC before growth of functional ZnO layer. The entire buffer is found to be around 10nm.

Figure 5.3 shows the SEM images of undoped and Ag doped ZnO. The insets are corresponding RHEED patterns. The samples were grown with Zn cell at 340ºC and oxygen flow at 3sccm for the functional layer. The RF plasma power was kept at 400W. The undoped and lightly Ag doped ZnO had relatively smooth surface, confirming the
information provided by RHEED patterns. However, pin holes are evidently visible in Figure 5.3b, and when Ag cell temperature was even higher, the surface becomes porous, as shown in Figure 5.3c.

XRD was again performed to investigate the film quality, as shown in Figure 5.4. For the undoped sample, only ZnO (002) and Sapphire (006) peaks are observed. No other ZnO growth directions were observed within detection limit. It is noticeable that Ag (111) peak is present in the doped sample, indicating phase segregation. However, no evident peak shift of the ZnO main peak is observed within detection limit, thus no significant change to the ZnO lattice is observed.

Figure 5.4 XRD of undoped and Ag doped ZnO on C-Sapphire. Ag (111) peak is observed.

Figure 5.5 Temperature dependent PL of undoped and Ag doped ZnO on C-Sapphire.
To further assert the Ag incorporation of this series of sample, temperature dependent photoluminescence was perform, as shown in Figure 5.5. Figure 5.5a is temperature dependent PL of the undoped sample. Only the free exciton peak at 3.377eV is observed, indicating very high film quality. Normally low temperature PL of ZnO would have multiple donor bound or acceptor bound exciton peaks originating from donor/acceptor levels [20]. The sole presence of free exciton indicates that optically active donors and acceptors have been suppressed in this sample. However, for the Ag doped sample (with Ag cell temperature at 750ºC) the low temperature PL still shows one singular peak at 3.375eV, very likely also a free exciton. Thus cohering with the XRD data, it is highly likely that Ag was not efficiently incorporated into ZnO lattice and formed segregated secondary phases.

Figure 5.6 Surface morphology of samples with different growth parameter.
With the aforementioned information, various attempts were performed to improve Ag incorporation without severely compromising surface morphology. The work was mainly focused on tuning Zn/O ratio to accommodate Ag doping. Figure 5.6 summarizes the experimental results of various growth recipes. For a given Zn/O growth condition, there exists a growth window for silver doping. When Ag cell temperature is low, thus Ag doping concentration is low, the samples would have smooth surface. However, while an undoped reference with background carrier concentration lower than $10^{17}$ cm$^{-3}$ is usually achieved, in doped samples usually a strong n-type (at the range of $10^{17}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$) is observed. The problem may be due to insufficient amount of Ag dopant, or insufficient activation of Ag dopant, while extra point defects were introduced through Ag doping. On the other hand, when Ag cell temperature is set too high, sample surface would tend to severely deteriorate, thus unfit for device applications. Within the two limits

![XRD Intensity (a.u.)](image)

**Figure 5.7** XRD of Ag doped ZnO p-type samples on C-Sapphire.
set by the aforementioned manner, p-type Ag doped ZnO can be sparsely observed.

Figure 5.7 is XRD spectra of a series of Ag doped ZnO. While all other growth parameter and procedures were kept the same, Ag cell temperature was varied within the range of 830°C to 870°C. XRD indicates that for some of the samples Ag phase segregation is still present. For the samples with Ag cell temperature 840°C and 850°C p-type conduction was observed. In these samples, it is noticeable that no Ag phase was observed within detection limit, and the ZnO main peak had larger FWHM at 14’ ~15’, in comparison to 10’ in the other two samples. Thus only those Ag incorporated into ZnO lattice can provide p-type conduction, as predicted.

Figure 5.8 is the Hall Effect data of the sample grown with Ag cell temperature 850°C. The sample had relatively high resistivity and was measured in a Hall bar configuration with varying field method. The positive slope of Hall resistance is extracted to calculate the hole concentration. However, such observed p-type switched back to n-type after extended storage in atmosphere, as typical in p-type ZnO researches.

To further investigate the sample, low temperature PL was performed, shown in Figure 5.9. At 20K the most prominent peak

![Figure 5.8 Hall Effect of Ag doped ZnO sample.](image-url)
is located at 3.358eV. This peak is very sharp and may be attributed to acceptor bound exciton (AX). Careful examination of temperature dependent PL indicated that another high energy peak exists, and persists with temperature higher than 50K. The energy is ~3.362eV at 50K, which is a typical donor bound exciton. Some of the other peaks match quite well as phonon replicas of the main peaks. A possible Donor Acceptor Pair (DAP) can be located at 3.217eV, with its stagnant/Blue-shift peak position supporting this assignment. Notice that the 3.362 DX peak becomes dominant at room temperature, thus indicating a substantial amount donor. The presence of native donors would compensate and reduce the p-type doping.

To further improve and achieve robust p-type doping, further tuning of growth recipe is still on going. Figure 5.10 shows some characterization results of one of the improved growth samples. As shown in Figure 5.10a, the sample has streaky RHEED and featureless SEM image for its surface. EDS measurement in Figure 5.10b indicates that no evident Ag signal was detected, thus incorporated Ag is less than 1%. This number is still valid for p-type doping, but would greatly reduce the chances of phase segregation. XRD
spectrum shown in Figure 5.10c confirms that no Ag secondary phases were observed within detection limit.

Through our experiments, we prove that Ag incorporation into ZnO through high quality epitaxial method is possible. Based on observed experimental results, Ag doping in ZnO does lead to deterioration of surface morphology when Ag amount is overly large. However, adequate amount of Ag doping can achieve high quality thin film. Phase segregation is prominent, even for some of the quasi-2D thin films, but with optimization it can be reduced to beyond detection limit of XRD. Also, as observed, when p-type is reached, Ag phase segregation would be limited. The major challenge for Ag doped p-type ZnO is still how to sustain robust p-type doping. With introduction of Ag doping, extra donors are still present, and thus threatens long term stability of the p-type conductivity.
Conclusion

We have investigated Ag doped ZnO on different sapphire substrates. Ag doping behavior is investigated and doping window was found for high quality Ag doped ZnO under different growth conditions. Ag phase segregation is observed and overcome by optimizing growth recipe. P-type Ag doped ZnO was observed but further optimization to achieve long term stability is necessary.

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Reference


Chapter 6
Magnetic Properties of Ag doped and Mn/Ag co-doped ZnO DMS

Introduction

TM-doped ZnO has been widely investigated since the prediction of ZnO as room temperature ferromagnetic DMS \(^1\),\(^2\). Classical theorem believes that magnetism rises from localized spin and coupling mechanism to form long range magnetic order \(^3\). The localized spin was mainly observed in partially filled d or f orbits, while naturally occurring magnets mainly fall within this category. Thus, it is natural that transition metals with partially filled d states (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) and rare earth elements with partially filled f states (e.g. Eu, Gd, Er) have been used as magnetic dopants in DMS. However, results have not been consistent or systematic for ZnO DMS. The field of ZnO DMS has been flooded with materials of all forms and fabrication methods. When doping with strong magnets (Fe, Co etc.), usually room temperature ferromagnetism is observed, but the origin of such signal usually leads to painful discussion. It has been proven that Co clusters beyond detection capability of typical XRD can provide ferromagnetism signals comparable to the reported weak ferromagnetism cases \(^4\). Gracia et al. have shown that weak extrinsic signals can rise from various routine MPMS measurement practices for powder form material, thus questioning the observed ferromagnetism of many reports \(^5\). The original p-d Zener coupling model has been addressed by its author as difficult to apply to oxide systems \(^3\). So it is now even more vital to investigate the true mechanism of
ferromagnetic ordering in DMS. To understand the mechanism of magnetic ordering in ZnO DMS, extrinsic factors need to be reduced. Single crystalline thin film is closest to bulk material and thus removes many considering factors for powder/poly-crystalline materials. We have demonstrated that magnetic moments larger than that is permitted by Hund’s law is observed in high quality Mn doped ZnO $^6$. Here we report further finding on Ag co-doping as a way to improve and manipulate ferromagnetism of Mn doped ZnO.

**Instrumentation**

Mn-doped ZnO thin films were grown using plasma enhanced MBE. Radical Knudsen effusion cells filled with elemental Zn (6N), Ag (6N) and Mn (5.5N) metals were used as Zn, Ag and Mn sources. The metal fluxes were controlled by the effusion cell temperatures. An RF plasma tube supplied with O$_2$ (6N) gas was used as the oxygen source, and the oxygen flow rate was precisely tuned by a mass flow controller.

For growths performed on R-sapphire, the substrates were cleaned in boiling aqua regia solution for 50 minutes before DI water rinsing and blown dry by nitrogen. Samples were then annealed in vacuum at 800$^\circ$C for 30 minutes. A low temperature ZnO buffer was grown at 450$^\circ$C. The buffer growth lasted 5 minutes with an estimated thickness of 1–2 nm. During functional layer growth the substrate temperature was 650$^\circ$C, and the growths lasted 2 hours. An annealing at 800$^\circ$C for 30 minutes was performed after growth in vacuum. For growths on C-Sapphire, the substrates were cleaned in boiling aqua regia solution for 50 minutes before DI water rinsing and blown dry by nitrogen. The samples
were grown with a two stage buffer to accommodate the larger lattice mismatch during
growths on sapphire. Firstly an MgO/MgZnO/ZnO low temperature buffer was grown at
450ºC, and then a thin ZnO was grown at 650ºC before growth of functional ZnO layer.
The entire buffer is found to be around 10nm.

The thickness of the films was measured using a Dektak 8 Surface Profilometer. X-ray
diffraction (XRD) measurements were performed using a Bruker D8 Advance X-ray
diffractometer. Photoluminescence (PL) study was carried out using a home-built PL
system with a Janis cryostat, a 325 nm He-Cd laser for the excitation source and a
photomultiplier tube for the PL detection. The magnetic properties of the samples were
characterized using a Quantum Design MPMS SQUID magnetometer. Magneto-transport
properties were investigated using a Quantum Design PPMS system.

Results and discussions

Ag was proposed as possible p-type dopant for ZnO [11,12]. Although no robust p-
type was achieved, we believe Ag does introduce acceptor levels. Under such occasions
interactions based on original p-d coupling mechanism might be possible. Figure 6.1 shows
the magnetic behaviors of purely Mn doped ZnO (Figure 6.1a) and Mn/Ag co-doped ZnO
(Figure 6.1a), grown on R-sapphire. For comparison, Mn/Ag co-doped sample had growth
parameter and procedures similar to that of the Mn doped sample, with the addition of Ag
doping to the functional layer growth. In Figure 6.1a, the Mn doped sample shows both in-
plane and off-plane magnetic anisotropy. This behavior is expected since epitaxial ZnO grown on R-Sapphire grows in (11-20) direction, with its (0001) direction different from that of the growth direction \[^9\]. The observance of both in-plane and off-plane magnetic anisotropy is a good support for intrinsic ferromagnetism. The details of the measurements can be found in ref 6. Same amount of thin film was measured each time to enable comparison of magnetic moment. We notice an in-plane strong axis, which has similar saturation moment and coercivity field as the off-plane measurement. The weak axis has both smaller saturation moment and smaller coercivity field. When Ag is introduced, while both in-plane and off-plane magnetic anisotropies are still observed, the behavior is different from purely Mn doped sample. Firstly, the maximum saturation moment is now approximately two times larger than the reference

![Figure 6.1](image)

*Figure 6.1* magnetic anisotropy of (a) Mn doped ZnO and (b) Mn/Ag co-doped ZnO.
MnZnO sample. While the in-plane strong axis still shows the same saturation moment as that of off-plane measurement, the coercivity field of the strong axis is now smaller than the weak axis.

This enhanced ferromagnetism by Ag co-doping is peculiar, and we investigated to rule out obvious factors. Both samples had similar thickness around 850nm, as measured by profilometer. To assert the film density, SEM was performed, as shown in Figure 6.2. Both samples had very smooth surface thus no significant difference in density is expected. The difference in ferromagnetism should rise from distributed dopants. EDX was performed on both samples but no Mn or Ag signal was detected on either sample. Figure 6.3 is EDX of the Mn/Ag co-doped sample, with the supposed position of Mn and Ag

![Figure 6.2 SEM of (a) Mn doped ZnO and (b) Mn/Ag co-doped ZnO.](image)

![Figure 6.3 EDX of Mn/Ag co-doped ZnO.](image)
peaks marked. This situation is similar to our previously published results on high quality MnZnO grown on R-sapphire \cite{6}, indicating very small amount of dopant to minimize any possible phase segregation.

To understand the phenomenon, purely Ag doped ZnO were grown. Difficulty was encountered when attempting to grow similarly smooth thin film on R-sapphire, so samples on C-sapphire was investigated. High quality Ag doped ZnO was successfully grown with optimized growth recipe, as mentioned in chapter 5. Samples all had n-type conductivity with an electron concentration between $10^{17}$ cm$^{-3}$ and $10^{18}$ cm$^{-3}$. Figure 6.4 is one typical examples of high quality Ag doped ZnO on C-sapphire. The SEM image shows that smooth and featureless surface is achieved. XRD spectrum shows only ZnO and Sapphire related peaks, with no Ag secondary phases present, proving proper incorporation of Ag into ZnO lattice.
Figure 6.4 is M-H response of Ag doped ZnO grown on C-
sapphire. Samples were all measured in in-plane geometry, with no in-plane magnetic anisotropy expected. Samples had other growth parameters and procedures kept the same, and had different Ag cell temperature during functional layer growth. It is clear that ferromagnetic hysteresis is observed in all samples, up to room temperature. Notice that the absolute strength of these samples are one order of magnitude smaller than previous Mn/Ag co-doped samples. This data fits our general expectation that no strong ferromagnetism will rise from Ag doping. But this is still first observation of ferromagnetism in high quality Ag doped ZnO thin
film. Previously there has only been a report on powder form Ag doped ZnO in which room temperature ferromagnetism was observed $^{[10]}$.

Temperature dependent cooling measurements were performed to identify possible magnetic phases within the samples. As shown in Figure 6.6, for the same samples as shown in Figure 6.5, fielded cooling measurements all had smooth trend without abrupt stepping in the data, indicating a magnetically singular phase for each sample, and a very high Currie Temperature well above 300K.

The largest saturation moment was observed in the sample with Ag cell 750$^\circ$C. Thus magnetic anisotropy measurement was attempted on this sample. Figure 6.7 shows in-plane and off-plane measurement results. The

**Figure 6.6** FC and ZFC measurements of Ag doped ZnO.
sample shows ferromagnetic hysteresis up to room temperature, with little change in saturation moment. For the in-plane measurement the coercivity field does increase as the temperature decreases. Similar to previous measurements, same amount of thin film was measured for the off-plane geometry. For the off-plane measurement, the saturation moment is around one order of magnitude smaller than the in-plane. But the coercivity field is found to be larger, and does not change with temperature. The observation of magnetic anisotropy is a good support for intrinsic ferromagnetism.

Finally a Mn/Ag co-doped ZnO sample was attempted on C-sapphire, with growth recipe based on the one mention in Figure 6.7. Figure 6.8 shows in-plane measurement results of Mn/Ag co-doped ZnO. In comparison to Figure 6.7a, the saturation moment remained similar, but coercivity field decreased significantly. One thing worth noting is

![Figure 6.7 Magnetic Anisotropy of Ag doped ZnO.](image)
that at 10K, the sample did not reach saturation within the measurement range (-6000Oe to 6000Oe), and the magnetic moment remained aligned to positive direction. The sudden increase of coercivity may indicate a different mechanism, and further measurements are necessary.

Ag has rarely been considered for magnetic doping since its d orbit is fully filled. A recent report of 2012 \cite{11} does consider Ag doped ZnO as possible ferromagnetic DMS, from theoretical point of view. Our observation of ferromagnetism confirms experimentally that Ag doped ZnO may be room temperature ferromagnetic. However, the exact mechanism remains to be verified by further investigation. The results we observed for Mn/Ag co-doping is of great significance for memory applications, since coercivity field can be manipulated by introduction of co-doping.

**Conclusion**

We observed room temperature ferromagnetism of high quality Ag doped ZnO. We have also noticed manipulation of coercivity behavior when Mn and Ag are co-doped into ZnO. Temperature dependent cooling measurements indicate that the Ag doped samples
are magnetically single phased, with a very high Currie Temperature. Magnetic anisotropy is observed on Ag doped and Mn/Ag co-doped ZnO, supporting claim of their intrinsic ferromagnetism.

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Reference


Chapter 7
Summary

Transition metal doped ZnO as diluted magnetic semiconductor exhibits great potential for optoelectronics and spintronic applications. The original prediction based on p-d Zener model predicted ZnO as a host material for room temperature DMS, thus rose great interest in developing ZnO DMS. While various methods have been utilized to fabricate ZnO DMS, molecular beam epitaxy prevails as high quality equilibrium growth method. When proper buffer and growth parameters are implemented, high quality ZnO thin films can be achieved.

Experimentally, while room temperature ferromagnetism is observed, the measured ZnO DMS does not necessarily comply with the parameters set by the original predictions. This is especially true in Mn doped ZnO. High quality epitaxial doped MnZnO is demonstrated by using MBE on both R-sapphire and C-sapphire. Mn concentration is found to be very low for such samples and no secondary phases or surface deterioration was observed. Both in-plane and off-plane magnetic anisotropy were observed, which supports intrinsic ferromagnetism. Large coercivity field was observed which makes the material more suitable for memory applications. One peculiar result observed is that the total magnetic moment, when quantized to $\mu_B$/ion based on Mn ion concentration, would exceed the maximum amount that is permitted by Hund’s law. Also considering the fact that these high quality MnZnO all showed evident n-type, thus does not satisfy the
condition for the p-d Zener model, a new understanding of the origin of the room temperature ferromagnetism is needed.

Furthermore, Ag doped ZnO was investigated as p-type dopant for high quality ZnO. Ag has the advantage as substitution dopant and thus is more suitable for high quality p-type ZnO. It is observed that Ag doping does suffer from evident phase segregation. But with optimization of growth parameters, phase segregation can be minimized and p-type was observed. However, for robust p-type doping further optimizations in suppression of donor levels are still necessary. Also, high quality Ag doped ZnO was found to be room temperature ferromagnetic. This finding experimentally verifies theoretical prediction and provides important insight into the mechanism of ZnO DMS. Also, co-doping of Mn and Ag into ZnO is found to increase saturation moment as well as modify magnetic anisotropy behavior. This co-doping thus provides valuable tool for memory applications, in which manipulation of saturation strength and coercivity field is vital.

As for the future of TM doped ZnO DMS, more research is still needed in clarifying the mechanism of room temperature ferromagnetism of DMS. Based on the improved knowledge through the scope of this thesis, it is highly possible that p-d Zener model does not account for the observed ferromagnetism. A new mechanism is needed to explain the exceedingly large $\mu$B/ion number. However, with the demonstration of manipulating saturation strength and coercivity field by either Mn doping concentration or Mn/Ag co-doping, memory devices now have a higher chance to realize. Further work on developing MTJ type memory devices can now be ventured.