Development of zinc oxide-based diluted magnetic semiconductor thin films and nanostructures possessing room temperature ferromagnetism

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**DEVELOPMENT OF ZINC OXIDE-BASED DILUTED
MAGNETIC SEMICONDUCTOR THIN FILMS AND
NANOSTRUCTURES POSSESSING ROOM
TEMPERATURE FERROMAGNETISM**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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Abstract

Spintronics has emerged as a new technology, which is based on electron spins rather than electron charges to carry information. Spintronics offers an opportunity for a new generation of devices combining standard microelectronics with spin-dependent effects that arise from the interactions between the spins of charge carriers and the magnetic properties of materials. In this project, pure ZnO thin films, Cu-doped ZnO thin films, Ni-doped ZnO thin films, pure ZnO nanostructures, and Co-doped ZnO nanostructures were developed as diluted magnetic semiconductor (DMS) materials for potential applications in spintronic devices.

Annealing effect under varying conditions on the structural and magnetic properties of the ZnO-based DMS thin films was investigated. A lattice deviation of both as-deposited and annealed pure ZnO thin films was observed through X-ray diffraction (XRD), which was attributed to oxygen vacancies and interstitial Zn in the films. Significant diffusion of O from the bottom to the top surface of the films occurred during annealing in Ar and air as revealed by X-ray photoelectron spectroscopy (XPS), which resulted in increased oxygen vacancies in the films after annealing. Furthermore, prolonged annealing could promote the diffusion of O and induce more oxygen vacancies in the films. Both the as-deposited and the annealed pure ZnO thin films displayed diamagnetism at room temperature, though the oxygen vacancies existed in all the films, indicating that the oxygen vacancies were necessary while only oxygen vacancies were not enough to induce room temperature ferromagnetism (RTFM) of ZnO-based DMS.

For the Cu-doped ZnO thin films, significant diffusion of O and Cu from the bottom to the top surface of the films was observed after annealing in Ar or air through XPS. Reduction of Cu occurred in the films annealed in Ar, while oxidization of Cu occurred in the films annealed in air. Extended annealing in air made a higher concentration of oxygen vacancies in the films, and also increased the amount of Cu^{2+} at Zn^{2+} sites of ZnO wurtzite lattice. The as-deposited Cu-doped ZnO thin film displayed RTFM that originated from Cu^{2+} based on the bound magnetic polaron (BMP) model. However, RTFM disappeared in the films annealed in Ar due to the disappearance of Cu^{2+} . Extended annealing of the Cu-doped ZnO films in air enhanced the saturation magnetization (M_s) of the films, which was attributed to a stronger BMP effect.

For the Ni-doped ZnO thin films, oxidization of metallic Ni to Ni^{2+} occurred in the film annealed in air at 600 °C, while reduction of Ni^{2+} to its metallic state occurred in the film annealed in Ar at 600 and 800 °C. In addition, there appeared to be significant diffusion of Ni from the bottom to the top surface of the film during annealing in Ar at 800 °C. Both as-deposited and annealed Ni-doped ZnO films displayed obvious RTFM which was from metallic Ni, Ni^{2+} or both with two distinct mechanisms. Furthermore, a significant improvement in M_s in the films was observed after annealing in air or Ar at 600 °C compared to that in the as-deposited film. An even higher M_s value was observed in the film annealed in Ar at 800 °C compared to that at 600 °C mainly due to the diffusion of Ni. The ultraviolet emission of the Ni-doped ZnO thin film was restored during annealing in Ar at 800 °C, which was also attributed to the diffusion of Ni.

Pure ZnO microrod arrays with different topographies were grown on bare silicon substrates through an electrochemical deposition method with varying potentials from -0.8 to -2.0 V. When the potential was -2.0 V, pure ZnO needle-shaped microrod arrays were formed. The applied potential played a key role in the nucleation and growth processes of the pure ZnO microrod arrays. Zn was in its two-valence oxidation state in the pure ZnO microrods grown with -0.8 V, while it was in its minor metallic and major two-valence oxidation states concurrently in the pure ZnO microrods grown with -1.2, -1.6, and -2.0 V. The reduced metallic Zn was doped into the interstices of ZnO wurtzite lattice and become interstitial metallic Zn. Furthermore, the concentration of interstitial metallic Zn increased in the pure ZnO microrods with the decreased potential. Diamagnetism was displayed by the pure ZnO microrod arrays grown with -0.8 V, while RTFM could be displayed by the pure ZnO microrod arrays grown with -1.2, -1.6, and -2.0 V. In addition, more negative potentials significantly enhanced the M_s of the pure ZnO microrod arrays. The RTFM in the pure ZnO microrod arrays could be attributed to the interstitial metallic Zn.

Diamagnetic pure ZnO nanorod arrays were formed on the silicon substrate with a ZnO seed layer through a chemical deposition method, while ferromagnetic Co-doped ZnO nanorod and microsphere arrays were synthesized on bare silicon substrates via an electrochemical deposition method, illustrating that the electrochemical deposition method rather than the chemical deposition method was capable of doping Co into ZnO matrix under a negative potential to synthesize Co-doped ZnO nano/micro structures with RTFM. The RTFM of the Co-doped ZnO nanorod and microsphere arrays could be properly interpreted using the BMP model.

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List of Nomenclatures

BMP	Bound Magnetic Polaron
$C_6H_{12}N_4$	Hexamethylenetetramine
$Co(NO_3)_2 \cdot 6H_2O$	Cobalt Nitrate Hydrate
DMS	Diluted Magnetic Semiconductor
FESEM	Field Emission Scanning Electron Microscopy
GMR	Giant Magnetoresistance Effect
H_c	Coercivity
M_r	Remanence
M_s	Saturation Magnetization
MRAM	Magnetoresistive Random Access Memory
MTJ	Magnetic Tunnel Junction
PL	Photoluminescence Spectroscopy
RTFM	Room Temperature Ferromagnetism
SEM	Scanning Electron Microscopy
T_C	Curie Temperature
TM	Transition Metal
VSM	Vibrating Sample Magnetometer
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
$Zn(NO_3)_2 \cdot 6H_2O$	Zinc Nitrate Hydrate
ZnO	Zinc Oxide

List of Publications

Journal

- (1) **X. Zhao**, E. J. Liu, R. V. Ramanujan, and J. S. Chen, “Effects of rapid thermal annealing on structural, magnetic and optical properties of Ni-doped ZnO thin films”, *Curr. Appl. Phys.* 12, 834 (2012).
- (2) Z. M. Wang, E. J. Liu, and **X. Zhao**, “Glassy carbon electrode modified by conductive polyaniline coating for determination of trace lead and cadmium ions in acetate buffer solution”, *Thin Solid Films* 519, 5285 (2011).
- (3) Y. Liu, R. V. Ramanujan, Z. W. Liu, C. Y. Tan, **X. Zhao**, E. J. Liu, and C. K. Ong, “The high frequency magnetic properties of self assembled Fe-Co-Si-N nanogranular thin films”, *Appl. Phys. A-Mater.* 100, 257 (2010).
- (4) **X. Zhao**, E. J. Liu et al., “Ferromagnetic pure ZnO needle-shaped microrod arrays”, In preparation.
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- (6) **X. Zhao**, E. J. Liu et al., “Effects of thermal annealing on structural and magnetic properties of Cu-doped ZnO thin films”, In preparation.

Conference

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Book Chapter

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Chapter 1. Introduction

1.1 Background

Spintronics (spin transport electronics or spin-based electronics) has emerged as a new technology, which is based on electron spins that carry information rather than electron charges. The spintronics offers opportunities for a new generation of devices combining standard microelectronics with spin-dependent effects that arise from the interactions between the spins of charge carriers and the magnetic properties of materials. Adding spin degrees of freedom to conventional charge-based semiconductor electronics or using spin degrees of freedom alone will substantially enhance the capabilities and performances to the electronic products. The advantages of these new devices are better nonvolatility, faster data processing, lower electric power consumption, and higher integration densities compared to conventional semiconductor devices [1].

The investigation on new materials for spintronics applications has drawn a lot of attention. The search for materials combining properties of the ferromagnet and the semiconductor has been a long-standing goal but an elusive one because of differences in crystal structure and chemical bonding [2, 3]. The major advantages of ferromagnetic semiconductors are their potential as spin-polarized carrier sources and easy integration into semiconductor devices. An ideal ferromagnetic semiconductor must possess a Curie temperature (T_C) above room temperature and must be able to incorporate not only p-type, but also n-type dopants. Eu chalcogenides are the most thoroughly studied early magnetic semiconductors. However, they failed in the

practical sense, because their ferromagnetic transition temperatures were much lower than room temperature [4]. The discovery of ferromagnetic order temperatures as high as 110 K in III-V-based diluted magnetic semiconductors (DMS) [5] has stimulated much interest.

DMS has been actively studied for the purpose of using both charges and spins of electrons in semiconductors [6-12]. In DMS, transition metal (TM) ions substitute the cations of the host semiconductor materials. Localized d electrons of the magnetic ions couple with the extended electrons in the semiconducting band. These couplings lead to a number of peculiar and interesting properties, such as magneto-optical and magneto-electrical effects [13]. Mn-doped III-V-based ferromagnetic semiconductors, such as InMnAs [14] and GaMnAs [15], have made it possible to fabricate spin injecting structures [16] as well as structures for electrical [17] or optical [18] control of ferromagnetism. However, the T_C up to 110 K of these materials is still far below room temperature required for practical device applications. Thus, a key challenge in spintronics is to increase T_C above room temperature [19]. There are theoretical predictions indicating that T_C above room temperature exists in several class of DMS materials, such as ZnO-based DMS [6].

Among DMS materials, ZnO-based DMS has drawn much attention since it is expected that ZnO-based DMS is a possible candidate to realize a ferromagnetic semiconductor with both a high T_C above 300 K and a large magnetization [19]. In 2000, Dietl et al. proposed that p-type ZnO-based DMS would achieve a high T_C above room temperature by means of hole mediation [6]. Sato and Katayama-Yoshida proposed that Co, Fe, or Ni doped n-type ZnO could possess room temperature

ferromagnetism (RTFM) [20]. However, there are still many challenges in ZnO-based DMS.

1.2 Challenges

According to references [13, 19, 21-28], contradictory experimental results on room temperature ferromagnetism (RTFM) in ZnO-based DMS systems have been reported, i.e., some researchers observed RTFM, but some others failed. Thus, it is a great challenge to explore the RTFM in ZnO-based DMS systems.

In addition, although some researchers have observed the RTFM in some ZnO-based DMS materials, the origin of RTFM still could not be satisfactorily interpreted. To properly understand the origin of RTFM in ZnO-based DMS materials is another challenge. In some cases, the RTFM in transition metal doped ZnO (TM-doped ZnO) was suggested to be a consequence of the precipitation of magnetic clusters or the formation of secondary magnetic phases [26, 29, 30] and some cases indicated that the RTFM in TM-doped ZnO could be intrinsic in origin [31-34]. A free carrier mediated exchange mechanism was proposed to induce the intrinsic RTFM in TM-doped ZnO [6, 31, 32]. However, TM-doped ZnO samples that are ferromagnetic are often poorly electrically conducting or even highly insulating, which can not be explained by the carrier-mediated model. The origin of RTFM for insulating oxide DMS has been widely explained by a bound magnetic polaron (BMP) model [35, 36], suggesting that the oxygen vacancies [10, 33, 37-39] or metallic interstitials [40, 41] in the oxide DMS materials can locally trap electrons to occupy orbitals interacting with the d subshells of doping TM neighbors, thus giving rise to the ferromagnetism.

Apart from TM-doped ZnO DMS, pure ZnO DMS has also attracted a lot of attention since RTFM was also observed in pure ZnO recently. Furthermore, the origin of the RTFM in pure ZnO has been attributed to the defects at Zn sites in ZnO thin films [42], interstitial Zn at the surface of ZnO nanorods [43], intrinsic defects in ZnO films [44], defects that cause a 469 nm emission [45], Zn nanoclusters embedded in ZnO nanowire matrices [46], and vacancies present in grain boundaries [47], etc. Hence, there is still a debate about the mechanism governing the ferromagnetic ordering in ZnO-based DMS.

Last but not least, nanostructures such as nanowires, nanorods, nanotubes and nanospheres are promising building blocks for miniaturized devices. Therefore, it is reasonable that the combination of nanostructures and RTFM in ZnO-based DMS materials would generate new functional nanomaterials useful for future miniaturized spintronic devices. However, much focus of DMS related researches has been put on thin films while limited attention has been paid to nanostructured ZnO-based DMS materials [48-51]. Thus, the investigation of nanostructured ZnO-based DMS systems forms the third challenge.

Facing such challenges, the project, development of zinc oxide-based diluted magnetic semiconductor thin films and nanostructures possessing room temperature ferromagnetism, is proposed.

1.3 Objectives

To cope with the major challenges as demonstrated in the preceding section, the thesis aims to develop zinc oxide-based diluted magnetic semiconductor (ZnO-based DMS) thin films and nanostructures possessing room temperature ferromagnetism (RTFM) for potential applications in spintronic devices with the following objectives:

- 1.) To develop pure ZnO and transition metal doped ZnO (TM-doped ZnO) DMS thin films possessing RTFM.
- 2.) To understand the origin of RTFM in the ZnO-based DMS materials.
- 3.) To develop novel pure ZnO and TM-doped ZnO DMS nanostructures possessing RTFM.

1.4 Scope

1.) Pure ZnO and TM-doped ZnO thin films are to be deposited using magnetron sputtering. The as-deposited thin films are to be annealed via rapid thermal processing or normal chamber furnace under various annealing conditions. The thermal annealing can influence the defects, the charge carriers, the distribution of elements, the chemical states of elements, and the secondary magnetic phases in the thin films, which can affect the magnetic property of the thin films. Thus, the effects of thermal annealing on the structural and magnetic properties of the thin films are to be studied to investigate the RTFM and its origin.

2.) Pure ZnO and TM-doped ZnO nanostructure arrays are to be fabricated using chemical deposition and electrochemical deposition methods. Different deposition conditions, such as different deposition methods, different solution concentrations, different potentials etc., will affect the morphology and magnetic property of the nanostructures. Thus, a comparative investigation is to be carried out to synthesize novel ZnO-based DMS nanostructures through chemical deposition and electrochemical deposition methods under different deposition conditions, which is helpful to investigate the RTFM and its origin.

3.) The surface morphology, crystal structure, chemical composition, magnetic properties and optical properties of the pure ZnO and TM-doped ZnO thin films and nanostructures will be characterized by means of scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), vibrating sample magnetometer (VSM), and photoluminescence spectroscopy (PL), respectively.

1.5 Significance

1.) In the literature, contradictory experimental results have been reported, i.e., some researchers observed the RTFM in ZnO-based DMS materials, but some others failed to find such a phenomenon. Facing such a big challenge, it is necessary to explore the RTFM in ZnO-based DMS systems.

2.) Although RTFM has been observed in some ZnO-based DMS materials, the origin of such ferromagnetism still could not be satisfactorily interpreted. Thus, it is

necessary to properly understand the origin of the RTFM in ZnO-based DMS materials.

3.) To date, most DMS related studies have been focused on thin films, while limited attention has been paid to the nanostructured ZnO-based DMS materials. Thus, it is very important to develop nanostructured ZnO-based DMS systems including patterned nanostructures arrays, which are potentially useful in spintronic devices such as data storage devices.

1.6 Novelty

1.) The RTFM in ZnO-based DMS thin films is investigated through studying the effect of thermal annealing on the structural and magnetic properties of pure ZnO thin films, Cu-doped ZnO thin films, and Ni-doped ZnO thin films. The research is carried out in terms of novel impact on the RTFM in ZnO-based DMS thin films, including the diffusion of O and TMs, the change of concentrations of oxygen vacancies and zinc interstices, and the variation of chemical states of TMs in the thin films during thermal annealing. As a result, both the Cu-doped ZnO thin films and Ni-doped ZnO thin films can display obvious RTFM, while pure ZnO thin films show room temperature diamagnetism. The origin of the RTFM is attributed to the interaction of oxygen vacancies and TMs through a bound magnetic polaron (BMP) model. Oxygen vacancies are necessary while only oxygen vacancies are not enough to induce the RTFM of ZnO-based DMS thin films.

2.) A comparative investigation is carried out to synthesize ZnO-based DMS nanostructures with RTFM through chemical deposition and electrochemical deposition methods, respectively. As a result, only the electrochemical deposition is capable of growing ferromagnetic ZnO-based DMS nanostructures with the help of a negative potential. Through the electrochemical deposition method, novel ZnO-based DMS nanostructures with RTFM are produced, including pure ZnO needle-shaped microrod arrays, Co-doped ZnO nanorod arrays, and Co-doped ZnO microsphere arrays.

1.7 Organization of Thesis

Chapter 1 highlights the background and challenges of ZnO-based DMS materials for spintronic applications, the research objectives, the scope, the significance, and the novelty of this project.

Chapter 2 surveys the state-of-the-art development of ZnO-based DMS for spintronic applications.

Chapter 3 describes the experimental details.

Chapter 4 presents and analyzes the experimental results related to ZnO-based DMS thin films, including pure ZnO thin films, Cu-doped ZnO thin films, and Ni-doped ZnO thin films.

Chapter 5 presents and analyzes the experimental results related to ZnO-based DMS nanostructures, including pure ZnO nanostructures and Co-doped ZnO nanostructures.

Chapter 6 concludes the thesis and recommends the future work.

Chapter 2. Literature Review

2.1 Magnetism

This section describes the classification of magnetic materials, especially the ferromagnetism.

2.1.1 Classification

The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials respond to magnetic fields. The main distinction is that in some materials there is no collective interaction of atomic magnetic moments, whereas in other materials there is a very strong interaction between atomic moments. The magnetic behavior of materials can be classified into the following five major groups: 1) Diamagnetism, 2) Paramagnetism, 3) Ferromagnetism, 4) Ferrimagnetism, and 5) Antiferromagnetism [52]. Diamagnetic or paramagnetic materials cannot exhibit collective magnetic interactions and are not magnetically ordered. Ferromagnetic, ferrimagnetic, or antiferromagnetic materials can exhibit long-range magnetic order below a certain critical temperature.

2.1.1.1 Diamagnetism

Diamagnetism is a fundamental property of all matter, although it is usually very weak. Diamagnetic substances are composed of atoms whose all orbital shells are

filled, so there are no unpaired electrons, no net magnetic moments, and no cooperative behavior of orbiting electrons when they are exposed to an applied magnetic field. However, a negative magnetization is produced and the susceptibility is negative when they are exposed to a magnetic field. The M-H graph can be plotted in Fig. 2.1. When the field is zero, the magnetization will be zero. The other characteristic behavior of diamagnetic materials is that the susceptibility is temperature independent as shown in Fig. 2.1.

Fig. 2.1. Schematic representations of diamagnetism [52].

2.1.1.2 Paramagnetism

For paramagnetic materials, some of the atoms or ions in the material have a net magnetic moment due to unpaired electrons in partially filled orbitals. However, the individual magnetic moments do not interact magnetically. When they are exposed to an applied magnetic field, there is a partial alignment of the atomic magnetic

moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility. However, the magnetization will be zero when the field is removed because there is no magnetic interaction between the individual magnetic moments. In addition, the efficiency of the field in aligning the moments is opposed by the randomizing effects of temperature. This results in a temperature dependent susceptibility, known as the Curie Law.

Fig. 2.2. Schematic representations of paramagnetism [52].

2.1.1.3 Ferromagnetism

For ferromagnetic materials, some of the atoms or ions in the material have a net magnetic moment due to unpaired electrons in partially filled orbitals. Unlike paramagnetic materials, the atomic moments in these materials exhibit very strong interactions. These interactions are produced by electronic exchange forces, resulting in a parallel or antiparallel alignment of atomic moments. The exchange force is a quantum mechanical phenomenon due to the relative orientation of the spins of two electrons. Ferromagnetic materials exhibit parallel alignment of magnetic moments,

resulting in large net magnetization even in the absence of a magnetic field, as shown in Fig. 2.3. The elements Fe, Ni, and Co and many of their alloys are typical ferromagnetic materials.

Fig. 2.3. Schematic representation of ferromagnetism [52].

2.1.1.4 Ferrimagnetism

Ferrimagnetism is similar to ferromagnetism. It exhibits all the hallmarks of ferromagnetic behavior, such as spontaneous magnetization, Curie temperatures, hysteresis, and remanence. However, ferrimagnetic materials have more complex forms of magnetic ordering than ferromagnetic materials. A simple representation of the magnetic spins in a ferrimagnetic oxide is shown in Fig. 2.4. The magnetic structure is composed of two magnetic sublattices, such as A and B, separated by oxygens. An exchange interactions between A and B are mediated by the oxygen anions, which are called indirect or superexchange interactions. The strongest superexchange interactions result in an antiparallel alignment of spins between the A

and B sublattice. However, the magnetic moments of the A and B sublattices are not equal, resulting in a net magnetic moment. Fe_3O_4 is a well known ferrimagnetic material.

Fig. 2.4. Schematic representation of ferrimagnetism [52].

2.1.1.5 Antiferromagnetism

Unlike ferrimagnetism, antiferromagnetism has opposite but exactly equal magnetic moments of the A and B sublattices as shown in Fig. 2.5, so the net magnetic moment is zero.

Fig. 2.5. Schematic representation of antiferromagnetism [52].

2.1.2 Characteristics of Ferromagnetism

The introduction to ferromagnetism includes magnetic domain, long range order in ferromagnet, Curie temperature, hysteresis, hysteresis loop, parameters in hysteresis loop, variations in hysteresis curves, and hysteresis in magnetic recording.

2.1.2.1 Magnetic Domain

In ferromagnetic materials, the microscopic ordering of electron spins leads to the regions of magnetic alignment called magnetic domains [53]. The unpaired electron spins line up parallel with each other in a magnetic domain. There is a high degree of magnetization within individual domains in ferromagnetic materials, but those domains are randomly oriented in the absence of external magnetic fields. A modest

applied magnetic field can cause a larger degree of alignment of the magnetic domains with the external field.

Fig. 2.6. Schematic representations of magnetic domains [53].

2.1.2.2 Long Range Order in Ferromagnet

Ferromagnetic materials exhibit a long-range ordering phenomenon at the atomic level which causes the unpaired electron spins line up parallel with each other in a domain [53]. The long range order which creates magnetic domains in ferromagnetic materials arises from a quantum mechanical interaction at the atomic level. This interaction locks the magnetic moments of neighboring atoms into a rigid parallel order over a large number of atoms in spite of the thermal agitation which tends to randomize any atomic-level order. Sizes of domains range from a 0.1 mm to a few mm. Within the individual domain of ferromagnetic material, the magnetic field is intense. However, the bulk material will usually be unmagnetized because the individual domain is randomly oriented with respect to one another in the bulk sample.

An external magnetic field can cause the magnetic domains to line up with each other and the material is magnetized. When an external magnetic field is applied, the domains already aligned in the direction of this field grow at the expense of their neighbors. The long range order in the ferromagnetic material abruptly disappears at a certain temperature which is called Curie temperature for the material.

2.1.2.3 Curie Temperature

The long range order in the ferromagnetic material abruptly disappears at a certain temperature which is called Curie temperature (T_C) for the material [53]. It is a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation. At the T_C , thermal energy eventually overcomes the electronic exchange forces and produces a randomizing effect in ferromagnets [52]. Below the T_C the ferromagnet is ordered, while above the T_C the ferromagnet is disordered. The T_C gives an idea of the amount of energy taken to break up the long range ordering in the material. The saturation magnetization goes to zero at the T_C . A typical plot of magnetization vs temperature for magnetite is shown in Fig. 2.7.

Fig. 2.7. Schematic representation of Curie temperature [52].

2.1.2.4 Hysteresis

When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the external magnetic field is removed. It must be driven back to zero by a magnetic field in the opposite direction. The lack of retraceability of the magnetization curve is the property called hysteresis [54]. Hysteresis is related to the existence of magnetic domains in the material. Once the magnetic domains are reoriented, it takes some energy to turn them back again. This property of ferromagnetic materials is useful as a magnetic memory.

2.1.2.5 Hysteresis Loop

When an alternating magnetic field is applied to the ferromagnetic material, its magnetization will trace out a loop called a hysteresis loop [54]. The magnetization M of the ferromagnet is plotted as a function of the magnetic field strength H in Fig. 2.8.

Fig. 2.8. Schematic representation of hysteresis loop [54].

2.1.2.6 Parameters in Hysteresis Loop

The saturation magnetization (M_s) is the maximum induced magnetic moment in a magnetic field [52]. In addition, beyond this magnetic field the magnetization will not further increase. M_s is an intrinsic property, independent of particle size but dependent on temperature. There is a big difference between paramagnetic and ferromagnetic susceptibility. Compared to paramagnetic materials, the magnetization in ferromagnetic materials is saturated in moderate magnetic fields at room temperature. A good ferromagnet should produce a high magnetic field with a low mass, and should be stable against the influences which would demagnetize it. The desirable properties are typically stated in terms of the remanence and coercivity of the ferromagnetic materials. When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the external magnetic field is removed. The amount of magnetization retaining at zero driving field is called remanence (M_r) [55]. It must be driven back to zero by a magnetic field in the opposite direction. The amount of reverse driving field required to demagnetize it is called coercivity (H_c) [55]. The materials with high remanence and high coercivity are magnetically hard to contrast with the magnetically soft materials.

Fig. 2.9. Schematic representation of hysteresis loop [55].

2.1.2.7 Variations in Hysteresis Curves

The variations in hysteresis curves of different magnetic materials are shown in Fig. 2.10.

Fig. 2.10. Schematic representation of variations in hysteresis curves [54].

2.1.2.8 Hysteresis in Magnetic Recording

An input signal at the level indicated by the dashed line in Fig. 2.11 could give a magnetization anywhere between C and D depending on the immediate previous history due to hysteresis. This unacceptable situation is remedied by the bias signal. The bias signal settles the magnetization down to zero if no signal is applied. If there

is a signal, it offsets the bias signal and leaves a remnant magnetization proportional to the signal offset.

Fig. 2.11. Schematic representation of hysteresis in magnetic recording [54].

2.2 Spintronics

Spintronics (spin transport electronics or spin-based electronics) has emerged as a new technology, which is based on electron spins that carry information rather than electron charges [1]. The spintronics offers opportunities for a new generation of devices combining standard microelectronics with spin-dependent effects that arise from the interactions between the spins of charge carriers and the magnetic properties of materials. Traditional approaches to using spin are based on the alignment of a spin which is up or down relative to a reference, such as an applied magnetic field or magnetization orientation of the ferromagnetic film. Device operations proceed with some quantity, such as electrical current, which depends on the degree of alignment in a predictable way. Adding the spin degree of freedom to conventional semiconductor charge-based electronics or using the spin degree of freedom alone will add

substantially more capability and performance to electronic products. The advantages of these new devices would be nonvolatility, increased data processing speed, decreased electric power consumption, and increased integration densities compared with conventional semiconductor devices. The success of spintronics depends on a deep understanding of fundamental spin interactions in solid state materials as well as the roles of dimensionality, defects, and semiconductor band structure in modifying these dynamics. If we can understand and control the spin degree of freedom in semiconductors, semiconductor heterostructures and ferromagnets, the prospect of high performance spintronics will be excellent.

2.2.1 Principles

The spintronic device principles includes spin-dependent transport, giant magnetoresistance effect (GMR), and spin-dependant transport structures.

2.2.1.1 Spin-Dependent Transport

Spin-polarized transport can occur in the material, if there is an imbalance of the spin populations at the Fermi level. This imbalance commonly occurs in ferromagnetic metals, because the density of states available to spin-up and spin-down electrons is often nearly identical, but the states are shifted in energy with respect to each other as shown in Fig. 2.12. This shift results in an unequal filling of the bands, which is the source of the net magnetic moment for the materials, but it can also cause the spin-up and spin-down carriers at the Fermi level to be unequal in number, character, and mobility. This inequality can produce a net spin polarization in an electron current

transport, resulting in the polarized current. The spin polarization of an electron current will be most readily visualized if the current is assumed to be 100% polarized as shown in Fig. 2.12. In this case, the spins of the carriers in the polarized current will only be parallel to the spin direction of the carriers at the Fermi level in the material. Therefore, there are continuing efforts to find 100% spin-polarized conducting materials which have only one occupied spin band at the Fermi level. However, materials are usually partially polarized, such as Fe, Co, Ni, and their alloys having a spin polarization P of 40 to 50%. The spin polarization P is defined in terms of the number of spin-up carriers ($n_{\uparrow}$) and the number of spin-down carriers ($n_{\downarrow}$), so $P = (n_{\uparrow} - n_{\downarrow}) / (n_{\uparrow} + n_{\downarrow})$. If the magnetization of the material is reversed, the spin direction of the carriers at the Fermi level will also reverse. Thus, depending on the magnetization direction of the material relative to the spin polarization of the current, the 100% spin-polarized conducting material can function as either a conductor or an insulator for electrons of a specific spin polarization. For the spin-polarized electrons, the magnetization of the material must be rotated 180° to stop electrical conduction.

Fig. 2.12. Schematic representations of the density of electronic states which are available to electrons in a normal metal and in a ferromagnetic metal whose majority spin states are completely filled [57]. E is the electron energy. E_F is the Fermi level. $N(E)$ is the density of states.

2.2.1.2 Giant Magnetoresistance Effect

The discovery of giant magnetoresistance effect (GMR) in 1988 [56] is considered the beginning of the spintronics. GMR is a quantum mechanical effect observed in layered thin-film structures which are composed of alternate ferromagnetic and nonmagnetic layers. When the magnetic moments of the ferromagnetic layers are parallel, the spin-dependent scattering of the carriers is minimized, and the resistance of the material is lowest. When the magnetic moments of the ferromagnetic layers are antiparallel, the spin-dependent scattering of the carriers is maximized, and the resistance of the material is highest. The directions of the magnetic moments can be manipulated by external magnetic fields applied to the materials. These materials can produce significant changes in resistance in response to relatively small magnetic fields at room temperature. Thus, the GMR has been applied to magnetic information storage [57].

Fig. 2.13 shows the basic action in a spin-polarized device using GMR. Electrons travel from a ferromagnetic metal, through a normal metal, and into a second ferromagnetic metal. When the magnetizations of the two ferromagnetic metals are in an aligned state, the resistance is low. However, when the magnetizations of the two ferromagnetic metals are in an antialigned state, the resistance is high. Actual devices are not easily fabricated in the orientation shown in Fig. 2.13, because they are made from thin films and the resistance perpendicular to the plane is too low. Another orientation provides more useful resistance as shown in Fig. 2.14, while the spin-polarized transport is more complicated. When the films are antialigned, the effect of the spin exclusion is still observed, but it results in high interface scattering and

channeling of the current into narrowed pathways. When the films are aligned, both of these resistance-generating mechanisms are removed, and the device resistance decreases.

Fig. 2.13. Schematic representations of spin-polarized transport from a ferromagnetic metal, through a normal metal, and into a second ferromagnetic metal for aligned and antialigned magnetic moments, where Ø represents the disallowed channel [57].

Fig. 2.14. 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 [57].

2.2.1.3 Spin-Dependant Transport Structures

Fig. 2.15. Schematic representations of spin-dependent transport structures: (A) spin valve, and (B) magnetic tunnel junction [1].

1.) Spin Valve

This simple GMR-based system is commonly referred to as a spin valve (Fig. 2.15A). A spin valve has two ferromagnetic layers sandwiching a thin nonmagnetic metal. The thin nonmagnetic metal is usually copper. The two ferromagnetic layers can be composed of alloys of iron, cobalt, and nickel. In addition, one of the two ferromagnetic layers is “pinned”, i.e., the magnetization in that layer is relatively insensitive to a moderate magnetic field, and the magnetic moment of that layer is very difficult to reverse in an applied magnetic field. The other ferromagnetic layer is called the “free” layer, i.e., its magnetization is relatively sensitive to a moderate magnetic field, and its magnetic moment is very easy to reverse in a relatively small magnetic field. Since the free layer is sensitive to manipulation by an external magnetic field it can act as the valve control. When the magnetizations in the two layers change from parallel to antiparallel alignment, the resistance of the spin valve typically rises from 5 to 10%. Thus, the spin valve can be used to measure or monitor the external magnetic fields. Pinning is usually accomplished by an antiferromagnetic layer which is in intimate contact with the pinned ferromagnetic layer. The two films form an interface which can resist changes in the magnetization of the pinned layer. The simple pinned layer can also be replaced with a synthetic antiferromagnet which consists of two magnetic layers separated by a very thin nonmagnetic conductor (usually Ru). The magnetizations in the two magnetic layers are strongly antiparallel coupled and are thus effectively immune to outside magnetic fields, resulting in improved stand-off magnetic fields and operation temperature of the spin valve.

2.) Magnetic Tunnel Junction

Magnetic tunnel junction (MTJ) is another GMR-based structure which is similar to the spin valve but uses spin-polarized tunneling. The pinned layer and the free layer are separated by a very thin insulating layer, commonly aluminum oxide, as shown in Fig. 2.15B. The concept of MTJ device is illustrated in Fig. 2.16. In any tunneling device, two conducting layers are separated by a very thin insulating layer. Upon applying a voltage, because the potential energy of the acceptor layer is lowered, the electron can quantum mechanically tunnel through the barrier and reappear on the acceptor layer. The tunneling probability linearly increases as the increased voltage. In normal tunneling device, normal metals are used as conducting contacts. However, in MTJ device, the two conductors are ferromagnetic. As a result, an additional barrier is introduced that is spin-dependent, and a spin-polarized tunneling occurs. Spin-polarized tunneling was first reported in 1975 as a low temperature effect in which Ge formed the tunneling barrier [62]. The technique was not used until the early 1990s, when spin-polarized tunneling through an alumina barrier was reported at room temperature [63]. Thus, the GMR effect also occurs. When the two ferromagnetic layers are magnetically aligned, the impedance is low. However, when they are antialigned, the impedance is high. The operational modes are similar to the spin valve, with one magnetically hard layer and one soft layer. However, the MTJ devices generally carry much lower currents than the all-metal GMR devices, which is an advantage for portable devices that have limited power. In addition, because the tunneling current density is usually small, MTJ devices tend to have high resistances. Thus, the large changes in device impedance ($\sim 30\%$) at room temperature have already permitted MTJ to be applied in device technology.

Fig. 2.16. Schematic representation of a magnetic tunnel junction formed by a thin insulating barrier separating two ferromagnetic metal films [57].

2.2.2 Devices

The GMR was discovered in 1988 [56]. The first commercial product using GMR was available in 1994, which is a magnetic field sensor [58]. The first products having a major economic impact are read heads for magnetic hard disk drives, which were announced by IBM in 1997 [59]. The next major economic impact from GMR is anticipated to come from nonvolatile magnetic computer memory. Honeywell Corporation announced the demonstration of GMR-based magnetoresistive random access memory (MRAM) in 1997 [60].

2.2.2.1 Read Heads for Magnetic Hard Disk Drives

The first application of GMR producing a substantially large economic impact is the GMR read heads for magnetic hard disk drives, which are components of every computer. GMR spin valve read heads are dominating applications in hard disk drives. The read head senses the magnetic bits stored on the disks. This information is stored in magnetized regions of the media called magnetic domains along tracks as shown in Fig. 2.17. Magnetization is stored as a “0” in one direction while as a “1” in the other direction. A domain wall exists between two oppositely magnetized domains, which is a microscopic region of 100 to 1000 Å. No magnetic field emanates from the interior of a magnetic domain. However, in the vicinity of the domain walls, uncompensated magnetic poles generate magnetic fields which extend out of the media. These magnetic fields are sensed by the GMR read head. Where the heads of two domains meet, uncompensated positive poles generate a magnetic field directing out of the media. Where the tails of two domains meet, uncompensated negative poles generate a magnetic field returning back into the media. The GMR read head is fabricated [61], in which the magnetic moment in the free layer lies parallel to the plane of the media in the absence of any applied fields, while the magnetic moment in the pinned layer is perpendicular to the plane of the media. When the GMR read head passes over a positive domain wall, the magnetic field pushes up the magnetic moment in the free layer. When the GMR read head passes over a negative domain wall, the magnetic field pulls down the magnetic moment in the free layer. The measured resistance of the GMR element increases for more antialigned layers while decreases for more aligned layers. The design goal for the GMR element is to obtain a maximum rate of change in the resistance corresponding to a change in the sensed

field. The resulting change in the resistance is sensed by the current i passing through the GMR read head.

Fig. 2.17. Schematic representation of a GMR read head (green) that passes over recording media containing magnetized regions [57].

2.2.2.2 Magnetoresistive Random Access Memory

The next application of GMR that is expected to have a large economic impact is nonvolatile memory. Nonvolatile means that the information storage does not evaporate when the power is removed from a system. Magnetic disks and tapes are the most widespread nonvolatile information storage media due to their long storage lifetime, low cost, and lack of any wear-out mechanism. Honeywell has demonstrated that GMR elements can be fabricated in arrays with lithographic processes to obtain nonvolatile memory which has speed and density approaching that of volatile semiconductor memory [60]. The structure of such an array is shown in Fig. 2.18. The GMR elements are essentially spin valve structures which are arranged in series and

connected by lithographic wires to form a sense line. The sense line stores the information and has a resistance which is the sum of the resistance of its GMR elements. When current runs through the sense line, amplifiers at the ends of the sense line detect changes in resistance in the GMR elements. The magnetizations of the GMR elements are manipulated by the magnetic fields which are provided by additional lithographic wires above and below the GMR elements. These lithographic wires cross the sense lines in a xy grid pattern and intersect with each GMR element.

These networks of lithographic wires are all electrically insulated. When current pulses run through them, they can generate magnetic fields acting on the magnetic elements in the GMR elements. A typical addressing scheme uses pulses in the overlay and underlay wires called word lines and bit lines which are half-select. Half-select means that the magnetic field associated with a word-line pulse can only half reverse the magnetization of a spin valve element. However, at any overlap of word line and bit line in the xy grid, the two half-select pulses can generate a combined magnetic field which is sufficient to completely reverse the free layer in the spin valve element. A higher current is also sufficient to reverse the pinned layer. Typically, one pulse rotates the layer 90° , and the second pulse rotates it the remaining 90° to complete the task. Through this xy grid, any GMR element of an array can be addressed to store information or be interrogated.

The information storage and addressing schemes may be varied. One scheme may store information in the free layer and interrogate information using “destroy” and “restore” procedures. For another scheme, high-current pulses are used to store information in the pinned layer, while low-current pulses can then be used to wiggle

the free layer to change resistance to interrogate information without destroying and restoring the information. There are many additional schemes depending on the specific requirements of the memory application including the power consumption, speed of reading, speed of writing, density of information stored, and cost of fabrication. Each application dictates the preferred approach.

Fig. 2.18. Schematic representation of MRAM that is constructed of GMR spin valve elements connected in series [57].

Compared to spin valve structures, MTJ structures have advantages including larger change in magnetoresistance and lower power consumption. Thus, IBM proposed an entirely different approach to obtain nonvolatile magnetic memory which is MTJ-based MRAM using spin polarized tunneling. The memory array architecture of MTJ-based MRAM is shown in Fig. 2.19. The high impedance of MTJ precludes the sense-line scheme used in the spin-valve-based MRAM. Instead, a xy intersecting grid array is used. A MTJ is located at every point of intersection. This approach provides a four-point probe arrangement. Two probes provide the current, while two probes

permit an independent voltage measurement. The leads can provide a dual service. As far as reading is concerned, the conducting wires provide current to the junctions and permit voltage measurements to be made. As far as writing is concerned, the conducting wires carry pulse currents running above and below MTJ rather than through the device to provide the magnetic fields to manipulate the magnetization directions in the ferromagnetic layers. This configuration is similar to the addressing scheme of the spin-valve-based MRAM. However, one problem is that such an array is multiply shorted through the elements. The electrical path from an input lead to an output lead can proceed through many elements, not just the one at the intersection. The solution to this old problem with grid arrays is to place a diode at every intersection. The current will pass in only one direction to eliminate alternative paths. Thus, the extremely high density MTJ-based MRAM will be constructed.

Fig. 2.19. Schematic representation of MRAM that is constructed of magnetic tunnel junctions connected together in a point contact array [57].

2.2.3 New Materials

The investigation on new materials for spintronics applications has drawn a lot of attention. One approach is to search new materials which can exhibit large carrier spin

polarization. Half-metal is definitely a good candidate. A half-metal is any substance that acts as a conductor to electrons of one spin orientation, but as an insulator or semiconductor to electrons of the opposite spin orientation. In half-metals, the valence band for one spin orientation is partially filled while there is a gap in the density of states for the other spin orientation, which means that the Fermi level intersects only one of the two spin bands while resides in a band gap of the other spin band, resulting in the conducting behavior for only electrons in the first spin orientation while insulating or semiconducting behavior for electrons in the other spin orientation. Some notable half-metals are magnetite (Fe_3O_4) [71], Heusler alloys [64, 65], lanthanum strontium manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) [67, 69, 70], and chromium dioxide (CrO_2) [66, 73]. Half-metallic Fe_3O_4 nanocontacts have show magnetoresistance which was interpreted in terms of very high spin polarization of the transport carriers [71]. There are efforts to produce magnetic Heusler alloys. The ferromagnetic single crystal alloy Ni_2MnGa has been grown on GaAs by molecular beam epitaxy [64]. NiMnSb has been used in spin-polarized tunneling junctions, while its conduction electron spin polarization was only about 28% contrary to the predicted value of 100% [65]. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is a good candidate for half-metals [67]. $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ has shown a spin polarization of 72% in spin-polarized tunneling junctions but at 0.3 K [69]. $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ has also shown a high spin polarization at low temperature, while this spin polarization decreased almost to zero near and above room temperature, indicating that the lanthanum strontium manganite will not provide spin polarized sources for room temperature applications [70]. CrO_2 is also a good candidate for half-metals [66]. Half-metallic CrO_2 has been capable of yielding a high spin polarization of about 96% which was determined by the point contact Andreev reflection, but at 1.85 K [73].

The search for materials combining properties of the ferromagnet and the semiconductor has been a long-standing goal but an elusive one because of differences in crystal structure and chemical bonding [2, 3]. The major advantages of ferromagnetic semiconductors are their potential as spin-polarized carrier sources and easy integration into semiconductor devices. An ideal ferromagnetic semiconductor must possess a Curie temperature (T_C) above room temperature and must be able to incorporate not only p-type, but also n-type dopants. Eu chalcogenides are the most thoroughly studied early magnetic semiconductors. However, they failed in the practical sense, because their ferromagnetic transition temperatures were much lower than room temperature [4]. The discovery of ferromagnetic order temperatures as high as 110 K in III-V-based diluted magnetic semiconductors (DMS) [5] has stimulated much interest. There are theoretical predictions indicating that T_C above room temperature exists in several class of DMS materials [6].

Thus, diluted magnetic semiconductors (DMS) have attracted a lot of attention as potential candidates for spintronic applications [1, 37, 57].

2.3 Diluted Magnetic Semiconductor

DMS has been actively studied for the purpose of using both charges and spins of electrons in semiconductors [6-12]. In DMS, transition metal (TM) ions substitute the cations of the host semiconductor materials. Localized d electrons of the magnetic ions couple with the extended electrons in the semiconducting band. These couplings lead to a number of peculiar and interesting properties, such as magneto-optical and magneto-electrical effects [13]. Mn-doped III-V-based ferromagnetic semiconductors,

such as InMnAs [14] and GaMnAs [15], have made it possible to fabricate spin injecting structures [16] as well as structures for electrical [17] or optical [18] control of ferromagnetism. However, the T_C up to 110 K of these materials is still far below room temperature required for practical device applications. Thus, a key challenge in spintronics is to increase T_C above room temperature [19]. There are theoretical predictions indicating that T_C above room temperature exists in several class of DMS materials, such as ZnO-based DMS [6].

ZnO-based DMS has drawn much attention since it is expected that ZnO-based DMS is a possible candidate to realize a ferromagnetic semiconductor with both a high T_C above 300 K and a large magnetization [19].

2.4 Zinc Oxide-Based Diluted Magnetic Semiconductor

This section describes the fundamental knowledge on pure ZnO and the development of ZnO-based DMS.

2.4.1 Zinc Oxide

There has been a great deal of interest in zinc oxide (ZnO) semiconductor materials. The interest in ZnO is fueled by its prospects in optoelectronics applications owing to its direct wide band gap ($E_g \sim 3.3$ eV at 300 K). Some optoelectronic applications of ZnO overlap with that of GaN. GaN is another wide-gap semiconductor ($E_g \sim 3.4$ eV at 300 K) which is widely used for production of green, blue-ultraviolet, and white light-emitting devices. However, ZnO has advantages over GaN, such as the

availability of high-quality ZnO bulk single crystals and a large exciton binding energy (~ 60 meV). ZnO also has much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices.

ZnO is an II-VI compound semiconductor whose ionicity resides at the borderline between covalent and ionic semiconductor. The crystal structures shared by ZnO are wurtzite (B4), zinc blende (B3), and rocksalt (B1), as shown in Fig. 2.20 [75]. At ambient conditions, the thermodynamically stable phase is wurtzite. The zinc-blende ZnO structure can be stabilized only by growth on cubic substrates. The rocksalt (NaCl) structure may be obtained at relatively high pressures.

Fig. 2.20. Stick and ball representations of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4) [75]. The shaded gray and black spheres denote Zn and O atoms, respectively.

The wurtzite structure has a hexagonal unit cell with two lattice parameters, a and c , in the ratio of $c/a = (8/3)^{1/2} = 1.633$ and belongs to the space group of C_{6v}^4 or $P6_3mc$. A schematic representation of the wurtzitic ZnO structure is shown in Fig. 2.21. The structure is composed of two interpenetrating hexagonal-close-packed (hcp) sublattices. Each hcp consists of one type of atom displaced with respect to each other along the threefold c -axis by the amount of $u = 3/8 = 0.375$ in fractional coordinates in an ideal wurtzite structure. The u parameter is defined as the length of the bond parallel to the c axis, in units of c . Each sublattice includes four atoms per unit cell and every atom of one kind (group-II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges of a tetrahedron. In a real ZnO crystal, the wurtzite structure deviates from the ideal arrangement by changing the c/a ratio or the u value.

Fig. 2.21. Schematic of a wurtzitic ZnO structure having lattice constants a in the basal plane and c in the basal direction [75]. The parameter u is expressed as the bond length or the nearest-neighbor distance b divided by c (0.375 in an ideal crystal), and α and β (109.47° in an ideal crystal) are the bond angles.

The wurtzite ZnO can be transformed to the rocksalt (NaCl) structure at relatively modest external hydrostatic pressures. The zinc-blende ZnO structure is metastable and can be stabilized only by heteroepitaxial growth on cubic substrates, such as ZnS, GaAs/ZnS, and Pt/Ti/SiO₂/Si, reflecting topological compatibility to overcome the intrinsic tendency of forming a wurtzite phase.

2.4.2 Zinc Oxide-Based Diluted Magnetic Semiconductor

In 2000, Dietl et al. predicted that p-type ZnO-based DMS would have a high T_C above room temperature [6], as shown in Fig. 2.22. However, contrary to Dietl's prediction that hole mediation is necessary for obtaining high temperature ferromagnetism, Sato and Katayama-Yoshida predicted that Co, Fe, Ni, doped n-type ZnO would display room temperature ferromagnetism [20]. Ferromagnetism of ZnO-based magnetic semiconductors was investigated by ab initio calculations based on the local density approximation. In a system of Mn atom doped ZnO, the ferromagnetic ordering of Mn magnetic moments was induced by hole doping. It was also found that 3d transition metal atoms of V, Cr, Fe, Co and Ni showed the ferromagnetic ordering of their magnetic moments in ZnO without any additional carrier doping treatments. Appearance of the ferromagnetism in these systems suggests possibility for a fabrication of a transparent ferromagnet which will have great impact on industrial applications in magneto optical devices. In addition, Sato et al. [76] suggested theoretically that the ferromagnetic state in Mn-, Fe-, Co-, and Ni-doped ZnO-DMS can be stabilized.

Fig. 2.22. Computed values of the Curie temperature T_C for various p-type semiconductors containing 5% of Mn and 3.5×10^{20} holes per cm^3 [6].

Thus, ZnO-based DMS has drawn much attention, the researchers have done a lot of work to produce the transition metal doped ZnO and obtain the room temperature ferromagnetism. Lately a few experimental results were reported [13, 19, 21-28]. However, through the experiments, some people obtained the room temperature ferromagnetism, but the others failed. Studies to date have been contradictory.

Therefore, can we obtain the room temperature ferromagnetism in ZnO-based DMS through the experiment? This is the first challenge we are facing in the ZnO-based DMS system.

2.4.2.1 Room Temperature Ferromagnetism in Zinc Oxide-Based Diluted Magnetic Semiconductor

The phenomenon of RTFM in ZnO-based DMS is not consistent through experiments.

1.) No Room Temperature Ferromagnetism

Ueda et al. formed n-type 3d-transition-metal-doped ZnO films ($\text{Zn}_{1-x}\text{TM}_x\text{O}$, TM = Co, Mn, Cr, and Ni) on sapphire substrates with the pulsed laser deposition [21]. However, the Mn, Cr, or Ni-doped ZnO films did not show RTFM. Only Co-doped ZnO films could display RTFM, but its reproducibility was less than 10%. Jin et al. employed combinatorial laser molecular beam epitaxy method to fabricate epitaxial ZnO thin films doped with all the 3d transition metal (TM: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) ions in a high throughput fashion [24]. However, contrary to the theoretical predictions, they have detected no indication of ferromagnetism for $\text{Zn}_{1-x}\text{TM}_x\text{O}$ (TM = Cr, Mn, Fe, Co, Ni, and Cu) films down to 3 K. Rao et al. reported the absence of ferromagnetism in Mn- and Co-doped ZnO [77]. The Mn- and Co-doped ZnO samples were prepared by the low temperature decomposition of acetate solid solutions, but they did not show RTFM. Tiwari et al. found no evidence for RTFM in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films [78]. The $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films were deposited on sapphire substrate by the pulsed laser deposition. However, those films could only show paramagnetism.

2.) Room Temperature Ferromagnetism

Lee et al. reported Co-doped ZnO DMS films [13]. The $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films were fabricated by the sol-gel method, which exhibited ferromagnetic behavior with a T_C higher than 350 K. Cho et al. investigated effects of rapid thermal annealing on the ferromagnetic properties of CoFe-doped ZnO thin films [19]. The $\text{Zn}_{1-x}(\text{Co}_{0.5}\text{Fe}_{0.5})_x\text{O}$ thin films were deposited by the reactive magnetron co-sputtering, and then annealed under vacuum with the rapid thermal annealing. Ferromagnetism was only observed below room temperature in the as-deposited thin films. However, the rapid thermal annealing led to a significant increase in T_C , resulting in RTFM with $T_C > 300$ K for the CoFe-doped ZnO thin films. Ramachandran et al. studied $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ DMS thin films [79]. The $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ thin films were grown on the c plane of sapphire single crystal substrates by pulsed laser deposition. Those films exhibited ferromagnetism at room temperature. Sharma et al. reported ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO [80]. The $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ bulk pellets were produced by sintering MnO_2 and ZnO powders in air. The $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin films were deposited on fused quartz substrates by a pulsed laser ablation technique. Both the bulk pellets and thin films displayed ferromagnetism above room temperature.

Although some researchers have obtained RTFM in ZnO-based DMS, they still cannot exactly explain the origin of the RTFM. What is the origin of the RTFM in ZnO-based DMS? This is the second challenge we are facing in the ZnO-based DMS system.

2.4.2.2 Origin of Room Temperature Ferromagnetism in Zinc Oxide-Based Diluted Magnetic Semiconductor

People did a lot of work to investigate the origin of the RTFM in ZnO-based DMS and proposed some possible explanations. In some cases, RTFM in TM-doped ZnO was suggested to be a consequence of the precipitation of magnetic clusters or the formation of secondary magnetic phases [26, 29, 30]. In some other cases, RTFM in TM-doped ZnO was suggested to be intrinsic in origin [31-34]. A free carrier mediated exchange mechanism was proposed to induce the intrinsic RTFM in TM-doped ZnO [6, 31, 32]. However, ferromagnetic TM-doped ZnO materials are often poorly electrically conducting or even highly insulating, which cannot be explained by the carrier-mediated model. The origin of RTFM for insulating oxide DMS has been widely explained by the bound magnetic polaron (BMP) model [35, 36], suggesting that oxygen vacancies [10, 33, 37-39] or metallic interstitials [40, 41] in oxide DMS materials locally trap electrons to occupy orbitals interacting with the d subshells of neighboring TM dopants, resulting in the ferromagnetism.

However, there is still a debate about the mechanism governing the ferromagnetic ordering in ZnO based DMS. Nobody can make sure which one is the most suitable explanation.

1.) Secondary Magnetic Phases

Zhou et al. considered crystalline Ni nanoparticles as the origin of ferromagnetism in Ni implanted ZnO crystals [81]. They reported the structural and magnetic properties

of ZnO single crystals implanted at 623 K with up to 10 at. % of Ni. As revealed by x-ray diffraction, crystalline fcc-Ni nanoparticles were formed inside ZnO. The ferromagnetism was observed in Ni implanted ZnO crystals at 10 K but not room temperature. The magnetic behavior of all samples is well explained by a magnetic Ni-nanoparticle system. Although the formation of Ni: ZnO based diluted magnetic semiconductor cannot be ruled out, the major contribution to the magnetic properties stems from crystalline Ni nanoparticles synthesized under these implantation conditions.

2.) Defects

Coey et al. proposed a defect (the oxygen vacancy) mediated mechanism to explain the ferromagnetism in Fe-doped SnO_2 thin films, which was F-center exchange as shown in Fig. 2.23 [9]. Thin films were grown by pulsed laser deposition, which had a high T_C of 610 K. Oxygen vacancies arose naturally to ensure charge neutrality when trivalent ions were substituted in SnO_2 . The Fe^{3+} -□- Fe^{3+} group was common in the structure, where □ denoted an oxygen vacancy. An electron would be trapped in the oxygen vacancy to constitute an F center. The trapped electron occupied an orbital which overlapped the d shells of both iron neighbors. Since 3d⁵ of Fe^{3+} only has unoccupied minority spin orbitals, the trapped electron would have spin down and the two iron neighbors would have spin up. This direct ferromagnetic coupling between the two iron neighbors was called F-center exchange, where the F-center was similar to Kasuya's bound magnetic polaron. Thus, the ferromagnetic coupling of ferric ions via an electron trapped in a bridging oxygen vacancy (F center) induced the ferromagnetism with the high T_C .

Fig. 2.23. Schematic representations of (a) superexchange and (b) F-center exchange [9].

Liu et al. systematically investigated effects of hydrogenated annealing on structural defects, conductivity, and magnetic properties of V-doped ZnO powders [82]. The V-doped ZnO powders had a mixed paramagnetic and ferromagnetic phase, which could be understood in the form of BMP model, as shown in Fig. 2.24. In the as-made V-doped ZnO powders, the defects were insufficient, so most of the V ions were distributed as uncoupled spins or isolated BMPs to form the paramagnetic phase, and only a small portion of BMPs could overlap to form the ferromagnetic phase, resulting in a predominant paramagnetic phase mixed with a minor ferromagnetic phase. Thus, the RTFM in the as-made V-doped ZnO powders was very weak. Hydrogenated annealing for oxides could be more efficient at removing oxygen,

reducing the valence state of 3d ions, and increasing the structural defects. In addition, the increased annealing temperature could produce more structural defects to connect more BMPs together to enhance the ferromagnetic phase and M_s for the V-doped ZnO powders. Thus, the M_s increased with increasing hydrogenated annealing temperature. In conclusion, it was suggested that the ferromagnetism in V-doped ZnO powders was correlated to the structural defects.

Fig. 2.24. Schematic representations of bounded magnetic polarons in V-doped ZnO powders: (a) as-made, (b) annealed at 300 °C, (c) annealed at 500 °C, and (d) annealed at 700 °C [82].

3.) Carriers

The carrier-induced ferromagnetism (RKKY or double exchange mechanism) is often reported for the III-V semiconductors [18, 83]. Ueda et al. reported that highly conducting n-type Co-doped ZnO films could display RTFM [21]. The $Zn_{1-x}Co_xO$

films were formed on sapphire substrates using a pulsed laser deposition technique, which exhibited ferromagnetism with a T_C higher than room temperature. The Co ions substituted for Zn sites in ZnO wurtzite lattice without changing the wurtzite structure. The T_C and the M_s of the films increased as the carrier concentration increased. Moreover, RTFM was only observed in the films with the high carrier density. Thus, the RTFM in the $Zn_{1-x}Co_xO$ films depended on the concentration of Co ions and carriers.

4.) Others

K. Potzger et al. have investigated the Fe implanted ferromagnetic ZnO [12]. Room-temperature ferromagnetism has been induced within ZnO single crystals by implant doping with Fe ions. For an implantation temperature of 623 K and an ion fluence of $4 \times 10^{16} \text{ cm}^{-2}$ (HFHT: high fluence and high temperature), very tiny Fe particles, formed inside the host matrix, are responsible for the ferromagnetic properties. On the other hand, Fe ions implanted at a temperature of 253 K and an ion fluence of $4 \times 10^{15} \text{ cm}^{-2}$ (LFLT: low fluence and low temperature) are incorporated into the host matrix and develop a room temperature diluted magnetic semiconductor. The ferromagnetic behavior of the LFLT sample results from an indirect exchange interaction between diluted Fe ions.

Norton et al. have reported the magnetic and structural properties of cobalt-implanted ZnO single crystals [85]. High-quality, (110)-oriented single-crystal Sn-doped ZnO substrates were implanted at $\sim 350^\circ\text{C}$ with Co to yield transition metal concentrations of 3-5 at. % in the near-surface ($\sim 2000 \text{ \AA}$) region. After implantation,

the samples were subject to a 5 min rapid thermal annealing at 700 °C. Magnetization measurements indicate ferromagnetic behavior, with hysteresis observed in the M vs H behavior at T = 55 K. Coercive fields were 100 Oe at this measurement temperature. Temperature-dependent magnetization measurements showed evidence for ordering temperatures of > 300 K, although hysteresis in the M vs H behavior was not observed at room temperature. Four-circle x-ray diffraction results indicate the presence of (110)-oriented hexagonal phase Co in the ZnO matrix. From the 2 θ full width at half maximum (FWHM) of the Co (110) peak, the nanocrystal size is estimated to be ~ 3.5 nm, which is below the superparamagnetic limit at room temperature. In-plane x-ray diffraction results show that the nanocrystals are epitaxial with respect to the ZnO host matrix. The magnetic properties are consistent with the presence of Co nanocrystals, but do not preclude the possibility that a component of the magnetism is due to Co substitution on the Zn site in the ZnO matrix.

Ramachandran et al. reported the effect of oxygen annealing on Mn doped ZnO diluted magnetic semiconductors [32]. They grew epitaxial single crystal $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.01, 0.05$ and 0.1) thin films on c-plane sapphire single crystals using pulsed laser deposition process and varied the electrical properties to investigate magnetic properties at two extremes in resistivity, namely, semiconducting (as-deposited films) and highly insulating (films annealed at 600 °C in flowing oxygen) states. The XRD and HRTEM results along with EELS convincingly excluded any possibility of nanosized clustering or secondary phase formation. Optical characterization using absorption spectroscopy indicated that the band gap increases with increasing Mn concentration, implying a uniform substitution of Mn ions for Zn in the lattice. They observed ferromagnetism at both the room and low temperatures in conducting

samples but in the insulating samples no sign of ordering was apparent except at very low temperatures and very low concentrations of the dopant. This is consistent with their hypothesis that ferromagnetic ordering is introduced through either carrier-mediated (electrons in this case) or defect-mediated (oxygen vacancies) processes. It was envisaged that in insulating samples, where free carriers are not present, the bound magnetic polaron (BMP) mechanism may be operative at very low temperatures and low Mn concentrations.

2.4.2.3 Copper-Doped Zinc Oxide Diluted Magnetic Semiconductor

TM-doped ZnO DMS has drawn much attention because of the T_C above room temperature [6]. Typical materials include ZnO doped with V, Cr, Mn, Fe, Co, or Ni [86]. A drawback of these materials is that the doped TM can segregate to form magnetic precipitates or clusters being responsible for the RTFM. The effect of such ferromagnetic clusters must be carefully examined before the usefulness of such materials can be determined for spintronic applications [87]. Thus, Cu-doped ZnO has drawn the attention, because the Cu^{2+} ion has a potential magnetic moment of $+1/2$, but metallic Cu is not magnetic and neither Cu_2O nor CuO is ferromagnetic [88]. The latter removes any possibility that the RTFM in the Cu-doped ZnO is from magnetic nanoclusters and secondary phases. Thus, Cu-doped ZnO has the possibility to be free of ferromagnetic precipitates and form an unambiguous DMS. In addition, both theoretical [89, 90] and experimental [91-94] reports have found RTFM in the Cu-doped ZnO. Initial theoretical studies indicated ZnO doped with 3.125% Cu [89] and 6.25% [95] should be ferromagnetic. Many experimental reports have found RTFM in the Cu-doped ZnO [91-94]. ZnO thin films doped with 0.3% Cu was suggested to be a

DMS [96]. ZnO powders doped with 2% and 5% Cu showed ferromagnetism [97]. In addition, it was suggested that there was no correlation between carrier concentration and ferromagnetic ordering and the free carrier mediated exchange was not playing a role in the RTFM of Cu-doped ZnO [37, 93, 98].

Buchholz et al. investigated the RTFM in Cu-doped ZnO thin films grown by the pulsed laser ablation [91]. The n-type films grown under an O₂ ambient were nonmagnetic, while p-type films grown under an N₂O ambient were ferromagnetic with a T_C above 350 K. It is consistent with the theoretical studies. Sato et al. indicated that the ferromagnetic ordering of Mn-doped ZnO is favored by p-type ZnO, while the antiferromagnetic ordering is favored by n-type ZnO [20]. Diel et al. suggested that holes are more effective in mediating ferromagnetic interactions in III-V and II-VI magnetic semiconductors [6]. Spaldin predicted that the robust ferromagnetism will only be obtained in p-type TM-doped ZnO [99].

Chakraborti et al. investigated the effect of oxygen annealing on Cu-doped ZnO and CuAl-doped ZnO DMS [37]. The thin films were grown epitaxially on a (0001) sapphire substrate by the pulsed laser deposition technique, and annealed in oxygen at 600 °C. The additional doping of Al in Cu-doped ZnO thin films increased the carrier concentration but did not alter the ferromagnetic ordering indicating that the free carrier mediated mechanism was not responsible for the RTFM. However, a decreased oxygen vacancies concentration after the annealing in oxygen had a large detrimental effect on the RTFM indicating that the defect mediated mechanism was responsible for the RTFM, such as the bound-magnetic-polaron mediated exchange. The role of oxygen vacancies in RTFM has been reported for a number of systems,

such as Fe-doped SnO₂ [100], Mn-doped ZnO [32], and Co-doped ZnO [39, 101]. Prater et al. [39] and Huang et al. [101] reported that the concentration of oxygen vacancies in Co-doped ZnO was reduced after annealing in oxygen which led to a reduction in ferromagnetic order. Hsu et al. reported that the increased oxygen vacancies enhanced the ferromagnetism in Co-doped ZnO films [33]. Rubi et al. reported that the annealing in N₂ enhanced while the annealing in O₂ suppressed the ferromagnetic ordering in Co-doped ZnO, indicating the native defects are responsible for the ferromagnetic ordering [102]. Apart from oxygen vacancies, another shallow donor, Zn interstitials, can also be responsible for the ferromagnetism [41, 103]. Ferromagnetic coupling due to native defects like oxygen vacancies can be explained by the formation of a F-centre or bound magnetic polaron (BMP) [41]. An electron loosely bound to a charged defect, e.g. the oxygen vacancy, occupies an extended orbital around the defect forming an F-centre or BMP. These overlap to form a spin-split impurity band. These electrons couple with the 3d spins of the magnetic dopant ions that lie within the extended orbital of the BMP. The Cu²⁺ exists in a 3d⁹ state and thus presents only one unoccupied orbital. The loosely bound electron will align in an anti-parallel configuration with the spin of the individual Cu²⁺ ion, inducing that the spins of the neighbouring Cu²⁺ ions align in a parallel configuration with each other, resulting in an effective ferromagnetic coupling between the Cu²⁺ moments. After annealing in oxygen, the oxygen content increased, the oxygen vacancy decreased, and the BMP concentration decreased in the thin films. The ferromagnetic exchange coupling between the 3d spins of the Cu²⁺ ions were weakened, so the M_s decreased. Thus, the defect (oxygen vacancy) mediated mechanism was responsible for the RTFM in the Cu-doped ZnO DMS, such as bound magnetic polaron mediated mechanism or F-centre exchange mediated mechanism.

2.4.2.4 Pure Zinc Oxide Diluted Magnetic Semiconductor

Apart from TM-doped ZnO DMS, pure ZnO DMS has also attracted a lot of attention since RTFM was also observed in pure ZnO recently. Furthermore, the origin of the RTFM in pure ZnO has been attributed to the defects at Zn sites in ZnO thin films [42], interstitial Zn at the surface of ZnO nanorods [43], intrinsic defects in ZnO films [44], defects that cause a 469 nm emission [45], Zn nanoclusters embedded in ZnO nanowire matrices [46], and vacancies present in grain boundaries [47], etc.

Hong et al. observed RTFM in laser-ablated ZnO thin films [42]. The RTFM in this type of compound does not stem from oxygen vacancies as in the case of TiO_2 and HfO_2 films, but from defects on Zn sites. Magnetization of very thin films is much larger than that of the thicker films, showing that defects must be located mostly at the surface and/or the interface between the film and the substrate. Results on Fe-doped ZnO and Mn-doped ZnO films reveal clearly that the metal-transition doping does not play any essential role in introducing the magnetism in ZnO.

Yan et al. reported the impact of annealing on morphology and ferromagnetism of ZnO nanorods [43]. RTFM has been observed in ZnO nanorods prepared by hydrothermal method. Annealing at 900 °C in air transformed the nanorods into twinning structures and weakened the magnetizations. The PL spectra indicated that the concentration of oxygen vacancy and singly negative charged zinc vacancy increased, while the concentration of interstitial zinc decreased after annealing. Since the magnetization of as-prepared sample decreased after annealing, the RTFM in the nanorods should not come from the oxygen vacancy but the interstitial zinc. The level

of interstitial zinc lies close to the bottom of the conduction band, which will induce strong interaction between the localized interstitial Zn 4s level and the conduction band. Thus, the interstitial zinc at the surface may contribute to the RTFM in ZnO nanorods.

Xu et al. reported Room temperature ferromagnetism in ZnO films due to defects [44]. ZnO films were prepared by pulsed laser deposition on *a*-plane sapphire substrates under N₂ atmosphere. Ferromagnetic loops were obtained with the superconducting quantum interference device at room temperature, which indicate a Curie temperature much above room temperature. No clear ferromagnetism was observed in intentionally Cu-doped ZnO films. This excludes that Cu doping into ZnO plays a key role in tuning the ferromagnetism in ZnO. 8.8% negative magnetoresistance probed at 5 K at 60 kOe on ferromagnetic ZnO proves the lack of *s-d* exchange interaction. Anomalous Hall effect (AHE) was observed in ferromagnetic ZnO as well as in nonferromagnetic Cu-doped ZnO films, indicating that AHE does not uniquely prove ferromagnetism. The observed ferromagnetism in ZnO is attributed to intrinsic defects.

Yan et al. reported surfactant-free fabrication of ZnO spheres and pseudospherical structures [45]. ZnO spheres and pseudospherical structures have been synthesized by a surfactant-free wet chemical method. The products were formed by a dissolution/precipitation mechanism. Room temperature ferromagnetism has been observed in the products, which could be affected not only by annealing but also by ultrasonic treatment. Photoluminescence measurement reveals that the ferromagnetism may relate to the defects that cause the 469 nm emission, and the products mainly show blue emission in the visible band after annealing. The low-cost

and high-yield synthesis method makes the products promising materials for optoelectronic and spintronic devices.

Yi et al. reported room temperature ferromagnetism in ZnO nanowires derived from electro-deposition on anodic aluminum oxide (AAO) template and subsequent oxidation [46]. ZnO nanowires were prepared by electro-deposition into an AAO template, and subsequent oxidation through annealing under air atmosphere. Zn nanowires were firstly formed during electro-deposition into the AAO template with nanometer-sized pores. The as-deposited Zn nanowires were non-ferromagnetic. ZnO nanowires were formed by oxidation of the Zn nanowires. ZnO nanowires with the presence of Zn clusters were found to be ferromagnetic at room temperature. When the Zn clusters disappeared (after the completion of oxidation), no room-temperature ferromagnetism was detected. Room temperature ferromagnetism was found in ZnO nanowires formed by incomplete oxidation of Zn wires, indicating that the ferromagnetism may be due to the unique structure-Zn nanoclusters embedded in a ZnO matrix. A similar microstructure was realized in PLD-derived ZnO films after subsequent deposition of Zn at elevated temperatures. It should be noted that the structure of Zn nanoclusters embedded in the ZnO matrix may induce room temperature ferromagnetism via interactions between Zn clusters and Zn clusters, or interactions between Zn clusters and ZnO matrix, or the interface effect between Zn clusters and ZnO matrix.

Similar to the surface effect, a grain-boundary effect has been proposed by Straumal et al. suggesting that grain boundaries and related vacancies are the intrinsic origin for RTFM [47]. In order to elucidate RTFM in ZnO, they analyzed a multitude of

experimental publications with respect to the ratio of grain-boundary area to grain volume. RTFM only appears if this ratio exceeds a certain threshold value S_{th} . Based on these important results, pure ZnO single crystals, pure and Mn-doped ZnO thin films consisting of dense equiaxial nanograins were grown. The pure ZnO single crystals show pure diamagnetic behavior without any evidence of RTFM since they do not contain any grain boundaries. However, for the nanograined pure and Mn-doped ZnO thin films, due to the extremely small mean grain sizes, their ratios of grain-boundary area to grain volume become high and exceed their respective S_{th} values. Consequently, they clearly reveal RTFM behaviors. It is strongly supported that RTFM originates through crystallographic imperfections, and the moments are located at vacancies present in grain boundaries. Furthermore, it is concluded that the crystalline ZnO grains are nonmagnetic and surrounded by a ferromagnetic foamlike grain-boundary network.

2.4.2.5 Nanostructures of Zinc Oxide-Based Diluted Magnetic Semiconductor

Nanoscale materials often exhibit physical and chemical properties that differ greatly from their bulk counterparts. One-dimensional (1D) nanostructures, such as nanotubes, nanowires, and nanorods, have attracted a great deal of attention as functional units for mediating the transport of electrons or optical excitation. Therefore, it is reasonable that the combination of low dimensionality and room temperature ferromagnetism in diluted magnetic oxides would generate new functional nanomaterials useful for future miniaturized devices. Synthesizing novel 1D ZnO-based DMS nanomaterials and probing their intrinsic properties are critical to assess their possible role in future nanodevice technology. Apart from the potential

applications, the fundamental understanding on the role of dimensionality in high- T_C ferromagnetism of DMSs also becomes an important ground for the synthesis of 1D nanostructured DMSs, because the quantum confinement may result in very interesting magnetic properties which are different from their bulk systems. For example, in general, the T_C of two-dimensional DMS is strongly suppressed compared with the T_C of corresponding three dimensional DMS. Until now, many efforts have been made to explore the synthesis and magnetic properties of ZnO-based DMS thin films; however, only a few research groups have reported the synthesis of ZnO-based DMS 1D nanostructures. In order to comprehend the role of dimensionality and to identify the origin of the ferromagnetism in ZnO-based DMS, it seems logical to investigate ZnO-based DMS 1D nanostructures. Some researches on ZnO-based DMS 1D nanostructures have been reported to exhibit interesting properties.

Chang et al. have investigated the synthesis, optical, and magnetic properties of diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanowires via vapor phase growth [48]. Diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanowires were synthesized via an in situ doping of manganese in ZnO nanowires using vapor phase growth at 500 °C, as shown in Fig. 2.25. The maximum content of the manganese in the ZnO is around 13 at. %, approaching the maximum thermal equilibrium limit of Mn solubility in ZnO at the growth temperature. Structure and composition analysis revealed that the manganese was doped into the lattice structure, forming solid solution instead of precipitation. Magnetic property measurements revealed that the as-doped $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanowires exhibit ferromagnetic behavior with Curie temperature around 37 K.

Fig. 2.25. (a) TEM image of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanowires, in which the inset shows the EDS spectrum of a typical $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanowire, and (b) HRTEM image of a single $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanowire [48].

Wu et al. have investigated the room-temperature ferromagnetism in well-aligned $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods [49]. Diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods with a Curie temperature higher than 350 K have been synthesized by in situ doping of Co in

ZnO nanorods using a simple thermal chemical vapor deposition method, as shown in Fig. 2.26. Structural analyses indicated that the nanorod possesses the single-crystalline wurtzite structure and there is no segregated cluster of impurity phase appearing throughout the nanorod. The transparency of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods in the visible region has been examined by UV-visible absorption. The fundamental absorptions of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods estimated from the absorption spectra do not reveal pronounced difference from that of pure ZnO nanorods.

Fig. 2.26. (a) SEM image of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods, and (b) XRD pattern of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods [49].

Cui et al. have investigated the electrodeposition and room temperature ferromagnetic anisotropy of Co and Ni-doped ZnO nanowire arrays [50]. Cobalt and nickel doped ZnO nanowire arrays were synthesized by an electrochemical process at a temperature of 90 °C, as shown in Fig. 2.27. Energy dispersive x-ray spectroscopy and x-ray diffraction show that the dopants are incorporated into the wurtzite-structure ZnO. Anisotropic ferromagnetism with an easy direction of magnetization either perpendicular or parallel to the wire axis, depending on the wire geometry and density, was observed in 1.7% Co and 2.2% Ni-doped ZnO nanowires at room temperature. The anisotropic magnetism was explained in terms of a competition between self-demagnetization and magnetostatic coupling among the nanowires.

Fig. 2.27. SEM images and EDX spectra of Co and Ni-doped ZnO nanowires [50].

Fig. 2.28. (a) SEM image of homogeneous Cu-doped ZnO nanowires, (b) SAED pattern of a single nanowire, and (c) HRTEM image of a single nanowire [104].

Fig. 2.29. (a) SEM image of inhomogeneous Cu-doped ZnO nanowires, (b) HRTEM image of an as-grown nanowire after coating a Cu overlayer. (c) HRTEM image of a 600 °C annealed nanowire. (d) HRTEM image of an 800 °C annealed nanowire [104].

Xing et al. reported a comparative study of RTFM in Cu-doped ZnO nanowires enhanced by structural inhomogeneity [104]. They argue that the formation of BMP is the origin of RTFM, and RTFM is not a homogeneous bulk property, but a surface effect by nature. Two distinct synthesis routes were designed to produce different levels of structural inhomogeneity. In the first approach, $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ powder was first synthesized by a conventional solid state reaction technique to achieve a homogeneous doping. Then homogeneous Cu-doped ZnO nanowires (Fig. 2.28) were grown on a silicon substrate by a vapor transport method with conditions similar to those used for growing undoped ZnO nanowires. In contrast with the first growth approach, the second approach starts and ends with samples with strong structural inhomogeneity (Fig. 2.29). Vertically well-aligned ZnO nanowires were first grown

on a-plane sapphire substrate and then a thin layer of Cu was coated on the nanowire surface by sputtering. Cu doping was achieved by annealing this ZnO/Cu core/shell nanowire heterostructure at temperature between 600 and 800 °C. After annealing at either 600 or 800 °C, the disappearance of the Cu shell is accompanied by the creation of a large amount of defects and distorted domains, which is attributed to the diffusion of Cu atoms. A striking feature of their magnetic properties is that the inhomogeneous nanowires with 2.2% Cu exhibited a much stronger RTFM than homogeneous nanowires with 4.9% Cu although they contain less Cu. The intriguing enhancement of RTFM in inhomogeneous nanowires is closely associated with its structural inhomogeneity. This correlation favors the formation of BMP as the origin of RTFM. Defects, such as oxygen vacancies, tend to form BMP that couple with 3d moments of the Cu^{2+} within their orbits. The overlapping of magnetic polarons induces spin-spin interaction between magnetic ions, eventually stabilizing the ferromagnetic ordering. During annealing, the low Zn-O bonding energy of 159 kJ mol^{-1} facilitates the formation of oxygen vacancies. The Cu diffusion might also contribute to a high level of oxygen vacancies on the surface of the inhomogeneous Cu-doped ZnO nanowires. On the other hand, the Cu doping only exists on the surface but not the volume of the inhomogeneous nanowires. The high concentrations of oxygen vacancies and Cu doping on the surface of the inhomogeneous nanowires yield a greater overall volume occupied by BMP, thus promoting the creation and percolation of ferromagnetic domains. In addition, the good vertical alignment of the inhomogeneous nanowires can cause a strong magnetic coupling between the surfaces of nanowires, which can strengthen the RTFM. Thus, the RTFM is absolutely from the surface but not the volume of the inhomogeneous nanowires. However, the homogeneous nanowires have no the high concentration of oxygen vacancies, especially in the volume of

nanowires, although they have a high concentration of homogeneous Cu doping. The low concentration of oxygen vacancies in the homogeneous nanowire form a low concentration of BMP, which causes that RTFM cannot be detected in a single homogeneous nanowire through the magnetic force microscopy measurement. Thus, the weak RTFM in the homogeneous nanowires is mainly from the magnetic coupling between the surfaces of nanowires. On the other hand, the poor alignment of the homogeneous nanowires weakens the magnetic coupling between the surfaces of nanowires. Thus, the RTFM is weaker in the homogeneous nanowires than that in the inhomogeneous nanowires. In conclusion, the RTFM is not a homogeneous bulk property, but a surface effect by nature.

Yao et al. demonstrated the magnetic property and spatial occupation of Co dopants in $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ nanowires [105]. Single phase Co-doped ZnO DMS nanowire was synthesized by a chemical solution method. They suggest that the Co ions are randomly doped into the ZnO matrix and located at the Zn sites. The magnetization measurement of the Co-doped ZnO nanowire shows the room temperature ferromagnetic characteristic with a relatively larger saturation magnetization. The saturation magnetization of $0.95 \mu_B/\text{Co}$ is much larger than that ($0.16 \mu_B/\text{Co}$) in the PLD-grown $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ thin film and also much larger than that in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ bulk modality with a perfect-crystal structure which are generally reported to be intrinsically paramagnetic. Peng et al. have reported that the size effect can be used to enhance hole-induced magnetization in the ZnO nanowire. Using the first-principles methods, they have shown that the size effect can reduce critical hole concentration for stabilizing the magnetization and that the critical hole (acceptor doping) concentration needed to induce ferromagnetism is less than 1/8 of that needed in bulk

materials. This means that the Zn vacancy will play an important role in the $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ nanowire and more Co dopants will be inside the BMP radius easily due to the size effect, thus increasing the probability of ferromagnetic coupling between two magnetic impurities within the same orbital. On the basis of BMP theory, the strong RTFM of the $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ nanowire can be attributed to the 1D size effect relevantly.

Fig. 2.30. (a) TEM image of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ nanowires, and (b) XRD pattern of the $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ nanowires [105].

Patra et al. reported structural and magnetic properties of Co-doped pyramidal ZnO nanorods synthesized by solution growth technique [106]. Large-area arrays of highly oriented Co-doped ZnO nanorods with pyramidal hexagonal structure are grown on polycrystalline glass slides by wet chemical method using $\text{Zn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{C}_6\text{H}_{12}\text{N}_4$ and ammonia solution in an aqueous medium. Further, the Co-doped ZnO nanorods show ferromagnetic behavior whereas the undoped ZnO nanorods show diamagnetic behavior at room temperature. In the absence of any unwanted precipitates, the RTFM requires exchange interaction between free delocalized carriers and localized d-spins of Co ions and therefore the presence of free carriers in the samples is a necessary condition for the observations of RTFM. The required free charge carriers might be made available by the presence of multivalence Co ions viz. Co^{2+} and Co^{3+} as well as oxygen vacancy centers.

Fig.2.31. SEM micrograph of Co-doped ZnO nanorods, where the insets show the enlarged views [106].

Fig. 2.32. FESEM images of high-vacuum annealed $\text{Zn}_{0.92}\text{Co}_{0.08}\text{O}$ nanowires with average diameters of (a) 38 nm and (b) 19 nm [107]. The inset in (a) is a HRTEM image of a single nanowire.

Chen et al. reported size effects on thermal treatments and room temperature ferromagnetism in high-vacuum annealed ZnCoO nanowires [107]. $\text{Zn}_{0.92}\text{Co}_{0.08}\text{O}$ nanowires with two different average diameters, 19 and 38 nm, have been made by the vapor transport and Co ion implantation method. The as-implanted nanowires were thermally annealed through multiple steps in a high vacuum. Electron energy

loss spectroscopy mapping revealed a homogeneous distribution of Co element in the high-vacuum annealed $\text{Zn}_{0.92}\text{Co}_{0.08}\text{O}$ nanowires and high-resolution transmission electron microscopy analysis indicated the absence of Co clustering in the nanowires. The multiple-step annealing process led to a transition from a weak to a strong RTFM. It was found that the ferromagnetic ordering depends strongly on high-vacuum annealing as well as on the nanowire diameter. The effect of annealing on the creation of a strong ferromagnetic state was observed to be much more pronounced in thinner nanowires. By comparison of magnetic properties between different-diameter nanowires, field-dependent magnetizations reveal considerably stronger ferromagnetism in the smaller diameter (19 nm) $\text{Zn}_{0.92}\text{Co}_{0.08}\text{O}$ nanowires than that in the larger diameter (38 nm) nanowires. It is believed that vacuum annealing generates either oxygen vacancies or zinc interstitials, which in turn induce stronger magnetic coupling between the Co ions. Obviously, thinner nanowires have a larger surface-to-volume ratio that benefits the diffusion of oxygen out from nanowires and helps to create a large amount of point defects. Thus, the high surface-to-volume ratio in thin nanowires facilitated the enhancement in ferromagnetism through the high-vacuum annealing process. However, it is found that the saturation magnetization of 19 nm nanowires does not further increase during further annealing after 3 h annealing, the saturation magnetization of 38 nm nanowires does not further increase during further annealing after 6 h annealing, and the saturation magnetization of 19 nm nanowires after 3 h annealing is larger than that of 38 nm nanowires after 6 h annealing. The further annealing does not cause further increased saturation magnetization, which can be attributed to the saturation of point defects corresponding to the Co ions. After saturating of point defects, the saturation magnetization of 19 nm nanowires is larger than that of 38 nm nanowires, which cannot be attributed to the amount of defects in

nanowires but the surface-to-volume ratio of nanowires. Because it is argued that the ferromagnetism is mainly from the surface but not volume of the nanowires, the larger surface-to-volume ratio of 19 nm nanowires causes its larger saturation magnetization.

Yan et al. reported the impact of annealing on morphology and ferromagnetism of ZnO nanorods [43]. RTFM has been observed in ZnO nanorods prepared by hydrothermal method. The magnetization reduced with the increase of the size. Annealing at 900 °C in air transformed the nanorods into twinning structures and weakened the magnetizations. Analysis indicated that the interstitial zinc at the surface may contribute to the ferromagnetism in ZnO nanorods.

Fig. 2.33. SEM images of as-prepared ZnO nanorods with the diameters of (a) 10 nm and (b) 20 nm, and TEM images of the as-prepared ZnO nanorods with the diameters of (c) 10 nm and (d) 20 nm [43].

However, the reverse size effect is also observed in some research works, which is that the RTFM is weakened with the decreased size of the ZnO-based DMS nanostructures. Liao et al reported size dependence of Curie temperature in Co^+ ion implanted ZnO nanowires [108]. ZnO nanowires with different diameters were grown on Si substrates, then implanted with 80 keV Co^+ ions at a dose of $3 \times 10^{16} \text{ cm}^{-2}$, and subsequently annealed at 700 °C for 5 min. No Co precipitates appeared in the ZnO nanowires according to the results observed using a high-resolution transmission electron microscope, revealing that the magnetism of the ZnO nanowires was independent of the Co precipitates. Hysteresis was observed at 10 K for all samples of ZnO nanowires with different sizes. The Curie temperature decreased from above 300 to 70 K with the reduction in the ZnO nanowires' diameters. It is very valuable to show that the quantum-confined effect appears gradually with decreasing size of the nanowires. The RKKY theory and quantum-confined effect were used to explain the phenomenon. According to RKKY theory, the magnetism is due to the exchange interaction between local spin-polarized electrons (such as the electrons of Co^+ ions) and conductive electrons. This interaction leads to the spin polarization of conductive electrons. Subsequently, the spin-polarized conductive electrons perform an exchange interaction with local spin-polarized electrons of other Co^+ ions. Thus after the long-range exchange interaction, almost all Co^+ ions exhibit the same spin direction. As a result, the material presents ferromagnetism. During this long-range interaction, the conductive electrons are regarded as the media to unify the spin direction of all Co^+ ions. In the results, as the diameters of nanowires decreased, the strength of the interaction between electrons and phonons became weak, resulting in a weaker long-range interaction between local spin-polarized electrons and conductive electrons. Therefore, the electrons were gradually confined around atoms. Thus the exchange

interaction between conductive electrons and local spin-polarized electrons was weakened so that the transition temperature of the second-order transition decreased.

Fig. 2.34. SEM images of ZnO nanowires with diameters of 55 (upper image) and 75 nm (lower image) [108].

Chapter 3. Experimental Details

This chapter describes the synthesis and the characterization of samples studied in this work.

3.1 Pure Zinc Oxide Thin Films

Pure ZnO thin films were grown on Si substrates by magnetron sputtering a pure Zn target with a DC power of 60 W. The temperature of the substrates was 300 °C. The gas used during the film depositions was a mixture of 10 sccm Ar and 10 sccm O₂ and the working gas pressure was about 5 mTorr. The deposition time of the films was 1 h. The first series of thin films were annealed in 1 atm of Ar gas environment at 600 °C using rapid thermal processing for 10 min and 20 min, respectively. The second series of thin films were annealed in 1 atm of air at 600 °C using rapid thermal processing for 10 min and 20 min, respectively. The third series of thin films were annealed in 1 atm of air at 600 °C using a normal box furnace for 3 h and 6 h, respectively. In the rapid thermal annealing, the temperature increasing rate is 50 °C/s, while it is 0.08 °C/s in the normal annealing. The structure of the films was characterized by means of X-ray diffraction (XRD, Empyrean, PANalytical) with a Cu K_α anode ($\lambda \approx 0.154$ nm). X-ray photoelectron spectroscopy (XPS, Kratos-Axis-ULTRA with a monochromatic Al K_α X-ray source, 1486.71 eV) was used to determine the chemical states of elements in the films after etching sample surfaces using low-energy Ar⁺ sputtering for 5 min. The magnetic properties of the films were measured with a vibrating sample magnetometer (VSM, Lake Shore Model 7404) at room temperature.

3.2 Copper-Doped Zinc Oxide Thin Films

Cu-doped ZnO thin films were grown on Si substrates by magnetron co-sputtering a pure Cu target and a pure Zn target with a DC power of 60 W applied to the Zn target and a DC power of 20 W applied to the Cu target. The temperature of the substrates was 300 °C. The gas used during the film depositions was a mixture of 10 sccm Ar and 10 sccm O₂ and the working gas pressure was about 5 mTorr. The deposition time of the films was 1 h. The first series of thin films were annealed in 1 atm of Ar gas environment at 600 °C using rapid thermal processing for 10 min and 20 min, respectively. The second series of thin films were annealed in 1 atm of air at 600 °C using rapid thermal processing for 10 min and 20 min, respectively. The third series of thin films were annealed in 1 atm of air at 600 °C using a normal box furnace for 3 h and 6 h, respectively. In the rapid thermal annealing, the temperature increasing rate is 50 °C/s, while it is 0.08 °C/s in the normal annealing. The structure of the films was characterized by means of X-ray diffraction (XRD, Empyrean, PANalytical) with a Cu K_α anode ($\lambda \approx 0.154$ nm). X-ray photoelectron spectroscopy (XPS, Kratos-Axis-ULTRA with a monochromatic Al K_α X-ray source, 1486.71 eV) was used to determine the chemical states of elements in the films. The XPS testing was carried out both before and after etching sample surfaces using low-energy Ar⁺ sputtering for 5 min. The magnetic properties of the films were measured with a vibrating sample magnetometer (VSM, Lake Shore Model 7404) at room temperature.

3.3 Nickel-Doped Zinc Oxide Thin Films

Ni-doped ZnO thin films were grown on Si substrates by magnetron co-sputtering a pure Ni target and a pure ZnO target with an RF power of 350 W applied to the ZnO target and a DC power of 11 W applied to the Ni target. An oxygen nonstoichiometry can appear in the Ni-doped ZnO thin films grown in pure Ar ambient due to the loss of oxygen during the sputtering process. Thus, the gas used during the film depositions was a mixture of 40 sccm Ar and 4 sccm O₂ and the working gas pressure was about 10 mTorr. The function of O₂ is to improve the oxygen stoichiometry in the films. The deposition rate of the films was about 33.2 nm/min. The films were annealed in 1 atm of air at 600 °C or in 1 atm of Ar gas environment at 600 °C and 800 °C using rapid thermal processing for 10 min. The structure of the films was characterized by means of X-ray diffraction (XRD, Empyrean, PANalytical) with a Cu K_α anode ($\lambda \approx 0.154$ nm). X-ray photoelectron spectroscopy (XPS, Kratos-Axis-ULTRA with a monochromatic Al K_α X-ray source, 1486.71 eV) was used to determine the chemical states of elements in the films. The XPS depth profiles of the sample surfaces were measured down to about 90 nm using low-energy Ar⁺ sputtering. The magnetic properties of the films were measured with a vibrating sample magnetometer (VSM, Lake Shore Model 7404) at room temperature. The optical properties of the films were measured using photoluminescence (PL) with an excitation wavelength of 325 nm at room temperature.

3.4 Pure Zinc Oxide Nanostructures

Pure ZnO nano/micro structures were produced on silicon substrate with ZnO seed layer through a chemical deposition method and on bare silicon substrates by an electrochemical deposition method, respectively. All experiments were carried out in same chemical solutions. In a representative procedure, zinc nitrate hydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) were dissolved in 50 mL deionized (DI) water and then the solution formed with 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$. In the chemical deposition, a ZnO thin film of about 100 nm was deposited on a bare silicon substrate using magnetron sputtering firstly, and then the substrate with ZnO seed layer was inserted in a sealed Teflon cell containing the chemical solution. The solution was heated to 90 °C using water bath and held at 90 °C for 2 h. In the electrochemical deposition, all experiments were carried out with a classical two-electrode Teflon cell. Bare silicon substrates were used as the cathode (-) and a platinum gauze was used as the anode (+). Both cathode and anode were inserted into the cell when the solution was heated to 90 °C using water bath. A negative potential of -0.8, -1.2, -1.6, and -2.0 V was respectively applied to silicon substrates during a two-hour growth of pure ZnO structures. The surface morphology, crystal structure, chemical composition, and magnetic properties of the pure ZnO nano/micro structures were characterized by means of field emission scanning electron microscopy (FESEM, JEOL JSM-7600F), X-ray diffraction (XRD, Empyrean, PANalytical with a Cu K_α anode, $\lambda \approx 0.154$ nm), X-ray photoelectron spectroscopy (XPS, Kratos-Axis-ULTRA with a monochromatic Al K_α X-ray source, 1486.71 eV), and vibrating sample magnetometer (VSM, Lake Shore Model 7404), respectively.

3.5 Cobalt-Doped Zinc Oxide Nanostructures

Co-doped ZnO nano/micro structures were produced on silicon substrate with ZnO seed layer through a chemical deposition method and on bare silicon substrates by an electrochemical deposition method, respectively. In a representative procedure, zinc nitrate hydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) and cobalt nitrate hydrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ were dissolved in 50 mL deionized (DI) water and then the solutions were formed with different concentrations. In the chemical deposition, a ZnO thin film of about 100 nm was deposited on a bare silicon substrate using magnetron sputtering firstly, and then the substrate with ZnO seed layer was inserted in a sealed Teflon cell containing the chemical solution with the concentration of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$. The solution was heated to 90 °C using water bath and held at 90 °C for 2 h. In the electrochemical deposition, all experiments were carried out with a classical two-electrode Teflon cell. Two solutions with different concentrations were carried out in the same condition, which are 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$ and 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$, respectively. Bare silicon substrates were used as the cathode (-) and a platinum wire was used as the anode (+). Both cathode and anode were inserted into the cell when the solution was heated to 90 °C using water bath. A negative potential of -0.8 V was respectively applied to silicon substrates during a two-hour growth of Co-doped ZnO structures. In order to rule out the possibility that the RTFM is from pure ZnO matrix, pure ZnO nanorod arrays were also synthesized by the electrochemical deposition in the same condition with the solution concentration of 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$. The surface morphology, crystal structure,

chemical composition, and magnetic properties of the Co-doped ZnO nano/micro structures were characterized by means of scanning electron microscopy (SEM, JEOL JSM-5600LV), field emission scanning electron microscopy (FESEM, JEOL JSM-7600F), X-ray diffraction (XRD, Empyrean, PANalytical with a Cu K $_{\alpha}$ anode, $\lambda \approx 0.154$ nm), X-ray photoelectron spectroscopy (XPS, Kratos-Axis-ULTRA with a monochromatic Al K $_{\alpha}$ X-ray source, 1486.71 eV), and vibrating sample magnetometer (VSM, Lake Shore Model 7404), respectively.

Chapter 4. Zinc Oxide-Based Diluted Magnetic Semiconductor Thin Films

Spintronics has emerged as a new technology, which is based on electron spins rather than electron charges to carry information, and has offered an opportunity for a new generation of devices combining standard microelectronics with spin-dependent effects that arise from interactions between spins of charge carriers and magnetic properties of materials [1]. For spintronics applications, diluted magnetic semiconductors (DMS) have attracted a lot of attention [1], especially ZnO-based DMS, due to the prediction of the existence of room temperature ferromagnetism (RTFM) in transition metals (TMs) doped ZnO by Dietl et al [6] and Sato et al [20]. However, contradictory experimental results have been reported on TM-doped ZnO, i.e., RTFM was observed in some studies [13, 19, 79, 80] while no RTFM was detected in some other studies [21, 24, 77, 78]. Interestingly, the RTFM in pure ZnO was also reported recently [42-47]. Although the RTFM in some ZnO-based DMS materials was observed, the origin of such RTFM still could not be satisfactorily interpreted. For TM-doped ZnO, in some cases, the RTFM was suggested to be a consequence of the precipitation of magnetic clusters or the formation of secondary magnetic phases [26, 29, 30], and in some other cases, RTFM was suggested to be intrinsic in origin [31-34]. A free carrier mediated exchange mechanism was proposed to induce the intrinsic RTFM in TM-doped ZnO [6, 31, 32]. However, TM-doped ZnO materials that are ferromagnetic are often poorly electrically conductive or even highly insulating, which cannot be explained by the carrier-mediated model. The origin of RTFM for insulating oxide DMS has been widely explained by a bound magnetic polaron (BMP) model [35, 36], suggesting that oxygen vacancies [10, 33,

37-39] or metallic interstitials [40, 41] in oxide DMS materials locally trap electrons to occupy orbitals interacting with the d subshells of neighboring TM dopants, resulting in the ferromagnetism. For pure ZnO, the origin of RTFM has been attributed to the defects at the Zn sites in ZnO thin films [42], the Zn nanoclusters embedded in ZnO nanowire matrices [46], the interstitial Zn at the surfaces of ZnO nanorods [43], the intrinsic defects in ZnO films [44], the defects that cause a 469 nm emission [45], and the vacancies present in grain boundaries [47], etc. It is still a challenge to properly understand the mechanisms governing the ferromagnetic ordering in ZnO-based DMS.

It was reported that post annealing would affect the magnetic properties of ZnO-based DMS thin films, so the annealing effect has been considered as a good way to investigate the RTFM of ZnO-based DMS. Chakraborti et al. reported a high temperature annealing in an oxygen atmosphere, which reduced the oxygen vacancy concentration in Cu-doped ZnO and CuAl-doped ZnO DMS thin films, and led to a large decrease in the ferromagnetic moment of the films, suggesting that an exchange mechanism mediated by BMPs formed by oxygen vacancies was responsible for the ferromagnetic ordering in the ZnO-based DMS thin films [37]. Liu et al. reported that the annealing in vacuum led to an increase in magnetic moment and annealing in air led to a decrease in magnetic moment, demonstrating that the magnetic behavior of Co-doped ZnO thin films was directly related to the presence of intrinsic defects, notably oxygen vacancies and interstitial Zn atoms [109]. However, these reports only focused on the change of magnetic properties after annealing, the systematical investigation of annealing effect on the structural and magnetic properties of ZnO-based DMS thin films has seldom been reported in the literature, such as the diffusion

of O and TM and the chemical state change of TM, as well as their effects on RTFM. In this chapter, annealing effect under varying conditions on the structural and magnetic properties of pure ZnO thin films, Cu-doped ZnO thin films, and Ni-doped ZnO thin films prepared via magnetron sputtering deposition was systematically investigated. The diamagnetism of the pure ZnO thin films indicated that oxygen vacancies were necessary while only oxygen vacancies were not enough to induce the RTFM of ZnO-based DMS. The RTFM of the Cu-doped ZnO and Ni-doped ZnO thin films was attributed to the BMP model.

4.1 Pure Zinc Oxide Thin Films

4.1.1 Introduction

Annealing effect under varying conditions on the structural and magnetic properties of pure ZnO thin films was systematically investigated. A lattice deviation of the pure ZnO thin films was observed both before and after annealing in Ar or air through XRD, which was attributed to oxygen vacancies and interstitial Zn in the thin films. Significant diffusion of O from the bottom to the top surface of thin films was observed after annealing in Ar or air through XPS, which resulted in increased oxygen vacancies in the thin films after annealing. Furthermore, increased annealing duration could strengthen the diffusion of O and increase the concentration of oxygen vacancies in the thin films. All the pure ZnO thin films displayed diamagnetism at room temperature both before and after annealing in Ar or air, although oxygen vacancies existed in all the films, indicating that oxygen vacancies were necessary while only oxygen vacancies were not enough to induce room temperature ferromagnetism of ZnO-based diluted magnetic semiconductors.

4.1.2 Results and Discussion

Fig. 4.1.1 shows the XRD spectra for the pure ZnO thin films both as-deposited and annealed under different conditions. Fig. 4.1.1(a) shows standard peak positions of pure ZnO powders. Only obvious peaks corresponding to ZnO is observed in the as-deposited film (Fig. 4.1.1(b)), indicating that a polycrystalline wurtzite phase with c-axis preferred orientation is formed in the film. However, it is interesting to notice

that all ZnO peaks of the as-deposited film shift toward left compared with standard peaks of pure ZnO powders. After annealing, still only obvious ZnO diffraction peaks are observed in the films (Fig. 4.1.1 (c)-(h)), but the peaks become sharper, indicating that the crystallinity of the films become better due to the growth of grains during annealing. It is more interesting to notice that all ZnO peaks of the annealed films shift toward right compared with standard peaks of pure ZnO powders. Thus, the standard peaks of ZnO powders locate between those of the as-deposited and annealed thin films, which means that the lattice constants are elongated in the as-deposited film and shortened in the annealed films. An elongated lattice constant indicates that the as-deposited film is in a state of tensile stress parallel to the corresponding axis. However, a shortened lattice constant in the annealed films reveals that the films after annealing are in a state of compressive stress parallel to the corresponding axis. Similar results have been reported by Gupta et al. [110] and Liu et al. [109]. Gupta et al. reported the influence of postdeposition annealing on the structural property of sputtered ZnO film. The as-deposited films are in a state of tensile stress parallel to the c-axis, the films become almost stress free after a postdeposition annealing treatment at 400 °C in air, and the films are in a state of compressive stress parallel to the c-axis after a postdeposition annealing treatment at 600 °C in air. The change in stress in the films after annealing is attributed to the interstitial oxygen. However, the interstitial oxygen is not the primary defect in ZnO crystal [75, 111]. Thus, Liu et al. developed Gupta's theory and reported the influence of annealing on microstructure of co-sputtered Co-doped ZnO thin films. The as-grown films are in a state of tensile stress parallel to the c-axis, the films become completely stress free after an annealing at 400 °C in vacuum, and the films are in a state of compressive stress parallel to the

c-axis after an annealing at 600 °C in vacuum. The change in stress in the films after annealing is explained using oxygen vacancies and interstitial zinc atoms.

Fig. 4.1.1. (a) Standard XRD peak positions of pure ZnO powders. XRD spectra of as-deposited and annealed pure ZnO thin films: (b) as-deposited, (c) annealed in Ar for 10 min, (d) annealed in Ar for 20 min, (e) annealed in air for 10 min, (f) annealed in air for 20 min, (g) annealed in air for 3 h, and (h) annealed in air for 6 h.

The change in stress in the films after annealing is primarily due to the defects produced during the film growth process. As the deposition rate of the films is high during the sputtering deposition, the zinc atoms are prone to enter the octahedral

interstices [75, 109, 111]. Simultaneously, the oxygen atoms have a tendency to deviate from their positions in the ZnO crystal lattice, so there are also a large number of oxygen vacancies in the films. On one hand, the interstitial zinc atoms and the zinc atoms at the normal sites in the ZnO crystal lattice exclude each other, which leads to the expansion of the film lattice. On the other hand, the existence of oxygen vacancies destroys the balance of attraction and repulsion between neighboring crystal planes, which leads to the contraction of the film lattice. Therefore, the lattice deviation of the pure ZnO films from that of the stress free ZnO powders may be a result of the formations of oxygen vacancies and interstitial Zn. There are relatively fewer oxygen vacancies but more Zn interstices in the as-grown pure ZnO film, which shows a state of tensile stress parallel to all axes, thus causing the elongation of all lattice constants. After annealing at 600 °C in Ar or air, the oxygen vacancies increase in the films. The thermal energy supplied in annealing motivates the migration of the zinc interstices to the normal crystal lattice sites, which reduces the number of interstitial zinc atoms. Consequently, the films after annealing at 600 °C in Ar or air are in a state of compressive stress parallel to all axes, which causes a contraction of all lattice constants.

XPS is performed to determine the chemical states of Zn and O in the pure ZnO films before and after annealing. Fig. 4.1.2 and Fig. 4.1.3 show the Zn 2p and O 1s spectra, respectively. In the Zn 2p spectra in Fig. 4.1.2, the peak at about 1021 eV is characteristic of $\text{Zn}^{2+} 2p_{3/2}$ state, so Zn is in its two-valence oxidation state in the films before and after annealing. In the O 1s spectra in Fig. 4.1.3, two O 1s peaks can be resolved by using a curve fitting procedure for each O 1s spectrum. The peak at 530 eV is attributed to O^{2-} ions present in a stoichiometric wurtzite ZnO structure, whereas

the 531 peak is associated with the specific chemisorbed oxygen, such as the adsorbed H_2O , $-\text{CO}_3$, and so on.

Fig. 4.1.2. XPS Zn 2p spectra of the pure ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

Fig. 4.1.3. XPS O 1s spectra of the pure ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

Fig. 4.1.4 is plotted to show the atomic concentrations of Zn and O in the pure ZnO thin films both as-deposited and annealed under different conditions determined by XPS. The atomic concentrations of Zn and O in the as-deposited film are about 56.6 % and 43.4 %, respectively. After annealing in Ar for 10 and 20 min, the atomic concentrations of O in the films decrease to about 39.1 % and 38.1 %, respectively. After annealing in air for 10 and 20 min, the atomic concentrations of O in the films decrease to about 40.9 % and 39.2 %, respectively. Thus, the O in the films is lost during annealing in Ar as well as air. Moreover, the longer the annealing duration is, the more serious the loss is. However, the loss of O is more serious during annealing in Ar than that in air. After annealing in air for 3 and 6 h, the atomic concentrations of O in the films further decrease to about 37.9 % and 36.5 %, respectively. The loss of O is most serious due to the longest annealing duration compared to those after rapid thermal annealing in Ar or air.

Fig. 4.1.4. XPS atomic concentrations of Zn and O in the pure ZnO thin films both as-deposited and annealed under different conditions.

The O decreases after annealing, which means that O in the films diffuses into the annealing ambient because of the concentration gradient of O in the film and the ambient during the annealing in Ar or air. The oxygen decomposed from the film matrix diffuses onto the film surface, and then departs the film surface and enters the environment. As a result of the O diffusion, oxygen vacancies will increase in the films which can explain the deviation of XRD pattern after annealing. Compared with annealing in Ar, annealing in air possesses a smaller concentration gradient of O in the film and the ambient, so the diffusion of O is slower, which can explain that the decrease of O is smaller after rapid thermal annealing in air than that after rapid thermal annealing in Ar. However, the normal annealing in air causes the most serious loss of O because of the longest annealing duration compared with rapid thermal annealing in Ar or air. Thus, oxygen vacancies increase in the films after annealing in Ar as well as air. Furthermore, the longer the annealing duration is, the more the increased oxygen vacancies in the films is.

Fig. 4.1.5 shows the magnetization of the pure ZnO thin films both as-deposited and annealed measured as a function of magnetic field at room temperature. All the films display diamagnetism, not room temperature ferromagnetism, although oxygen vacancies exist in all the films through XRD and XPS measurements. RTFM has been observed in some pure ZnO-based DMS materials [42-47, 113], and its origin has been attributed to the defect of oxygen vacancies in pure ZnO [113], but this work indicates that only oxygen vacancies are not enough to induce RTFM of ZnO-based DMS. In order to satisfactorily interpret the RTFM of ZnO-based DMS, further theoretical and experimental investigation is necessary.

(a)

(b)

(c)

(d)

(e)

Fig. 4.1.5. Room-temperature M-H hysteresis loops of the pure ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

4.1.3 Summary

Annealing effect under varying conditions on the structural and magnetic properties of pure ZnO thin films was investigated. A lattice deviation of the pure ZnO thin films was observed both before and after annealing in Ar or air through XRD, which was considered as a result of formations of oxygen vacancies and interstitial Zn in the thin films. An elongation of ZnO wurtzite lattice constants was observed in the as-grown pure ZnO thin film compared to that of the stress free ZnO powders, which could be attributed to relatively fewer oxygen vacancies but more Zn interstices in the as-deposited thin film. However, a contraction of ZnO wurtzite lattice constants was observed in the thin films after annealing in Ar or air compared to that of the stress free ZnO powders, which could be assigned to increased oxygen vacancies but decreased interstitial zinc atoms. Significant diffusion of O from the bottom to the top

surface of thin films was observed after annealing in Ar or air through XPS, which resulted in increased oxygen vacancies in the thin films after annealing. Furthermore, increased annealing duration could strengthen the diffusion of O and increase the concentration of oxygen vacancies in the thin films. All the pure ZnO thin films displayed diamagnetism at room temperature both before and after annealing in Ar or air, although oxygen vacancies existed in all the thin films, indicating that oxygen vacancies were necessary while only oxygen vacancies were not enough to induce room temperature ferromagnetism of ZnO-based diluted magnetic semiconductors.

4.2 Copper-Doped Zinc Oxide Thin Films

4.2.1 Introduction

Annealing effect under varying conditions on the structural and magnetic properties of Cu-doped ZnO thin films was systematically investigated. A lattice deviation of the Cu-doped ZnO thin films was observed both before and after annealing in Ar or air through XRD, which was assigned to oxygen vacancies and interstitial Zn in the thin films. Significant diffusion of O and Cu from the bottom to the top surface of thin films was observed after annealing in Ar or air through XPS. The O diffusion resulted in increased oxygen vacancies in the thin films after annealing. Reduction of Cu occurred in the thin films annealed in Ar, while oxidization of Cu occurred in the thin films annealed in air. Increased annealing duration in air increased the concentration of oxygen vacancies in the thin films, also increased the amount of Cu^{2+} at Zn^{2+} sites of ZnO wurtzite lattice. The as-deposited thin film displayed obvious room temperature ferromagnetism (RTFM) that originated from Cu^{2+} through bound magnetic polaron (BMP) model. However, RTFM disappeared in the thin films after annealing in Ar due to the disappearance of Cu^{2+} . On the contrary, a significant improvement in saturation magnetization (M_s) in the thin films was observed after annealing in air compared to that in the as-deposited thin film. Furthermore, the longer the annealing duration in air was, the larger the M_s was. The increase of M_s in the thin films annealed in air was attributed to a stronger BMP effect with increased concentrations of oxygen vacancies in the thin films and Cu^{2+} at Zn^{2+} sites of ZnO wurtzite lattice.

4.2.2 Results and Discussion

Fig. 4.2.1 shows the XRD spectra for the Cu-doped ZnO thin films both as-deposited and annealed under different conditions. Fig. 4.2.1(a) shows standard peak positions of pure ZnO powders. Only obvious peaks corresponding to ZnO is observed in the as-deposited film (Fig. 4.2.1(b)), indicating that a polycrystalline wurtzite phase with c-axis preferred orientation is formed in the film. However, it is interesting to notice that all ZnO peaks of the as-deposited film shift toward left compared with standard peaks of pure ZnO powders. After annealing, still only obvious ZnO diffraction peaks are observed in the films (Fig. 4.2.1 (c)-(h)), but the peaks become sharper, indicating that the crystallinity of the films become better due to the growth of grains during annealing. It is more interesting to notice that all ZnO peaks of the annealed films shift toward right compared with standard peaks of pure ZnO powders. Thus, the standard peaks of ZnO powders locate between those of the as-deposited and annealed thin films, which means that the lattice constants are elongated in the as-deposited film and shortened in the annealed films. An elongated lattice constant indicates that the as-deposited film is in a state of tensile stress parallel to the corresponding axis. However, a shortened lattice constant in the annealed films reveals that the films after annealing are in a state of compressive stress parallel to the corresponding axis. Similar results have been reported by Gupta et al. [110] and Liu et al. [109]. Gupta et al. reported the influence of postdeposition annealing on the structural property of sputtered ZnO film. The as-deposited films are in a state of tensile stress parallel to the c-axis, the films become almost stress free after a postdeposition annealing treatment at 400 °C in air, and the films are in a state of compressive stress parallel to the c-axis after a postdeposition annealing treatment at 600 °C in air. The change in

stress in the films after annealing is attributed to the interstitial oxygen. However, the interstitial oxygen is not the primary defect in ZnO crystal [75, 111]. Thus, Liu et al. developed Gupta's theory and reported the influence of annealing on microstructure of co-sputtered Co-doped ZnO thin films. The as-grown films are in a state of tensile stress parallel to the c-axis, the films become completely stress free after an annealing at 400 °C in vacuum, and the films are in a state of compressive stress parallel to the c-axis after an annealing at 600 °C in vacuum. The change in stress in the films after annealing is explained using oxygen vacancies and interstitial zinc atoms.

The change in stress in the films after annealing is primarily due to the defects produced during the film growth process. As the deposition rate of the films is high during the sputtering deposition, the zinc atoms are prone to enter the octahedral interstices [75, 109, 111]. Simultaneously, the oxygen atoms have a tendency to deviate from their positions in the ZnO crystal lattice, so there are also a large number of oxygen vacancies in the films. On one hand, the interstitial zinc atoms and the zinc atoms at the normal sites in the ZnO crystal lattice exclude each other, which leads to the expansion of the film lattice. On the other hand, the existence of oxygen vacancies destroys the balance of attraction and repulsion between neighboring crystal planes, which leads to the contraction of the film lattice. Therefore, the lattice deviation of the Cu-doped ZnO films from that of the stress free ZnO powders may be a result of the formations of oxygen vacancies and interstitial Zn. There are relatively fewer oxygen vacancies but more Zn interstices in the as-grown Cu-doped ZnO film, which shows a state of tensile stress parallel to all axes, thus causing the elongation of all lattice constants. After annealing at 600 °C in Ar or air, the oxygen vacancies increase in the films. The thermal energy supplied in annealing motivates the migration of the zinc

interstices to the normal crystal lattice sites, which reduces the number of interstitial zinc atoms. Consequently, the films after annealing at 600 °C in Ar or air are in a state of compressive stress parallel to all axes, which causes a contraction of all lattice constants.

Fig. 4.2.1. (a) Standard XRD peak positions of pure ZnO powders. XRD spectra of as-deposited and annealed Cu-doped ZnO thin films: (b) as-deposited, (c) annealed in Ar for 10 min, (d) annealed in Ar for 20 min, (e) annealed in air for 10 min, (f) annealed in air for 20 min, (g) annealed in air for 3 h, and (h) annealed in air for 6 h.

Fig. 4.2.2. (a) Standard XRD peak positions of pure ZnO powders. Enlarged XRD spectra of as-deposited and annealed Cu-doped ZnO thin films: (b) as-deposited, (c) annealed in Ar for 10 min, (d) annealed in Ar for 20 min, (e) annealed in air for 10 min, (f) annealed in air for 20 min, (g) annealed in air for 3 h, and (h) annealed in air for 6 h.

Small diffraction peaks are unobvious in Fig. 4.2.1, so Fig. 4.2.1 is enlarged, as shown in Fig. 4.2.2. No diffraction peaks attributed to Cu-related secondary phases are observed in the as-deposited film (Fig. 4.2.2(b)), implying that Cu atoms might substitute for Zn atoms in the ZnO wurtzite lattice or any occurrence of Cu should be

below the resolution of the XRD measurements. After annealing in Ar, apart from ZnO phase, Cu₂O (200) peaks appear, as shown in Fig. 4.2.2(c) and Fig. 4.2.2(d). However, after annealing in air, CuO (111) peaks appear, as shown in Fig. 4.2.2 (e)-(h). The precipitation of Cu₂O and CuO indicates that the Cu deviates from Zn²⁺ sites in ZnO wurtzite lattice, and then aggregations of Cu-related phases occur in the films during the annealing. Moreover, a reduction of copper occurs in the film annealed in Ar. On the contrary, an oxidation of copper occurs in the film during the annealing in air. The precipitation of Cu₂O and CuO phases in the ZnO matrix can be further explained by XPS.

XPS is performed to determine the atomic concentration for each element at the surface of the Cu-doped ZnO thin films, as shown in Fig. 4.2.3. In addition, the x value is termed the mole fraction of Cu in the Cu-doped ZnO (Zn_{1-x}Cu_xO) film, so Fig. 4.2.4 shows the x values in the Zn_{1-x}Cu_xO films before and after annealing in different conditions. The atomic concentrations of Zn, Cu, and O in the as-deposited film are about 44.35, 2.61, and 53.04 %, respectively. Its x is 0.0556.

Fig. 4.2.3(a) and Fig. 4.2.4(a) show the rapid thermal annealing effect in Ar on the atomic concentration for each element at the surface of the films. After annealing in Ar for 10 min, the atomic concentrations of Zn, Cu, and O in the film become about 39.08, 9.61, and 51.31 %, respectively. Its x increases to 0.1975. After annealing in Ar for 20 min, the atomic concentrations of Zn, Cu, and O in the film become about 38.14, 11.45, and 50.41 %, respectively. Its x further increases to 0.2308. Thus, the concentration of O decreases and Cu increases at the surface of the films after annealing in Ar. Moreover, the longer the annealing duration is, the larger the

concentration change is. Fig. 4.2.3(b) and Fig. 4.2.4(b) show the rapid thermal annealing effect in air on the atomic concentration for each element at the surface of the films. After annealing in air for 10 min, the atomic concentrations of Zn, Cu, and O in the film become about 44.22, 3.35, and 52.43 %, respectively. Its x increases to 0.0706. After annealing in air for 20 min, the atomic concentrations of Zn, Cu, and O in the film become about 43.78, 4.68, and 51.54 %, respectively. Its x further increases to 0.0966. Thus, the concentration of O also decreases and Cu also increases at the surface of the films after annealing in air. Moreover, the longer the annealing duration is, the larger the concentration change is. However, the concentration changes of O and Cu are smaller after annealing in air than those after annealing in Ar. Fig. 4.2.3(c) and Fig. 4.2.4(c) show the normal thermal annealing effect in air on the atomic concentration for each element at the surface of the films. After annealing in air for 3 h, the atomic concentrations of Zn, Cu, and O in the film become about 51.51, 3.17, and 45.33 %, respectively. Its x increases to 0.058. After annealing in air for 6 h, the atomic concentrations of Zn, Cu, and O in the film become about 52.67, 3.37, and 43.97 %, respectively. Its x further increases to 0.0601. Thus, the concentration of O also decreases and Cu also increases at the surface of the films after annealing in air. Moreover, the longer the annealing duration is, the larger the concentration change is. The loss of O is most serious due to the longest annealing duration compared with that after rapid thermal annealing in Ar or air. However, the concentration changes of Cu are smallest than those after rapid thermal annealing in Ar or air.

The O decreases after annealing, which means that O in the films diffuses into the annealing ambient because of the concentration gradient of O in the film and the ambient during the annealing in Ar or air. The oxygen decomposed from the film

matrix diffuses onto the film surface, and then departs the film surface and enters the environment. As a result of the O diffusion, oxygen vacancies will increase which can explain the deviation of XRD pattern after annealing. Compared with annealing in Ar, annealing in air possesses a smaller concentration gradient of O in the film and the ambient, so the diffusion of O is slower, which can explain that the decrease of O is smaller after rapid thermal annealing in air than that after rapid thermal annealing in Ar. However, the normal annealing in air causes the most serious loss of O because of the longest annealing duration compared with rapid thermal annealing in Ar or air.

The Cu increases after annealing, which indicates a significant diffusion of Cu from the bottom to the top surface of the film during annealing. The Cu doping can increase system free energy of the Cu-doped ZnO films compared with pure ZnO films, which causes that the Cu-doped ZnO films are in an unstable state. During annealing, the thermal energy supplied motivates the migration of Cu in ZnO matrix. In order to decrease the system energy and return to stable state of the films, Cu deviates from the position in ZnO matrix and diffuses from the bottom to the top surface of the films. As a result of the diffusion of Cu, the concentration of Cu increases at the surface, while decreases at the bottom of the film. Thus, the aggregations of Cu-related phases occur at the surface of the films, which causes the appearance of Cu₂O and CuO phases in the ZnO matrix after annealing. The annealing in Ar possesses a most significant Cu diffusion compared with annealing in air. In addition, the rapid thermal annealing in air causes a more distinct Cu diffusion than the normal annealing in air. The difference of Cu diffusion after different annealing conditions will be discussed later using chemical states of Cu in the films through XPS.

(a)

(b)

(c)

Fig. 4.2.3. XPS atomic concentrations of Zn, Cu and O at the surfaces of annealed Cu-doped ZnO thin films with reference to as-deposited films: (a) annealed in Ar for 10 and 20 min, (b) annealed in air for 10 and 20 min, and (c) annealed in air for 3 and 6 h.

(a)

(b)

(c)

Fig. 4.2.4. x values in annealed $Zn_{1-x}Cu_xO$ films with reference to as-deposited films:

(a) annealed in Ar for 10 and 20 min, (b) annealed in air for 10 and 20 min, and (c) annealed in air for 3 and 6 h. The x value is the mole fraction of Cu in the $Zn_{1-x}Cu_xO$ film.

Fig. 4.2.5. XPS Zn 2p spectra at the top surfaces of the Cu-doped ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

Fig. 4.2.6. XPS O 1s spectra at the top surfaces of the Cu-doped ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

Fig. 4.2.7. XPS Cu 2p spectra at the top surfaces of the Cu-doped ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

The chemical states of Zn, Cu and O in the films are studied also using XPS. Figures 4.2.5, 4.2.6, and 4.2.7 show the Zn 2p, O 1s, and Cu 2p spectra respectively, which are measured at the surface of the Cu-doped ZnO films before and after annealing. In the Zn 2p spectra in Fig. 4.2.5, the peak at about 1021 eV is characteristic of Zn^{2+} $2p_{3/2}$ state, so Zn is in its two-valence oxidation state in the films before and after annealing. In the O 1s spectra in Fig. 4.2.6, two O 1s peaks can be resolved by using a curve fitting procedure for each O 1s spectrum. The peak at 530 eV is attributed to O^{2-} ions present in a stoichiometric wurtzite ZnO structure, whereas the 531 peak is associated with the specific chemisorbed oxygen, such as the adsorbed H_2O , $-\text{CO}_3$, and so on.

Fig. 4.2.7(a) shows the Cu 2p spectrum in the as-deposited thin film. The Cu $2p_{3/2}$ peak can be fitted with two peaks. One peak is at 933 eV, corresponding to Cu^{2+} $2p_{3/2}$ peak. The other peak at 932 eV is characteristic of Cu^{1+} $2p_{3/2}$ peak. Thus, it illustrates that the Cu is in its one and two-valence oxidation states simultaneously in the as-deposited film. It is expected that Cu^{1+} and Cu^{2+} has been effectively doped into the ZnO wurtzite lattice at the Zn^{2+} sites. After annealing in Ar or air, Cu still exists in its one and two-valence oxidation states simultaneously. However, the Cu^{1+} $2p_{3/2}$ peaks become stronger after annealing in Ar as shown in Fig. 4.2.7(b, c), indicating that a reduction of Cu occurs during annealing. On the contrary, Cu^{2+} $2p_{3/2}$ peaks become predominant after annealing in air as shown in Fig. 4.2.7(d-g), illustrating that an oxidation of Cu occur during annealing. XRD and XPS measurements have found that the loss of oxygen from the film during the annealing in Ar or air. The reduction of Cu is caused by the loss of oxygen from the film during the annealing in the inert gas. The Cu^{2+} or Cu^{1+} at the Zn^{2+} sites in the ZnO wurtzite lattice is easier to lose oxygen

and then be reduced to Cu^{1+} even metallic form than Zn^{2+} in the film. Thus, the Cu^{2+} or Cu^{1+} is reduced to Cu^{1+} even metallic Cu in the film. The reduction of copper in the films is consistent with the precipitation of Cu_2O but not CuO after annealing in Ar through XRD results. Although the loss of oxygen from the film also occurs during the annealing in air, the oxidation of Cu still can occur. Compared with annealing in Ar, annealing in air possesses a smaller concentration gradient of O in the film and the ambient, which induces that the diffusion of oxygen is slower during annealing in air. Thus, the loss of oxygen from Cu^{2+} or Cu^{1+} at the Zn^{2+} sites in the ZnO wurtzite lattice and the oxidation of copper by the oxygen in the crystal lattice occur at the same time, but the oxidation of copper is dominant, so Cu^{1+} is gradually oxidized to Cu^{2+} . The oxidation of copper in the films is consistent with the precipitation of CuO but not Cu_2O after annealing in air through XRD results.

The chemical states of metallic elements at the surface of thin films are easily influenced by air when the sample is stored in the air environment, because they can be oxidized by the oxygen in air. It is necessary to remove the top surface of the thin films and test the subsurface chemical states of each element in the films. Thus, the subsurface chemical states of Zn, Cu and O in the films are further investigated by XPS after etching sample surfaces using low-energy Ar^+ sputtering for 5 min. Figures 4.2.8, 4.2.9, and 4.2.10 show the Zn 2p, O 1s, and Cu 2p spectra respectively, which are measured at the subsurface of the Cu-doped ZnO films before and after annealing. In the Zn 2p spectra in Fig. 4.2.8, no significant differences have been observed, the Zn $2p_{3/2}$ peak is still at about 1021 eV, so Zn is also in its two-valence oxidation state in the volume of the films before and after annealing. In the O 1s spectra in Fig. 4.2.9, two O 1s peaks can also be resolved by using a curve fitting procedure for each O 1s

spectrum. Compared with the chemical state of O at the top surface, the peak associated with the chemisorbed oxygen becomes lower, because the chemisorbed oxygen is much more at the top surface than that in the volume of the thin films.

Fig. 4.2.8. XPS Zn 2p spectra of the subsurfaces of the Cu-doped ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

Fig. 4.2.9. XPS O 1s spectra of the subsurfaces of the Cu-doped ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

Fig. 4.2.10. XPS Cu 2p spectra of the subsurfaces of the Cu-doped ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h.

(a)

(b)

Fig. 4.2.11. Fitting results of the XPS spectra shown in Fig. 4.2.10, indicating the mean percentages of Cu, Cu¹⁺ and Cu²⁺ in the volumes of the annealed Cu-doped ZnO films with reference to the as-deposited films: (a) annealed in Ar for 10 and 20 min, and (b) annealed in air for 10 min, 20 min, 3 h, and 6 h.

Fig. 4.2.10(a) shows the Cu 2p spectrum in the subsurface of the as-deposited thin film, which is obviously different from the Cu 2p spectrum at the top surface of the film in Fig. 4.2.7(a). In the Cu 2p spectrum at the top surface of the film, the major component is Cu^{2+} , and the minor component is Cu^{1+} . However, in the Cu 2p spectrum in the subsurface of the film, the Cu $2p_{3/2}$ peak is fitted with a major component of $\text{Cu}^{1+} 2p_{3/2}$ at about 932 eV and a minor component of $\text{Cu}^{2+} 2p_{3/2}$ at about 933 eV. Fitting results indicate that the mean percentages of Cu^{1+} and Cu^{2+} are 84.3% and 15.7%, respectively. The major component of Cu^{1+} in the subsurface is transferred to Cu^{2+} at the top surface of the film, which can be attributed to the further oxidation of Cu^{1+} by the oxygen in the air when the sample is stored in the air environment. Cu is in its one and two-valence oxidation states simultaneously in the volume of the as-deposited film. It is expected that Cu^{1+} and Cu^{2+} has been effectively doped into the ZnO wurtzite lattice at the Zn^{2+} sites.

The chemical states of Cu display larger differences after annealing between subsurface and top surface of the films. After annealing in Ar, the Cu $2p_{3/2}$ peak can be fitted with two peaks, as shown in figures 4.2.10(b, c). One minor peak is at about 932 eV, corresponding to $\text{Cu}^{1+} 2p_{3/2}$ peak. One major peak at about 931 eV is characteristic of metallic Cu $2p_{3/2}$ peak. It illustrates that the Cu is in its major metallic and minor one-valence oxidation states simultaneously in the film after annealing in Ar. No peak corresponding to $\text{Cu}^{2+} 2p_{3/2}$ peak is observed anymore like at the top surface of the films in figures 4.2.7(b, c). Because there is a big difference on the chemical states of Cu at the top surface from that in the subsurface of the films, the reduction process should be further completed. The loss of oxygen from the film occurs during the annealing in the inert gas, which can cause the reduction of Cu. The

Cu^{2+} or Cu^{1+} at the Zn^{2+} sites in the ZnO wurtzite lattice is easier to lose oxygen and then be reduced to Cu^{1+} even metallic form than Zn^{2+} in the films. Thus, the Cu^{2+} is completely reduced to Cu^{1+} even metallic Cu, while the Cu^{1+} is partially reduced to metallic Cu in the films. It should be reasonable that the Cu is in its major metallic and minor one-valence oxidation states simultaneously both in the subsurface and top surface of the films after annealing in Ar. However, obvious one and two-valence oxidation states of Cu are observed at the top surface of the films. The reason is that the reduced metallic Cu and Cu^{1+} at the top surface of the film are oxidized again by the oxygen when the sample is stored in the air environment. In the subsurface of the films, the concentration of Cu is much lower than that at the top surface due to the Cu diffusion, and the aggregation of metallic Cu is not distinct, so the precipitation of Cu_2O at the top surface but not metallic Cu in the subsurface is observed in the films after annealing in Ar through XRD results. Fitting results in Fig. 4.2.11(a) indicate that the mean percentages of metallic Cu are 0.0%, 61.3% and 77.0% in the films as-deposited, annealed in Ar for 10 min, and annealed in Ar for 20 min, respectively. It illustrates that the longer the annealing duration is, the more serious the loss of oxygen is, and the more serious the reduction of Cu is.

After annealing in air, the Cu 2p spectra in the subsurface (figures 4.2.10(d-g)) are also different from those at the top surface of the films (figures 4.2.7(d-g)), but similar to that in the subsurface of the as-deposited film (Fig. 4.2.10(a)). In the Cu 2p spectrum in the subsurface of the film annealed in air, the Cu $2p_{3/2}$ peak is also fitted with a component of $\text{Cu}^{1+} 2p_{3/2}$ at about 932 eV and a component of $\text{Cu}^{2+} 2p_{3/2}$ at about 933 eV. Compared with the subsurface, the top surface of the films also shows increased component of Cu^{2+} , which can also be attributed to the further oxidation of

Cu^{1+} by the oxygen in the air when the sample is stored in the air environment. Fitting results in Fig. 4.2.11(b) indicate that the mean percentages of Cu^{2+} are 15.7%, 23.4%, 37.4%, 48.3%, and 55.4% in the films as-deposited, annealed in air for 10 min, annealed in air for 20 min, annealed in air for 3 h, and annealed in air for 6 h, respectively. It illustrates that the longer the annealing duration is, the more serious the loss of oxygen is, but the more serious the oxidation of Cu is. In other words, the increased annealing duration in air can increase the concentration of oxygen vacancies in the films, also increase the amount of Cu^{2+} at Zn^{2+} sites of ZnO wurtzite lattice.

The chemical states of Cu in the subsurface are their real states in the volume of the films. They can explain the difference of Cu diffusion after different annealing conditions. The annealing in Ar possesses a most significant Cu diffusion compared with annealing in air, which can be attributed to the reduction of Cu. Through XPS, it indicates that Cu is in its major metallic and minor one-valence oxidation states simultaneously in the volume of the films after annealing in Ar. Cu^{2+} or Cu^{1+} at Zn^{2+} sites of ZnO wurtzite lattice is reduced to metallic Cu and gets rid of the restriction of oxygen in the crystal lattice during the annealing in Ar. The metallic Cu has to deviate from the Zn^{2+} sites of ZnO wurtzite lattice and enter the grain boundaries. Without the restriction of oxygen in the ZnO wurtzite lattice, the reduced Cu is easy to diffuse from the bottom to the top surface of the films. On the contrary, Cu is in its one and two-valence oxidation states simultaneously in the volume of the films after annealing in air. Cu^{1+} at Zn^{2+} sites of ZnO wurtzite lattice is gradually oxidized to Cu^{2+} during annealing in air. The restriction of oxygen in the lattice is stronger for Cu^{2+} than Cu^{1+} , so the restriction of oxygen in ZnO wurtzite lattice for Cu becomes stronger and stronger during the annealing in air. With the strengthened restriction of oxygen in the

ZnO wurtzite lattice, Cu^{1+} and Cu^{2+} become more and more difficult to diffuse from the bottom to the top surface of the films. Thus, Cu diffusion during annealing in Ar is most significant compared with those during annealing in air.

In addition, the rapid thermal annealing in air causes a more distinct Cu diffusion than the normal annealing in air. Through XPS, Cu^{1+} at Zn^{2+} sites of ZnO wurtzite lattice is gradually oxidized to Cu^{2+} during annealing in air. The oxidation can inhibit the diffusion of Cu. In the rapid thermal annealing, the temperature increasing rate is $50\text{ }^{\circ}\text{C/s}$, while it is $0.08\text{ }^{\circ}\text{C/s}$ in the normal annealing. With the high temperature increasing rate, the oxidation and diffusion of Cu almost start at the same time during the rapid thermal annealing. However, with the low temperature increasing rate, the oxidation should start earlier than the diffusion of Cu, because the oxidation can be motivated by lower energy or temperature than the diffusion. During the slow increasing temperature, the oxidation of Cu has started at lower temperature. On the contrary, the diffusion of Cu can start at higher temperature during the increasing temperature, even during the holding duration. The early oxidation of Cu can more efficiently inhibit the diffusion of Cu, so the diffusion of Cu is less distinct after the normal annealing than the rapid thermal annealing in air.

Fig. 4.2.12 shows the magnetization of the Cu-doped ZnO thin films both as-deposited and annealed measured as a function of magnetic field at room temperature. The as-deposited film displays obvious room temperature ferromagnetism (RTFM), as shown in Fig. 4.2.12(a). However, the RTFM disappears in the films after annealing in Ar, and diamagnetism is observed instead (figures 4.2.12(b, c)). On the contrary, significant improvements in saturation magnetization (M_s) and coercivity in the films

are observed after rapid thermal annealing in air compared to that in as-deposited film, as shown in figures 4.2.12(d, e). Furthermore, even stronger M_s and coercivity are observed after normal thermal annealing in air compared to that after rapid thermal annealing in air (figures 4.2.12(f, g)). The longer the annealing duration in air is, the larger the M_s and coercivity are. Fig. 4.2.13 is plotted to show the change of M_s in the films with different annealing conditions.

The XPS spectrum in Fig. 4.2.10(a) has illustrated that Cu is in its major one-valence (Cu^{1+}) and minor two-valence (Cu^{2+}) oxidation states simultaneously in the volume of the as-deposited film. The pure ZnO thin films do not show RTFM, which has been investigated in Section 4.1. Thus, the RTFM of the as-deposited film is from Cu^{1+} or Cu^{2+} . The electronic configuration of Cu^{1+} is $3d^{10}4s^0$ and that of Cu^{2+} is $3d^94s^0$. Since Cu in one-valence oxidation state has no unpaired spins, it has no contribution to net ferromagnetic moment. Thus, only Cu in two-valence oxidation state will contribute to the RTFM. The origin of RTFM for ZnO-based DMS has been widely explained by a bound magnetic polaron (BMP) model, suggesting that oxygen vacancies in ZnO-based DMS materials locally trap electrons to occupy orbitals interacting with the d subshells of neighboring TM dopants, resulting in the ferromagnetism. In this work, the RTFM in Cu-doped ZnO thin films can also be understood in the framework of BMP model. In the BMP model, an electron loosely bound to a charged defect, e.g. the oxygen vacancy, occupies an extended orbital around the defect forming a BMP. These overlap to form a spin-split impurity band. These electrons couple with the 3d spins of the magnetic dopant ions that lie within the extended orbital of the BMP. The Cu^{2+} exists in a $3d^9$ state and thus presents only one unoccupied orbital. The loosely bound electron will align in an anti-parallel configuration with the spins of the

individual Cu^{2+} ions resulting in the spins on the neighboring Cu^{2+} ions to align in a parallel configuration with each other, thus, leading to an effective ferromagnetic coupling between the Cu^{2+} moments.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Fig. 4.2.12. Room-temperature M-H hysteresis loops of the Cu-doped ZnO thin films: (a) as-deposited, (b) annealed in Ar for 10 min, (c) annealed in Ar for 20 min, (d) annealed in air for 10 min, (e) annealed in air for 20 min, (f) annealed in air for 3 h, and (g) annealed in air for 6 h. The insets show the magnified portions of the respective plots near the origins.

(a)

(b)

Fig. 4.2.13. M_s of the annealed Cu-doped ZnO films vs. annealing conditions with reference to the as-deposited films: (a) annealed in Ar for 10 and 20 min, and (b) annealed in air for 10 min, 20 min, 3 h, and 6 h.

It was reported that annealing in Ar could enhance the RTFM of TM-doped ZnO films due to the increased structural defects [33]. However, in this work, the annealing in Ar induces the disappearance of RTFM in the Cu-doped ZnO films because of the chemical state change of Cu. After annealing in Ar, it indicates that Cu is in its major metallic and minor one-valence oxidation states simultaneously in the volume of the films through XPS. Cu^{2+} can cause RTFM, but it is completely reduced to Cu^{1+} or metallic Cu. Metallic Cu is not magnetic, and Cu^{1+} has no contribution to RTFM, so RTFM disappears in the films after annealing in Ar.

It was reported that the M_s of TM-doped ZnO films declined after annealing in air due to the decreased oxygen vacancies [33, 109]. However, in this study, an enhanced M_s is observed in the Cu-doped ZnO films annealed in air because of the chemical state change of Cu and the diffusion of O. After annealing in air, Cu is in its one-valence (Cu^{1+}) and two-valence (Cu^{2+}) oxidation states simultaneously in the volume of the films. XPS fitting results in Fig. 4.2.11(b) have indicated that the mean percentages of Cu^{2+} increase from 15.7% in the as-deposited films to 23.4% after annealing in air for 10 min, 37.4% after annealing in air for 20 min, 48.3% after annealing in air for 3 h, and 55.4% after annealing in air for 6 h, respectively. The concentration of Cu^{2+} in the films increases with the increased annealing duration in air. Both XRD and XPS measurements have illustrated that the annealing in air can induce the loss of oxygen from the films and the increased oxygen vacancies in the films. Furthermore, the longer the annealing duration in air is, the higher the concentration of oxygen vacancies in the films is. In short, the increased annealing duration in air can increase the concentration of oxygen vacancies in the films, also increase the amount of Cu^{2+} at Zn^{2+} sites of ZnO wurtzite lattice. With the BMP model, higher densities of oxygen

vacancies and Cu^{2+} species yield a greater overall area occupied by the BMPs, thus activating more Cu^{2+} and oxygen vacancies to migrate into the ferromagnetic domains and enhancing the RTFM of the film. The strengthened RTFM obtained from BMP model is consistent with the change of M_s in the films with different annealing conditions plotted in Fig. 4.2.13(b). In Fig. 4.2.13(b), a significant improvement of M_s in the films has been observed after annealing in air compared to that in as-deposited film. In addition, the longer the annealing duration in air is, the larger the M_s is. Thus, the BMP model is acceptable through this work.

4.2.3 Summary

Annealing effect under varying conditions on the structural and magnetic properties of Cu-doped ZnO thin films was investigated. A lattice deviation of the Cu-doped ZnO thin films was observed both before and after annealing in Ar or air through XRD, which was considered as a result of formations of oxygen vacancies and interstitial Zn in the thin films. An elongation of ZnO wurtzite lattice constants was observed in the as-grown Cu-doped ZnO thin film compared to that of the stress free ZnO powders, which could be attributed to relatively fewer oxygen vacancies but more Zn interstices in the as-deposited thin film. However, a contraction of ZnO wurtzite lattice constants was observed in the thin films after annealing in Ar or air compared to that of the stress free ZnO powders, which could be assigned to increased oxygen vacancies but decreased interstitial zinc atoms. Significant diffusion of O and Cu from the bottom to the top surface of thin films was observed after annealing in Ar or air through XPS. The O diffusion resulted in increased oxygen vacancies in the thin films after annealing. Reduction of Cu occurred in the thin films

annealed in Ar, while oxidization of Cu occurred in the thin films annealed in air. Increased annealing duration in air increased the concentration of oxygen vacancies in the thin films, also increased the amount of Cu^{2+} at Zn^{2+} sites of ZnO wurtzite lattice. The as-deposited thin film displayed obvious room temperature ferromagnetism (RTFM) that originated from Cu^{2+} through bound magnetic polaron (BMP) model. However, RTFM disappeared in the thin films after annealing in Ar due to the disappearance of Cu^{2+} . On the contrary, a significant improvement in saturation magnetization (M_s) in the thin films was observed after annealing in air compared to that in the as-deposited thin film. Furthermore, the longer the annealing duration in air was, the larger the M_s was. The increase of M_s in the thin films annealed in air was attributed to a stronger BMP effect with increased concentrations of oxygen vacancies in the thin films and Cu^{2+} at Zn^{2+} sites of ZnO wurtzite lattice.

4.3 Nickel-Doped Zinc Oxide Thin Films

4.3.1 Introduction

Annealing effect under varying conditions on the structural, magnetic and optical properties of Ni-doped ZnO thin films was systematically investigated. A deviation of the lattice constant c in the Ni-doped ZnO thin films was observed both before and after annealing in air or Ar at 600 °C, which was assigned to oxygen vacancies and interstitial Zn in the thin films. Oxidization of metallic Ni from its metallic state to two-valence oxidation state occurred in the film annealed in air at 600 °C, while reduction of Ni^{2+} from its two-valence oxidation state to metallic state occurred in the film annealed in Ar at 600 and 800 °C. In addition, there appeared to be significant diffusion of Ni from the bottom to the top surface of the film during annealing in Ar at 800 °C. Both as-deposited and annealed thin films displayed obvious room temperature ferromagnetism (RTFM) which was from metallic Ni, Ni^{2+} or both with two distinct mechanisms. Furthermore, a significant improvement in saturation magnetization (M_s) in the films was observed after annealing in air or Ar at 600 °C compared to that in as-deposited film. An even higher M_s value was observed in the film annealed in Ar at 800 °C compared to that at 600 °C mainly due to the diffusion of Ni. The ultraviolet emission of the Ni-doped ZnO thin film was restored during annealing in Ar at 800 °C, which was also attributed to the diffusion of Ni.

4.3.2 Results and Discussion

Fig. 4.3.1 shows the XRD spectra for the Ni-doped ZnO thin films both as-deposited and annealed under different conditions. Only the peak corresponding to ZnO(002) is observed in the as-deposited film, indicating that a polycrystalline wurtzite phase with c-axis preferred orientation is formed in the film. No diffraction peaks attributed to Ni-related secondary phases are observed, implying that the Ni atoms might substitute for the Zn atoms or any occurrence of Ni should be below the resolution of the XRD measurements. After annealing in Ar or air at 600 °C, the ZnO(002) peak still exists but shifting toward right. Moreover, the standard peak position of ZnO powders (34.4°) located between those of the as-deposited (34.2°) and annealed (34.6°) thin films, which means that the lattice constant c is elongated in the as-deposited film and shortened in the annealed films. The stress σ in the plane of the film can be calculated using the estimated lattice constant c using the following expression [109],

$$\sigma = 4.5 \times 10^{11} (c_0 - c) / c_0$$

where c_0 is the lattice constant of bulk ZnO. An elongated c indicates that the as-deposited film is in a state of compressive stress parallel to the (002) plane and tensile stress parallel to the c-axis. However, a shortened c in the annealed films reveals that the films after annealing are in a state of tensile stress parallel to the (002) plane and compressive stress parallel to the c-axis. Similar results have been reported by Gupta et al. [110] and Liu et al. [109]. The change in stress in the films after annealing was attributed to interstitial oxygen by Gupta et al. However, the interstitial oxygen is not

the primary defect in ZnO crystal [75, 111]. Thus, Liu et al. developed Gupta's theory and attributed it to oxygen vacancies and interstitial zinc atoms.

Fig. 4.3.1. XRD spectra of as-deposited and annealed Ni-doped ZnO thin films.

The change in stress in the films after annealing is primarily due to the defects produced during the film growth process. As the deposition rate of the films is high during the sputtering deposition, the zinc atoms are prone to enter the octahedral interstices [75, 109, 111]. Simultaneously, the oxygen atoms have a tendency to deviate from their positions in the ZnO crystal lattice, so there are also a large number of oxygen vacancies in the films. On one hand, the interstitial zinc atoms and the zinc atoms at the normal sites in the ZnO crystal lattice exclude each other, which leads to the expansion of the film lattice. On the other hand, the existence of oxygen vacancies destroys the balance of attraction and repulsion between neighboring crystal planes,

which leads to the contraction of the film lattice. Therefore, the lattice deviation of the Ni-doped ZnO films from that of the stress free ZnO powders may be a result of the formations of oxygen vacancies and interstitial Zn. There are relatively fewer oxygen vacancies but more Zn interstices in the as-grown Ni-doped ZnO film, which shows a state of compressive stress parallel to the (002) plane and tensile stress parallel to the c-axis, thus causing the elongation of the lattice constant c . After annealing at 600 °C in Ar or air, the oxygen vacancies increase in the films. The thermal energy supplied in annealing motivates the migration of the zinc interstices to the normal crystal lattice sites, which reduces the number of interstitial zinc atoms. Consequently, the films after annealing at 600 °C in Ar or air are in a state of tensile stress parallel to the (002) plane and compressive stress parallel to the c-axis, which causes a contraction of lattice constant c .

In addition, the grain growth can also induce the change in stress. For the as-deposited film, the film grows with a columnar structure along the c-axis due to a (002) preferential orientation during the sputtering deposition [109]. The columnar grains squeeze each other in a direction parallel to the (002) plane, which leads to a restraint of grain growth and a compressive stress along the direction. After annealing, the zinc atoms released from the interstitial positions result in a grain growth along the c-axis due to the lowest binding energy in the [002] direction of ZnO when they revert to the crystal lattice sites. However, the grain growth is simultaneously restrained along the c-axis because of the existing film, which causes a compressive stress along the c-axis.

After annealing in Ar at 800 °C, the ZnO(002) peak disappears and no other obvious diffraction peaks are observed, which means that the ZnO matrix in the film has been

degraded. During the annealing in Ar at 800 °C, the decomposition of the ZnO matrix occurs substantially because of the inert environment and high temperature. As a result, the grains are damaged and the grain size becomes smaller, which have caused the diminished diffraction peaks. The decomposition of the ZnO matrix is also confirmed by the loss of oxygen from the film during the annealing in the inert gas through XPS.

XPS is performed to determine the depth profile of atomic concentration for each element in the Ni-doped ZnO thin films, as shown in Fig. 4.3.2. The atomic concentrations of Zn, Ni, and O in the as-deposited film are uniform along the depth profile, which are about 47.26, 2.25, and 50.49 %, respectively (Fig. 4.3.2(a)). After the annealing in air at 600 °C, no significant differences have been observed (Fig. 4.3.2(b)). After the annealing in Ar at 600 °C, the atomic concentrations of each element in the film are still uniform along the depth profile, while the O decreases to about 44.55 % (Fig. 4.3.2(c)), which means that the O in the film diffuses into the inert gas because of the concentration gradient of O in the film and the ambient during the annealing in Ar. The oxygen decomposed from the film matrix diffuses onto the film surface, and then departs the film surface and enters the Ar gas environment. It is more interesting to notice that after the annealing in Ar at 800 °C, the atomic concentrations of each element in the film become not uniform any more along the depth profile (Fig. 4.3.2(d)). The O is from about 31.56 to 41.88 % at the etching depth from 10 to 90 nm in the film, which is much lower than 44.55 % in the film annealing in Ar at 600 °C. The annealing in Ar at higher temperature of 800 °C causes a more severe loss of oxygen from the film compared to the annealing in Ar at 600 °C. The more severe loss of oxygen confirms the decomposition of the ZnO matrix

through XRD. Apart from the diffusion of O, a significant diffusion of Ni from the bottom to the top surface of the film during annealing in Ar at 800 °C is also observed from Fig. 4.3.2(d). The Ni becomes 23.97 % at the etching depth of 10 nm, while 0 % at the etching depth of 90 nm in the film. As a result of the diffusion of Ni, the concentration of Ni increases at the surface, while the pure ZnO is left at the bottom of the film.

Fig. 4.3.2. XPS atomic concentration depth profiles for Zn, Ni, and O in Ni-doped ZnO thin films: (a) as-deposited, (b) annealed in air at 600 °C, (c) annealed in Ar at 600 °C, and (d) annealed in Ar at 800 °C.

The x value is the mole fraction of Ni in the Ni-doped ZnO ($\text{Zn}_{1-x}\text{Ni}_x\text{O}$) film. Fig. 4.3.3 shows the x values in the films before and after annealing as a function of the

etching depth. The x values in the as-deposited film are uniform along the depth profile, which are around 0.045 (Fig. 4.3.3(a)). No significant differences have been observed after annealing in air (Fig. 4.3.3(b)) or Ar (Fig. 4.3.3(c)) at 600 °C, which indicates that there is no diffusion of Ni during the annealing. However, after the annealing in Ar at 800 °C, the x values become nonuniform along the depth (Fig. 4.3.3(d)). The x is about 0.35 at the depth of about 10 nm, and near 0 at the depth of about 90 nm in the film, which shows a significant diffusion of Ni from the bottom to the top surface of the film during annealing in Ar at 800 °C.

Fig. 4.3.3. Ni mole fraction x vs. etching depth of $Zn_{1-x}Ni_xO$ films: (a) as-deposited, (b) annealed in air at 600 °C, (c) annealed in Ar at 600 °C, and (d) annealed in Ar at 800 °C.

The chemical states of nickel in the films are studied also using XPS. Fig. 4.3.4 shows the Ni 2p depth profiles measured from the Ni-doped ZnO films before and after annealing. In the XPS spectra, the peaks at about 852.5 and 855 eV are characteristic of metallic Ni 2p_{3/2} and Ni²⁺ 2p_{3/2} states, respectively. Although the noises in the Ni 2p spectra are relatively high due to the low nickel contents in the films, they are not obstructing the effective information. The Ni 2p spectra measured from the top surfaces of the films are noisier than those measured from near bottom locations of the films due to the contamination of the top surfaces. Fig. 4.3.4(a) is the Ni 2p depth profile measured from the as-deposited film. The metallic Ni 2p_{3/2} peak at 852.2 eV and the Ni²⁺ 2p_{3/2} peak at 854.4 eV illustrate that the nickel is in its metallic and two-valence oxidation states simultaneously in the as-deposited film. It is expected that Ni²⁺ has been effectively doped into the ZnO wurtzite lattice at the Zn²⁺ sites, while the metallic Ni exists in the interstices of the ZnO wurtzite lattice or the grain boundaries of the ZnO matrix.

Fig. 4.3.4(b) shows the Ni 2p depth profile measured from the film annealed in air at 600 °C. The unique Ni²⁺ 2p_{3/2} peak at 854.6 eV indicates that the nickel is only in its two-valence oxidation state in the film. The metallic Ni is oxidized to the Ni²⁺ in the film after annealing in the air. The XRD results in Fig. 4.3.1 have indicated that the interstitial Zn atoms revert to the crystal lattice sites during annealing in air at 600 °C. The metallic Ni as well as the interstitial Zn atoms can diffuse into the Zn²⁺ sites in the ZnO wurtzite lattice because of the small diffusion barriers. As a result, the metallic Ni in the film is oxidized to Ni²⁺ by the oxygen in the lattice, and the concentration of Ni²⁺ at the Zn²⁺ sites in the ZnO wurtzite lattice increases. However, the activation energy for oxygen diffusion is much larger than that for the diffusion of

the interstitial Zn atoms and metallic Ni, and no significant oxygen diffusion from air into the film has been observed in Fig. 4.3.2(b), so no enough oxygen atoms from air diffuse in the lattice to fill up the new oxygen vacancies caused by the increased Zn^{2+} and Ni^{2+} , oxygen vacancies increase. Thus, after annealing in air at 600 °C, the concentration of oxygen vacancies is increased in the film, which is consistent with the XRD results.

Fig. 4.3.4. XPS Ni 2p depth profiles of Ni-doped ZnO films: (a) as-deposited, (b) annealed in air at 600 °C, (c) annealed in Ar at 600 °C, and (d) annealed in Ar at 800 °C.

On the contrary, the unique metallic Ni 2p_{3/2} peak at 852.0 eV indicates that the nickel is only in its metallic state in the film annealed in Ar at 600 °C, as shown in Fig. 4.3.4(c). The Ni²⁺ is reduced to the metallic Ni in the film, which is caused by the loss of oxygen from the film during the annealing in the inert gas (Fig. 4.3.2(c)). The Ni²⁺ at the Zn²⁺ sites in the ZnO wurtzite lattice is easier to lose oxygen and then be reduced to metallic form than Zn²⁺ in the film. Thus, the Ni²⁺ is reduced to the metallic Ni in the film. The metallic Ni reduced locates at the grain boundaries rather than in the interstices of the ZnO wurtzite lattice, which can be explained by the XRD results as shown in Fig. 4.3.1. The interstitial Ni can elongate the lattice constant *c* of the ZnO like interstitial Zn, but the lattice constant *c* is shortened with annealing in Ar at 600 °C as depicted by the XRD results, so the metallic Ni exists at the grain boundaries of the ZnO matrix.

During the annealing in Ar at 800 °C, the reduction of Ni²⁺ and the diffusion of Ni atoms occur in the film, as shown in Fig. 4.3.4(d). Below 10 nm in depth in the film, the metallic Ni 2p_{3/2} peaks at 852.5 eV indicate that the nickel mainly exists in the form of metallic Ni due to the reduction of Ni²⁺ in the inert Ar. From the XRD (Fig. 4.3.1) and XPS (Fig. 4.3.2(d)) measurements for the film annealed in Ar at 800 °C, it has been found that the decomposition of the ZnO matrix and the more severe loss of oxygen from the film obviously occur during the annealing. The more severe loss of oxygen from the film causes a more complete reduction of Ni²⁺. Usually, only the reduction of Ni²⁺ occurs in the inert gas, but at the top surface of the film, only strong Ni²⁺ 2p_{3/2} peak at 855 eV is observed, which means that the metallic Ni is fully oxidized to Ni²⁺. The reason is that the reduced metallic Ni at the top surface of the film is oxidized again by the oxygen when the sample is stored in the air environment.

The diffusion of Ni from the bottom to the top surface of the film during annealing in Ar at 800 °C is also observed from Fig. 4.3.4(d). At the film surface, the peaks corresponding to nickel are very strong, but no peak for nickel is observed near the bottom of the film. The diffusion of Ni has also been confirmed by the depth profile of atomic concentration for Ni using XPS in Fig. 4.3.2(d). Thus, there is metallic Ni with higher concentration near the surface of the film annealed in Ar at 800 °C, which causes the aggregation of more metallic Ni and the formation of more and larger metallic Ni clusters at the grain boundaries near the film surface.

Fig. 4.3.5. Room-temperature M-H hysteresis loops of as-deposited and annealed Ni-doped ZnO films.

Fig. 4.3.5 shows the magnetization of the Ni-doped ZnO thin films both as-deposited and annealed measured as a function of magnetic field at room temperature. Both the as-deposited and annealed films can display obvious room temperature ferromagnetism (RTFM). Furthermore, a significant improvement in saturation

magnetization (M_s) in the films is observed after annealing in air or Ar at 600 °C compared to that in as-deposited film. An even stronger M_s is observed after annealing in Ar at 800 °C compared to that at 600 °C.

The XPS spectra in Fig. 4.3.4(a) have illustrated that nickel is in its metallic and two valence oxidation (Ni^{2+}) states simultaneously in the as-deposited film, so the RTFM of the as-deposited film is from the metallic and ionized nickel at the same time with two distinct mechanisms. The metallic Ni nanoclusters should exist at the grain boundaries, which may have certain RTFM but cannot be detected within the sensitivity of the XRD system used. The RTFM from Ni^{2+} can be explained using a bound magnetic polaron (BMP) model. The defects, such as oxygen vacancies, locally trap electrons to occupy the orbitals interacting with the d subshells of the neighboring Ni dopants, leading to the formation of a ferromagnetic network.

It was reported that the M_s of TM-doped ZnO films declined after annealing in air due to the decreased oxygen vacancies in ZnO [33, 109]. However, in this study, an enhanced M_s is observed in the film annealed in air at 600 °C, which is attributed to a stronger BMP effect. The XRD and XPS measurements in Fig. 4.3.1 and Fig. 4.3.4(b) illustrate that the oxygen vacancies increase after annealing in air at 600 °C. In addition, the XPS spectra indicate that the concentration of Ni^{2+} at the Zn^{2+} sites in the ZnO wurtzite lattice also increases after annealing in air at 600 °C. With the BMP model, higher densities of oxygen vacancies and Ni^{2+} species yield a greater overall area occupied by the BMPs, thus activating more Ni^{2+} and oxygen vacancies to migrate into the ferromagnetic domains and enhancing the RTFM of the film [33].

Annealing in the Ar environment at 600 °C has a similar effect on the M_s of the film. It was reported that the increased structural defects after annealing in Ar, such as oxygen vacancies, were considered as a reason for the increased M_s [33], but this work shows that the higher M_s can be attributed to the increased metallic Ni nanoclusters. The metallic Ni at the grain boundaries is increased after annealing in Ar at 600 °C according to the XPS and XRD results. More metallic Ni nanoclusters are formed at the grain boundaries by the aggregation of the increased metallic Ni, which enhances the M_s . The two distinct strengthening mechanisms on M_s after annealing in air and Ar at 600 °C further identify that the RTFM is from metallic Ni, Ni^{2+} or both with two distinct mechanisms in this work.

An even higher M_s is observed in the film annealed in the Ar environment at 800 °C compared to that at 600 °C. On one hand, annealing at a higher temperature in Ar induces a more complete reduction of Ni^{2+} and a more production of metallic Ni. On the other hand, according to the XPS measurement, Ni diffuses from the bottom to the surface of the film during annealing in Ar at 800 °C, leading to a higher concentration of metallic Ni near the film surface. Thus, more metallic Ni aggregates at the grain boundaries near the film surface, which promotes the formation of more and larger metallic Ni clusters. The more and larger metallic Ni clusters enhance the M_s of the film annealed at 800 °C compared to that at 600 °C.

Room temperature PL spectra of the Ni-doped ZnO thin films both as-deposited and annealed are shown in Fig. 4.3.6. The films as-deposited and annealed in air or Ar at 600 °C show very weak ultraviolet (UV) peaks centered at about 380 nm (3.26 eV). The UV emission is attributed to the near band-edge excitonic emission. Interestingly,

a significant strengthening in the intensity of UV emission peak is observed in the film annealed in Ar at 800 °C. In addition, this UV emission peak is centered at about 377 nm, which exhibits a blue shift of 3 nm compared to the 380 nm observed from the others. Usually, Ni doping in ZnO may result in a weaker peak and a red shift of UV emission [112]. The stronger UV emission and its blue shift of the film annealed in Ar at 800 °C show the depletion of Ni in the ZnO matrix. However, the total Ni concentration in the film is constant, thus it is a local depletion of Ni in the ZnO matrix near the bottom of the film due to the diffusion of the Ni from the bottom to the top surface of the film, which has been confirmed by the XPS measurement. As a result, the pure ZnO left at the bottom causes the stronger UV emission and its blue shift. Thus, the annealing in Ar at 800 °C simultaneously restores the optical property of the Ni-doped ZnO thin film when it enhances the magnetic property of the film.

Fig. 4.3.6. Room-temperature PL spectra of as-deposited and annealed Ni-doped ZnO films.

4.3.3 Summary

XPS depth profiles were used to investigate the effect of rapid thermal annealing under varying conditions on the structural, magnetic and optical properties of Ni-doped ZnO thin films. A deviation of the lattice constant c in the Ni-doped ZnO thin films was observed both before and after annealing in air or Ar at 600 °C, which was considered as a result of formations of oxygen vacancies and interstitial Zn in the thin films. An elongation of ZnO wurtzite lattice constant c was observed in the as-grown Ni-doped ZnO thin film compared to that of the stress free ZnO powders, which could be attributed to relatively fewer oxygen vacancies but more Zn interstices in the as-deposited thin film. However, a contraction of ZnO wurtzite lattice constant c was observed in the thin films after annealing in air or Ar at 600 °C compared to that of the stress free ZnO powders, which could be assigned to increased oxygen vacancies but decreased interstitial zinc atoms. Oxidization of metallic Ni atoms occurred in the film annealed in air at 600 °C, while reduction of Ni^{2+} ions occurred in the film annealed in Ar at 600 and 800 °C. Significant diffusion of Ni from the bottom to the top surface of the film during annealing in Ar at 800 °C was observed. Both the as-deposited and annealed thin films displayed obvious room temperature ferromagnetism (RTFM) that originated from metallic Ni, Ni^{2+} or both with two distinct mechanisms. Furthermore, a significant improvement in saturation magnetization (M_s) in the films was observed after annealing. The increase in M_s in the film annealed in air at 600 °C was attributed to a stronger bound magnetic polaron (BMP) effect. A similar improvement in M_s in the film annealed in Ar at 600 °C was attributed to increased metallic Ni nanoclusters. An even more significant M_s was observed from the film annealed in Ar at 800 °C compared to that at 600 °C, which

was attributed to more and larger metallic Ni clusters at the grain boundaries near the film surface mainly due to the diffusion of Ni in the film. A significant strengthening in the intensity and a blue shift of the ultraviolet emission peak were observed in the film annealed in Ar at 800 °C, which was attributed to the local depletion of Ni in the ZnO matrix near the bottom of the film due to the diffusion of Ni in the film. Thus, the annealing of the Ni-doped ZnO thin film in Ar at 800 °C simultaneously restored the optical property of the film when it enhanced the magnetic property of the film.

Chapter 5. Zinc Oxide-Based Diluted Magnetic Semiconductor Nanostructures

Nanoscale materials often exhibit physical and chemical properties that greatly differ from their bulk counterparts. Nanostructures such as nanowires, nanorods, nanotubes and nanospheres are promising building blocks for miniaturized devices. It is thus expected that a combination of the nanostructure with the RTFM of ZnO-based DMS materials would generate new functional nanomaterials with a potential for making future miniaturized spintronic devices. Apart from the potential applications, the fundamental understanding of the origin of RTFM in ZnO-based DMS has also become an important ground for the synthesis of nanostructured DMS, because the quantum confinement may result in very interesting magnetic properties which can be significantly different from their bulk systems. However, most DMS related researches have been focused on thin films while limited works on nanostructured ZnO-based DMS materials have been reported [48-51]. Thus, there is a need to investigate nanostructured ZnO-based DMS systems. In this chapter, ZnO-based DMS nanostructures possessing RTFM were synthesized through an electrochemical deposition method, including pure ZnO needle-shaped microrod arrays, Co-doped ZnO nanorod arrays, and Co-doped ZnO microsphere arrays. The RTFM of the pure ZnO microrod arrays was attributed to interstitial metallic Zn, while that of the Co-doped ZnO nanorod or microsphere arrays was attributed to the BMP model.

5.1 Pure Zinc Oxide Nanostructures

5.1.1 Introduction

Pure ZnO needle-shaped nanorod arrays were synthesized on the silicon substrates having a ZnO seed layer through the chemical deposition. The needle shape of the nanorods was formed due to the preferred orientation of ZnO[002]. Pure ZnO microrod arrays with different morphologies were grown on the bare silicon substrates through the electrochemical deposition with the help of different potentials of -0.8, -1.2, -1.6, and -2.0 V, respectively. When the potential was -2.0 V, pure ZnO needle-shaped microrod arrays were obtained. The potential played a key role in the nucleation process as well as the growth process of the pure ZnO microrod arrays. Zn was in its two-valence oxidation state in pure ZnO needle-shaped nanorod synthesized by chemical deposition as well as the pure ZnO microrod grown through electrochemical deposition at the potential of -0.8 V, while it was in its minor metallic and major two-valence oxidation states simultaneously in the pure ZnO microrod grown at the potentials of -1.2, -1.6, and -2.0 V. The reduced metallic Zn was doped into the interstices of ZnO wurtzite lattice and became interstitial metallic Zn. Furthermore, the concentration of interstitial metallic Zn increased in the pure ZnO microrod with the decreased potential. Diamagnetism was displayed by the pure ZnO needle-shaped nanorod arrays synthesized by the chemical deposition as well as the pure ZnO microrod arrays grown through the electrochemical deposition at -0.8 V, while RTFM could be displayed by the pure ZnO microrod arrays grown at the potentials of -1.2, -1.6, and -2.0 V. In addition, significant improvements in saturation magnetization (M_s) were observed in the pure ZnO microrod arrays with the

decreased potential applied in the electrochemical deposition. The RTFM in the pure ZnO microrod arrays could be attributed to the interstitial metallic Zn.

5.1.2 Results and Discussion

Figures 5.1.1-5.1.5 show typical FESEM micrographs of pure ZnO nano/micro structures synthesized by the chemical deposition and the electrochemical deposition methods, respectively. Through the chemical deposition method, pure ZnO nanorod arrays with high density and regular structure are obtained, as shown in Fig. 5.1.1. The nanorods have a well-defined hexagonal cross section with tip diameter of about 100 nm. In addition, the diameter of the hexagonal cross section is smaller at the tip than that at the bottom of the rods. When a potential of -0.8 V is applied in the electrochemical deposition process, dense microrod arrays are grown instead of nanorod arrays as shown in Fig. 5.1.2. The tip diameter of the well-defined hexagonal cross section is about 500 nm, and its bottom diameter is also much larger compared to its tip diameter. With the decreased potential, the tip diameter becomes smaller and smaller, and the difference between the tip and bottom diameters becomes larger and larger. As shown in figures 5.1.3-5.1.5, the tip diameters of the rods reduce to about 470, 200, and 100 nm when the potential is -1.2, -1.6, and -2.0 V, respectively. Fig. 5.1.6 shows the decreased tip diameter of the microrods with the decreased potential applied in the electrochemical depositions.

Fig. 5.1.1. (a) Low and (b) high magnification FESEM images of pure ZnO nano/micro structures grown with chemical deposition.

Fig. 5.1.2. (a) Low and (b) high magnification FESEM images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -0.8 V.

Fig. 5.1.3. (a) Low and (b) high magnification FESEM images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -1.2 V.

Fig. 5.1.4. (a) Low and (b) high magnification FESEM images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -1.6 V.

Fig. 5.1.5. (a) Low and (b) high magnification FESEM images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -2.0 V.

Fig. 5.1.6. Tip diameters of pure ZnO nano/micro rods synthesized with both chemical and electrochemical deposition methods.

Figures 5.1.7-5.1.11 show typical FESEM cross-sectional micrographs of pure ZnO nano/micro structures synthesized by the chemical deposition and the electrochemical deposition methods, respectively. Through the chemical deposition method, pure ZnO nanorod arrays are vertically aligned to the surface of silicon substrate with ZnO seed layer, as shown in Fig. 5.1.7. The length of nanorods is about 2.5 μm . In addition, it is confirmed that the diameter is smaller at the tip than that at the bottom of rods. Since the diameter of rod gradually decreases from bottom to top and the shape looks like a needle, it is named after needle-shaped nanorod. When the potential of -0.8 V is applied in the electrochemical deposition process, microrod arrays are vertically aligned to the surface of bare silicon substrate instead of nanorod arrays as shown in Fig. 5.1.8. The length of microrods is about 3.6 μm , which is much longer than that of nanorods in Fig. 5.1.7, indicating that the growth rate of pure ZnO nano/micro rods is much larger in the electrochemical deposition with the help of potential than that in the chemical deposition. Furthermore, it is also confirmed that the tip diameter of the microrod is much smaller compared to its bottom diameter. With the decreased potential, the length of the microrods increases. As shown in figures 5.1.9-5.1.11, the length of the microrods increase to about 4.0, 4.9, and 6.7 μm when the potential is -1.2, -1.6, and -2.0 V, respectively. Fig. 5.1.12 shows the increased length of the microrods with the decreased potential applied in the electrochemical depositions, illustrating that the potential can promote the growth of the pure ZnO microrods. In addition, with the decreased potential, the tip diameter becomes smaller and smaller, and the difference between the tip and bottom diameters becomes larger and larger. When the potential is -2.0 V, the bottom of microrod becomes very thick, while the tip becomes very small and sharp, so it is termed needle-shaped microrod. It is interesting to notice that the tips of the pure ZnO nano/micro rods separate, while the

bottoms connect each other even aggregate. The aggregation of rod bottoms is more obvious in the electrochemical deposition, and the thickness of the aggregation increases with decreased potential.

Fig. 5.1.7. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO nano/micro structures grown with chemical deposition.

Fig. 5.1.8. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -0.8 V.

Fig. 5.1.9. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -1.2 V.

Fig. 5.1.10. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -1.6 V.

Fig. 5.1.11. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO nano/micro structures grown with electrochemical deposition at the potential of -2.0 V.

Fig. 5.1.12. Lengths of pure ZnO nano/micro rods synthesized with both chemical and electrochemical deposition methods.

Fig. 5.1.13 shows XRD patterns for the nano/micro rods synthesized by the chemical deposition and electrochemical deposition methods. Fig. 5.1.13(a) shows standard peak positions of pure ZnO powders. Only obvious peaks corresponding to ZnO is observed in the nano/micro rods (figures 5.1.13(b-f)), indicating that a pure ZnO wurtzite phase with c-axis preferred orientation is formed in the rods. The strongest ZnO(002) peak indicates that the pure ZnO nano/micro rods are vertically aligned on the substrates with the preferred orientation of ZnO[002].

XPS measurements are performed to determine the atomic concentrations of Zn and O in the pure ZnO nano/micro rod arrays as shown in Fig. 5.1.14. The atomic concentrations of Zn and O are respectively about 48.51 and 51.49 % in the pure ZnO needle-shaped nanorod arrays synthesized by the chemical deposition. In the O-rich condition, the defect of oxygen vacancies should not dominate. However, the atomic concentrations of Zn and O become respectively about 50.02 and 49.98 % in the pure

ZnO microrod arrays synthesized by the electrochemical deposition when the potential is -0.8 V. Furthermore, the concentration of Zn increases to 50.96, 51.68, and 52.49 %, when the potential decreases to -1.2, -1.6, and -2.0 V, respectively. Thus, in the Zn-rich conditions, the defect of oxygen vacancies should dominate. In addition, the concentration of oxygen vacancies should increase with the decreased potential applied in the electrochemical deposition.

Fig. 5.1.13. (a) Standard XRD peak positions of pure ZnO powders and (b-f) XRD spectra of (b) nanorod arrays synthesized with chemical deposition, and (c-f) microrod arrays synthesized with electrochemical deposition at the potentials of (c) - 0.8, (d) -1.2, (e) -1.6, and (f) -2.0 V.

Fig. 5.1.14. XPS atomic concentrations of Zn and O in the pure ZnO nano/micro rod arrays synthesized with both chemical and electrochemical deposition methods.

The chemical states of Zn and O in the pure ZnO nano/micro rod arrays are studied also using XPS. Fig. 5.1.15 and Fig. 5.1.16 respectively show the Zn 2p and O 1s spectra, which are measured at the surface of rod arrays. In the Zn 2p spectrum in Fig. 5.1.15(a), the peak at about 1021 eV is characteristic of $\text{Zn}^{2+} 2p_{3/2}$ state, so Zn is in its two-valence oxidation state in the pure ZnO needle-shaped nanorod synthesized by the chemical deposition. In the O 1s spectrum in Fig. 5.1.16(a), two O 1s peaks can be resolved by using a curve fitting procedure. The peak at 530 eV is attributed to O^{2-} ions present in a stoichiometric wurtzite ZnO structure, whereas the 531 peak is associated with the specific chemisorbed oxygen, such as the adsorbed H_2O , $-\text{CO}_3$, and so on.

Fig. 5.1.15. XPS Zn 2p spectra of (a) nanorod arrays synthesized with chemical deposition, and (b-e) microrod arrays synthesized with electrochemical deposition at the potentials of (b) -0.8, (c) -1.2, (d) -1.6, and (e) -2.0 V.

Similar Zn 2p and O 1s spectra are observed in the pure ZnO microrod arrays grown through the electrochemical deposition when the potential is -0.8 V, as shown in Fig. 5.1.15(b) and Fig. 5.1.16(b). However, when the potential is decreased to -1.2 V, Zn 2p spectrum displays obvious differences. In Fig. 5.1.15(c), the Zn 2p_{3/2} peak can be fitted with two peaks. One peak is at about 1021 eV, corresponding to Zn²⁺ 2p_{3/2} peak. The other peak at about 1019 eV is characteristic of metallic Zn 2p_{3/2} peak. It

illustrates that Zn is in its minor metallic and major two-valence oxidation states simultaneously in the pure ZnO microrod. Zn in two-valence oxidation state must be at the Zn^{2+} sites of ZnO wurtzite lattice, while metallic Zn is expected to locate in interstices of ZnO wurtzite lattice and become interstitial metallic Zn. Fitting results indicate that the mean percentages of metallic Zn and Zn^{2+} are about 9.00 % and 91.00 %, respectively.

Fig. 5.1.16. XPS O 1s spectra of (a) nanorod arrays synthesized with chemical deposition, and (b-e) microrod arrays synthesized with electrochemical deposition at the potentials of (b) -0.8, (c) -1.2, (d) -1.6, and (e) -2.0 V.

When the potential is further decreased to -1.6 and -2.0 V, Zn is also in its minor metallic and major two-valence oxidation states simultaneously in the pure ZnO microrod, as shown in figures 5.1.15(d) and 5.1.15(e). Corresponding to XPS fitting results plotted in Fig. 5.1.17, the concentration of interstitial metallic Zn increases to 19.65 % and 24.49 % when the potential decreases to -1.6 and -2.0 V, respectively.

Fig. 5.1.17. Fitting results of XPS Zn 2p spectra of pure ZnO nano/micro rod arrays synthesized using both chemical and electrochemical deposition methods.

The formation of pure ZnO needle-shaped nanorod arrays synthesized by the chemical deposition involves nucleation and growth processes. The nucleation and growth mechanisms can be explained as follows:

$\text{C}_6\text{H}_{12}\text{N}_4$ in the solution is decomposed to HCHO and NH_3 according to Eq. (1). NH_3 reacts with H_2O through Eq. (2) to form hydroxide ions. Subsequently, Eqs. (3) and (4) occur in the solution, which produces a large amount of ZnO. Since the nucleation energy barrier of ZnO is very low on the silicon substrate with ZnO seed layer, ZnO in the solution easily nucleates on the ZnO seed layer. In the growth process following nucleation, due to the preferred orientation of ZnO[002], the growth rate is fastest along ZnO[002] compared to those along the other directions. As a result, pure ZnO needle-shaped nanorod arrays are obtained.

Pure ZnO nano/micro rod arrays cannot be synthesized on bare silicon substrate without potential, but can be obtained with potential. In addition, with the decreased potential, the tip diameter of the pure ZnO microrod becomes smaller and smaller, the difference between its tip and bottom diameters becomes larger and larger, and its growth rate becomes faster and faster. When the potential is -2.0 V, pure ZnO needle-shaped microrod arrays are obtained. In order to understand the growth mechanism of pure ZnO microrod arrays on bare silicon substrate through electrochemical deposition method, a series of experiments were carried out with a potential of -2.0 V and different durations of 0.5, 1, 2, and 6 h.

Figures 5.1.18-5.1.25 show typical FESEM top-view (figures 5.1.18-5.1.21) and cross-sectional (figures 5.1.22-5.1.25) micrographs of pure ZnO nano/micro structures synthesized by the electrochemical deposition method with different durations of 0.5, 1, 2, and 6 h, respectively. The changes of the tip diameter and length of pure ZnO microrod with duration are plotted in figures 5.1.26 and 5.1.27. As shown in Fig. 5.1.26, its tip diameter decreases from about 430 nm with 0.5 h duration to about 300, 100, and 20 nm when the duration increases to 1, 2, and 6 h, respectively. In Fig. 5.1.27, its length increase from about 2.7 μm with 0.5 h duration to about 4.5, 6.7, and 9.2 μm when the duration increases to 1, 2, and 6 h, respectively. When the duration is 0.5 h, short pure ZnO microrod arrays are grown. The tip hexagonal cross section with small islands is not flat but big. The difference between its top and bottom diameters is small. The microrods separate at their tips. At their bottoms, some microrods separate while some start to connect each other and aggregate. When the duration is 1 h, its tip becomes smaller, and length becomes longer. The difference between its top and bottom diameters becomes larger. In addition, the microds has completely aggregated at their bottoms. When the duration is increased to 2 h and 6 h, its length further becomes longer, its tip further becomes smaller, its bottom aggregation becomes thicker, the difference between its top and bottom diameters further becomes larger, and pure ZnO needle-shaped microrod arrays are synthesized. With the increased duration, the length of the pure ZnO microrod becomes longer and longer, its bottom aggregation becomes thicker and thicker, its tip hexagonal cross section becomes smaller and smaller, and the difference between its top and bottom diameters becomes larger and larger.

Fig. 5.1.18. (a) Low and (b) high magnification FESEM images of pure ZnO microrod arrays grown with electrochemical deposition at potential of -2.0 V for 0.5 h.

Fig. 5.1.19. (a) Low and (b) high magnification FESEM images of pure ZnO microrod arrays grown with electrochemical deposition at potential of -2.0 V for 1 h.

Fig. 5.1.20. (a) Low and (b) high magnification FESEM images of pure ZnO microrod arrays grown with electrochemical deposition at potential of -2.0 V for 2 h.

Fig. 5.1.21. (a) Low and (b) high magnification FESEM images of pure ZnO microrod arrays grown with electrochemical deposition at potential of -2.0 V for 6 h.

Fig. 5.1.22. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO microrod arrays grown with electrochemical deposition at the potential of -2.0 V for 0.5 h.

Fig. 5.1.23. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO microrod arrays grown with electrochemical deposition at the potential of -2.0 V for 1 h.

Fig. 5.1.24. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO microrod arrays grown with electrochemical deposition at the potential of -2.0 V for 2 h.

Fig. 5.1.25. (a) Low and (b) high magnification FESEM cross-sectional images of pure ZnO microrod arrays grown with electrochemical deposition at the potential of -2.0 V for 6 h.

Fig. 5.1.26. Tip diameters of pure ZnO microrods synthesized using electrochemical deposition for different durations.

Fig. 5.1.27. Lengths of pure ZnO microrods synthesized using electrochemical deposition for different durations.

The formation of the pure ZnO microrod arrays through the electrochemical deposition also involves nucleation and growth processes. The nucleation and growth mechanisms can be explained as follows:

The $\text{C}_6\text{H}_{12}\text{N}_4$ in the solution is decomposed to HCHO and NH_3 according to Eq. (5). NH_3 reacts with H_2O through Eq. (6) to form hydroxide ions. OH^- is also produced during the electroreduction of nitrate to nitrite ions according to Eq. (7), which causes the increased OH^- ions at the bare silicon substrate surface (cathode). At the same time, Zn^{2+} is attracted to the substrate surface by negative potentials, which increases

the concentration of cations at the substrate surface. Subsequently, Eqs. (8) and (9) occur in the solution, especially at the substrate surface due to the high concentrations of OH^- and Zn^{2+} , which produces a large amount of ZnO at the substrate surface. The potential applied can assist in overcoming the high nucleation energy barrier of ZnO on the bare silicon substrate. Thus, negative potential promotes nucleation of the ZnO microrods, leading to a higher nucleation density compared to that in the absence of electric potential.

In the growth process following nucleation, due to the preferred orientation of ZnO[002], the growth rate is fastest along ZnO[002] compared to those along the other directions. As a result, short pure ZnO microrod arrays are separately grown on the bare silicon substrate in the beginning of the growth process. The diameter of the microrod gradually decreases from its bottom to top due to the fastest growth rate along ZnO[002], but the difference on diameters is small in the beginning of the growth process. With the increased duration, the growth of microrod simultaneously occur parallel and perpendicular to ZnO[002] direction, but the longitudinal growth is much faster than the transverse growth due to the preferred orientation of ZnO[002], so the length of the pure ZnO microrod increases, its tip hexagonal cross section becomes smaller, its bottom cross section becomes bigger, and the difference between its top and bottom diameters becomes larger. With a long enough duration, pure ZnO needle-shaped microrod arrays can be obtained. As a result of the bigger bottom cross section, the separate microrods start to connect each other. With the increased duration, the microrods aggregate at their bottoms. The longer the duration is, the thicker the bottom aggregation is.

The potential plays a key role in the nucleation process as well as in the growth process of the pure ZnO microrod arrays. The decreased potential can strengthen the attraction of the substrate to Zn^{2+} , increase the concentrations of OH^- and Zn^{2+} at the substrate surface, and supply enough energy to promote the growth of microrods. Thus, it has been observed that decreased potential can increase the growth rate of the microrods through FESEM, especially along ZnO[002] direction. With the accelerated growth rate parallel to ZnO[002] direction, the decreased tip diameter of microrods is also accelerated. It is consistent with the FESEM results that the tip diameter of microrods becomes smaller and the difference between the tip and bottom diameters becomes larger with the decreased potential. With the accelerated growth rate perpendicular to ZnO[002] direction, the aggregation of microrod bottoms is accelerated. It is also consistent with the FESEM results that the thickness of the aggregation increases with the decreased potential.

XPS measurements have indicated that Zn is in its two-valence oxidation state in the pure ZnO microrod grown at the potential of -0.8 V, while in its minor metallic and major two-valence oxidation states simultaneously in the pure ZnO microrod grown at the potential of -1.2, -1.6, and -2.0 V. Furthermore, the concentration of interstitial metallic Zn increases with the decreased potential in the pure ZnO microrod corresponding to XPS fitting results plotted in Fig. 5.1.17. It illustrates that the potential of -1.2 V is capable of motivate the reduction of Zn^{2+} in the solution according to Eq. (10). The reduced metallic Zn is doped into the interstices of ZnO wurtzite lattice and become interstitial metallic Zn. With the decreased potential, the reduction of Zn^{2+} in the solution becomes more serious, so the concentration of interstitial metallic Zn increases in the pure ZnO microrod.

Fig. 5.1.28. Room-temperature M-H hysteresis loops of (a) pure ZnO nanorod arrays synthesized using chemical deposition, and (b-e) pure ZnO microrod arrays grown through electrochemical deposition at the potentials of (b) -0.8 , (c) -1.2 , (d) -1.6 , and (e) -2.0 V.

Fig. 5.1.29. M_s of pure ZnO nanorod arrays synthesized using chemical deposition and pure ZnO microrod arrays grown through electrochemical deposition at different potentials.

Fig. 5.1.28 shows the magnetizations of the pure ZnO nanorod arrays synthesized by the chemical deposition method and the pure ZnO microrod arrays grown through the electrochemical deposition method at different potentials, which are measured as a function of magnetic field at room temperature. As shown in Fig. 5.1.28(a), diamagnetism is observed in the pure ZnO needle-shaped nanorod arrays synthesized by the chemical deposition. Likewise, the pure ZnO microrod arrays grown through the electrochemical deposition at -0.8 V are also diamagnetic (Fig. 5.1.28(b)). However, when the potential is decreased to -1.2 V, weak RTFM starts to be displayed by the microrod arrays (Fig. 5.1.28(c)). With the potential decreased to -1.6 V, a significant improvement in saturation magnetization (M_s) is observed in the microrod arrays compared to that at -1.2 V, as shown in Fig. 5.1.28(d). When the potential is further decreased to -2.0 V, the pure ZnO needle-shaped microrod arrays

possess an even stronger M_s compared to that at -1.6 V (Fig. 5.1.28(e)). The RTFM of pure ZnO microrod arrays are strengthened by the potential applied in the electrochemical deposition. Fig. 5.1.29 is plotted to show the values of M_s in the pure ZnO nano/micro arrays.

Although similar RTFM was also observed in some pure ZnO-based DMS materials [42-47, 113], the origin of such RTFM still could not be satisfactorily interpreted. For pure ZnO, the origin of the RTFM has been attributed to the defects at Zn sites in ZnO thin films [42], Zn nanoclusters embedded in ZnO nanowire matrices [46], interstitial Zn at the surface of ZnO nanorods [43], intrinsic defects in ZnO films [44], defects that cause a 469 nm emission [45], and vacancies present in grain boundaries [47], oxygen vacancies [113], etc. It is still a challenge to properly understand the mechanisms governing the ferromagnetic ordering in pure ZnO-based DMS. In this work, RTFM cannot be displayed by the pure ZnO needle-shaped nanorod arrays synthesized by the chemical deposition as well as the pure ZnO microrod arrays synthesized by the electrochemical deposition at -0.8 V. Both of them do not contain interstitial metallic Zn. On the contrary, RTFM starts to appear accompanying with the appearance of interstitial metallic Zn in the pure ZnO microrod grown through the electrochemical deposition at -1.2 V. In addition, the RTFM of pure ZnO microrod arrays are strengthened by the decreased potential of -1.6 and -2.0 V applied in the electrochemical deposition, which is consistent with the trend that the concentration of interstitial metallic Zn is increased in the pure ZnO microrod by the decreased potential of -1.6 and -2.0 V. Thus, RTFM in the pure ZnO microrod arrays can be attributed to the interstitial metallic Zn. The interstitial metallic Zn induces RTFM via interactions between interstitial metallic Zn and interstitial metallic Zn, or interactions

between interstitial metallic Zn and oxygen vacancies, or interactions between interstitial metallic Zn and ZnO matrix. Hence, the mechanism of RTFM needs to be further investigated.

5.1.3 Summary

Pure ZnO needle-shaped nanorod arrays were synthesized on the silicon substrate with ZnO seed layer by the chemical deposition method. The needle shape of the nanorod was formed due to the preferred orientation of ZnO[002]. Pure ZnO microrod arrays with different morphologies were grown on bare silicon substrates through the electrochemical deposition method with the help of different potentials of -0.8, -1.2, -1.6, and -2.0 V, respectively. Decreased potential could increase the growth rate of the pure ZnO microrods, resulting in the accelerated decrease of microrod tips, the accelerated aggregation of microrod bottoms, and the larger difference between the tip and bottom diameters of microrod. When the potential was decreased to -2.0 V, pure ZnO needle-shaped microrod arrays were grown on the bare silicon substrate. The potential played a key role in the nucleation process as well as the growth process of the pure ZnO microrod arrays. Zn was in its two-valence oxidation state in pure ZnO needle-shaped nanorod synthesized by chemical deposition as well as the pure ZnO microrod grown through electrochemical deposition at the potential of -0.8 V. The potential of -1.2 V started to be capable of motivate the reduction of Zn^{2+} in the solution, so Zn was in its minor metallic and major two-valence oxidation states simultaneously in the pure ZnO microrod grown at the potential of -1.2, -1.6, and -2.0 V. The reduced metallic Zn was doped into the interstices of ZnO wurtzite lattice and became interstitial metallic Zn. With the decreased potential, the reduction of Zn^{2+} in

the solution became more serious, so the concentration of interstitial metallic Zn increased in the pure ZnO microrod. Both the pure ZnO needle-shaped nanorod arrays synthesized by the chemical deposition and the pure ZnO microrod arrays grown through the electrochemical deposition at -0.8 V were diamagnetic. However, when the potential was decreased to -1.2 V, weak RTFM started to be displayed by the microrod arrays. With the potential decreased to -1.6 V, a significant improvement in saturation magnetization (M_s) was observed in the microrod arrays compared to that at -1.2 V. When the potential was further decreased to -2.0 V, the pure ZnO needle-shaped microrod arrays possessed an even stronger M_s compared to that at -1.6 V. The RTFM of pure ZnO microrod arrays were strengthened by the potential applied in the electrochemical deposition. The RTFM in the pure ZnO microrod arrays could be attributed to the interstitial metallic Zn.

5.2 Cobalt-Doped Zinc Oxide Nanostructures

5.2.1 Introduction

Diamagnetic pure ZnO nanorod arrays were formed on silicon substrates having a ZnO seed layer through the chemical deposition, while ferromagnetic Co-doped ZnO nanorod and microsphere arrays were synthesized on bare silicon substrates using the electrochemical deposition, illustrating that the electrochemical deposition method but not the chemical deposition method was capable of effectively doping Co into the ZnO matrix by means of a negative potential to synthesize Co-doped ZnO nano/micro structures possessing room temperature ferromagnetism (RTFM). In the electrochemical deposition, the potential played a key role in the both nucleation and growth processes of the Co-doped ZnO nanorod and microsphere arrays. The RTFM of the Co-doped ZnO nanorod or microsphere arrays was attributed to the bound magnetic polaron (BMP) model.

5.2.2 Results and Discussion

Fig. 5.2.1 shows typical SEM micrographs of pure and Co-doped ZnO nano/micro structures produced through the chemical deposition and the electrochemical deposition methods, respectively. Through the chemical deposition method, nanorod arrays with high density and regular structure are obtained, as shown in Fig. 5.2.1(a). The nanorod is vertically aligned to the substrate surface and has a well-defined hexagonal cross section with diameter of about 100 nm. When a potential of -0.8 V is applied in the electrochemical deposition process, similar dense nanorod arrays are

grown with the solution of 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$ as shown in Fig. 5.2.1(b). The diameter of the well-defined hexagonal cross section is about 200 nm. When 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is added in the solution, similar dense nanorod arrays are also synthesized with the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$ as shown in Fig. 5.2.1(c). However, the diameter of the hexagonal cross section is about 400 nm, which is larger than that in Fig. 5.2.1(b). It is interesting to notice that when the solution of 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$ is used, loosely distributed microspheres are formed instead of the dense nanorods in Fig. 5.2.1(c). It can be seen from Fig. 5.2.1(d) that spherical microcluster consists of microrods and has a diameter of about 4.5 μm .

Fig. 5.2.2 displays XRD patterns taken from the nanorods and microspheres, respectively. Compared to standard peak positions of pure ZnO powders, only obvious peaks corresponding to ZnO are observed in figures 5.2.2(a-d), indicating that a pure ZnO wurtzite phase with c-axis preferred orientation is formed in the nanorods and microspheres. In the XRD spectra of both nanorods and microspheres, no diffraction peak can be attributed to Co-related secondary phases within the sensitivity of the XRD measurements, implying that the nanorods and microspheres are single phase and that Co atoms substitute for Zn atoms in the ZnO lattice if Co has been doped into the ZnO matrix.

Fig. 5.2.1. SEM micrographs of (a) nano/micro structure arrays formed through chemical deposition in the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (b-d) nano/micro structure arrays synthesized using electrochemical deposition in the solutions of (b) 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, (c) 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (d) 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$.

Fig. 5.2.2. XRD spectra of (a) nano/micro structure arrays formed through chemical deposition in the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (b-d) nano/micro structure arrays synthesized using electrochemical deposition in the solutions of (b) 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, (c) 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (d) 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$.

The chemical states of Zn, O, and Co in the nanorods and microspheres are studied using XPS. In the Zn 2p spectra in Fig. 5.2.3, the peak at about 1021 eV is characteristic of $\text{Zn}^{2+} 2p_{3/2}$ state, so Zn is in its two-valence oxidation state in the nanorods and microspheres, which are at the Zn^{2+} sites of ZnO wurtzite lattice. In the O 1s spectra in Fig. 5.2.4, two O 1s peaks can be resolved by using a curve fitting procedure for each spectrum. The peak at 530 eV is attributed to O^{2-} ions present in a stoichiometric wurtzite ZnO structure, whereas the 531 peak is associated with the specific chemisorbed oxygen, such as the adsorbed H_2O , $-\text{CO}_3$, and so on. Fig. 5.2.5 shows Co 2p spectra measured from the nanorods and microspheres. In Fig. 5.2.5(a), no peak related to Co is observed, indicating that Co has not been doped into the ZnO matrix of the nanorod arrays synthesized by the chemical deposition method with the solution of $0.005 \text{ M Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} - 0.05 \text{ M Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} - 0.05 \text{ M C}_6\text{H}_{12}\text{N}_4$. Thus, the chemical deposition method is not capable of doping Co into ZnO matrix to grow Co-doped ZnO nano/micro structures, which is contrary to report by Patra et al. [106] while consistent to report by Cui et al. [50]. However, with the help of the potential in the electrochemical deposition, Co has been successfully doped into the ZnO matrix of the nanorod arrays and microsphere arrays, as shown in figures 5.2.5(c and d). In the Co 2p spectra, the peaks at about 780 and 796 eV are characteristic of $\text{Co}^{2+} 2p_{3/2}$ and $\text{Co}^{2+} 2p_{1/2}$ states, respectively. The others are accompanying peaks. It illustrates that the cobalt is in its two-valence oxidation state (Co^{2+}) in the Co-doped ZnO nanorods and microspheres. It is expected that Co^{2+} has been effectively doped into the ZnO wurtzite lattice at the Zn^{2+} sites. Thus, the electrochemical deposition method is capable of doping Co into ZnO matrix to synthesize Co-doped ZnO nano/micro structures, which is consistent to report by Cui et al. [50].

Fig. 5.2.3. XPS Zn 2p spectra of (a) nano/micro structure arrays formed through chemical deposition in the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (b-d) nano/micro structure arrays synthesized using electrochemical deposition in the solutions of (b) 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, (c) 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (d) 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$.

Fig. 5.2.4. XPS O 1s spectra of (a) nano/micro structure arrays formed through chemical deposition in the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (b-d) nano/micro structure arrays synthesized using electrochemical deposition in the solutions of (b) 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, (c) 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (d) 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$.

Fig. 5.2.5. XPS Co 2p spectra of (a) nano/micro structure arrays formed through chemical deposition in the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (b-d) nano/micro structure arrays synthesized using electrochemical deposition in the solutions of (b) 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, (c) 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (d) 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$.

The formation of pure or Co-doped ZnO nanorods and microspheres by the chemical deposition and electrochemical deposition methods involves nucleation and growth processes. The nucleation and growth mechanisms can be explained as follows:

- (1) $\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} = 6\text{HCHO} + 4\text{NH}_3$
- (2) $\text{NH}_3 + 6\text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$
- (3) $\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- = \text{NO}_2^- + 2\text{OH}^-$
- (4) $\text{Zn}^{2+} + 2\text{OH}^- = \text{Zn}(\text{OH})_2$
- (5) $\text{Zn}(\text{OH})_2 = \text{ZnO} + \text{H}_2\text{O}$
- (6) $\text{Co}^{2+} + 2\text{OH}^- = \text{Co}(\text{OH})_2$

Pure ZnO nanorod arrays are formed through the chemical deposition method with the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and Co has not been doped into ZnO matrix. $\text{C}_6\text{H}_{12}\text{N}_4$ in the solution is decomposed to HCHO and NH_3 according to Eq. (1). NH_3 reacts with H_2O through Eq. (2) to form hydroxide ions. Subsequently, Eqs. (4) and (5) occur in the solution, which produces a large amount of ZnO. Since the nucleation energy barrier of ZnO is very low on the silicon substrate with ZnO seed layer, ZnO in the solution easily nucleates on the ZnO seed layer. In the growth process following nucleation, due to the preferred orientation of ZnO[002], the growth rate is fastest along ZnO[002] compared to those along the other directions. As a result, pure ZnO nanorod arrays are obtained. Although Co^{2+} exists in the solution, no extra energy is supplied to support Co^{2+} to enter the Zn^{2+} sites in the ZnO wurtzite lattice of nanorods, so Co^{2+} only participates in the form of $\text{Co}(\text{OH})_2$ in the solution.

On the contrary, Co-doped ZnO nanorod arrays are synthesized by the electrochemical deposition method with the same solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and Co has been doped into ZnO matrix. In the electrochemical deposition, OH^- is also produced during the

electroreduction of nitrate to nitrite ions according to Eq. (3) except for Eqs. (1) and (2), which causes the increased OH^- ions at the bare silicon substrate surface (cathode). At the same time, Zn^{2+} and Co^{2+} are attracted to the substrate surface by negative potentials, which increases the concentration of cations at the substrate surface. Subsequently, Eqs. (4) and (5) occur in the solution, especially at the substrate surface due to the high concentrations of OH^- and Zn^{2+} , which produces a large amount of ZnO at the substrate surface. The potential applied can assist in overcoming the high nucleation energy barrier of ZnO on the bare silicon substrate. Thus, negative potential promotes nucleation of the ZnO nanorods, leading to a higher nucleation density compared to that in the absence of electric potential. The potential plays a key role in the nucleation process as well as in the growth process of the nanorod arrays. The potential can strengthen the attraction of the substrate to Zn^{2+} , increase the concentrations of OH^- and Zn^{2+} at the substrate surface, and supply enough energy to promote the growth of nanorods. In the growth process following nucleation, due to the preferred orientation of ZnO[002], the growth rate is fastest along ZnO[002] compared to those along the other directions. As a result, pure ZnO nanorod arrays matrix can be obtained. Because Co^{2+} also exists in the solution, and is also attracted to the substrate surface by the negative potential, with the help of the extra energy supplied by the potential, Co^{2+} continuously enters the Zn^{2+} sites in the ZnO wurtzite lattice during the growth process of ZnO nanorods. As a result, Co-doped ZnO nanorod arrays are obtained. At the same time, partial Co^{2+} also participates in the form of $\text{Co}(\text{OH})_2$ in the solution.

When $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is increased to 0.025 M and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ are proportionally decreased to 0.03 M each in the solution, the loosely distributed Co-

doped ZnO microsphere arrays are formed instead of dense nanorod arrays. Though the concentration of nitrate anions remains unchanged in these experiments, increased $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and decreased $\text{C}_6\text{H}_{12}\text{N}_4$ result in lower concentration of OH^- in the solution, because the Co^{2+} ions can consume the OH^- to form $\text{Co}(\text{OH})_2$ through Eq. (6) and $\text{C}_6\text{H}_{12}\text{N}_4$ can lower OH^- concentration through Eqs. (1) and (2). The decrease of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ reduces the concentration of free Zn^{2+} in the solution. Thus, lower OH^- and free Zn^{2+} in the solution reduce the nucleation density of ZnO on the substrate surface. When the nucleation density of ZnO is high on the silicon substrate, the nanorod arrays with high density are obtained. However, when the nucleation density of ZnO is low on the substrate surface, subsequent nucleation and growth of ZnO is easier on the existing ZnO rather than on the bare silicon substrate. Therefore, microrods aggregate together and form the microspheres. Thus, the nucleation density decreases with increasing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and decreasing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$, which leads to the transformation of the structure from denser nanorod arrays to less dense microsphere arrays.

The magnetic properties of the pure or Co-doped ZnO nanorod and microsphere arrays are measured by vibrating sample magnetometer at room temperature, as shown in Fig. 5.2.6. Diamagnetisms are observed in the pure ZnO nanorod arrays formed through the chemical deposition (Fig. 5.2.6(a)) and electrochemical deposition (Fig. 5.2.6(b)) methods, respectively. However, obvious room temperature ferromagnetisms are displayed by the Co-doped ZnO nanorod (Fig. 5.2.6(c)) and microsphere (Fig. 5.2.6(d)) arrays synthesized by the electrochemical deposition method, respectively. Thus, pure ZnO matrix of the Co-doped ZnO nanorods or

microspheres has no contribution to the RTFM, and the RTFM can be attributed to Co doped in the ZnO matrix.

Fig. 5.2.6. Room-temperature M-H hysteresis loops of (a) nano/micro structure arrays formed through chemical deposition in the solution of 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (b-d) nano/micro structure arrays synthesized using electrochemical deposition in the solutions of (b) 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, (c) 0.005 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.05 M $\text{C}_6\text{H}_{12}\text{N}_4$, and (d) 0.025 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –0.03 M $\text{C}_6\text{H}_{12}\text{N}_4$.

Through XRD and XPS measurements, no Co-related secondary phase is observed and Co is in its two-valance state at the Zn^{2+} sites in the ZnO matrix, so it can be ruled

out that the Co-related secondary phase, such as metallic Co, is the source of RTFM. The RTFM of Co-doped ZnO nanorod or microsphere arrays can be explained using a bound magnetic polaron (BMP) model. There are many defects such as oxygen vacancies and zinc interstitials in the nanorods or microspheres. The defects locally trap electrons to occupy orbitals interacting with the d subshells of the neighboring Co dopants, leading to the formation of a ferromagnetic grain-boundary network. The electron loosely bound to a charged defect, e.g. the oxygen vacancy, occupies an extended orbital around the defect forming a BMP. These overlap to form a spin-split impurity band. These electrons couple with the 3d spins of the magnetic dopant ions that lie within the extended orbital of the BMP. The Co^{2+} exists in a $3d^7$ state and thus presents three unoccupied orbitals. The loosely bound electron will align in an anti-parallel configuration with the spins of the individual Co^{2+} ions resulting in the spins on the neighboring Co^{2+} ions to align in a parallel configuration with each other, thus, leading to an effective ferromagnetic coupling between the Co^{2+} moments. Through the BMP model, the Co-doped ZnO nanorod or microsphere arrays possess RTFM.

5.2.3 Summary

Diamagnetic pure ZnO nanorod arrays were formed on the silicon substrate with ZnO seed layer through the chemical deposition method, indicating that the chemical deposition method was not capable of doping Co into ZnO matrix to grow Co-doped ZnO nano/micro structures. Ferromagnetic Co-doped ZnO nanorod and microsphere arrays were synthesized on bare silicon substrates by the electrochemical deposition method, illustrating that the electrochemical deposition method was capable of doping Co into ZnO matrix with the help of negative potential to synthesize Co-doped ZnO

nano/micro structures. The potential played a key role in the nucleation process as well as the growth process of the Co-doped ZnO nanorod and microsphere arrays. The room temperature ferromagnetism of the Co-doped ZnO nanorod or microsphere arrays was explained using the bound magnetic polaron (BMP) model.

Chapter 6. Conclusions and Recommendations

6.1 Conclusions

Annealing effect under varying conditions on the structural and magnetic properties of pure ZnO thin films, Cu-doped ZnO thin films, and Ni-doped ZnO thin films prepared via magnetron sputtering deposition was systematically investigated. Lattice deviations of the thin films both as-deposited and annealed were observed through XRD spectra, which were attributed to the formation of oxygen vacancies and zinc interstices in the films. An elongation of the ZnO wurtzite lattice was observed from the as-grown thin film with reference to that of the stress free ZnO powders, which could be attributed to relatively fewer oxygen vacancies but more Zn interstices in the as-deposited film. However, a contraction of the ZnO wurtzite lattice was observed in the films after annealing in Ar and air compared to that of the stress free ZnO powders, which could be due to increased oxygen vacancies but decreased zinc interstices. A significant diffusion of O from the bottom to the top surface of the thin films annealed in Ar and air was observed through XPS spectra, which resulted in increased oxygen vacancies in the films. Furthermore, a prolonged annealing could promote the diffusion of O, thus increasing the number of oxygen vacancies in the films.

As far as the Cu-doped ZnO thin film was concerned, a significant diffusion of Cu from the bottom to the top surface of the films annealed in Ar and air was also observed through XPS spectra. Reduction of Cu occurred in the films annealed in Ar, while oxidization of Cu occurred in the films annealed in air. An extended annealing in air increased the concentration of oxygen vacancies and the amount of Cu^{2+} at the

Zn^{2+} sites of the ZnO wurtzite lattice in the films. As for the Ni-doped ZnO thin films, a significant diffusion of Ni from the bottom to the top surface of the films annealed in Ar at 800 °C was also observed from the XPS depth profiles. Oxidization of metallic Ni atoms occurred in the film annealed in air at 600 °C, while reduction of Ni^{2+} ions occurred in the films annealed in Ar at 600 and 800 °C.

All the pure ZnO thin films both as-grown and annealed in Ar and air displayed diamagnetism at room temperature, though the oxygen vacancies existed in all the films, indicating that the oxygen vacancies were necessary but not enough to induce the room temperature ferromagnetism (RTFM) of the ZnO-based diluted magnetic semiconductors (DMS). The as-deposited Cu-doped ZnO thin film displayed obvious RTFM that originated from Cu^{2+} through bound magnetic polaron (BMP) model. However, RTFM disappeared in the films after annealing in Ar due to the disappearance of Cu^{2+} in the films. On the contrary, a significant improvement in saturation magnetization (M_s) of the films was observed after annealing in air compared to that of the as-deposited film. Furthermore, the longer the annealing in air, the larger the M_s was. The increase of M_s in the films annealed in air was attributed to a stronger BMP effect with the increased amounts of oxygen vacancies and Cu^{2+} at the Zn^{2+} sites of the ZnO wurtzite lattice in the films. Both the as-deposited and annealed Ni-doped ZnO thin films displayed obvious RTFM that originated from Ni^0 , Ni^{2+} or both with two distinct mechanisms. Furthermore, a significant improvement in M_s of the films was observed after annealing. The increase in M_s of the film annealed in air at 600 °C was attributed to a stronger BMP effect with higher amounts of oxygen vacancies and Ni^{2+} at the Zn^{2+} sites of the ZnO wurtzite lattice in the film. A similar improvement in M_s of the film annealed in Ar at 600 °C was attributed to

increased metallic Ni nanoclusters. An even more significant M_s was observed from the film annealed in Ar at 800 °C compared to that at 600 °C, which was attributed to more and larger metallic Ni clusters at the grain boundaries near the film surface mainly due to the diffusion of Ni in the film. A significant increase in intensity and a blue shift of the ultraviolet emission peak were observed in the film annealed in Ar at 800 °C, which was attributed to the local depletion of Ni in the ZnO matrix near the bottom of the film due to the diffusion of Ni in the film. Thus, the annealing of the Ni-doped ZnO thin film in Ar at 800 °C restored the optical property of the film at the time when it enhanced the magnetic property of the film.

Pure ZnO needle-shaped nanorod arrays were synthesized on the silicon substrates having a ZnO seed layer using a chemical deposition method. The needle shape of the nanorod was due to the preferred orientation of ZnO[002]. Pure ZnO microrod arrays with different topographies were grown on bare silicon substrates through a electrochemical deposition method at different potentials of -0.8, -1.2, -1.6, and -2.0 V. More negative potentials could accelerate the growth of the pure ZnO microrods, resulting in the finer microrod tips, faster aggregation of microrod bottoms, and larger difference between the tip and bottom diameters of the microrod. When the potential was decreased to -2.0 V, pure ZnO needle-shaped microrod arrays were grown on the bare silicon substrate. The potential played a key role in the both nucleation and growth processes of the pure ZnO microrod arrays. Zn was in its divalence oxidation state in the pure ZnO needle-shaped nanorods synthesized by the chemical deposition as well as in the pure ZnO microrods grown through the electrochemical deposition at the potential of -0.8 V. The potential of -1.2 V started to be capable of motivating the reduction of Zn^{2+} in the solution, so Zn was in its minor metallic and major divalence

oxidation states simultaneously in the pure ZnO microrods grown at the potentials of -1.2, -1.6 and -2.0 V. The reduced metallic Zn took up the interstices of the ZnO wurtzite lattice of the microrods. At more negative potentials, the reduction of Zn^{2+} in the solution became more significant, leading to higher concentrations of interstitial metallic Zn in the pure ZnO microrods. Both the pure ZnO needle-shaped nanorod arrays synthesized by the chemical deposition and the pure ZnO microrod arrays grown through the electrochemical deposition at -0.8 V were diamagnetic. However, when the potential was decreased to -1.2 V, weak RTFM started to be displayed by the microrod arrays. With the potential decreased to -1.6 V, a significant improvement in M_s was observed in the microrod arrays compared to that obtained at -1.2 V. When the potential was further decreased to -2.0 V, the pure ZnO needle-shaped microrod arrays possessed an even stronger M_s compared to that produced at -1.6 V. The RTFM of the pure ZnO microrod arrays was strengthened by the potential applied during the electrochemical deposition, which could be attributed to the interstitial metallic Zn.

That the diamagnetic pure ZnO nanorod arrays were formed on the silicon substrates having a ZnO seed layer through the chemical deposition indicated that the chemical deposition method was not capable of doping Co into the ZnO matrix. That the ferromagnetic Co-doped ZnO nanorod and microsphere arrays were synthesized on the bare silicon substrates using the electrochemical deposition illustrated that the electrochemical deposition method was capable of doping Co into the ZnO matrix with the help of negative potential. The RTFM of the Co-doped ZnO nanorod or microsphere arrays was explained using the BMP model.

6.2 Recommendations

It would be interesting in comparative study of the RTFM of ZnO-based DMS thin films and nanostructures, including pure ZnO thin films and nanostructures, Cu-doped ZnO thin films and nanostructures. In addition, annealing effect under varying conditions on the structural and magnetic properties of ZnO-based DMS thin films and nanostructures also deserves a comparative investigation.

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