Ferromagnetic copper-doped ZnO for spintronics

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Ferromagnetic Copper-Doped ZnO for Spintronics

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2008

To my wife, Sheryl Gui and my beloved parents

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Summary

Intensive research is being carried out in the field of spintronics, which aims at utilizing the spin degree of freedom of electrons along with its charge to get multifunctional opto-electronic devices. Efforts are being made to find a semiconductor with a high Curie temperature (T_c) by doping it with suitable transition metal ions in order to achieve the so-called diluted magnetic semiconductor (DMS). Along this direction, copper-doped zinc oxide (ZnO:Cu) is a specially promising material not only because of numerous interesting properties of ZnO but also due to Cu as a potential magnetic ions in ZnO. Moreover, there are no known ferromagnetic compounds of Cu/Zn or Cu-O and Cu element itself is nonmagnetic, making this system clean in terms of ferromagnetic inclusions, clusters or segregated secondary phases. This motivates researchers to study ZnO:Cu films as well as its nanostructures to exploit their potential in spintronics.

A series of ZnO:Cu films were prepared by filtered cathodic vacuum arc (FCVA) technique and the magnetic properties of the samples were studied as a function of deposition temperature and Cu concentration. The magnetic moment of $\sim 0.4 \mu_B/\text{Cu}$ was obtained for the room temperature deposited films having a Cu concentration of ~ 1 at.%. The presence of Zn interstitials in the films is related to the ferromagnetic ordering in the ZnO:Cu samples. In addition, the magnetic moment of the ZnO:Cu films decreases with an increase of Cu concentration which is attributed to the formation of anti-ferromagnetic precipitates.

One of the advantages of the FCVA technique over other deposition methods is its low temperature process which enables the growth of high-quality films on any

substrates including plastics. Ferromagnetic, flexible, and transparent ZnO:Cu films on plastic substrates with a magnetic moment of $0.28 \mu_B/\text{Cu}$ were obtained. The magnetic anisotropy of the samples was studied under various strain conditions. It is found that stress may lead to lattice distortion and produces magneto-elastic-driven anisotropy.

The magnetization of the ZnO:Cu films can be enhanced significantly by annealing the samples in N_2O ambient. After the annealing treatment, the ferromagnetism of the samples was improved by up to 100%. The magnetic properties of the annealed samples became relatively stable as compared to the as-grown sample in terms of temperature and storage time. It is found that the presence of N promotes the substitution of high spin Cu^{2+} ions into Zn^{2+} sites which leads to the enhanced ferromagnetism in the ZnO:Cu. The cyclic annealing experiments of the ZnO:Cu films in air, N_2O and Zn vapor suggested that Zn interstitial defects were crucial to the N incorporation.

Most of the ZnO based ferromagnetic materials including ZnO:Cu are either insulator or poor conductor, these materials would not be suitable for spin injector in devices such as spin light emitting diodes (spin-LED). We discovered that the conductivity of the ZnO:Cu films can be increased substantially using a biasing technique during deposition. The electron concentration and conductivity of the samples can be increased from 10^{16} to 10^{20} cm^{-3} and 0.31 to $194 (\Omega\text{-cm})^{-1}$ respectively, using the biasing technique. Several heterostructures LEDs have been fabricated using the conductive ZnO:Cu as an electron injector and a *p*-type GaN as hole injector. Electroluminescent from these LEDs can be detected.

Magnetic semiconductor nanostructures are expected to have a longer coherence time and spin lifetime as compared to the thin film counterpart. One-dimensional ferromagnetic ZnO:Cu nanoneedles were prepared by an ion-beam technique using Cu plate and ZnO film at room temperature. A saturated magnetization moment of 0.698 emu/cm^3 was found in the nanoneedles when a field was applied perpendicular to the substrate, which was 15% larger than when the field applied parallel to the substrate. The magnetic ordering of the nanoneedles was enhanced significantly to 0.968 emu/cm^3 after annealing at 400°C for 20 mins. However, the magnetic anisotropy at high field is vanished but an “easy plane” FM shows up in low fields. The magnetic anisotropy of the ZnO:Cu nanoneedles at high magnetic field may not be related to the shape and orientation of the nanoneedles but rather the distribution of Cu^{2+} and defect density.

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Abbreviations

1D	One dimensional
AFM	Atomic force microscopy
AGM	Alternating gradient magnetometer
ALD	Atomic layer deposition
BMP	Bound magnetic polaron
DMS	Diluted magnetic semiconductor
EL	Electroluminescence
FCVA	Filtered cathodic vacuum arc
FM	Ferromagnetism
GaN	Gallium Nitride
H_c	Coercity
LED	Light emitting diode
MOCVD	Metal-organic chemical vapor deposition
M_s	Saturated magnetic moment
PL	Photoluminescence
PLD	Pulsed laser deposition
RT	Room temperature
SAED	Selected area electron diffraction
SEM	Scanning Electron Microscopy
Si	Silicon substrate
spin-LED	Spin-light emitting diode
T_c	Curie temperature
TEM	Transmission Electron Microscopy
TM	Transition metal ions
XPS	X-ray photoelectron diffraction
XRD	X-ray diffraction
Zn_i	Zn interstitial
ZnO:Co	Cobalt-doped ZnO
ZnO:Cu	Copper-doped ZnO

Abbreviations

ZnO:Fe	Iron-doped ZnO
ZnO:Mn	Manganese-doped ZnO
ZnO:TM	Transition metal-doped ZnO

Chapter 1: Introduction

1.1 Background

Devices continue to diminish in size in order to achieve higher speed and packaging density. As this shrinkage occurs, the design parameters are impacted in such a way that the materials in current use are pushed to their limits.¹ An alternative solutions would be to render the individual components multifunctional, which would reduce the device size, low power consumption, higher integration density, high data processing speed, non-volatility and exploit multifunctional properties of materials.^{2,3} One of the hot research topic today is to utilize the electron spin to obtain new functionalities in conventional electronics and semiconductors technology. Today, the information technology made of the ferromagnetic materials, used for mass data storage application (hard disks, magnetic tapes, magneto-optical disks) has had great success in using electrons spin in ferromagnetic materials. One advantage of spin over charge is that spin can be easily manipulated by externally applied magnetic field, a property already in use in magnetic storage technology.^{4,5} The tomorrow's technology may combine magnetism (spin), and semiconductivity (charge) in one device that exploits both charge and spin to process, and store the information. Such a device called “spintronic device”. Alternatively, we may be able to inject spin-polarized current into semiconductors to control the spin state of carriers, which may allow us to carry out qubit (quantum bit) operations required for quantum computing.⁶ However, there are good reasons why this has not yet been widely integrated with existing semiconductor devices. The semiconductors used for devices and integrated

circuits, such as silicon (Si), gallium arsenide (GaAs) and silicon carbide (SiC), do not contain magnetic ions and their magnetic g factors are generally rather small. In order for them to be a useful difference in energy between the two possible electron spin orientations, the magnetic fields that would have to be applied are too high for everyday use. Moreover, the crystal structures of magnetic materials are usually quite different from that of the semiconductors used in electronics, which makes both materials incompatible with each other.⁶

One of the approaches to produce a ferromagnetic semiconductor is to introduce transition metal (TM) ions such as Mn, Cr, Co, Fe, Cu, etc into non-magnetic semiconductors. In these ferromagnetic semiconductors, a part of the lattice is made up of substitution magnetic atoms; thereby it is called diluted magnetic semiconductors (DMSs).⁷ There has been an extensive research towards introducing magnetic ions into semiconductors to realize a new class of DMS materials, such as (Ga,Mn)As and (In,Mn)As. The low Curie temperature (T_c) and debatable origin of ferromagnetism (FM) in these materials have limited its practical application.^{8,9} To a real DMS, it is necessary to show that the carrier population is spin polarized. This can be done through transport measurements, especially the observation of the anomalous Hall effect (AHE) or by observation of polarized light emission from a quantum well using the DMS material as a spin injector.¹⁰

The quest for a room temperature (RT) ferromagnetic semiconductor, gained momentum, following a theoretical prediction by Dietl *et al.*, that ZnO and GaN would exhibit FM above RT with a hole density $>10^{20} \text{ cm}^{-3}$.¹¹ This prediction initiated intensive experimental work on ZnO:TM. The values T_c at or above RT has been reported in ZnO:Co,¹² ZnO:Fe,¹³ and ZnO:Mn¹⁴. But the origin of FM in these

materials is controversial as it is suspected that its FM is induced by TM precipitates and its clustering. Hence non-magnetic element of Cu is a preferred choice to avoid controversies regarding the ferromagnetic ordering due to Cu related precipitates and secondary phases such as CuO and Cu₂O or clustering, making this system clean of metal precipitate induced FM. Buchholz *et al.*¹⁵ demonstrated RT FM in ZnO:Cu films, which prepared by pulsed laser deposition (PLD) under N₂O ambient and the origin of the FM was believed to be hole-mediated. On the other hand, we have demonstrated RT FM in ZnO:Cu deposited at RT by the filtered cathodic vacuum arc (FCVA) technique under pure O₂ ambient.^{16,17} Thus hole doping is not essential for the observation of FM in the ZnO:Cu. Despite uncertainty in the mechanism of FM in ZnO:Cu, and the fact that the obtained magnetization is lower than the theoretically predicted value in most of the reports appearing in literature, the results reported thus far, provide a pathway for exploring Cu-doped ZnO. This discrepancy is partly attributed to substitution of magnetic “silent” of Cu¹⁺ state into Zn site, formation of antiferromagnetism Cu-related secondary phases in the ZnO:Cu. It is however, imperative to understand the underlying mechanism of FM in order to improve the magnetic moment and stability towards the realization of commercially applicable devices.

1.2 Motivations

1.2.1 Why ZnO?

GaN and ZnO have attracted intense attention in the searching for high T_c DMS materials as it is predicted that GaN and ZnO could potentially exhibit FM when doped with TM or rare earths ions with unpaired partially empty $3d$ and $4f$ shells, respectively. Although theoretical calculation predicted that GaN ($T_c \sim 400\text{K}$) would exhibit higher T_c compared to ZnO ($T_c \sim 350\text{K}$),¹¹ ZnO is the choice in this study because of its intriguing advantages relative to GaN such as (a) its availability in bulk (b) larger exciton binding energy (~ 60 meV, cf. ~ 25 meV for GaN) for brighter luminescence at RT, (c) higher electron mobility, (d) higher saturation velocity, and (e) ZnO also has much simpler crystal-growth technology.^{18,19} Furthermore, n -ZnO type has relatively long room temperature spin-coherence time (~ 190 ps at RT) as compared to GaN (~ 35 ps at RT)²⁰ is advantageous in spintronics applications.²¹ The basic properties of ZnO are shown in Table 1 and its typical wurtzite structure is shown in Figure 1-1. Two types of atoms, Zn and O, are tetrahedrally coordinated to each other and are therefore equivalent in position. The Zn-O distance is $1.992 \text{ \AA}$ parallel to the c -axis and $1.973 \text{ \AA}$ in the other three directions of the tetrahedral arrangement of nearest neighbors.²²

In addition, a potential application and the integrity of ZnO with conventional electronics application is also the prime consideration in the choice of host materials. A ZnO based DMS would be very promising because of its widespread application in electronic devices such as gas sensors, varistors, surface acoustic wave devices, optical wave guides, acousto-optic modulators/deflectors, ultraviolet laser source, and detectors.^{3,19,23}

Property	Value
Lattice parameters at 300 K	
a_0	0.32495 nm
c_0	0.52069 nm
c_0/a_0	1.602 (ideal hexagonal structure shows 1.633)
Density	5.606 g/cm ³
Stable phase at 300 K	Wurtzite
Melting point	1975 °C
Thermal conductivity	0.6, 1-1.2 W/cm K
Linear expansion coefficient (/°C)	$a_0 = 6.5 \times 10^{-6}$ $c_0 = 3.0 \times 10^{-6}$
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy gap	3.4 eV, direct
Intrinsic carrier concentration	$<10^6 \text{ cm}^{-3}$
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron Hall mobility at 300K for low n -type conductivity	200 cm ² /Vs
Hole effective mass	0.59
Hole Hall mobility at 300K for low p -type conductivity	5-50 cm ² /Vs

Table 1: Basic properties of ZnO.²²

Figure 1-1: Wurtzite structure of ZnO.

1.2.2 Why ZnO:Cu?

Numerous TM ions such as Mn, Co, Cr, Ni, V or Fe has incorporated into ZnO.²⁴ A drawback to this approach is that the dopant material can segregate to form precipitates or clusters that are actually responsible for the ferromagnetic properties. The effect of such ferromagnetic clusters must be examined more carefully before the usefulness of such materials for spintronics applications can be determined.²⁵ Interestingly, copper-doped zinc oxide (ZnO:Cu) has been predicted to be ferromagnetic²⁶⁻²⁹ and some initial experiments have shown signs of magnetic behavior at 5 K.³⁰ Because metallic copper is not magnetic, and neither Cu₂O nor CuO is ferromagnetic, ZnO:Cu has the possibility of being free of ferromagnetic precipitates and hence form an clean ferromagnetic semiconductor system. Until 2004 there was no report on room temperature FM in ZnO:Cu, which motivated us to investigate ZnO:Cu system using FCVA technique. Furthermore, Cu is also well known as a potential *p*-type dopant with high reproducibility that aroused our interest to realize FM in ZnO:Cu films.^{31,32} The use of hole doping has been predicted by Dietl *et al.*¹¹ that ZnO-based DMS could exhibit FM above RT with incorporation of hole doping.

Controversies of underlying physical origin in DMS is another momentum for us to explore the ferromagnetic ZnO:Cu. In early day, a carrier-mediated mechanism has been proposed to explain the FM in oxide DMS.²⁴ However, the TM-doped oxide films with ferromagnetic properties are sometimes poor in conduction or highly insulating.^{33,34} The *sp-d* exchange mechanism between the *sp* free carriers and the *d* states of the TM doping elements is therefore inapplicable in these cases. Double exchange mechanism between *d* states of TM elements is another possible candidate

to induce FM in magnetic oxide. However, in many cases the low doping concentration and single valence state of magnetic elements have been observed to exclude the double exchange mechanism. A synopsis of ZnO based DMS theory will be presented in Chapter 2.2.3. Hence, we have carried out a series of experiment to examine the role of defect in the films and proposed the possible underlying mechanism of observed FM in the ZnO:Cu.

It is worthy to highlight that one of the prime advantages of the FCVA technique over other deposition methods is its low temperature process which enables the growth of high-quality films on any substrates including plastics, thereby transparent and flexible ZnO:Cu films on plastic substrates have been demonstrated with reasonable high magnetic moment ($0.28 \mu_B/\text{Cu}$).

1.3 Objectives

The main aim of the present thesis is to obtain room temperature FM in ZnO:Cu films by tailoring the process parameters. We have also pursued various experimental and characterization techniques:

1. to study the effect and role of Cu in ZnO.
2. to understand the underlying physical origin of the observed FM in ZnO:Cu.
3. to develop the highly transparent and flexible ZnO:Cu films on plastic substrates. The magnetic, structural, electrical and optical properties of ZnO:Cu on plastic substrate were investigated.
4. to realize conductive and ferromagnetic ZnO:Cu.
5. to demonstrate ZnO:Cu based heterojunction light-emitting diodes.

6. to fabricate ZnO:Cu nanoneedles and to study the magnetic anisotropy associated with it.

1.4 Major contribution of the thesis

The main contributions of this work are as follows:

1. It is the first time that ZnO:Cu prepared on silicon under pure O₂ ambient showed room temperature FM.
2. Zn interstitial was identified to play a crucial role in mediating FM in ZnO:Cu films. The FM is not related to oxygen vacancy.
3. The enhancement of magnetic ordering and stability has been achieved by the incorporation of N through N₂O annealing. The role of N in enhancing the FM in ZnO:Cu was proposed.
4. The important interplay between high spin Cu²⁺ ions, N and Zn interstitials in ZnO:Cu was studied. They are essential to the magnetic enhancement.
5. Highly transparent and flexible ferromagnetic ZnO:Cu films on plastic substrates have been developed and characterized.
6. Demonstrated conductive and ferromagnetic ZnO:Cu films with electron concentration greater than 10²⁰cm⁻³ using a biasing technique.
7. ZnO:Cu based heterojunction LED was demonstrated.
8. An ion-beam technique has been employed to fabricate ZnO:Cu nanoneedles on silicon substrates at room temperature. The possible mechanism of the observed magnetic anisotropy was proposed.

1.5 Organization

The dissertation begins with Chapter 1, which describes the background, motivation and the objectives of the research. The main contributions of the thesis are also presented in this chapter.

The literature review is depicted in Chapter 2. The fundamental concepts, basic principle of the spintronics and DMS materials have been reviewed. In the end of this chapter, the state-of-the-art of the ZnO based DMS, in particular ZnO:Cu is illustrated in details.

Chapter 3 describes the fabrication methods and characterization approaches adopted in this work.

The physical origin of the observed FM in the ZnO:Cu is a central of Chapter 4. The bound magnetic polarons (BMP) model and the role of Zn interstitial in the ferromagnetic ZnO:Cu are studied. In the end of this chapter, the enhancement of magnetic moment and stability of ZnO:Cu by N₂O annealing are realized. The interplay of Cu ions, Zn interstitials and N in mediating FM in ZnO:Cu is investigated.

Chapter 5 provides the detailed fabrication and characterization of transparent and flexible ZnO:Cu on plastic substrates. The possible mechanism of the magnetic anisotropy of the stressed samples is proposed.

Chapter 6 describes the fabrication of conductive and ferromagnetic ZnO:Cu films by the biasing technique. The structural, magnetic, electrical and optical properties of the ZnO:Cu prepared by biasing technique are investigated. The detailed fabrication and optical properties of the ZnO:Cu based heterojunction LED are studied.

The fabrication and characterization of ZnO:Cu nanoneedles on Si substrates are addressed in Chapter 7. The magnetic anisotropy of the ZnO:Cu nanoneedles is presented.

The dissertation ends in Chapter 8 with a summary of the main conclusions and recommendations for further research.

Chapter 2: Literature review

2.1 What is spintronics?

In 21st century, the data storage and Si integrated circuit (IC) industry advance at a rapid pace. In the storage industry, the overall bit density on a magnetic head has increased at an annual rate of 60–100%. The key parameter of magnetic storage is the electron spin, as spin can be thought of as the fundamental origin of magnetic moment.⁵ The electrons spin itself is manifested as two state magnetic energy system (spin up or spin down). When electron spins are aligned and interact, they can create a large magnetic moment. In the case of IC industry, the IC operates by controlling the flow of carriers through the semiconductor by applied electric fields. The key parameter therefore is the charge of the electrons or holes.⁵ The number of transistors on a chip doubles about every 18 months according to Moore's law. However, Moore's law will subsequently lose its momentum as the size of individual bit approaches dimensions of an atom. It has motivated researchers to exploit charge and spin degrees of freedom of electrons in semiconductors, with the hope of developing a remarkable new generation of devices, which are smaller, more versatile and less power consumption than the current charge–current based devices.⁴ Thus emerges a new field of electronics called spintronics^{35,36} short for spin electronics, an area concerned with the storage and transfer of information by means of electrons spins in addition to electron charge as in conventional electronics.

The advantages of spin over charge are (a) spin can be easily manipulated by external applied magnetic fields and (b) spin has longer life time and coherence time (~190 ps for ZnO at RT). Once created spin tends to stay that way for a long time, unlike charge states, which are easily destroyed by scattering or collision with defects,

impurities or other charges.⁴ In order to store and process information, the spin of an electron must be relatively robust, in particular spin relaxation time which is the time it takes for the spin to 'relax.' When spin relaxes, the information encoded in it is lost. It is widely expected that new functionalities for electronics and photonics can be derived if injection, transfer and detection of carrier spin can be controlled over room temperature. These characteristics open the possibility of developing devices that could be much smaller, consume less electricity and be more powerful for certain types of computations than is possible with electron-charge-based systems. A proposed new class of spin related devices are spin transistors, spin-LED, fast non-volatile semiconductor memory and integrated magnetic/electronic/photonic devices ("electromagnetism-on-a-chip") as shown in Figure 2-1.⁵

Figure 2-1: A technology tree for Spin-based devices.⁵

Spin relaxation (how spins are created and disappear) and spin transport (how spins move in metals and semiconductors) are fundamentally important not only as basic physics understandings but also because of their demonstrated applications in electronic technology. The first acknowledged breakthrough in spintronics was the exploitation of giant magnetoresistance (GMR), a technology now employed in the read heads of most hard drives. GMR can be used to detect extremely small magnetic fields by using a nonmagnetic material sandwiched between two magnetic plates as shown in Figure 2-2. Depending on the relative orientation of the magnetizations in the magnetic layers, the electrical resistance through the layers changes from small (parallel magnetizations) to large (antiparallel magnetizations).

Figure 2-2: Schematic representations of transport that is parallel to the plane of a layered magnetic metal sandwich structure for aligned (low resistance) and antialigned (high resistance) orientations.³⁷

The realization of functional spintronics devices requires materials with ferromagnetic ordering at operational temperatures compatible with existing semiconductor materials. In addition, there are a number of essential requirements for achieving practical spintronics devices. These include (a) the ability to transport the carriers with high transmission efficiency within the host materials, (b) the ability to detect or collect the spin-polarized carriers and (c) ability to control the transport

through external means such as biasing of a gate contact on a transistor structure.⁵ The search of new materials which exhibits above mentioned criteria is a challenge to the researchers around the world. A diluted magnetic semiconductor (DMS) is one of potential ferromagnetic semiconductors for future spintronics application. In the next session, we focus on the development of DMS.

2.2 Diluted magnetic semiconductors

The term of dilute magnetic semiconductor (DMS) refers to the fact that some fraction of the atoms in a nonmagnetic semiconductor host such as ZnO are replaced by ‘3d’ or ‘4f’ magnetic ions.^{7,38} The schematic representation of DMS is shown in Figure 2-3. In DMS materials, ‘3d’ or ‘4f’ magnetic ions are randomly substituted for the cations of the host, the resultant electronic structure is influenced by strong hybridization of the, ‘3d’ or ‘4f’ orbitals of the magnetic ion and mainly the p orbitals of the neighboring host anions. This hybridization gives rise to the strong magnetic interaction between the localized magnetic ion spins and the carriers in the host valence band. A consequence of hybridization and its ternary nature are that the several properties of these materials such as lattice constant, energy gap and other band parameters can be tuned by varying the concentration of the magnetic ions in the host materials.⁷ The possibility thus exists to tailor the properties of the DMS materials and hence they become important materials in the field of device technology. However, to be considered a true DMS, it is necessary to show that the carrier population is spin polarized. This can be done through transport measurements, especially the observation of the anomalous Hall effect (AHE) or by observation of polarized light emission from a quantum well using the DMS material as a spin injector.¹⁰ In addition, it is the

necessity that the DMS must exhibit FM with a critical temperature above RT in order to have practical applications in spintronics devices. The Curie temperature (T_C) is naturally deemed to be the bottleneck issue. The other criteria of ideal DMS are:³⁹

- A close connection between the FM and the population of a spin-split band of carriers.
- A choice of p or n type doping.
- High mobility and long spin diffusion length, needed for lateral heterostructures.
- Magneto-optic effects including magnetic circular dichroism (MCD).

No material yet exists which ticks all the criteria. Dilute magnetic oxides have proved disappointing, except in the observation of room temperature FM. No clear link has yet been established between carrier concentration and FM.³⁹

Figure 2-3: Three types of semiconductors: (A) a magnetic semiconductor, in which a periodic array of magnetic element is present; (B) a diluted magnetic semiconductor, an alloy between nonmagnetic semiconductor and magnetic element; and (C) a nonmagnetic semiconductor, which contains no magnetic ions.⁶

The study of DMS began in late 1960s resulted in various exciting findings. The most common DMSs are II-VI compounds (such as CdTe, ZnSe, CdSe, CdS, etc.) doped with TM ions. There are also DMS based on IV-VI compound (e.g. PbTe,

SnTe) and III-V (e.g. GaAs, InSb). In order to ensure this thesis self contained, we will begin by recalling the history of DMS; as well as by summarizing the current research of DMS.

2.2.1 History of DMS

In early stage of DMS development, it was II–VI compounds (such as CdTe, ZnSe, CdSe, CdS, etc.) doped with TM ions which are most common and thoroughly studied DMS.^{38,40} A study of II–VI DMS have centered mostly on manganese-based II–VI DMS, $A_{1-x}^{II}Mn_xB^{VI}$ compounds (e.g. $Cd_{1-x}Mn_xT$, $Cd_{1-x}Mn_xSe$, etc.) in which the valence of the cations matches that of the Mn ions. Although this phenomenon makes II–VI DMS relatively easy to prepare in bulk form as well as in thin epitaxial layers, these DMSs have been difficult to dope to create *p*- and *n*-type, which made the material less attractive for applications. Moreover, the magnetic interaction in II–VI DMS is dominated by the antiferromagnetic exchange among the Mn spins, which results in the paramagnetic, antiferromagnetic, or spin-glass behavior of the material. It was not possible until very recently to make an II–VI DMS ferromagnetic at low temperature in modulation doped QW structures exploiting Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism.⁴¹ RKKY is a coupling mechanism of nuclear magnetic moments or localized inner *d* or *f* shell electron spins in a metal by means of an interaction through the conduction electrons, describing (*d*-electron spin)-(*d*-electron spin), (nuclear spin)-(nuclear spin) as well as (*d*-electron spin)-(nuclear spin) interactions.^{42,43} The details of RKKY mechanism will be presented in Section 2.2.3. The most significant of RKKY theory has been to GMR application in explaining ferromagnetic/antiferromagnetic oscillation phenomenon.

Another class of semiconductor materials is III-V compounds (such as GaAs, InAs, etc) are widely used in optoelectronics and high speed electronic applications. Therefore, the introduction of magnetic III-V semiconductors opens up the possibility of using a variety of magnetic phenomena not present in conventional nonmagnetic III-V semiconductors in the optical and electrical devices already established. However the magnetism of III-V compounds has not been studied intensively in the early stage because of the low solid solubility of TM ions into these materials, typically $\sim 10^{18} \text{cm}^{-3}$ or less.⁴⁴ Beyond a certain doping level, the surface segregation, and in extreme cases phase separation would occur and impede further incorporation of high concentration of magnetic ions into the crystals. Therefore, preparation of ternary alloys to form DMS of III-V semiconductors is an extremely difficult task. No III-V based DMS was reported until the discovery of low temperature non-equilibrium film growth technique using molecular beam epitaxy (MBE).^{45,46} Ohno *et al.* reported FM in epitaxial films of InMnAs grown by MBE in 1992 and GaMnAs ($T_c \sim 110 \text{ K}$) in 1996.^{45,46} When a high concentration of magnetic elements is introduced in excess of the solubility limit, formation of the secondary phase occurs if conditions are near equilibrium. However, when the crystal is grown at low temperature by MBE, there is not enough thermal energy available to form the secondary phase, and yet there still exists a local potential landscape that allows epitaxial growth of a single-crystal alloy.

The narrow gap IV-VI compounds (e.g. PbMnTe, MnTe and GeMnTe) is another well known DMS material, attributing to its intriguing feature of free carrier induced magnetism.³⁸ Unlike II-VI and III-V DMSs, these materials can be grown with higher concentration of free band carriers and its magnetic properties can be controlled by modifying the carrier concentration through control of native defects.

Story *et al.* demonstrated effect of carrier concentration toward the magnetic properties of PbSnMnTe.⁴⁷ The T_c could be increased by increasing the carrier concentration. In addition, the early study revealed that the antiferromagnetic interaction between magnetic ions in these materials were considerable weaker than comparable narrow gap II-VI compounds, resulting improved magnetic ordering.^{48,49}

2.2.2 ZnO and ZnO:Cu based DMS – the states of the arts

In recent year, a key development of DMS is focused in the wide bandgap semiconductor as being most promising candidates for practical spintronics application. Theoretical calculation predicted that wide bandgap semiconductors, in particular ZnO and GaN containing 5% Mn with the hole concentration above 10^{20} cm^{-3} could exhibit room temperature FM.¹¹ The schematic of predicted T_c for the doped semiconductors is shown in Figure 2-4. This prediction initiated remarkable research interest in TM-doped ZnO (II-VI compounds) and GaN (III-V compounds). However, in this dissertation, the discussion mainly centered on copper-doped ZnO due to intriguing features of ZnO over GaN and distinctiveness of copper in ZnO as illustrated in chapter 1.2.

Figure 2-4: Predicted Curie temperatures for *p*-type semiconductors.¹¹

Table 2 summarizes the recent reports of magnetic properties of TM-doped ZnO. The experimental results in TM-doped ZnO have been rather controversial, ranging from spin-glass behavior and paramagnetism to the FM below or above room temperature.²⁴ Some groups reported the FM is intrinsic,^{16,50} while others believed TM related clusters, precipitates or secondary phases are responsible for the observed magnetic properties.^{51,52} This variation can potentially be explained by the small total magnetization typically found in the samples, the very dilute nature of the dopants, and the potential for artifacts, such as clustering of magnetic dopants. The effect of such ferromagnetic clusters must be examined more carefully before the usefulness of such materials for spintronics applications can be determined. The distribution of TM elements in the host ZnO is also an important issue to be addressed in DMS system. Consequently, the origin of ferromagnetism in TM-doped ZnO is not well understood. Interestingly, ZnO:Cu has been predicted to be promising candidate displaying room temperature FM and some initial experiments have shown signs of magnetic behavior. The fact of Cu and its oxides (CuO and Cu₂O) are non-ferromagnetic⁵³ removes any possibility of FM arising from the presence of secondary magnetic phases in this system. The reports of uniqueness of Cu in ZnO led to many efforts on synthesis of ZnO:Cu, as detailed in Table 2.

Initial theoretical studies of ZnO doped with 25% Cu by Sato and Katayama-Yoshida²⁶ predicted ZnO:Cu to be nonmagnetic. Later theoretical studies at lower Cu doping levels of 6.25%²⁷ and 3.125%²⁸ indicated ZnO:Cu should be ferromagnetic. The discrepancies can be reconciled by noting the proximity of the Cu atoms with respect to each other in the different studies. The above simulations are based on supercells that contain 8 or 16 molecules of ZnO and replacing the appropriate number of Zn atoms with Cu to obtain the doping concentration of interest. For

simulations involving 6.25% and 3.125% Cu the nearest-neighbor copper atoms were at least 6.1 Å apart. In the study by Sato and Katayama-Yoshida, for 25% Cu concentration, it was necessary to place Cu atoms such that they were both above/below each other in adjacent basal planes (separated by the c -axis constant of 5.20 Å) and on adjacent cation positions within a single basal plane (separated by the a -axis constant of 3.25 Å). Feng looked at the effect of Cu separation and the stability of the ferromagnetic state in ZnO:Cu.⁵⁴ For the case where the Cu atoms were separated by 5.20 Å along the c -axis the ferromagnetic state was favored, but for the case where the Cu atoms were separated by 3.25 Å within the basal plane the antiferromagnetic state was favored.

Experimentally, magnetic circular dichroism spectra of ZnO thin films doped with 0.3% Cu suggested it was a DMS.³⁰ Additionally, a saturable component of the magnetization has been observed in M - H curves of ZnO powders doped with 2% and 5% Cu and interpreted as ferromagnetism.³² However, there is report of RT ferromagnetic M - H behavior in ZnO:Cu thin films till 2005. Buchholz *et al.*¹⁵ first reported room temperature FM in ZnO:Cu grown by PLD in N₂O ambient. The ZnO:Cu magnetic properties has been confirmed by our group and we are first showed the room temperature FM in ZnO:Cu synthesized in O₂ at RT.¹⁶ The magnetization of ZnO:Cu is found to be related to Cu concentration, defects level, Cu atom separation distance, crystallography and materials solid solubility. In general, the magnetization reduces with an increase of Cu concentration. The experimental studies^{15,55,56} reported the high resistivity and low carrier concentration of ZnO:Cu, envisaging its magnetism is related to bound magnetic polaron interaction. Recently, Ye *et al.* showed theoretically that ZnO:Cu system could display 100% polarization of local Cu²⁺, and Huang *et al.* predicted that certain types of defect states may help

stabilize this spin polarization. Near 100% spin polarization of the localized 3d spins of the Cu has been obtained experimentally by Chakraborti *et al.*⁵⁷ Thereafter, ZnO:Cu has received significant attention to study its magnetic properties and origin of ferromagnetism as shown in Table 2. However, the mechanism of FM in ZnO:Cu is not well understood. Sudakar *et al.*⁵⁸ reported the large magnetic moment of 1.6 μ_B /Cu grown by magnetron co-sputtering, which is attributed to inclusion of nanophases and it is not intrinsic FM. A better understanding of the underlying physics and mechanism of FM in ZnO:Cu DMS will certainly provide guidance of developing functional semiconductors system with high T_c . The next session describes the fundamental theories forwarded the mechanism involving DMS, delving into the theoretical studies specific to ZnO:Cu.

Chapter 2 : Literature Review

Compound	TM content (at. %)	Fabrication method	T _c (K)	Magnetic moment	Ref
ZnO:Mn	0.0221	PLD	> 425	0.05 emu/g single phase	14
ZnO:Mn	0.022	RF magnetron sputtering	> 350	0.55 μ_B /Mn	59
ZnO:Mn	0.07	Sputtering		Paramagnetism	60
ZnO:Mn	0.03	ALD		Paramagnetism	61
ZnO:Mn:Sn	Mn 0.03 Sn < 0.1	PLD	> 300	Ferromagnetism	62
ZnO:Mn:N	~ 0.05	Reactive magnetron cosputtering	> 300	0.35 μ_B /Mn	63
ZnO:Co	0.01	Pulsed injection MOCVD	900	18.9 μ_B /Co	64
ZnO:Co	0.048	Thermal diffusion		Antiferromagnetism and paramagnetism	65
ZnO:Co	0.05	PLD		1.04 μ_B /Co	66
ZnO:Co	0.04	Reactive magnetron cosputtering	790	6.1 μ_B /Co	67
ZnO:Co:Al	Co 0.05 Al 0.03	Sol gel	> 360	0.48 μ_B /Co	68
ZnO:Fe		Ion implantation	> 300	0.13 μ_B /Fe	69
ZnO:Fe	0 - 0.1	Sol gel with hydrogen treatment	> 300	0.099 μ_B /Fe	70
ZnO:Ni	0.01 - 0.25	PLD		Superparamagnetism or paramagnetism	71
ZnO:Ni	0.01	Wet chemical reaction	> 300	0.05 emu /g	72
ZnO:V	0.05	PLD	> 300	Ferromagnetism	73
ZnO:Cu	0.05	Magnetron sputtering	360	0.52 μ_B /Cu	74
ZnO:Cu	0.0186	Solvothermal	> 300	0.013 μ_B /Cu	75
ZnO:Cu	0.05 – 0.82	FCVA	> 300	0.28 μ_B /Cu for ZnO:Cu (1.3%) on plastic	56
ZnO:Cu	0.02 -0.12	DC reactive magnetron cosputtering		1.8 μ_B /Cu for ZnO:Cu (2%)	76
ZnO:Cu	0.01	Reactive magnetron cosputtering	> 300	1.6 μ_B /Cu	58
ZnO:Cu	0.02 - 0.1	PLD	> 300	0.75 μ_B /Cu for ZnO:Cu (2%)	57
ZnO:Cu	0.013	FCVA	> 300	1.249 emu / cm ³	17
ZnO:Cu	0 to 0.016	PLD	> 350	0.4 μ_B /Cu at 200K (Cu = 1 at. %)	15
ZnO:Cu	0.024	FCVA	> 300	0.037 μ_B /Cu	16
ZnO:Cu	0.013	FCVA	> 300	0.4 μ_B /Cu	77
ZnO:Cu	0 – 0.05	Sol gel		paramagnetism	32
ZnO:Cu:Co	Cu 0 – 0.2 Co 0 – 0.2	PLD	> 300	0.75 μ_B /Cu for ZnO:Cu (2%)	78
ZnO:Mn:Cu	Mn 0.1 Cu 0.05	PLD	400	0.1 μ_B /Mn	79
ZnO:Fe:Cu	Fe < 0.07 Cu < 0.01	Solid state reaction	550	0.75 μ_B /Fe	13

Table 2: Recent reported magnetic properties of transition metal doped ZnO. PLD, pulsed laser deposition; ALD, atomic layer deposition; FCVA, filtered cathodic vacuum arc; MOCVD, metal-organic chemical vapor deposition.

2.2.3 A synopsis of ZnO based DMS theory

In ZnO based DMS, a random substitution of TM element into cations sites of ZnO gives rise to localized moments in the semiconductor matrix. The presence of TM ions affects the free carrier behavior through the $sp-d$ exchange interaction between the localized magnetic moments and the spins of the itinerant carriers.⁷ The $3d$ TM elements are partially filled (up or down) with valence electrons corresponding to the $4s$ orbital as shown in Figure 2-5.²⁴ The d bands of TM ions hybridize with the host valence bands (O- p bands in ZnO) to form the tetrahedral bonding ($s-p^3$). This hybridization gives rise the exchange interaction between the localized $3d$ spins and the carriers in the host valence band, leading to the observed magnetic moments.

Figure 2-5: Electronic configuration of the $3d$ -states and $4s$ -states of transition metal elements.²⁴

The most important characteristic in DMS or ferromagnetic material is its spontaneous magnetization below T_c . As shown in Figure 2-6, for ferromagnetic materials the d band is divided into spin-up and spin-down sub-bands. The up and down states are displaced in energy with respect to one another, so that the spin-up band is filled first, and the spin-down states contain the remaining. The difference in

the number of spin-up and spin-down electrons leads to the observed spontaneous magnetic moment. Above T_c , the ferromagnetic material loses its permanent magnetism due to thermal agitations. Thus, it is essential to have a T_c well above RT for DMS materials to be practical spintronics application.

Figure 2-6: A schematic representation of the density of electronic states that are available to electrons in a normal metal and in a ferromagnetic metal whose majority spins states are completely filled. E , the electron energy; E_F , the Fermi level; $N(E)$, density of states.³⁷

The mechanisms pertinent to magnetism in DMS are direct superexchange,⁸⁰ indirect superexchange,⁸¹ Ruderman-Kittel-Kasuya-Yoshida (RKKY), double exchange mechanism⁸² and magnetic polarons.⁸³ Table 3 gives a comparison of the magnetic interactions. The basic idea behind the RKKY interaction is based on the exchange coupling between the magnetic ions and the conduction band electrons. The conduction electron is magnetized in the vicinity of the magnetic ion, with the polarization decaying with distance from the magnetic ion in an oscillatory fashion. This oscillation causes an RKKY interaction between two magnetic ions on the nearest or next nearest magnetic neighbors. This coupling may result in a parallel (ferromagnetic) or an anti-parallel (antiferromagnetic) setting of the moments dependent on the separation of the interacting atoms. This theory give complete

description on (*d*-electron spin)-(*d*-electron spin), (nuclear spin)-(nuclear spin) as well as (*d*-electron spin)-(nuclear spin) interactions.^{42,43} The derived exchange interaction takes the following form:

$$H(\mathbf{R}_{ij}) = \frac{\mathbf{I}_i \cdot \mathbf{I}_j}{4} \frac{|\Delta k_m k_m|^2 m^*}{(2\pi)^3 R_{ij}^4 \hbar^2} [2k_m R_{ij} \cos(2k_m R_{ij}) - \sin(2k_m R_{ij})]$$

where H represents the Hamiltonian, R_{ij} is the distance between the nuclei i and j , $\mathbf{I}_j$ is the nuclear spin of atom i , $\Delta k_m k_m$ is a term that represents the strength of the hyperfine interaction, m^* is the effective mass of the electrons in the crystal, and k_m is the wave vector of the conduction electrons.

Another class of magnetic interaction model in DMS is the double-exchange mechanism – a theory that predicts the relative ease with which an electron may be exchanged between two species (valence state). For example, consider the 180 degree interaction of Mn-O-Mn in which the Mn "eg" orbitals are directly interacting with the O "2p" orbitals as illustrated in Figure 2-7. Hence, double-exchange predicts that electron movement from one species to another will be facilitated more easily if the electrons do not have to change spin direction in order to conform with Hund's rules when on the accepting species. The ability to hop (to delocalize) reduces the kinetic energy. Hence the overall energy saving can lead to ferromagnetic alignment of neighboring ions.

Figure 2-7: Double exchange mechanism of Mn-O-Mn.

In the superexchange mechanism, magnetic ions modify the wave functions of connecting “ligands” giving them a magnetic character, allowing indirect exchange interactions with neighboring ions as shown in as shown in Figure 2-8 (b). However, anti-ferromagnetic state is favored, if the two neighboring magnetic ions are direct coupling through overlap of magnetic orbital as shown in Figure 2-8 (a). To date, the origin of FM in oxide DMS remains a very controversial topic. There is no single theory can well accord with the experimental results. However, it is desirable to have a DMS to be due to carrier-induced FM such as double exchange, so that magnetic properties of DMS can be manipulated by external means (holes or electron concentration). In the subsequent chapter, we will investigate the underlying physical origin of our ZnO:Cu films prepared by FCVA technique based on the fundamental magnetic knowledge.

Figure 2-8: The (a) direct and (b) indirect superexchange interaction.

Interaction	Definitions
RKKY	• Indirect exchange coupling of magnetic moments over relative large distance via conduction band electrons due to the Coulomb exchange. • The coupling between two magnetic ions on the nearest or next nearest magnetic neighbors. • It becomes efficient when high concentration of free carriers is present. • The coupling may result in a parallel (ferromagnetic) or an anti-parallel (antiferromagnetic) dependent the separation of the interacting atoms.
Direct superexchange	• Direct coupling of magnetic ions through overlap of magnetic orbital. • Resultant the antiferromagnetism.
Indirect superexchange	• Spins of two magnetic ions are correlated due to the exchange interaction between each of the two ions and the valence p-band. • Resultant of interaction could be ferromagnetism.
Double exchange	• Couples magnetic ions in deferent charge state by virtual hopping of the “extra” electron form one ion to the other through interaction with p-orbital as illustrated in Figure 2-7. • Predicts that electron movement from one species to another will be facilitated more easily if the electrons do not have to change spin direction in order to conform with Hund's rules when on the accepting species. • Ferromagnetism will be observed.

Table 3: A comparison of magnetic interactions

In addition to the models mentioned in Table 3, bound magnetic polaron (BMP) model has been widely used to interpret the magnetic properties in oxide DMS system such as TM-doped ZnO.⁸³⁻⁸⁵ The bound magnetic polarons are formed by interaction of many TM spins with that of much lower number of weakly bound carrier such as excitons. The localized holes/electrons of the polarons act on the TM impurities surrounding them, creating an effective magnetic field and aligning all the spins as illustrated in Figure 2-9. As temperature decreases the interaction distance increases and neighboring magnetic polarons overlap via magnetic impurities to form correlated clusters of polarons. The ferromagnetic transition occurs when the size of the overlapping clusters reaches that of the size of the sample. This model is inherently attractive for low carrier density systems such as many of the electronic oxides; it is applicable to both p - and n -type host materials.⁸⁶ Even though the direct exchange interaction of the localized holes is antiferromagnetic,

the interaction between BMP may be ferromagnetic for sufficiently large concentrations of magnetic impurities. This enables ferromagnetic ordering in the insulating or semi-insulating material.

Figure 2-9: Representation of magnetic polarons in TM-doped ZnO. A donor electron couples its spin anti-parallel to impurities with a half-full or more than half full $3d$ shell. Cation sites are represented by small circles. Oxygen is not shown; the unoccupied oxygen sites are represented by squares.⁸³

The first-principle calculations also suggested that the n -type doping in ZnO can increase the Curie temperature of TM-doped ZnO samples when the effects of disorder are taken account by what is called the coherent potential approximation.⁸⁷⁻⁹⁰ Considering than n -type ZnO is readily available and the intrinsic defects such as O-vacancies and Zn-interstitials form donor states, it was concluded that ZnO:TM are promising candidates for high T_c ferromagnetic.

Chapter 3: Experimental and methodology

3.1 Filtered cathodic vacuum arc (FCVA) technique

The vacuum arc is a low voltage, high current plasma discharge that takes place between two metallic electrodes in vacuum. The idea of generating the coating by vacuum arc was first proposed by Thomas Edison in 1892.⁹¹ The first “modern” study of the properties of metal coatings deposited from vacuum arc began in 1965 by *Kikushi et al.*⁹² Thereafter, many research groups progressively worked on this technique to understand the cathodic arc and plasma processes, with direct applications in the deposition of hard coatings. To date, vacuum arc deposition equipment is one of the most important commercial available techniques for high quality thin films deposition.

The major obstacle for the cathodic vacuum arc deposition was the generation of microparticles in the plasma.⁹¹ To circumvent this issue, *Aksenov et al.*⁹³ designed a magnetic filter in the cathodic vacuum arc system to remove particles from plasma. Thus, this deposition technique is well known as filtered cathodic vacuum arc (FCVA). *Shi et al.*⁹⁴ improved the efficiency of microparticles removal by double bend filter. Films of metal and alloys, including non-equilibrium alloys, high quality diamond-like carbon, ceramics of many different kinds, semiconductors, high-temperature superconductors, and other materials have been fabricated, both as single layer films and multilayer structures by vacuum arc technique.⁹¹ However, to the best of our knowledge, it is the first time that FCVA technique is being used to prepare ferromagnetic ZnO:Cu films.

The formation of high energy ions from the cathode material is one of important advantages of the cathodic arc process over other physical vapor deposition

techniques. The ions generated by the cathodic arc are multiply charged and with a near optimal kinetic energy for forming dense and adherent coatings on complex shapes. The high degree of ionization in the plasma (usually close to 100%) means that the impact energy of the depositing ions at the growth surface can be readily controlled using electric fields. For instance, by adding bias voltage on the substrate, the energy of deposition species could be increased and thus the film morphology and structure can be optimized.⁹¹

Figure 3-1 illustrates the double bend FCVA system. The system mainly consists of cathodic arc source, plasma-filtering duct and a deposition chamber. A rotary-cryogenic pump system is connected to the chamber for pumping down to the desired pressure during the deposition. The cathodic vacuum arc source has five main parts: the anode wall, the power supply, the arc trigger, the target and the target cooling system. A radial electric field is formed via the toroidal duct, coupled with a curvilinear axial magnetic field on the curved toroidal duct that forms a crossed electric-magnetic field filtering assembly. The plasma, which is steered by the field, passes through the duct to the substrate and results in the deposition of films free from any macroparticles.

High purity, typically 99.99%, metal target (i.e., Zn and ZnCu alloy targets) was used as the cathode material and oxygen was used as the reactant gas. The chamber base pressure was kept at $\sim 2 \times 10^{-6}$ Torr. When the trigger is struck on the metal target with an arc current of 60 A, energetic plasma ions from the metal target are formed. The plasma beam was steered by a magnetic field produced by copper coils wrapped around the filter and was kept at ~ 25 mT. Oxygen is introduced inside the filtering duct through an outlet along the filter such that metal-oxide plasma can be formed. The oxygen partial pressure in the deposition process is set to 3×10^{-5} Torr.

The ZnO and ZnO:Cu films were prepared at substrate temperatures ranging from RT to 400 °C.

Figure 3-1: The schematic of Filtered Cathodic Vacuum Arc (FCVA) system.

3.2 Ion beam sputtering

Recently, various methods have been reported for the fabrication of one dimensional (1D) ferromagnetic ZnO:TM nanostructures such as direct hydrothermal synthesis,⁹⁵ vapor transport,^{96,97} chemical vapor deposition,^{98,99} thermal evaporation,¹⁰⁰ combustion,¹⁰¹ laser-ablation methods,¹⁰² etc. These techniques usually use catalysts and additives to control the nanostructure growth, leading to suspicious observed FM. Exploring simple, cheap, catalyst-free, low-temperature methods of synthesizing vertically aligned 1D ZnO nanostructures remains a challenge. Energetic ions are an excellent tool for the creation of nanostructures on a surface or in the surface-near region of any kind of solid at room temperature.¹⁰³ The fabrication mechanism induced by sputtering of solid surfaces and the formation

kinetics is mainly determined by etching instead of growth.¹⁰⁴ In modern sputtering model, surface atoms are ejected into a vacuum from an ion-impacting point via a collision cascade in the projectile-implanted subsurface. The ion beam sputtering technique has been proved to entail the formation of nanosized ripples, pyramids, conical protrusions and whiskers structures of carbon, Si and Au.^{104,105} In this study, ion beam sputtering technique was used to fabricate ZnO:Cu nanoneedles.

The ZnO:Cu nanoneedles were fabricated in an ultra-high vacuum (UHV) system comprising micro-beam ion gun (JEOL; MIED) and an arc-plasma gun (ULVAC; APG-1000).¹⁰⁶ The ion gun operated under an UHV ambient with 1 keV Ar⁺ ions was irradiated at an incidence angle of 45° to the Cu plate and the ZnO surface for 4 min inside a vacuum system. The schematic of experimental setup is shown in Figure 3-2. Simultaneously, Cu was doped into the host material during nanoneedles formation. Prior to ion beam irradiation, a thin carbon layer was deposited onto the ZnO films which enhances the formation of nanostructures during sputtering. The chamber was pumped down to $\sim 10^{-7}$ Torr, and the pressure remained at 10^{-6} Torr during the sputtering process. Prior to characterization, the residue of carbon layer was removed by ethanol.

Figure 3-2: Schematic diagram of the fabrication of ZnO:Cu nanoneedles.

Ion beam bombardment of thin films surfaces provides a controlled and cost effective process for the formation of regular aligned nanostructures array. This ion beam sputtering technique offers several advantages over other fabrication methods: (1) room temperature fabrication, (2) catalyst-free, (3) selectively growth of nanostructures, and (4) on any substrates.

3.3 Sample characterization methodology

3.3.1 Alternating gradient magnetometer (AGM)

Alternating gradient magnetometer (AGM) was used heavily in this work in order to characterize the magnetic properties of ZnO:Cu. The schematic and configuration of AGM is shown in Figure 3-3. The instrument is 1000 times more sensitive than a conventional vibrating sample magnetometer (VSM) with comparable working space and is much quicker to use than a semiconductor quantum interface device (SQUID) magnetometer.¹⁰⁷ The magnetic sample is mounted on the end of a cantilevered rod that incorporates a piezoelectric element. The sample is magnetized by a dc field (variable in magnitude), and is simultaneously subjected to a small alternating field gradient. The alternating field gradient exerts an alternating force on the sample, proportional to the magnitude of the field gradient, dh'_x/dy and to the magnetic moment of the sample. The resulting deflection of the cantilever rod is measured by the voltage output, V of the piezoelectric element. By operating at or near a mechanical resonance frequency of the cantilever, the output signal is greatly amplified. The sensitivity of AGM goes down to 10 pAm^2 with accuracy of 2% and repeatability of 1%. The mechanical and acoustic noise in the environment limits the sensitivity.

The magnetic moment, m_x of sample which located at the tip of the extension rod can be determined by $\frac{V}{m_x} = 3G(l_b + l_c)g_{31}(1 - \frac{\delta^2}{t_b^2}) \frac{(dh_x'/dy)10^{-3}}{2w_bt_b}$ where the t_b is thickness of bimorph, l_b length of bimorph, l_c length of cantilever, G is mechanical gain, w_b is width of bimorph, g_{31} is the transverse piezoelectric modules or voltage efficient, and δ is thickness of the brass vane in the bimorph.¹⁰⁷

Figure 3-3: Configuration of (a) bimorph extension, (b) electrical circuitry, (c) variable magnet pole and (d) gradient coil arrangement. (e) The outlook of an AGM.

3.3.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is one of the useful and precise tools for microstructure characterization of thin films and nanostructure. It provides the information of size, shape and arrangement of the particles / atoms in the sample

as well as their relationship to each other on the scale of atomic diameter. In the scope of ferromagnetic semiconductor, it is widely use to determine the presence of TM-related precipitates, clustering and secondary phases in the films. Plane-view and cross-sectional samples were thinned to electron transparency by Ar ion milling. The detailed study of the TEM in this work was done by using TEM (JEOL JEM-2010) operating at 200 kV. The magnification of our TEM is 50 to 150000 times with its resolution of 0.1940 nm. The accelerating voltage used ranging from 80 to 200 kV.

3.3.3 Scanning Electron Microcopy (SEM)

Scanning electron microscopy (SEM) forms an image of the surface of materials by scanning a fine electron beam. Both secondary and backscattered electrons can be collected giving information about the surface topography and atomic weight of the sample. The surface morphologies of our samples were studied using SEM (JEOL JSM-5910 LV). The resolution of SEM is 3 nm with its accelerating voltage ranging form 0 to 30 KeV.

3.3.4 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials, which provides information on structures, phases, preferred crystal orientations (texture) and other structural parameters such as average grain size, crystallinity, strain and crystal defects. All the XRD measurements were carried out by Cu K α ($\lambda = 0.154$ nm) radiation on X-ray diffractometer (Siemen) (40 kV, 40 mA). The grain size, t can be calculated from Scherrer's equation,

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$t = \frac{C\lambda}{B \cos \theta}$ where λ is the x-ray wavelength (nm), B is the full width at half maximum (FWHM) of the peak (radians) corrected for instrumental broadening, θ is the Bragg angle, C is a factor (typically 1.0) that depends on the crystallite shape, and t is the crystallite size (nm).

3.3.5 X-ray photoelectron spectroscopy (XPS)

The Cu concentration and its chemical bonding state in the ZnO:Cu samples were determined by x-ray photoelectron spectroscopy (XPS). The XPS experiment was carried out by a Kratos-Axis spectrometer with Dual-Anode Al Ka (1486.6 eV) X-ray radiation (150 W, 15 kV and 10 mA) and hemispherical electron energy analyzer on the surface of the samples. The base vacuum of the chamber is 2×10^{-9} Torr. The survey spectra in the range of 0-1100 eV were recorded in 1 eV step followed by high-resolution spectra over different element peaks in 0.1 eV step, from which the detailed composition was calculated. Curve fitting was performed after a Shirley background subtraction by non-linear least square fitting using a mixed Gauss/Lorentz function. To remove surface contamination layer, Ar ion bombardment was carried out for 480 seconds using a differential pumping ion gun (Kratos Macro Beam) with an accelerating voltage of 4 keV and a gas pressure of 1×10^{-7} Torr. The detection limit can be as small as 0.1 at. %.

3.3.6 Photoluminescence spectroscopy (PL)

The light energy can be dissipated as radiation, which results in a luminescence emission of semiconductor material, called photoluminescence (PL). PL

is a very important technique used to study the electronic band structure of semiconductors. The intensity and spectral content of PL is a direct measure of various important material properties.¹⁰⁸ The PL spectra of the ZnO:Cu at RT were studied under optical excitation by a Nd:YAG (355 nm: YAG: yttrium aluminum garnet) laser operating in pulsed mode (6 ns, 10 Hz). Optical pumping was achieved by using a cylindrical lens to focus a pump stripe of length ~ 5 mm and width ~ 50 μm in a direction parallel to the surface of the samples. The emission was obtained from the surface of the sample using an objective lens.

3.3.7 Hall effect measurement

The importance of the Hall effect is underscored by the need to determine accurately carrier density, electrical resistivity, and the mobility of carriers in semiconductors. The transport properties of ZnO:Cu films were investigated using the van der Pauw method in the temperature range from 80 K up to 300 K (HL5500 PC). HL5500PC is a turnkey, high performance Hall System for the measurement of resistivity, carrier concentration, and mobility in semiconductors. It has both low and high resistivity measurement capabilities, with optional cryostats extending the temperature range from below 4K to as high as 600° C. The system has a uniform 0.32 T field over a radius of ~ 12 mm and easily accommodates typical samples of area 3 cm square. Prior to measurement, the indium contact pads were made at the corner of samples. Then ohmic characteristic of the samples were tested before the Hall effect measurement.

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This dissertation is devoted to the study of the room temperature FM in the ZnO:Cu. We shall first look at the fabrication, characterization and physical origin of FM in the ZnO:Cu films. In particular, it is imperative to understand the underlying mechanism of FM in the ZnO:Cu in order to improve the magnetic moment and stability towards the realization of practical devices.

The room temperature FM of the ZnO:Cu has already been reported. However, the experimental results and the origin of FM in ZnO:Cu have been rather controversial, ranging from paramagnetism³² to FM below or above room temperature.^{16,17,56,58,76,78} The results are sensitive to preparation methods and process conditions leading to different moments or ordering temperatures. The FM is usually only found in samples, at doping levels below the percolation threshold for nearest-neighbor cation interactions¹⁰⁹ and sapphire is the choice of substrate due to its small lattice constant mismatch with ZnO. However, in order to integrate spintronics devices with conventional silicon semiconductor process technology, ZnO:Cu has to be fabricated on Si substrate. In this chapter, the role of Cu, Zn interstitial defects, and N in the ZnO:Cu films have been investigated. The detailed discussion on structural, magnetic, optical and transport properties of the ZnO:Cu have been traced in this chapter. In a similar vein, the magnetic moment and stability enhancement of the ZnO:Cu are discussed.

4.1 Role of Cu

4.1.1 Introduction

Since the emergence of magnetism in ZnO:Cu, there has been considerable interest in this class of material as seen in Table 2. However, despite this interest, the effect and role of Cu in ZnO:Cu is still unclear. Buchholz *et al.*¹⁵ suggested the substitution of Cu²⁺ ions to Zn²⁺ sites induced the magnetic ordering. On the other hand, Lee *et al.* proposed that FM in ZnO:Cu could be attributed to the structural distortion.³² In this section, the effect and role of Cu in ZnO:Cu films are investigated.

Undoped ZnO and ZnO:Cu films were prepared on Si substrates at RT by the FCVA technique (i.e., details can be found in Chapter 3.1).¹¹⁰ Zn:Cu alloy targets containing 0.5, 1, 2, 3, 5 and 7 at.% of Cu were used, the corresponding Cu content in the films were 0.5, 1.3, 2, 3.1, 4.4 and 8.2 at.%, respectively, as determined by XPS. The typical thickness of the ZnO:Cu films were ~ 250 nm, as measured by surface profiler (Tencor P-10) with a resolution of 0.1 nm.

4.1.2 Structural properties

Figure 4-1 shows the XRD spectra of the as-prepared ZnO:Cu films as a function of Cu content. All XRD peaks are perfectly indexed and they are corresponding to ZnO wurtzite structure with predominately *c*-axis (002) orientation. The degradation of XRD intensity and its resolution are observed with increasing Cu concentration. A pronounced multiple peaks of (100), (101), (110) and (113) appeared with an increase of Cu concentration to 8.2 at.%, showing a random crystal growth orientation. The incorporation of 3*d* transition ions generally deteriorates the

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crystallinity of ZnO, which is attributed to their low solubility and various valence states.¹¹¹ It is noted that the (002) peak was shifted toward higher angle, 2θ , with an increase in Cu concentration, indicating the reduction of lattice parameter c . It is due to the substitution of the smaller Cu^{2+} ions (0.057 nm) into Zn^{2+} (0.06 nm) sites.¹¹² Table 4 summarizes the structural properties of our ZnO:Cu films extracted from XRD data. The variation of lattice parameter a and c as a function of Cu concentration is illustrated in Figure 4-2 and Table 4. However, the lattice parameter a and c does not decrease linearly with increasing Cu concentration when Cu content > 2 at. %, which might be attributed to limited solubility of Cu in ZnO. Within the sensitivity of XRD, no secondary phases were detected when Cu concentration is ≤ 4.4 at.%. However, the CuO phase was detected in the structurally poor ZnO:Cu (8.2 at.%) which is commonly related to the limited solubility of Cu in ZnO, typically 1 at.%.²⁷ The grain sizes along the c -axis are summarized in Table 4, which indicate that the Cu doping has little effect on the Cu concentration, which is consistent with ZnO:Cu films grown by sputtering technique.¹¹³ The average grain size of our films is 22.155 nm with the nominal strain of 1.834×10^{-4} .

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Figure 4-1: X-ray diffraction patterns of the room temperature prepared undoped ZnO and ZnO:Cu films on Si. (*) indicates the secondary phase of CuO.

Figure 4-2: *c*-axis lattice constant of the ZnO:Cu as a function of Cu concentration.

Sample	(002) position (°)	Grain size (nm)	<i>a</i> (nm)	<i>C</i> (nm)	Strain
ZnO	34.21	21.17	0.32445	0.52370	2.368E-04
ZnO:Cu (0.5%)	34.27	20.56	0.32389	0.52280	1.96E-04
ZnO:Cu (1.3%)	34.31	22.86	0.32353	0.52222	2.242E-04
ZnO:Cu (2.0%)	34.34	23.97	0.32326	0.52179	1.176E-04
ZnO:Cu (4.4%)	34.22	22.05	0.32439	0.52360	1.299E-04
ZnO:Cu (8.2%)	34.15	20.34	0.32503	0.52464	2.492E-04

Table 4: Grain size, lattice parameters and strain of undoped ZnO and ZnO:Cu films.

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In order to examine the thorough structural and chemical bonding effect of Cu in ZnO, the samples were characterized by XPS. All the indexed peaks are corresponding to C, Cu, O and Zn; there are no foreign impurities detected. Figure 4-3 (a) depicts the binding energy (BE) of Zn $2p_{3/2}$ states centered at 1021.95 ± 0.18 eV.^{114,115} The O $1s$ state exhibited broad and asymmetric peaks which could be well fitted by two Gaussian curves as shown in Figure 4-3 (b). The peak centered at 530.44 ± 0.15 eV can be attributed to O-Zn bound formation; whereas peak centered at 531.47 ± 0.08 eV are associated with the loosely bond oxygen (e.g., adsorbed O_2 , -OH) chemisorbed on the surface and/or grain boundary of the polycrystalline film.^{116,117} As seen in Figure 4-3 (c), the Cu $2p_{3/2}$ peak appears at 933.41 ± 0.24 eV, showing the Cu^{2+} ion state.¹¹⁸ Thus, it is reasonable to propose that Cu^{2+} ions have substituted into Zn^{2+} sites. The remarkable shift of Cu $2p_{3/2}$ peak from 933.65 to 933.16 eV with an increase of Cu concentration, suggesting the formation of metallic Cu^0 (~933 eV)¹¹⁸ cluster at high Cu concentration. Furthermore, the appearance of a satellite structure¹¹⁹ at around 9.8 eV above the main peak was detected in ZnO:Cu (8.2 at. %) as shown in Figure 4-3 (d), elucidating the existence of CuO phase. It is in good agreement with its XRD spectrum as shown in Figure 4-1. More importantly, the whole spectrum of the core levels peak of Zn $2p$, Cu $2p$ and O $1s$ were shifted toward lower BE by ~ 0.3 eV with an increase of the Cu concentration, implying the valence band and its core levels band toward the Fermi level. The observed BE shift toward lower energy typically suggests an upward band bending of energy core level as illustrated in Figure 4-4. In this case, the BE shift could indicate that Cu element change the band structure of the ZnO:Cu as Cu is well known as a potential hole dopant for ZnO.^{32,120}

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Figure 4-3: XPS spectra of (a) Zn 2p, (b) O 1s and (c) Cu 2p core level for the ZnO:Cu films. (d) The corresponding satellite peak of Cu 2p in the ZnO:Cu films.

Figure 4-4: Schematic representation of Cu concentration toward the band structure of the ZnO:Cu samples.

4.1.3 Magnetic properties

Magnetic measurements of the ZnO:Cu films were performed at RT using an AGM. To eliminate the spurious magnetic data, the ZnO:Cu samples and tweezers used were cleaned with acetone prior to magnetic measurement. It is confirmed that no FM can be detected from the undoped ZnO sample and Si substrate. All the measurements were corrected for substrate effects. The saturated magnetic moment (M_s) of the RT prepared ZnO:Cu films as a function of Cu concentration is shown in Figure 4-5. All the samples show ferromagnetic ordering at RT, implying it is not necessary to co-dope ZnO with Cu and N in order to obtain FM.¹⁶ The M_s reaches a maximum ($0.4 \mu_B/\text{Cu}$) with a clear hysteresis loop when Cu content is ~1.3 at. % as illustrated in the inset of Figure 4-5. Then the M_s decreases with further increase of Cu concentration, which could be due to an increased occurrence of antiferromagnetic coupling between Cu pairs occurring at shorter separation distances, which has been predicted in earlier theoretical studies.¹²¹ The low M_s for the 8.2% Cu film could be attributed to the formation of the secondary phase Cu_2O , which is antiferromagnetic.⁵³ The moment per Cu atom is less than the theoretical value of $1.00 \mu_B/\text{Cu}$ for Cu^{2+} because Cu exhibits a mixed valence state of Cu^{1+} and Cu^{2+} .^{27,121} The $3d$ orbital in Cu^{1+} ($3d^{10}4s^0$) are fully filled and hence do not contribute to FM (“ferromagnetic silent”).

Having obtained a clear picture that the presence of Cu^{2+} states favors the magnetic ordering, we now turn to investigate the correlation between Cu concentration, magnetic moment and Cu^{2+} states in the ZnO:Cu films. As shown in Figure 4-6, the ratio of $\text{Cu}^{2+}/\text{Cu}^{1+}$ (area under the XPS curve) decrease remarkably with an increase of Cu concentration. The film with Cu concentration of 1.3 at.%, 4.4 at.% and 8.2 at.% possess the $\text{Cu}^{2+}/\text{Cu}^{1+}$ ratio of 2.32, 0.65 and 0.19 respectively as

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listed in Table 5, showing the domination of high spin Cu^{2+} ions in the low Cu content films. The substitution of high spin Cu^{2+} ions into Zn^{2+} sites results in the enhancement of crystal field splitting of $3d$ states into t_{2g} and e_g state, leading to strong FM.

Cu concentration (at. %)	$\text{Cu}^{2+} / \text{Cu}^+$ ratio
1.3	2.32
4.4	0.65
8.2	0.19

Table 5: The ratio of $\text{Cu}^{2+}/\text{Cu}^+$ valence state for various Cu concentrations.

Figure 4-5: Saturated magnetic moment of the ZnO:Cu deposited at room temperature as a function of Cu concentration. Inset: M-H curve of the ZnO:Cu (1.3 at.%).

Figure 4-6: XPS spectra of Cu $2p_{3/2}$ for the ZnO:Cu with various Cu contents. The ratio of $\text{Cu}^{2+}/\text{Cu}^{+}$ decreases with an increase of Cu concentration.

4.1.4 Microstructure

The detailed morphology and microstructure of the ZnO:Cu (1.3 at. %) films were investigated using SEM, SAED and HRTEM as shown in Figure 4-7. The surface of ZnO:Cu (1.3 at. %) is very smooth with no clustering formation as shown in Figure 4-7(a). The interplanar distance of fringes is 0.26 nm which is corresponding to the (002) planes of wurtzite ZnO as shown in Figure 4-7 (b). This is in good agreement with the XRD result as (002) plane is dominant in the ZnO:Cu films. Figure 4-7 (c) shows the SAED patterns of the ZnO:Cu and the inset is a simulated SAED ring pattern of ZnO. The SAED pattern of the film is matched with the simulated ZnO pattern, implying the film exhibited the ZnO wurtzite structure. By combining the results shown in SEM, HRTEM, XRD and XPS, the possibility of Cu

cluster / secondary phases formation in ZnO:Cu (1.3%) thin film is extremely low as there is no physical and chemical detection of metallic Cu clusters / secondary phases.

Figure 4-7: (a) SEM image of the ZnO:Cu (1.3 at. %). (b) HRTEM image of the ZnO:Cu (1.3 at. %) showing (002) planes. (c) Comparison of the SAED patterns of ZnO:Cu with the simulated patterns of ZnO. (d) TEM image at the interface of ZnO:Cu (1.3 at. %) and Si.

4.1.5 Magnetic homogeneity

Concerning the homogeneity and interface distortion of the film, the cross-sectional HRTEM was performed in the ZnO:Cu (1.3 at. %). The interface between the ZnO:Cu and Si substrate is sharp and smooth as shown in Figure 4-7 (d). It appears that the FM is not due to interface distortion or impurity at the interface.¹⁰⁹ In order to verify the FM in the ZnO:Cu is a bulk effect rather than surface/interface effect, ZnO:Cu films were grown at identical conditions with various thicknesses ranging from 100 nm to 350 nm. The M_s is almost constant at $\sim 0.38 \pm 0.02 \mu_B/\text{Cu}$ for various thicknesses as shown in Figure 4-8, reflecting the FM is not due to interface

distortion or surface/interface magnetization. This result also suggests that the ZnO:Cu samples are homogeneous with Cu ions uniformly distributed in the film.

Figure 4-8: Saturated magnetization of the as-grown ZnO:Cu (1.3 at. %) as a function of film thickness.

4.1.6 Electrical properties

The transport properties of ZnO:Cu is another important aspect to understand the magnetic mechanism. As seen in Figure 4-9, the incorporation of Cu into ZnO leads to dramatic reduction in conductivity and carrier concentration. The resistivity of the ZnO:Cu (2 at.%) ($49 \Omega\text{-cm}$) is 2 orders of magnitude more than the undoped ZnO ($0.36 \Omega\text{-cm}$). The ZnO:Cu films become highly resistive if the Cu content is more than 2 at.%. Although Cu is a well known potential hole dopant in ZnO, the ZnO:Cu films exhibited *n*-type behavior. The electron concentration reduces 4 orders of magnitude from $8.04 \times 10^{19} \text{ cm}^{-3}$ to $7.5 \times 10^{15} \text{ cm}^{-3}$ for ZnO and ZnO:Cu (2.0 at.%),

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respectively. This phenomenon is an indication that the dopant element is at deep acceptor levels.³² This might be explained by the presence of a fraction of Cu in 1+ state which acts as a deep level acceptor, thus compensating the electrons arising from the oxygen vacancies or Zn interstitial in the as-grown ZnO, which is *n* type in nature. In addition, Cu in a 2+ state acts as a trap for electrons because of the presence of the 3*d* hole states.⁷⁸ Therefore, the high resistive ZnO:Cu films lead us to envisage its FM is not related to free-carrier, but bound magnetic polarons (BMPs) mechanism.^{83,84,122} In the context of BMPs model, the FM not only constituted by Cu ions, but it is correlated to donor defects (such as Zn interstitial or oxygen vacancies) which are present in the films grown by the FCVA at RT.⁸³ In the next section, the possible defects that present in the ZnO:Cu and its roles in mediating magnetic ordering are discussed.

Figure 4-9: Carrier concentration and resistivity as function of Cu concentration.

4.2 Defects related ferromagnetism

4.2.1 Introduction

Our previous experimental results reveal that the incorporation of Cu ions into ZnO could exhibit room temperature FM. In addition to the Cu doping effect, defects such as oxygen vacancy and Zn interstitial (Zn_i) were proposed to influence the ferromagnetic state of the oxide magnetic semiconductors. The origin of the FM in ZnO:Cu is still not adequately understood. Theoretical^{29,123} and experimental^{124,125} studies suggest that oxygen vacancies can alter the band structure of a host oxide and make a significant contribution to the FM. However a number of recent experiments showed a correlation between the ferromagnetic behavior and Zn_i in ZnO:Co system, giving an evidence that FM in ZnO:Co is mediated by donor-bound carriers.¹²⁶⁻¹²⁸ Furthermore, the formation of shallow spin-split impurity band upon coalescence of BMPs constituted by donor defects (i.e. oxygen vacancy and Zn_i) have also been proposed to explain the origin of RT FM for oxide based materials.⁸³ In this section, the role and effect of defects in ZnO:Cu are investigated. It is found out that Zn_i defect plays a dominant role in mediating ferromagnetic ordering in ZnO:Cu films.

As seen in Figure 4-5, the magnetization decreases with an increase of Cu concentration and it was found that the ZnO:Cu (1.3 at. %) exhibited the highest M_s among all other Cu concentration. Hence ZnO:Cu (1.3 at. %) was chosen for the substrate temperature dependence and annealing experiments. In this section, we will only discuss the ZnO:Cu (1.3 at. %) samples unless otherwise stated.

4.2.2 Identification of defects

Figure 4-10 shows the XRD patterns of the ZnO:Cu films prepared at various substrate temperatures. All XRD peaks are perfectly indexed and they are

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corresponding to ZnO wurtzite structure with predominately *c*-axis (002) orientation. No secondary phases were detected within the sensitivity of XRD. The samples prepared at RT exhibited polycrystalline structure. The pronounced (002) peak was observed when the samples were prepared at temperatures from 100 to 400 °C. The full width at half maximum (FWHM) of the (002) peak decreased from 0.53° to 0.37° when the substrate temperature increased from RT to 400 °C. This may be due to smaller crystal sizes resulting from a lower deposition temperature, or the strains in the film and crystal symmetry that were affected by the substrate temperature during the deposition process. When the crystal size is reduced, the higher surface to volume ratio can lead to more surface related defects. Therefore it is a clear signature that ZnO:Cu films deposited at RT exhibited poorer crystallinity and smaller grain size as compared with samples prepared at higher temperatures.

Figure 4-10: XRD spectra of ZnO:Cu deposited at substrate temperature ranging from RT to 400 °C.

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The M_s of the ZnO:Cu films measured at 300 K as a function of substrate temperature is shown in Figure 4-11. The M_s reduces with an increase in substrate temperature. The ZnO:Cu film deposited at RT exhibits a M_s of $0.40 \mu_B/\text{Cu}$. Inset of Figure 4-11 shows the magnetization curve of samples deposited at RT and 400°C . The magnetic exchange of structurally superior ZnO:Cu film deposited at 400°C is weakened by 35% to a M_s of $0.26 \mu_B/\text{Cu}$. The magnetic moment does not go along with its enhanced crystallinity.

Figure 4-11: The M_s of the ZnO:Cu films deposited (filled square) and annealed (open square) at various temperatures. Inset: the magnetization curves of ZnO:Cu films deposited at RT and 400°C .

A series of RT deposited ZnO:Cu films were annealed in open air (under air ambient with atmosphere pressure) from 100°C to 900°C . The M_s of the annealed ZnO:Cu films is shown in Figure 4-11. The M_s of the ZnO:Cu samples decrease with an increase in annealing temperature. After annealed at 300°C , the M_s of the ZnO:Cu film was reduced by 40 % to $0.24 \mu_B/\text{Cu}$. Then the M_s remains almost constant from

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300 °C to 600 °C. The M_s drops rapidly to $\sim 0.12 \mu_B/\text{Cu}$ with further increases in annealing temperature to 900 °C. The M_s values of the annealed samples (≤ 400 °C) are consistent with the samples deposited at the corresponding temperatures. The result seems to suggest that native defects inherited from the RT deposited samples could associate with the enhanced FM. The high temperature instability of FM in the ZnO:Cu, even at temperature below 200 °C, leads us to propose that Zn_i could play a significant role in the FM. It is because Zn_i has low diffusion barriers and easy to diffuse into the lattice at relatively low temperature as compared with other defects.¹²⁹ Erhart and Albe reported that Zn_i is the most mobile defect among other defects.¹³⁰ The ZnO:Cu films prepared at RT were found to be *n*-type with resistivity and electron concentration of $6.7 \Omega\text{cm}$ and $7.6 \times 10^{16} \text{cm}^{-3}$, respectively. The intrinsic *n*-type ZnO:Cu is believed to be due to Zn_i or O vacancies. Wang *et al.* reported that Zn_i were the dominant defects in ZnO films prepared by the FCVA at RT.¹¹⁰ The energetic Zn ions produced by the cathodic arc and the low substrate temperature favored the formation of Zn_i in the ZnO films. Since our ZnO:Cu films were deposited at RT with similar growth conditions as the ZnO films, large concentration of Zn_i might be presented in our samples. The resistivity of ZnO:Cu films prepared at RT can be changed several orders of magnitude by increasing substrate temperature or annealing temperature to 200 °C ($> 1 \times 10^5 \Omega\text{cm}$). This indicates that large concentration of Zn_i is present in the RT deposited ZnO:Cu films. Since the unstable Zn_i can diffuse into the ZnO:Cu lattice at elevated temperatures (below 200 °C) which correlate with the reduction of magnetic moment as shown in Figure 4-11. During the high temperature annealing process, it is more favorable to generate vacancy than interstitial defects, if an energy and chemical balance between the film and the ambient gas is considered. Since magnetic moment of the ZnO:Cu remains almost

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constant between the annealing temperatures of 300 and 600 °C, we may rule out vacancy defects as candidates responsible for the enhanced FM. The pronounced reduction in magnetic moment for annealing temperature above 700 °C may be attributed to the out-diffusion of Cu^{2+} ions from the substitution Zn^{2+} site, which degraded the magnetic exchange significantly¹³¹.

In order to confirm Zn_i play a dominant role in the FM in ZnO:Cu films, a series of ZnO:Cu films deposited at RT were annealed at 400°C under various ambient conditions (vacuum, open air and oxygen-rich). Annealing temperature of 400 °C is chosen for the study because the magnetic moment is reasonable large; and it can avoid the out-diffusion of Cu^{2+} from the substitutional sites. Figure 4-12 shows the M_s of the annealed ZnO:Cu films in vacuum, open air and oxygen-rich ambient. In principle, annealing in oxygen-rich atmosphere should reduce the oxygen vacancies concentration. If oxygen vacancy is responsible for the FM, the M_s value should change after annealed in oxygen-rich environment. Apparently the M_s of the ZnO:Cu films are the same ($0.27 \mu_B/\text{Cu}$) regardless of ambient conditions.

Figure 4-12: Room temperature M_s of the ZnO:Cu films annealed at 400°C in various ambient conditions.

4.2.3 Zn vapor annealing

According to density functional theory calculations by Sluiter *et al.*, electron doping with Zn_i enhances the ferromagnetic properties of ZnO:Mn and ZnO:Co.¹³² Schwanz *et al.* demonstrated that Zn_i enhances FM in ZnO:Co by exposing the samples to Zn vapor.¹³³ In order to test the role of Zn_i in enhancing the FM of our ZnO:Cu, our sample was exposed to Zn vapor by heating metallic Zn foil to 420 °C in a quartz tube in reduced ambient for an hour. The M_s of the sample was enhanced by ~30% after annealing with the presence of Zn vapor as shown in Figure 4-13. The sample has been annealed for several cycles, the M_s value increases after Zn vapor annealing, indicating Zn_i favors FM. It should be noted that no FM can be observed in undoped ZnO films annealed in Zn vapor. The intriguing results indicated that the substitution of Cu^{2+} ions into ZnO lattice is essential for the FM. The annealing experiment confirms that Zn_i is the most likely candidate responsible for the enhanced FM.

Figure 4-13: Variation of M_s for ZnO:Cu film sequentially annealed at 420°C in open air and Zn vapor ambient.

4.2.4 Transport properties

Now let us consider the relationship between magnetic and electrical properties of the ZnO:Cu (1.3 at.%). Figure 4-14 (a) shows the temperature dependence of electrical conductivity (σ) on undoped ZnO and ZnO:Cu films. The σ increases with temperature, where ZnO and ZnO:Cu films exhibit metallic and semiconductor behavior, respectively. For the temperature between 200 K and 300 K, the conductivity gives linear Arrhenius plot indicating band conduction of carrier electrons.¹³⁴ The activation energies (E_a) of the undoped ZnO, ZnO:Cu (0.5 at.%) and ZnO:Cu (1.3 at.%) were determined to be 0.45 meV, 7.32 meV and 28 meV respectively, in the temperature range between 200 and 300 K. The increase in E_a is due to decrement of the carrier concentration with increasing Cu content. It is because Cu introduces the deep acceptor level and it traps electrons from the conduction band.²² As evident, Hall effect measurement depicts that the undoped ZnO, ZnO:Cu (0.5 at.%) and ZnO:Cu (1.3 at.%) exhibited electron concentration of $8.04 \times 10^{19} \text{ cm}^{-3}$, $2.42 \times 10^{18} \text{ cm}^{-3}$ and $7.6 \times 10^{16} \text{ cm}^{-3}$ at RT respectively. The result is corroborated by the observed upward band bending of the core levels with increasing Cu concentration as illustrated in Chapter 4.1. Indeed, the E_a value ($\sim 28 \text{ meV}$) is in good agreement with the Zn_i empirical activation level as observed by Natsume *et al.*¹³⁴ However, the conductivity of the ZnO:Cu deviates from the Arrhenius plot at temperature lower than 200 K. Hence, the data were re-plotted and it is evident that the $\ln(\sigma)$ is linear as a function of $T^{-1/2}$ for temperature below 200 K as illustrated in Figure 4-14 (b). The linearity of $\ln(\sigma)$ versus $T^{-1/2}$ is qualitatively consistent with the prediction of magnetic polaron (MP) variable range hopping (VRH) in the presence of electron-electron interaction.¹³⁵ Variable range hopping is a model elucidating a low temperature

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conduction in strongly disordered systems with localized states.¹³⁶ In disordered systems, when electronic states are localized in the Anderson sense near the Fermi level, E_F , that the electric conduction does not obey the classic process of diffusion, but follows the VRH. According to this theory, electrons are “somewhat intelligent” since in the conduction process they hop from an initial site “ i ” to another “ j ” with an energy hop as low as possible. According to this model, the conductivity $\sigma = \sigma_0 \exp\{-2\alpha R - W/kT\}$, where σ_0 is a factor weakly T-dependent, k is the Boltzmann constant, T is the temperature, W is the hopping energy, α^{-1} is the wave function decay length and R is the distance separating sites i and j .¹³⁶ In the context of ZnO:Cu, the VRH mechanism provides a reasonable explanation of transport behavior in magnetic semiconductors and has been applied to model magnetoresistance (MR) observed in DMS. Indeed, MR of ZnO:Cu films have been observed at temperature ranging from 5 to 300 K.¹³⁷ The existence of MP in the ZnO:Cu films may shed light on the FM mechanism.

Figure 4-14: (a) Arrhenius plots of conductivity of ZnO, ZnO:Cu (0.5 at.%) and ZnO:Cu (1.3 at.%). (b) The plot of $\ln(\sigma)$ as a function of $T^{-1/2}$ for ZnO:Cu (0.5 at.%) and ZnO:Cu (1.3 at.%).

4.2.5 Bound Magnetic Polarons (BMPs) mechanism

Considering all the XRD, XPS, SEM and HRTEM results in the previous sections, it is reasonable to rule out the possibility of magnetic impurities in ZnO:Cu which could lead to observed FM. Moreover, the sharp and smooth interface between the ZnO:Cu film and Si substrate as shown in Figure 4-7 (d), suggesting the FM is not due to interface distortion or impurity at the interface. This fact has been confirmed by the thickness dependence magnetization experiment (Figure 4-8), revealing that there is no surface/interface effect in the ZnO:Cu and Cu is uniformly substituted into ZnO. Thus, the observed FM is attributed to the substitution of Cu^{2+} into Zn^{2+} sites.

Concerning the FM model in ZnO:Cu, it is noteworthy that low carrier concentration in the ZnO:Cu films (electron concentration $\sim 10^{16} \text{ cm}^{-3}$) as illustrated in Section 4.2.4, may not link to carrier-mediated mechanism such as double exchange or an RKKY mechanism. The FM of ZnO:Cu prepared at RT is proposed to be invoked super coupling mechanism based on BMP model (as discussed in Chapter 2.2.3),⁸³ which is supported by the presence of magnetic polarons in the ZnO:Cu. Shallow donor of Zn_i are located throughout the lattice at arbitrary distances with respect to Cu^{2+} sites. We expect $\text{Cu}^{2+}-\square-\text{Cu}^{2+}$ groups will be common in the structure, where $\square$ denotes a Zn_i . The shallow donor state of Zn_i defects¹³⁸ occupies an orbital and overlaps the d shells of both Cu ions; constitutes BMPs formation.⁸³ Based on the BMPs model, the magnetic properties of the ZnO:Cu films could be tuned through Cu and defects concentration which are in good agreement with our experimental results. The understanding of the underlying mechanism of the FM in ZnO:Cu would lead us to improve the magnetic properties of ZnO:Cu.

4.3 Nitrogen enhanced ferromagnetism

4.3.1 Introduction

A considerable works have been carried out to study the origin of FM in the ZnO:Cu. Fueled by our experimental results, the roles and effects of Cu and Zn_i in the ZnO:Cu system have adequately determined in the section 4.1 and 4.2. However, the magnetization of our ZnO:Cu is considerably weak and the moment per Cu atom is less than the theoretical value of $1.00 \mu_B/\text{Cu}$. According to the theoretical study,⁵⁴ it is believed that hole doping could improve magnetic moment and stabilize FM, thereby potential hole dopant of N_2O was introduced into ZnO:Cu system. Buchholz *et al.*¹⁵ reported that ferromagnetic ZnO:Cu films prepared by PLD could only be obtained when N_2O gas was used during deposition. However it is not clear whether the ferromagnetic samples exhibited *p*-type behavior as N_2O is believed to be a *p*-type dopant source for ZnO.¹³⁹ As illustrated from the previous section, ferromagnetic ZnO:Cu could be prepared by FCVA technique using a Zn:Cu alloy target and O_2 gas only. The role of N_2O toward the observed FM in ZnO:Cu is therefore not well understood. In this section, the role and effect of N in ZnO:Cu through N_2O annealing is investigated. It is found that the magnetic moment of the N_2O annealed ZnO:Cu films not only can be enhanced by more than 100 %, but its magnetic stability also improved significantly.

4.3.2 Effect of N_2O

Figure 4-15 shows the magnetization curves of the as-grown ZnO:Cu films. The ZnO:Cu film demonstrated FM at RT with a M_s of $0.4 \mu_B/\text{Cu}$. The M_s of the as-

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grown ZnO:Cu film is comparable to PLD-deposited ZnO:Cu with N₂O gas.¹⁵ This result elucidates that N is not necessary for the observation of FM in ZnO:Cu. In order to study the effect of N₂O on the FM in ZnO:Cu, a series of ZnO:Cu films were annealed in N₂O ambient at temperatures ranging from 100 °C to 900 °C with N₂O gas pressure of ~0.4 bar for one hour. Surprisingly, the M_s of the annealed ZnO:Cu were enhanced by more than 100% in the temperature range of 400 to 600 °C as shown in the Figure 4-16 (a). The M_s of the annealed samples at various temperatures are normalized by the corresponding as-grown samples, where $M_n = M_s(T)/M_s(as-grown)$. When annealing temperature increases gradually to 200 °C, M_n is less than 1. The M_n increases rapidly to above 2 when the annealing temperature increase from 300 to 600 °C. Beyond 600 °C, the M_n decreases drastically and even less than 1 at 900 °C. Since the decomposition temperature of N₂O is above 260 °C,¹³⁹ the degradation of M_s at temperature below 300 °C should not be related to N₂O. Indeed the degradation of FM can also be observed from samples annealed in air or N₂ ambient at temperature above 100 °C. The reduction of FM could be related to defect-mediated FM which has been discussed in Section 4.2. The M_s of the ZnO:Cu increases substantially when annealed at temperatures between 400 to 600 °C. The enhancement of FM in the ZnO:Cu films should be related to the N₂O annealing. The first-principles calculations by Yan *et al.* suggest that the N substitution for the O site in the ZnO:Mn can change the magnetic interaction from antiferromagnetic to ferromagnetic and enhanced the magnetic moment.¹⁴⁰ When the annealing temperature reaches 700 °C, the M_s reduces drastically. This observation could be attributed to the out-diffusion of Cu to the surface at temperature above 700 °C. From the XPS analysis as shown in Figure 4-16 (b), the Cu content in the ZnO:Cu is increased substantially from 1.3 to 10 at.% when annealing temperatures increase

from RT to 800 °C. This suggests that the Cu content is out-diffusing into the sub-surface layers, resulting in the reduction of Cu in the film. As a result of a decrease in Cu^{2+} concentration, this leads to weakening of magnetic ordering. The sample became paramagnetic after annealing at 1000 °C. This is because most Cu has escaped from the surface of the film, since no Cu can be detected by XPS. It is an indication that Cu is essential for the observed FM.

Figure 4-15: Magnetization curves of the as-grown and N_2O annealed ZnO:Cu films measured immediately and after a storage period of 6 months.

Figure 4-16: (a) Normalized saturated magnetic moment ($M_n = [M_s(T)/M_s(\text{as-grown})]$) of ZnO:Cu films annealed at temperatures from RT to 900 °C. (b) The Cu concentration (at. %) at the surface as a function of annealed temperature from 600 °C to 1000 °C.

XRD spectra of the as-grown, open air and N₂O annealed ZnO:Cu films at 400 °C are shown in Figure 4-17. All the diffraction peaks are corresponding to ZnO wurtzite structure with predominately *c*-axis (002) texture. The annealed ZnO:Cu films exhibited stronger XRD peak intensity and narrower peak wide as compared to the as-prepared samples, indicating annealing improve the crystallinity of the samples. There is no structural variation between open air and N₂O annealed samples. Thus the

enhancement of FM could not be due to the improved crystal structure of ZnO:Cu as the FM degraded once the sample was annealed in open air.

Figure 4-17: XRD spectra of the as-grown, open air and N₂O annealed ZnO:Cu.

The surface morphology and microstructure of the as-grown and N₂O annealed ZnO:Cu films were investigated by SEM and HRTEM. Figure 4-18 (a), (b) and (c) show the SEM images of the as-grown, 400 °C and 900 °C N₂O annealed ZnO:Cu films, respectively. The as-grown sample exhibits smooth surface, however, the grain structure become apparent when the samples were annealed at 400 and 900 °C. The grain size is about 50 nm and 200 nm for the 400 °C and 900 °C annealed samples, respectively. This is consistent with the XRD results as shown in Figure 4-17 that the crystallinity of the samples improved with annealing temperature. Figure 4-18 (d) reveals the HRTEM image of the ZnO:Cu annealed at 400 °C in N₂O ambient with its interplanar distance of 0.26 nm corresponding to the ZnO wurtzite structure. SAED patterns of the as-grown, 400 °C and 900 °C N₂O annealed samples

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are shown in Figure 4-18 (e), (f) and (g) respectively. CuO-related diffraction spots could be found in the as-grown and 400 °C annealed samples only but no CuO spot was observed from the sample annealed at 900 °C as shown in Figure 4-18 (g). The disappearance of CuO might be attributed to the out-diffusion of Cu under elevated temperature. As evident from the XPS result (Figure 4-16(b)), Cu could leave the surface of the ZnO:Cu at around 900 °C, thus no CuO can be found. It should be noted that there is no obvious difference before the surface morphology and microstructure of the samples annealed in air or N₂O ambient.

Figure 4-18: SEM images of (a) as-grown, (b) 400 °C and (c) 900 °C annealed ZnO:Cu films. (d) HRTEM image of ZnO:Cu film annealed at 400 °C in N_2O ambient and the inset shows the cross-sectional image of the sample at the interface. SAED patterns of (e) as-grown, (f) 400 °C and (g) 900 °C annealed ZnO:Cu films.

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In order to investigate the role of N₂O or N in the enhancement of FM, *in-situ* XPS measurements were carried out on the ZnO:Cu. The as-prepared ZnO:Cu sample was first scanned by the XPS. The sample was then annealed at 400 °C in the XPS analysis chamber for 1 hr in N₂O ambient. XPS scan was performed at RT after the N₂O annealing process. The XPS full scan revealed core level peaks that correspond to Cu, O, N and Zn, with no other impurity being detected. The annealed sample exhibited similar M_s value as compared to the sample annealed in the tube furnace. The incorporation of Cu and N in the N₂O annealed sample is clearly revealed by the core level spectra of Cu 2p and N 1s as shown in Figure 4-19(a) and (b) respectively. The Cu 2p_{3/2} peak appears at 933.5 eV, which can be observed from both as-grown and N₂O annealed samples, indicating a divalent state of Cu.^{118,141} Chakraborti *et al.* reported that the Cu 2p_{3/2} peak could also be an indication of Cu²⁺ ions substituted into ZnO lattice sites.⁵⁷ A weak N 1s peak can only be observed from the N₂O annealed sample. The N 1s band consists of two components as depicted in Figure 4-19 (b). The peaks at 399.3 eV and 401.45 eV can be attributed to Zn-N and N-O bond respectively. These indicate that N is incorporated in the ZnO:Cu after N₂O annealing. The incorporation of N in the ZnO:Cu may also relate to the enhancement of FM.

Figure 4-19: (a) XPS spectra of Cu 2p for as-grown and N₂O annealed ZnO:Cu film. (b) XPS spectrum of N 1s core level for the N₂O annealed ZnO:Cu film.

4.3.3 Interplay between N and Zn interstitial

It has been reported that Zn_i defect plays a significant role in the FM in ZnO:Co.^{126,127} The FM of ZnO:Co can be enhanced after exposing it in a Zn vapor at elevated temperature. Our ZnO:Cu samples also exhibited similar behavior after exposed to Zn vapor as illustrated in Chapter 4.2. In order to study the interplay between Zn_i and N in the ZnO:Cu, the as-grown ZnO:Cu samples, denoted sample A and B were undertaken a series of annealing in various ambient (i.e. open air, N₂O or Zn vapor) at 420 °C for an hour. Annealing temperature of 420 °C is chosen because it is the minimum temperature required to generate a Zn vapor and magnetic response

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of the sample is considerably large. The M_s of sample A increases substantially to $\sim 0.73 \mu_B/\text{Cu}$ after the first N_2O annealing as shown in Figure 4-20. The subsequent annealing cycles in air and N_2O do not have significant effect on the M_s (reduced by $\sim 6\%$). Besides the enhancement of FM, the stability of M_s with temperature seems to improve after the N_2O annealing. For sample B, the M_s reduces by $\sim 15\%$ to $0.30 \mu_B/\text{Cu}$ after open air annealing (number 1), which is attributed to the reduction of Zn_i at elevated temperature. Surprisingly, there is no magnetic ordering improvement as compared to sample A after the subsequent N_2O annealing (number 2). However, the M_s increases to $0.35 \mu_B/\text{Cu}$ which is close to the as-grown sample after exposed to the Zn vapor (number 3). The result corroborates with the recent experimental¹²⁶ study that Zn_i is associated with FM ordering. The M_s increases further to $0.47 \mu_B/\text{Cu}$ with the subsequent N_2O annealing (number 4). These intriguing results seem to suggest that there must have a relationship between Zn_i and N. According to first-principles total energy calculations by Yan *et al.*¹⁴², N from N_2O source could be incorporated spontaneously and controllably into ZnO if the sample is in Zn-rich condition. In contrast, N is unlikely to be incorporated into ZnO under O-rich condition. This may explain why FM can only be enhanced in ZnO:Cu with the present of Zn_i and N. Zn_i will lead to instability of FM in ZnO:Cu, but it is also crucial and essential to the FM enhancement with incorporation of N. To further examine the magnetic stability of the N_2O annealed sample, the M_s of the N_2O treated and untreated samples were measured again after a storage period of 6 months. As shown in Figure 4-15, the M_s of the N_2O treated and untreated samples after 6 months have reduced by $\sim 11\%$ ($0.65 \mu_B/\text{Cu}$) and $\sim 60\%$ ($0.16 \mu_B/\text{Cu}$) respectively as compared to their initial values. Our results elucidate N plays a vital role in enhancing the FM and improving the stability of ZnO:Cu.

Figure 4-20: Variation of M_s for ZnO:Cu films in different annealing sequences. Sample A: $\text{N}_2\text{O} \rightarrow \text{Open air} \rightarrow \text{N}_2\text{O} \rightarrow \text{Open air}$. Sample B: $\text{open air} \rightarrow \text{N}_2\text{O} \rightarrow \text{Zn vapor} \rightarrow \text{N}_2\text{O}$.

Having obtained a clear picture that the presence of Zn_i favors N incorporation into the ZnO:Cu, we now turn to investigate the correlation between N and Cu. As shown in Figure 4-19 (a), the ratio of $\text{Cu}^{2+}/\text{Cu}^{1+}$ (area under the curve) for the as-grown and N_2O annealed samples are 2.32 and 3.18, respectively. It indicates that the high spin state of Cu^{2+} component has indeed increased upon N_2O annealing. The introduction of N element increases the substitutional Cu^{2+} concentration, resulting in the enhancement of crystal field splitting of $3d$ states into t_{2g} and e_g state. However, the moment per Cu atom is less than the theoretical value of $1 \mu_B/\text{Cu}$ ^{27,121}. It may be due to the existence magnetic “silent” state of Cu^{1+} ($3d^{10}4s^0$) in the films as its $3d$ orbital are fully filled, thus not contributing to the magnetic moment. The evidence of N-Zn bond in the N_2O annealed ZnO:Cu as shown in Figure 4-19 (b) suggested that

N stabilizes Zn_i states through N-Zn bonding which improved the magnetic stability in term of storage time and temperature. The high resistivity of ZnO:Cu led us to envisaged its magnetism is related to BMP mechanism.^{83,84} However, further research is needed to understand the exact role of N and its underlying mechanism for the enhancement of FM.

4.4 Summary

In summary, the RT deposited ZnO:Cu exhibited M_s of $0.4 \mu_B/\text{Cu}$ at RT for 1.3 at.% of Cu, showing the incorporation of Cu ions into ZnO system could induce the ferromagnetic ordering. However, the magnetization is related to Cu concentration. An increase of Cu concentration could suppress the magnetic ordering, which is attributed to (1) the formation of secondary phases, (2) reduction of high spin Cu^{2+} concentration in the films and (3) increased occurrence of antiferromagnetic coupling between Cu pairs occurring at shorter separation distances. In addition, the structural properties of film would be degraded with increasing Cu concentration due to limited solubility of Cu in ZnO. The Hall effect experiment reveals that Cu acts as a deep acceptor in ZnO, which led to reduction of conductivity and carrier concentration of the ZnO:Cu. Moreover, the shift of binding energy toward lower energy suggests an upward band bending of energy core level, indicating Cu element could change the band structure of the ZnO:Cu and its “hole” behavior.

In addition to the role of Cu in inducing FM in ZnO:Cu, the presence of Zn_i plays essential role in enhancing magnetic ordering of the ZnO:Cu as depicted in Chapter 4.2. However, it is found that the Zn_i is high diffusive and unstable element and it can diffuse into the lattice at elevated temperatures which results in the degradation of FM. In order to improve the magnetic moment and stability of

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ZnO:Cu, a potential hole dopant of N ions are incorporated into ZnO:Cu system by N₂O annealing as illustrated in Chapter 4.3. The magnetic moment has been enhanced by ~ 100% with high magnetic stability. In addition, there is an importance interplay between Cu, N and Zn_i in ZnO:Cu system. The presence of Zn_i is essential to the FM enhancement and it is prerequisite to the incorporation of N. The incorporation of N increases the substitution of high spin state of Cu²⁺ concentration into Zn²⁺ sites and stabilizes the highly diffusive Zn_i through N-Zn bonding.

The low temperature Hall effect measurement was carried out to study the ZnO:Cu transport properties and its underlying mechanism of FM. The ZnO:Cu films are generally highly resistive or insulating in nature due to the incorporation of deep acceptor of Cu or/and N atom. The transport mechanism of ZnO:Cu is related to variable range hopping (VRH) with the presence of magnetic polarons. The highly resistive ZnO:Cu film and existence of magnetic polarons have led us to envisaged the FM in ZnO:Cu is correlated to bound magnetic polarons (BMP) model. The magnetic properties of the ZnO:Cu films could be tuned through Cu and defects concentration according to BMP model.

Chapter 5: Ferromagnetic ZnO:Cu on plastic substrates

5.1 Introduction

As presented in chapter 4, the ferromagnetic ZnO:Cu films deposited on Si has been demonstrated. The investigation of oxide magnetic semiconductors, includes ZnO:Cu were commonly based on the films deposited on rigid substrates such as silicon and sapphire.²⁴ The ZnO:TM deposited on a flexible and low temperature substrate have received relatively less attention due to high processing and preparation temperature by PLD,⁷⁸ sputtering,¹⁴³ and MOCVD.⁶⁴ The FCVA technique is capable of fabricating relatively good crystal-quality ZnO:Cu at RT, which led us to investigate the properties of ZnO:Cu deposited on plastic substrates. In this chapter, we investigate the magnetization of ZnO:Cu films deposited on plastic substrates subjected to various bending conditions and magnetic field directions. Indeed the advent of plastic electronics is another momentum for us to explore flexible ferromagnetic semiconductors. ZnO/polymer heterojunction light emitting diodes (LEDs)¹⁴⁴ and ZnO thin film transistors (TFTs)¹⁴⁵ have been demonstrated using processing temperature of ~100 °C which is comparable with large area fabrication on plastic substrates. The demonstration of ferromagnetic and semiconductor properties of ZnO:Cu thin films on plastic substrate may facilitate the development of plastic spintronics.

5.2 Structural properties

ZnO:Cu films were prepared on plastic (polycarbonate) substrates at RT by the FCVA technique. The flexible and transparent polycarbonate substrates were

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chosen because of its high heat resistance and superior dimensional stability. The typical thickness of the polycarbonate substrate is 0.16 mm. Zn:Cu alloy targets containing 0.5, 1, 3, 5 and 7 at.% of Cu were used, the corresponding Cu content in the films were 0.5, 1.3, 3, 4.4 and 8.2 at.%, respectively, as determined by XPS. The details of the FCVA apparatus have been described in Chapter 3.1. The typical thickness of the ZnO:Cu films were ~220 nm.

Figure 5-1 shows the XRD patterns of ZnO:Cu films prepared at RT on plastic substrates as a function of Cu concentration. The films exhibit predominately *c*-axis (002) texture at ~34.3° corresponding to a ZnO wurtzite structure. The degradation of XRD intensity and its resolution are observed with increasing Cu concentration, indicating the increase in structural disorder of the ZnO:Cu films at higher Cu content. The incorporation of 3*d* transition ions generally deteriorates the crystallinity of ZnO, which is due to their low solubility and various valence states.¹¹¹ Within the sensitivity of XRD, no secondary phases were detected when Cu concentration is ≤ 4.4 at.%. The appearance of CuO phase in the structurally poor ZnO:Cu (8.2 at.%) is an indication that the solid solubility of Cu in ZnO has been exceeded. The XRD results of the ZnO:Cu films on plastic substrates are similar to that of samples on Si substrates.

Figure 5-1: XRD spectra of the ZnO and ZnO:Cu films prepared at room temperature on plastic substrates. The weak intensity mark (*) indicates the presence of CuO phase.

5.3 Magnetic properties

The typical magnetization curves of ZnO:Cu (1.3 at%) films prepared on plastic substrates with applied field parallel and perpendicular to the sample are shown in Figure 5-2 (a). Well-defined hysteresis loops with coercivity (H_c) about 90 Oe are observed from the sample. The sample exhibits no magnetic anisotropy at high magnetic field region (10 kOe) but an “easy plane” FM is apparent at low field (< 2 kOe) with field perpendicular to the sample as shown in the inset of Figure 5-2 (a). As proposed by Sati *et al*, the “easy plane” FM in ZnO:Cu may be considered as a signature of intrinsic FM where Cu^{2+} ions in ZnO possess a strong single ion

anisotropy¹⁴⁶. Chanier *et al* reported the tetrahedral and trigonal crystal field of ZnO, together with spin-orbit coupling, lead to a magnetic anisotropy.¹⁴⁷

As shown in Figure 5-2 (b), room temperature FM is observed from samples with Cu contents up to 4.4 at.%. The ZnO:Cu (1.3 at.%) film exhibits the strongest magnetic ordering with a M_s of 0.28 μ_B/Cu among all other Cu concentrations. The H_c and M_s reduce with an increase of Cu content. The M_s reduces significantly to 0.072 μ_B/Cu for Cu content of 3.0 at.%. This appears that an increase of lattice disorder at high Cu content degrades the magnetic properties of the ZnO:Cu films. The paramagnetism is observed in ZnO:Cu (8.2 at.%), which may be attributed to the formation of anti-ferromagnetic CuO phases¹⁴⁸ and its poor crystallinity. It is worthwhile to highlight that the diamagnetic background of the substrate has been subtracted from all the magnetization data shown here. No magnetic ordering could be detected in the plastic substrate, confirming the plastic substrate is not responsible for the observed FM in the samples even down to 5K. In addition, there is no trace of magnetism in the undoped ZnO film on plastic substrate. It is noted that the observed M_s of ZnO:Cu films on plastic substrate are compatible to other ZnO based DMS on Si and sapphire substrates.²⁴ Furthermore, the ZnO:Cu films exhibit RT FM without co-doped with other transition metal elements (such as Fe or Mn)⁷⁹ or N.¹⁵ The M_s of ZnO:Cu (1.3 at.%) on plastic substrate was weakened by 30% as compared with the sample prepared on Si substrate ($M_s \sim 0.4 \mu_B/\text{Cu}$ as shown in Figure 4-5) under identical growth conditions by the FCVA technique. The magnetic properties of the ZnO:Cu on Si has been discussed in details in the Chapter 4. The relatively lower M_s of the ZnO:Cu on plastic substrate could be attributed to the relatively poor crystal quality of the sample as compared with the one prepared on Si.

Figure 5-2: (a) Magnetization vs. H curve of ZnO:Cu (1.3 at.%) film on plastic substrates at 300K. The inset shows the magnified magnetization vs. H curve at low applied field region. (b) Saturated magnetization and coercivity as a function of Cu concentration.

5.4 Film grown in N_2O and O_2 ambient

Next, we focus on the magnetization enhancement of the ZnO:Cu films on plastic. In Chapter 4.3, it is found that magnetization of ZnO:Cu on Si could be enhanced by incorporation of N element through N_2O annealing at 400 °C. However, the low

melting point of plastic substrate made N_2O annealing technique not possible. It is noted that the decomposition of N_2O is possible under the high ionization energy of cathodic plasma.^{139,149} In this direction, ZnO:Cu was prepared under a mixture of O_2/N_2O (50 sccm:30 sccm) at RT on plastic substrates. Figure 5-3 shows the magnetic curves of the ZnO:Cu prepared from pure O_2 and O_2/N_2O mixture. Distinct RT ferromagnetic ordering was observed in both samples. The M_s of the film prepared under O_2/N_2O ambient is enhanced by ~75% to $0.46 \mu_B/Cu$ as compared to the ZnO:Cu prepared under pure O_2 ambient. The result implies that N improves the magnetic ordering in the ZnO:Cu. It is in good agreement with our previous observation that N can enhance the magnetic ordering. The underlying physical origin and role of N in ZnO:Cu could be similar to what we have discussed in details in Chapter 4.3.

Figure 5-3: M-H curve for ZnO:Cu (1.3 at.%) thin films prepared under pure O_2 and mixture of O_2 and N_2O ambient.

5.5 Effect of stress on magnetic anisotropy

One of the most remarkable aspects of ZnO:Cu on plastic substrates is its flexibility. Since the ZnO:Cu films can be bent to various shapes, which may be useful for the study of magnetic properties under strain conditions. The ZnO:Cu samples were bent to about 40° from the base plane with radius of curvature of 5.7 mm using non-magnetic “C” shaped plastic tube as a holder. The sample mounting position and method is shown in Figure 5-4. The schematic diagrams of the ZnO:Cu films under compressive and tensile stress are shown in Figure 5-5 (a) and (b), respectively. The magnetic anisotropy of the samples under compressive (inward bending) and tensile (outward bending) stress were studied. Figure 5-5 (c) and (d) show the magnetization curves of the ZnO:Cu (1.3 at.%) films under compressive and tensile stress with M_s of 0.24 μ_B/Cu and 0.26 μ_B/Cu respectively. The M_s of the ZnO:Cu (1.3 at.%) at applied field of 10 kOe under strain conditions is tabulated in Table 6. It is recalled that no magnetic anisotropy in the flat ZnO:Cu sample can be observed at the applied field of 10 kOe. However, the magnetic anisotropy at high applied field becomes apparent for the samples under strain conditions. For the compressive stressed sample, the M_s can be different by ~8% when the field applied parallel and perpendicular to the sample. In addition, the M_s of the sample can be reduced by 15% when compared with the flat sample under parallel field. The observed magnetic anisotropy of the stressed samples can be attributed to strain in the ZnO:Cu films. The internal strain could lead to lattice distortion and produce magneto-elastic-driven anisotropy. The results indicate that strain play a role in the magnetic anisotropy of the ZnO:Cu films.

Chapter 5: Ferromagnetic ZnO:Cu deposited on plastic substrates

Figure 5-4: Schematic diagrams of sample mounting position under (a) compressive and (b) tensile bending. A rubber and non-magnetic holder were employed to ascertain the uniform magnetic field applied to the samples.

Figure 5-5: Schematic diagrams of ZnO:Cu films under (a) compressive and (b) tensile stress. Magnetic properties of ZnO:Cu (1.3 at.%) under (c) compressive stress and (d) tensile stress with external magnetic fields applied parallel and perpendicular to the samples. (e) Photograph of ZnO:Cu on plastic substrate under strain.

Table 6: The saturated magnetic moment of the ZnO:Cu (1.3 at.%) under various bending conditions with magnetic field of 10 kOe applied parallel and perpendicular to the film.

Applied magnetic field direction	Flat (μ_B/Cu)	Compressive (μ_B/Cu)	Tensile (μ_B/Cu)
	0.28	0.26	0.27
	0.28	0.24	0.26

5.6 Microstructure characterization

Photograph in Figure 5-5 (e) shows the fully transparent ZnO:Cu (1.3 at.%) on plastic substrate at bending condition. HRTEM studies were carried out to ascertain the microscopic homogeneity of the ZnO:Cu films. Figure 5-6 (a) reveals that the interface between ZnO:Cu (1.3 at.%) film and plastic substrate is smooth and sharp. It appears that no interface distortion or impurity at the interface. Taking together the weak magnetic anisotropy and TEM images, it is reasonable to rule out the possibility of localized interface defects which could lead to the observed FM.¹⁰⁹ A well oriented (0002) plane of ZnO:Cu (1.3 at.%) with its interplanar distance of 0.26 nm is shown in Figure 5-6 (b). There are no detectable traces of any secondary phases or clusters of any ferromagnetic oxide or Cu related precipitates, indicating good crystallinity and homogeneity of the sample. The inset of Figure 5-6 (b) shows the selected area electron diffraction (SAED) pattern of the ZnO:Cu which reflects the polycrystalline structure.

Figure 5-6: (a) TEM image at the interface of ZnO:Cu (1.3 at.%) film and plastic substrate. (b) HRTEM image of ZnO:Cu (1.3 at.%) on plastic substrate and its corresponding SAED pattern.

5.7 Magnetic stability and electrical properties

In order to study the stability of FM in the ZnO:Cu on plastic substrates, low temperature ($\sim 100^\circ\text{C}$) annealing for 1 to 3 hours in vacuum were carried out. A low annealing temperature of 100°C is crucial to ensure there is no plastic deformation in the substrate. The polycarbonate substrate retained its diamagnetism after annealing of 100°C . The M_s of the annealed ZnO:Cu (1.3 at.%) reduces to $0.20 \mu_B/\text{Cu}$ ($\sim 29\%$ reduction) after 3 hours of annealing as illustrated in Figure 5-7. The gradual reduction of magnetic properties is further explored by structural and electrical study on the annealed ZnO:Cu films. XRD reveals that no obvious changes in the structural properties of the as-deposited and annealed sample (3 hours) as shown in the inset of Figure 5-7. The influence of structural defects or disorder toward FM is trivial under low annealing temperature. On the other hand, the resistivity of the ZnO:Cu films increases slightly with annealing time. The electron concentration of the samples is reduced to $4.2 \times 10^{16} \text{ cm}^{-3}$, $3.1 \times 10^{16} \text{ cm}^{-3}$ and $1.7 \times 10^{16} \text{ cm}^{-3}$ after annealed for 1, 2 and 3 hours respectively. The above results suggest that the resistivity, carrier concentration and magnetic moment are correlated. The gradual decrement of carrier concentration with annealing duration may be attributed to out-diffusion of shallow donor defect such as Zn_i to second nearest neighbor position. This observation depicts the significant role played by Zn_i in ZnO:Cu, which is in good agreement with the ZnO:Cu deposited on Si as illustrated in Chapter 4.2. The FM observed in the ZnO:Cu samples are expected to possess the identical magnetic property with ZnO:Cu on Si samples, suggesting the BMP mechanism. The detailed BMP mechanism in the ZnO:Cu is discussed in Chapter 4.2.

Figure 5-7: Variation of saturated magnetic moment and resistivity of ZnO:Cu (1.3 at. %) film annealed at 100 °C for various times in vacuum ambient. Inset: XRD spectra of the as-deposited and annealed ZnO:Cu (1.3 at.%) films.

5.8 Summary

In summary, we have demonstrated room temperature FM in flexible and transparent ZnO:Cu films on plastic substrates. The ZnO:Cu (1.3 at.%) film exhibited saturated magnetic moment of 0.28 μ_B/Cu . The annealing experiment showed that the observed FM is linked to Zn_i which plays a crucial role in mediating the FM in the ZnO:Cu films. The magnetization could be enhanced using $\text{O}_2/\text{N}_2\text{O}$ mixture gas during deposition. The realization of ferromagnetic properties of ZnO:Cu on plastic substrates may open up new prospect of plastic spintronics such as spin-LEDs and spin-transistors.

Chapter 6: Ferromagnetic and conductive ZnO:Cu

6.1 Introduction

The coexistence of magnetic and semiconductor properties in ferromagnetic semiconductors are expected to meet emerging spintronics technological demands where conventional electronics cannot provide a solution.^{35,37,150} Examples of typical spintronics application include spin-LED, spin-transistor, and magnetic random access memory (MRAM).^{24,37,151,152} However, the performance of many above RT ferromagnetic oxides, including ZnO:Cu, has been insufficient for use as functional materials owing to their poor electrical properties. As mentioned in Chapter 4.1, the carrier concentration and conductivity reduce significantly with the incorporation of Cu. One of the possible ways to improve the conductivity of the ZnO-based sample is the utilization of substrate biasing technique during the film deposition. Xu *et al.* and Lim *et al.* reported that biasing technique can improve the electrical properties of ZnO.^{153,154} The electron concentration of the ZnO:Cu samples have been improved from 10^{16} to 10^{20} cm^{-3} by applying the biasing technique. The comprehensive study of the conductive and ferromagnetic ZnO:Cu is presented in Chapter 6.2.

The realization of the conductive ZnO:Cu film is an essential step in the effort to exploit its electron injection by fabricating a LED. However, reproducible and stable *p*-type ZnO material with sufficiently high conductivity and carrier concentration is still in a development phase. Therefore, the fabrication of ZnO homojunction, continues to be problematic.^{19,22} In an alternative approach, the electron injection behavior of ZnO:Cu might be best exploited by constructing ZnO:Cu/GaN:Mg heterojunction LED. GaN based films are considered good candidates for the *p*-type layer because they are readily available and they have the

same crystal structure (wurtzite) as ZnO with a small in-plane lattice mismatch (~1.8% for GaN) and the same stacking sequence (2H).¹⁵⁵ The fabrication and characterization of ZnO:Cu/GaN:Mg heterojunction LED are described in Chapter 6.3.

6.2 Highly conductive ZnO:Cu

A series of ZnO:Cu films were prepared on Si substrates at RT by the FCVA technique under identical oxygen flow rate, partial pressure, filter magnetic field and arc current as prescribed in chapter 3.1. Zn:Cu alloy target containing 1 at. % of Cu was used in this experiment. To investigate the biasing effect, the substrate and sample holder were biased under various applied voltages, ranging from -200 to + 200 V by a DC power supply during the film deposition. In order to compare the effectiveness of this method for electrical properties improvement, an unbiased ZnO:Cu film (i.e. control sample) was also prepared under the identical conditions on Si substrate.

The XRD patterns of the ZnO:Cu films are illustrated in Figure 6-1. The XRD peaks of (100), (002), (010), and (110) peaks are perfectly indexed and they are corresponding to ZnO wurtzite structure. No secondary phases were detected within the sensitivity of XRD. It can be seen that the film deposited at RT without bias exhibited predominately *c*-axis (002) orientation. However, the intensity and full width half maximum (FWHM) of (002) peak degrade with an increase of positive biased voltage. For the negative bias < -40V, the (002) peak disappears and the films changed its predominated orientation to (100) direction with poor crystallinity as indicated by the broad and weak diffraction peak. A positive (negative) biased voltage

is thought to attract negatively (positively) charged ions; the bombardment by these charged ions could deform the c -axis orientation and create an imperfect structure with large density of defects (i.e. structural, Zn_i and/or O vacancies).^{154,156} It is noted from Figure 6-1 that negative biased samples showed poorer structural properties as compared to its positive biased counterpart. A heavier mass of positively charged particles (i.e. Cu and Zn) could generate higher impingement force to the negative biased samples, leading to dramatic deformation of structural properties. These results are consistent with Suzuki *et al.*¹⁵⁶ and Xu *et al.*¹⁵³ that the crystal orientation of ZnO is dependent on biased voltage and the negative biased samples are generally exhibited poorer crystallinity as compared to positive biased samples. The (002) peak is shifted to a lower angle with an increase in biasing voltage which indicates the samples exhibited larger lattice parameter, c . Defects and imperfection in the grain of the biased ZnO:Cu leads to higher compression stress exerted on lattice resulting in a larger c .¹¹⁰

Figure 6-1: XRD patterns of ZnO:Cu films deposited at various biasing conditions.

As illustrated in Chapter 4.1, the incorporation of Cu into ZnO reduces its conductivity as Cu introduces deep acceptor level and it traps electrons from the conduction band.²² However, with the biasing technique, all the prepared ZnO:Cu films are conductive with *n*-type behavior and its electrical properties are depicted in Figure 6-2. The resistivity and carrier concentration of unbiased ZnO:Cu are 6.7 $\Omega\text{-cm}$ and $7.6 \times 10^{16} \text{ cm}^{-3}$, respectively. The carrier concentration of the biased ZnO:Cu increases drastically by 4 orders of magnitude to $\sim 1.2 \times 10^{20} \text{ cm}^{-3}$, whereas the resistivity reduces to $\sim 3.7 \times 10^{-2} \Omega\text{-cm}$. As the biased voltage increase, a flux of energetic atoms impinging on the substrate with increasing kinetic energy would cause a deviation from crystallinity, accompanied by a change of electrical properties. The structural defective ZnO:Cu led us to envisage the enhanced electrical properties are related to the presence of defects (i.e. structural, Zn_i or/and O vacancies) in the films. The improved electrical properties in the ZnO:Cu film by the biasing technique is a common characteristic of doped ZnO film.^{154,157}

Figure 6-2: Electrical resistivity and electron concentration as a function of bias voltage.

Figure 6-3 shows the magnetic properties of the biased ZnO:Cu films. A well defined hysteresis loop was observed for the +100 V biased ZnO:Cu film with M_s of $0.32 \mu_B/\text{Cu}$ and H_c of 98.5 Oe as shown in the inset of Figure 6-3, showing a room temperature FM. The M_s of the ZnO:Cu samples prepared at various biasing conditions are normalized by the corresponding unbiased sample, where $M_n = M_s(V)/M_s(\text{unbiased})$. The unbiased ZnO:Cu prepared at RT possessed the $M_s(\text{unbiased})$ of $0.4 \mu_B/\text{Cu}$. As depicted in Figure 6-3, the M_s reduces with an increase of biased voltage. All the biased films possess weaker magnetic moment as compared to the unbiased ZnO:Cu film, M_n is less than 1. These results elucidate that magnetic ordering depends on the applied bias; the transformation of the crystal orientation and quality would lead to transition of FM to paramagnetism. Theoretical modeling of the ZnO:Cu system indicates that the location of the Cu atoms relative to each other and its substituted sites in host lattice can strongly affect the magnetic properties of the system.^{26,27,54} Feng studied the effect of Cu separation and the stability of the ferromagnetic state in ZnO:Cu.⁵⁴ The FM is only possible to occur if two Cu^{2+} substitute two Zn^{2+} sites in c -plane, which gives well separation distance at lowest total energy at RT. However, if two Cu^{2+} ions are separated within the ab plane the anti-ferromagnetic state is favored, as evidenced by the absence of FM in the predominated (100) films. Taking the XRD and magnetic data together, it is noted that the magnetic moment reduce with increasing structural disorder. The presence of structural defects could suppress the magnetic ordering, which is in good agreement with recent literature.^{100,158}

Figure 6-3: Normalized saturated magnetic moment M_n of the ZnO:Cu films as a function of biasing voltage. Inset: Magnetization curve of the ZnO:Cu prepared at + 100V.

In addition to the Cu atom placement, the Zn_i also plays a significant role in enhancing and mediating magnetic ordering in the ZnO:Cu. To investigate the role of Zn_i in the biased sample, the + 100 V biased ZnO:Cu films were annealed at 200 and 400 °C under oxygen rich ambient for an hour. The magnetic moment has been reduced by ~30% ($0.22 \mu_B/\text{Cu}$) and ~45 % ($0.18\mu_B/\text{Cu}$) for the samples annealed at 200 and 400 °C, respectively. It is attributed to the out diffusion of Zn_i to second nearest neighbor position as Zn_i has low diffusion barriers and easy to diffuse into the lattice at relatively low temperature.¹²⁹ As expected, the electrical properties of the films degrade with an increase in annealing temperature as shown in Figure 6-4. After annealing treatment at 400 °C, the electron concentration of the biased ZnO:Cu reduced to $9.33 \times 10^{17} \text{ cm}^{-3}$ with the resistivity of $0.353 \Omega\text{-cm}$. This result suggests that the deficiency of Zn_i in ZnO:Cu could degrade the magnetic ordering as well as electrical properties, which is consistent with the unbiased ZnO:Cu.

Figure 6-4: Electrical resistivity and electron concentration of the +100 V annealed ZnO:Cu film as a function of annealing temperature.

6.3 Heterojunction LED

Now, let us consider the practical application of the conductive and ferromagnetic ZnO:Cu film. Among the biased samples, it is found that the ZnO:Cu prepared at the biased voltage of +100 V exhibited the highest M_s , considerably superior structural and electrical properties, thereby it was chosen for the heterojunction LED fabrication, acting as electron injection layer.

Figure 6-5: Schematic illustration of the n -ZnO:Cu/ p -GaN heterojunction LED structure.

Figure 6-5 shows the schematic diagram of the proposed *p-n* heterojunction diode (ZnO:Cu /*p*-GaN) with the size of 6 mm x 5 mm. A 150 nm thick ZnO:Cu (1 at.%) was deposited on 1 μm -thick *p*-GaN:Mg/sapphire (Technologies and Devices International, Inc.). The + 100 V biased ZnO:Cu is preferred as the electron injection active layer due to its optimal carrier concentration ($> 7 \times 10^{19} \text{ cm}^{-3}$) as presented in chapter 6.2. The contact layer of Ti (100 nm) and Ni (100 nm) were then e-beam evaporated onto the *p* and *n* layers, respectively.

The electrical properties of the diode was analyzed by HP 4155 semiconductor parameter analyzer. The diode shows a rectifying behavior with the threshold voltage of $\sim 3 \text{ V}$ as shown in Figure 6-6. The non-linear I-V characteristic of diode is well described by Shockley's law, $I = I_s \left[\exp \left(\frac{V}{V_T} \right) - 1 \right] \approx I_s e^{V/V_T}$, where I_s is the saturation current of the diode and V_T is threshold voltage. Next, the diode was biased under rectangle pulse voltage source (with repetition rate and pulse width of 12.6 and 60 ms, respectively) at RT and its corresponding light-voltage curve (measured by home made EL spectrum meter), which shows a rectifying behavior with turn on voltage of $\sim 16 \text{ V}$, is plotted in Figure 6-6. Large turn on voltage might be attributed to interface defects between ZnO:Cu and GaN layer, and the high ohmic resistance from Ti/Ni contact on the *p*-GaN:Mg and ZnO:Cu, respectively. The interface defects and high contact resistance will reduce the light emission efficiency.

Figure 6-6: Current–voltage and light–voltage characteristic of the ZnO:Cu/*p*-GaN heterojunction LED.

Figure 6-7 shows the electroluminescence (EL) spectra of the diode at different forward-biased voltages. The EL spectra obtained in the sample are fitted by two Gaussian curves, which is dominated by broad blue and green luminescence band peaking at 466 nm and 554 nm respectively.¹⁹ The peak intensity increases with an increase of biased voltage, indicating the diode exhibits effective band radiative recombination. The appearance of EL signal provides important insight that the conductive *n*-ZnO:Cu is significant for electron injection in the heterojunction LED. Rogers *et al.* demonstrated that *n*-ZnO/*p*-GaN:Mg heterojunction LED, showing the room temperature EL spectrum at ~ 375 nm.¹⁵⁹ On the other hand, Leong observed the room temperature EL peaked at ~ 385 nm for *n*-ZnO:Al/*i*-ZnO/*p*-GaN:Mg heterojunction LED.¹⁶⁰ Hence the broad EL spectra in our *n*-ZnO:Cu/*p*-GaN:Mg may not be attributed to *p*-GaN:Mg, but it could be originated from the conductive ZnO:Cu.

The photoluminescence (PL) measurement was carried out on the ZnO:Cu film deposited on SiO₂/Si substrate to examine the origin of EL emission and center of radiative recombination. As expected, the PL spectrum consists of two components as depicted in Figure 6-8. The peaks at 486 nm and 568 nm can be attributed to blue

and green luminescence band respectively. The PL spectrum is dominated by the green luminescence, whereas blue luminescence dominates the EL spectra. The deviation of the PL and EL spectrum might be attributed to the influence of the hetero-interface defect. Till now, the origin of this green emission is rather controversial.¹⁹ Dingle *et al.*¹⁶¹ reported the green luminescence was attributed to the introduction of Cu ions into ZnO, which has been supported by recent experimental observation by Alivov *et al.*¹⁶² and Leiter *et al.*¹⁶³ In contrast, Studenikin *et al.*¹⁶⁴ assigned the green luminescence to a donator-acceptor transition (D, A) from oxygen vacancy (O_V) to Zn vacancies (Zn_V). A transition between Zn_V and Zn_i was suggested by Xu *et al.*¹⁶⁵ On the other hand, Kang *et al.* ascribed the appearance of the green luminescence to transitions involving deep-levels within the band gap associated with oxygen vacancies.¹⁶⁶ The annealing process revealed FM in our ZnO:Cu could be partially associated to the presence of Zn_i , thereby we proposed the broad green band would come from multiple energy levels in the forbidden band due to Cu or/and Zn_i . There is no ultraviolet (UV) peak observed in either PL or EL spectra. The observation is consistent to the recent reports that the incorporation of Cu into ZnO could suppress the UV peak.^{96,162}

To understand the origin of the blue emission band, the PL of the as-deposited GaN:Mg films was studied. Figure 6-9 shows the PL spectrum of the GaN:Mg film on sapphire substrate. A sharp peak at ~362 nm is observed with a tail extending to ~520 nm. The curve can be fitted by two Gaussian curves at ~363 and ~400 nm. The emission at ~363 nm is attributed to the near band edge emission of GaN:Mg whereas emission at ~400 nm is likely to be the transition from the conduction band to the Mg acceptor level.^{160,167} Hence, it is believed that the EL emission is not emerged from the GaN:Mg film.

Figure 6-7: EL spectra of the ZnO:Cu /p-GaN heterojunction LED at various forward bias.

Figure 6-8: PL spectrum of the ZnO:Cu on SiO₂/Si substrate.

Figure 6-9: PL spectrum for GaN:Mg film on sapphire substrate. The PL spectrum is fitted with two Gaussian curves with peak wavelength at ~363 nm and ~413 nm.¹⁶⁰

The proposed energy band diagram of n -ZnO:Cu/ p -GaN:Mg is presented in Figure 6-10. In this diagram, the electron affinity (χ) for ZnO:Cu and GaN:Mg are taken as ~ 4.35 eV and ~ 3.9 eV, respectively. The bandgap (E_g) for ZnO:Cu is assumed as ~ 3.3 eV and ~ 3.51 eV for GaN:Mg.¹⁶⁸ As can be seen from the diagram, the energetic barrier ΔE_C for electrons is $\Delta E_C = \chi_{(\text{ZnO:Cu})} - \chi_{(\text{GaN:Mg})} = (4.35 - 3.9) \text{ eV} = 0.45 \text{ eV}$, while the energetic barrier ΔE_V for holes is $\Delta E_V = E_{g(\text{ZnO:Cu})} + \Delta E_C - E_{g(\text{GaN:Mg})} = (3.3 + 0.45 - 3.51) \text{ eV} = 0.24 \text{ eV}$. Thus, the energetic barrier for holes ΔE_V is ~ 2 times less than the barrier for electrons ΔE_C , showing a much small barrier for holes than that which exists for electrons. Thus, it is suggested that the EL emission emerges from the ZnO region of the device.

Figure 6-10: Energy band diagram of the n -ZnO:Cu/ p -GaN:Mg heterojunction.

It is recalled that the relatively high-resistive unbiased ZnO:Cu films exhibit higher magnetic moment as compared to the conductive films, though the latter possess a higher carrier concentration, thereby the FM in the conductive ZnO:Cu may

not be carrier-mediated.¹⁶⁹ The experimental results indicate that Zn_i , crystal-quality and crystal orientation play an important role in the magnetic moment of the conductive ZnO:Cu films. In this case, the highly non-equilibrium process of FCVA-biasing technique makes the Zn_i defects located throughout the lattice in the films; the interaction between Zn_i and Cu^{2+} ions in the lattice at the appropriate distance and density¹⁷⁰ will give rise to magnetic ordering in the ZnO:Cu according to the BMP model as discussed in chapter 4.2.⁸³ The annealing process have provided important insight into the role played by Zn_i in the ZnO:Cu system. It is worthy to highlight that the crystal orientation is crucial to the FM in the ZnO:Cu films in addition to Zn_i - Cu^{2+} interaction, a (002) crystal orientation appears to be essential to the observation of magnetic ordering. However, it is not clear why conductive ZnO:Cu film will give a lower magnetic moment as compared to relatively high-resistive films, which is also a common characteristic for the conductive ZnO:Co films.^{171,172} Till now, the explanation of this phenomenon is rather controversial. Venkatesen *et al.*¹⁷¹ reported that reduction of magnetization in the conductive ZnO:Co was attributed to absent of cobalt nanoclusters; whereas Song *et al.*¹⁷² suggested that presence of the structure defects could enhance FM in insulating ZnO:Co films as compared to semiconducting films. In the context of BMP, we propose that the deviation of magnetic moment could be related to the defect density of the sample as certain critical defect density will lead to the optimized magnetic couplings.¹⁷⁰ Based on the BMP model, the magnetic properties of the ZnO:Cu films could be tuned through Cu and defects concentration, which are in good agreement with our results.

6.4 Summary

In summary, conductive and ferromagnetic ZnO:Cu have been demonstrated using the biasing technique. The magnetization of the biased ZnO:Cu is correlated to its structural properties, crystal orientation and biasing voltage. The structural properties of the ZnO:Cu degrade with an increase of biasing voltage, and leads to the transition of FM to paramagnetism. Furthermore, it is found that the crystal orientation (i.e. (002) oriented) and defect density are crucial to the FM in the ZnO:Cu. A *n*-ZnO:Cu/*p*-GaN:Mg heterojunction LED has been demonstrated. The heterojunction exhibited room temperature EL, showing the blue and green band luminescence. The appearance of EL signal is an important insight that the conductive ZnO:Cu could be acted as electron injector for LED. The realization of ZnO:Cu based LEDs may open up new prospect for spin-LEDs.

Chapter 7: Ferromagnetic ZnO:Cu nanoneedles

7.1 Introduction

The last few chapters have considered the fabrication and study of the thin-film ZnO:Cu. The advent of room temperature FM in ZnO:Cu films together with the recent development of nanotechnology have brightened our effort to exploit ZnO:Cu nanostructures. Ferromagnetic semiconductors having nanostructure are expected to have a longer coherence time, which may provide a pathway for increasing the spin lifetime for practical spintronics applications.¹⁷³ In particular, one-dimensional (1D) ferromagnetic semiconductors systems in the nanometre scale are believed to be good candidates for future nanospintronics devices because of their efficient injection of spin-polarized carriers, large magnetic anisotropy energy and application to building blocks for nanometre-scale devices.¹⁷⁴ However, to date, most of the research on ferromagnetic ZnO:Cu have been focused on thin films and bulk materials. In this chapter, we report the magnetic anisotropy in the ferromagnetic ZnO:Cu nanoneedles prepared by the ion beam technique at RT. This approach should shed light to the selectively growth of ferromagnetic semiconductors on any substrate for functional spintronics devices.

7.2 Fabrication and characterization

ZnO and ZnO:Cu films with thickness of 850 nm and 1100 nm respectively, were prepared on Si substrates at RT by the filtered cathodic vacuum arc (FCVA) technique. Then the samples were exposed to ion beam irradiation for nanoneedles fabrication. The details of ion beam irradiation procedures have been described in

Chapter 3.2 and its schematic of nanoneedles fabrication is shown in Figure 3-2. In order to compare the effectiveness of this method for doping, ZnO:Cu nanoneedles were also prepared by the similar ion beam technique but the starting material was a FCVA-deposited ferromagnetic ZnO:Cu film.¹⁶ In this case, no Cu plate was used in the ion beam irradiation. The ZnO:Cu nanoneedle samples were labeled as N1 and N2 for the ZnO and ZnO:Cu films used as starting materials, respectively. The Cu content in samples N1 and N2 was estimated to be ~2.1 and ~1.3 at.% respectively, by the energy dispersive x-ray spectroscopy attached in the SEM.

The surface morphology and structural properties of sample N1 are presented here as sample N2 exhibited similar structural properties of N1. The typical ZnO:Cu nanoneedle array is shown in Figure 7-1 (a). The lengths of the cone-like structures ranged from 250 nm to 500 nm. The nanoneedles are oriented around ~45° to the substrate, which is similar to the ion beam irradiation direction. The average diameter of the nanoneedles in the stem part was ~100 nm with considerably sharp morphology as illustrated in Figure 7-1 (b). Figure 7-1 (c) shows a well oriented (0002) plane of an individual nanoneedle with its interplanar distance of 0.26 nm, suggesting high crystallinity of the ZnO:Cu nanoneedles. Figure 7-1 (d) shows the SAED patterns of a nanoneedle and the inset is a simulated SAED ring pattern of ZnO by using the computer program JECPP/PCED.¹⁷⁵ The SAED pattern of the nanoneedle is matched with the simulated ZnO pattern, implying the nanoneedle exhibited the ZnO wurtzite structure. However, some weak diffraction spots of CuO could be seen in the pattern.

Figure 7-1: (a) A typical cross-sectional SEM image of ZnO:Cu nanoneedles (sample N1). (b) TEM image of a ZnO:Cu nanoneedle and its corresponding HRTEM image is shown in (c). (d) Comparison of the SAED patterns of ZnO:Cu nanoneedles with the simulated patterns of ZnO. Some weak diffraction spots related to CuO were detected.

Figure 7-2 shows the XRD spectra of as-grown ZnO, ZnO:Cu, N1 and N2. All samples exhibited prominent (002) peak corresponding to ZnO wurtzite structure. The degradation of XRD intensities is observed with the incorporation of Cu into ZnO, elucidating the increase in structural disorder. It is because the incorporation of $3d$ transition ions, such as Cu generally deteriorates the crystallinity of ZnO due to their low solubility and various valence states. Although sample N1 exhibited higher Cu content than N2, the XRD peak intensity of N1 is higher than that of N2. This

discrepancy may be attributed to the crystal quality of the starting material as the XRD peak intensity of ZnO film is stronger than ZnO:Cu. As shown in the inset of Figure 7-2, the (002) peak of the nanoneedles were shifted to higher angles by $0.02^\circ \sim 0.06^\circ$ as compared to ZnO film ($2\theta = 34.34^\circ$), indicating the reduction of lattice parameter c . It is attributed to the substitution of the smaller Cu^{2+} ions into Zn^{2+} sites as Cu^{2+} ions have radii of 0.057 nm as compared to 0.06 nm for Zn^{2+} ions.¹¹²

Figure 7-2: XRD pattern of ZnO film, ZnO:Cu film and as-fabricated ZnO:Cu nanoneedles on Si (100) substrate. Inset shows an enlarged (002) peak of ZnO:Cu samples.

7.3 Magnetic anisotropy

Figure 7-3 shows the typical magnetization curves of sample N1. A well defined hysteresis behavior is observed in the ZnO:Cu nanoneedles, magnetic ordering with H_c and M_s of 100 Oe and 0.698 emu/cm^3 , respectively when the magnetic field was applied perpendicular to the substrate. The saturated magnetization of all samples measured with magnetic field applied parallel ($M_s^\parallel$) and

perpendicular ($M_s^\perp$) to the substrate at 10 kOe is listed in Table 7. The $M_s^\perp$ of sample N2 is about 19% less than N1. Since the M_s values have been normalized by the volume of the thin film or nanoneedles, the difference of $M_s^\perp$ between sample N1 and N2 may be attributed to the higher Cu content in sample N1 than in N2. It is noted that the $M_s^\perp$ of N2 is 15% less than that of the ZnO:Cu film, the interfacial defects created by the ion beam irradiation and the orientation of the ZnO:Cu nanoneedles may be attributed to the reduction of the $M_s^\perp$ after irradiation. It seems that ion beam irradiation is an effective method to dope Cu into ZnO and make it become ferromagnetic.

Figure 7-3: Magnetization hysteresis loops of as-fabricated and annealed ZnO:Cu nanoneedles for sample N1 measured at 300K. Inset shows the magnetization ratio of $M_s^\perp / M_s^\parallel$ before and after annealing for samples N1, N2 and ZnO:Cu film.

Table 7: The saturated magnetization of as-fabricated and annealed samples N1, N2 and ZnO:Cu film measured at applied field of 10 kOe.

Applied magnetic field direction	Sample N1 (emu /cm ³)		Sample N2 (emu /cm ³)		ZnO:Cu film (emu /cm ³)	
	As-fabricated	Annealed	As-fabricated	Annealed	As-grown	Annealed
	0.698	0.968	0.562	0.773	0.665	1.249
	0.593	0.966	0.431	0.773	0.628	1.242

The magnetic anisotropy in transition element substituted ZnO is a common characteristic of oxide semiconductors.¹⁷⁶ Sati *et al.* reports that the magnetic anisotropy in ZnO:Co could be considered as a signature of intrinsic FM.¹⁴⁶ Thus the magnetic anisotropy of the ZnO:Cu nanoneedles and thin film samples were studied. As shown in the inset of Figure 7-3, the ratio of the $M_s^\perp / M_s^\parallel$ for the three samples is greater than 1, indicating the anisotropy nature of the samples. The anisotropy of the $M_s^\perp$ in the ZnO:Cu nanoneedles can be 30% larger than $M_s^\parallel$. The stronger anisotropy of the ZnO:Cu nanoneedles as compared to the thin film sample could be due to the shape and orientation of the nanoneedles as the nanoneedles are oriented $\sim 45^\circ$ to the substrate. In order to verify whether the shape or orientation of the nanoneedles will play a role in the anisotropy, the samples were annealed at 400 °C for 20 min. Under these optimal annealing conditions, the $M_s^\perp$ of the ZnO thin films will be the highest ($M_s^\perp = 1.2$ emu/cm³). It is not clear why such conditions will give the highest $M_s^\perp$, but it may be related to the defect density of the sample as certain critical defect density will lead to the optimized magnetic couplings.¹⁷⁰ Surprisingly, after annealing

the magnetization ratio $M_s^\perp / M_s^\parallel$ of all the samples is equal to ~ 1 at the applied field of 10 kOe as shown in the inset of Figure 7-3. However, it should be noted that “easy plane” FM can still be observed in all the samples at applied field less than 5 kOe. The typical magnetization curve of the annealed sample N1 is shown in Figure 7-3. The “easy plane” is along the perpendicular axis of the substrate which may be attributed to the magnetocrystalline anisotropy in our samples as they are predominately (002) oriented. The structural properties of the annealed nanoneedles have been examined by XRD and SEM but no obvious difference can be observed in terms of XRD peak positions and surface morphology as compared to the as-fabricated samples. Thus, the changes of the magnetization ratio $M_s^\perp / M_s^\parallel$ after annealing are unlikely related to the structural properties of the samples. In addition, the anisotropy of the samples at high applied field does not seem to be due to the shape and orientation of the nanoneedles. The mild but yet optimized annealing conditions has a significant effect on the saturated magnetization and anisotropy of the samples. The annealing temperature of 400 °C should be sufficient to redistribute inhomogeneous Cu^{2+} ions in ZnO since our samples were prepared under non-equilibrium condition (i.e. low growth temperature). A homogeneous distribution of Cu^{2+} ions in ZnO would favor FM and it should lead to enhanced magnetization. On the other hand, the intrinsic defects in ZnO such as O vacancies and Zn_i may be affected by annealing where Zn_i is more likely to be annealed out at 400 °C than O vacancies. It is due to the low diffusion energy of Zn_i , it can diffuse into the lattice at relatively low temperature as compared with other defects.¹⁷⁷ The Zn_i defect density may somehow play a role on the enhanced FM after annealing as a critical defect density will lead to optimized magnetic coupling.¹⁷⁰ It is not clear whether the “easy plane” ferromagnetic state in the annealed Cu doped ZnO samples is related to single

ion anisotropy as proposed by Sati *et al.*¹⁴⁶ A theoretical calculation is sought to verify the effect of single ion anisotropy of Cu^{2+} in ZnO. It should be noted that the “easy plane” FM of N1 and N2 samples is stronger than that of the thin film sample. Thus the effect of shape anisotropy in the ZnO nanoneedles at low field cannot be ruled out. It is due to the ion beam bombardment, the interfacial defects and inhomogeneous distribution of Cu^{2+} ions in the nanoneedles samples are expected to be higher than that in the ZnO:Cu film. It may account for the larger changes in magnetization ratio $M_s^\perp / M_s^\parallel$ in the nanoneedle samples than in the thin film as interfacial defects and inhomogeneous distribution of Cu^{2+} can be removed by annealing.

7.4 Summary

In summary, an ion beam technique has been employed to dope Cu into ZnO and makes it become ferromagnetic at RT. The magnetic anisotropy of the ZnO:Cu nanoneedles at high magnetic field may not be related to the shape and orientation of the nanoneedles but rather the distribution of Cu^{2+} and defect density.

Chapter 8: Conclusions and recommendations

8.1 Conclusions

The room temperature FM in the ZnO:Cu on Si as well as plastic substrates has been achieved by tailoring the process parameters. The studies have shown that incorporation of Cu into ZnO could induce the magnetic ordering and its magnetization is related to Cu concentration, crystal orientation, structural properties, Zn interstitial (Zn_i) defect and high spin Cu^{2+} . The key to observe FM in this system is the RT processing at relatively low Cu concentration (~ 1 at.%), which (1) prevents formation of clusters and secondary phases, and (2) prevent the substitutional of Cu^{2+} at the shorter separation distances in a - b plane of Zn^{2+} sites.

More in-depth studies on the ZnO:Cu system has been carried out to investigate the origin of FM. The experimental data reveals that the presence of Zn_i could enhance the magnetic moment, but it would lead to magnetic instability at elevated temperature due to its high diffusive nature. In order to improve the magnetic moment and stability of ZnO:Cu, a potential hole dopant of N are incorporated into ZnO:Cu system by N_2O annealing. As a result, the magnetic moment can be enhanced by $\sim 100\%$ with high magnetic stability. In addition, the studies have shown an importance interplay between Cu, N and Zn_i in ZnO:Cu system. It is found that Zn_i is prerequisite to the incorporation of N into ZnO:Cu. The incorporation of N could increase the high spin state of Cu^{2+} in the ZnO:Cu and stabilize the highly diffusive Zn_i through N-Zn bonding.

The low temperature conductivity measurement was carried out to study the ZnO:Cu transport properties and its underlying mechanism of FM. The ZnO:Cu films are generally highly resistive in nature due to the incorporation of deep acceptor of Cu

and/or N atom. The transport mechanism of the ZnO:Cu is related to variable range hopping (VRH) with the presence of magnetic polarons. The highly resistive ZnO:Cu film with the existence of magnetic polarons have led us to envisage the FM in ZnO:Cu is correlated to bound magnetic polarons (BMP) model. The magnetic properties of the ZnO:Cu films could be tuned through Cu and defects concentration according to BMP model.

The investigation of ZnO:Cu on plastic substrate reveals its magnetic properties is weaker as compared to its counterpart on Si substrate, which is attributed to poor crystallinity and substrate effect. The magnetic anisotropy was observed in the stressed films under various bending conditions, which can be attributed to strain in the ZnO:Cu films. The internal strain could lead to lattice distortion and produce magneto-elastic-driven anisotropy.

The poor electrical performance of ZnO:Cu has been insufficient for use as functional materials. To circumvent this issue, the biasing technique was used to improve the conductivity and carrier concentration of ZnO:Cu. However, it is found that the biased films exhibit weakened magnetization, which is attributed to its defective structural properties. To demonstrate the usefulness of the ferromagnetic and conductive ZnO:Cu film, a *n*-ZnO:Cu/*p*-GaN:Mg heterojunction LED has been fabricated which showed room temperature EL luminescence. The appearance of EL signal is an important insight that the conductive ZnO:Cu could be acted as electron injector for LED.

One-dimensional ferromagnetic ZnO:Cu nanoneedles prepared by an ion-beam technique at RT has been achieved. The nanoneedles exhibit higher magnetic moment when a field was applied perpendicular to the substrate than when the field applied parallel to the substrate. The magnetic anisotropy of the ZnO:Cu nanoneedles

at high magnetic field may not be related to the shape and orientation of the nanoneedles but the distribution of Cu^{2+} and defect density.

8.2 Recommendations for future works

The studies presented in this dissertation are mainly focused on the investigation of ferromagnetic ZnO:Cu film. Although comprehensive studies have been carried out to understand its physical origin of FM, the underlying mechanism is still rather debatable. Keavney *et al.*¹⁷⁸ reported a robust FM in ZnO:Cu, but no magnetic circular dichroism (MCD) signal consistent with FM originating from Cu 3d, O 2p and Zn 3d state. For practical ferromagnetic semiconductor material, the ZnO:Cu is required to exhibit Anomalous Hall effect (AHE), ferromagnetic resonance (FMR) and MCD signal. These characterizations should be part of the future works.

A more thorough study of the ferromagnetic and conductive ZnO:Cu is needed in order to understand the FM mechanism. If the structural and magnetic properties of the biased samples can be improved without compromising the electrical properties, this will pave the way to enhance the efficiency of spin-injection and open up the pathway to practical devices.

The demonstration of electrically driven ZnO:Cu based heterojunction LED is an essential extension of this presented dissertation, suggest an interesting research direction. It is highly desirable to fabricate more efficient electrically pumped ZnO:Cu based LED structures. The key step to achieve more efficient electrically pumped LED is the fabrications of the P-I-N junction structure, which can be obtained by fabricating, *n*-ZnO:Cu/*i*-ZnO/*p*-GaN:Mg heterojunction structures as shown in Figure

8-1. The optimization of ohmic contract is another key in achieving high efficient LED.

Figure 8-1: Schematic diagram of the proposed n -ZnO:Cu/ i -ZnO/ p -GaN:Mg heterojunction structures.

It is strongly believed that the success of implementing the above recommendation, practical spintronics devices such as spin-LED and spin-transistor can be realized in the future.

Appendix I: List of Publications

1. **T.S. Herng**, S.P. Lau, S.F. Yu, H.Y. Yang, L. Wang, M. Tanemura, and J.S. Chen, "Magnetic anisotropy in the ferromagnetic Cu-doped ZnO nanoneedles," *Appl. Phys. Lett.*, **90**, 032509 (2007).
2. **T.S. Herng**, S.P. Lau, S.F. Yu, H.Y. Yang, K.S. Teng, and J.S. Chen, "Ferromagnetic copper-doped ZnO deposited on plastic substrates," *J. Phys.: Condens. Matter*, **19**, 236214 (2007).
3. **T.S. Herng**, S.P. Lau, S.F. Yu, J.S. Chen and K.S. Teng, 'Zn-interstitial-enhanced ferromagnetism in Cu-doped ZnO films', *J. Magn. Magn. Mater.*, **315**, 107(2007).
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5. **T.S. Herng**, S.P. Lau, S.F. Yu, H.Y. Yang, X.H. Ji, J.S. Chen, N. Yasui, and H. Inaba, "Origin of room temperature ferromagnetism in ZnO:Cu films," *J. Appl. Phys.*, **99**, 086101 (2006).
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Appendix II: Bibliography

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