Cu AND Mn EMBEDDED-ZnO NANOCLUSTER ASSEMBLED FILMS AND NANOCOMPOSITES:
FABRICATION, CHARACTERIZATION AND PROPERTIES

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Abstract

The experiments of this master’s degree project are divided into five parts: (1) the magnetic and optical properties of Cu nanocluster-embedded ZnO thin film; (2) the magnetic and optical properties of Zn\textsubscript{0.94}Cu\textsubscript{0.06}O nanocluster assembled films and (3) ZnO:Cu-SiO\textsubscript{2} nanocomposite; and (4) the magnetic and optical properties of Zn\textsubscript{0.94}Mn\textsubscript{0.06}O nanocluster assembled films and (5) ZnO:Mn-SiO\textsubscript{2} nanocomposite.

Transition metals such as Cu and Mn do not contribute to the ferromagnetism of samples since they themselves and their secondary phases are non-ferromagnetic phases due to fully-occupied d-orbitals or fully-filled majority-spin states. In order to investigate possibility of occurrence of ferromagnetism in non-ferromagnetic and insulating diluted magnetic semiconductor oxide system, Cu and Mn nanoclusters were embedded in ZnO in the form of nanocluster assembled films (without matrix) and nanocomposites (with SiO\textsubscript{2} matrix). Room temperature ferromagnetism can be induced in Cu embedded-ZnO thin films as suggested by small coercivities of their M-H curves. From XRD and TEM results, no substitution of Cu and Mn nanoclusters over Zn cation site was detected, instead they were surrounded by Zn and O atoms to form nanocluster-matrix interface. XRD and high resolution TEM and SADP analysis excluded the possibility of presence of ferromagnetic phases in the samples. The XPS result suggests Cu in the +1 valence state is the most favorable condition for the occurrence of ferromagnetism. Through comparison of Cu and Cu-oxides embedded SiO\textsubscript{2} system with Cu and Cu-oxides embedded ZnO system, the interaction of nanoclusters with their environment was proved to be important for the enhanced ferromagnetism. However, PL (photoluminescence) analysis indicated the presence of oxygen vacancies greatly enhanced the M\textsubscript{s} value of samples.
The magnetic and optical properties of ZnO:Cu nanoclusters under the influence of nanocluster volume fraction and the annealing temperature were studied by using various characterization tools. Maximum room temperature saturation magnetization ($M_s$) of 2.64 emu/cm$^3$ was obtained for as-deposited 0.4 vol. % Cu-ZnO nanocluster assembled films. Only ZnO phases were detected in XRD analysis while high resolution TEM and selected area diffraction patterns indicate the existence of secondary phases non-ferromagnetic CuO and Cu$_2$O in the as-deposited and annealed nanocluster-assembled films. Cu atoms were surrounded by ZnO matrix and the interface effect caused overlapping of p-orbital from O contributed by ZnO and d-orbital contributed by Cu as suggested by XPS and UV-Vis absorbance results. Photoluminescence results also suggest the existence of oxygen vacancies in the samples may contribute to the enhancement of magnetic moment. Hence the defect-mediated room temperature ferromagnetism was thought responsible for the enhanced ferromagnetic behavior in the samples.

ZnO:Cu-SiO$_2$ nanocomposite were prepared by using nanocluster beam deposition technique combined with RF sputtering. The effects of both volume fraction of ZnO:Cu nanocluster in nanocomposite and annealing temperatures on the magnetic and optical properties were studied. Maximum saturation magnetization 6.98 emu/cm$^3$ were obtained for as-deposited 50 vol. % ZnO:Cu-SiO$_2$ nanocomposite. The most prominent surface plasmon resonance was appeared around visible green wavelength in the 600$^\circ$C vacuum-annealed ZnOCu:SiO$_2$ nanocomposite Photoluminescence results suggest the existence of oxygen vacancies in the samples may contribute to the enhancement of magnetic moment. High resolution TEM indicates only the existence of secondary phases antiferromagnetic CuO, Cu$_2$O and nonmagnetic Zn$_2$SiO$_4$ in the as-deposited and annealed nanocomposites. Thus the defect-mediated room temperature ferromagnetism was thought responsible for the enhanced ferromagnetic behavior.
High resolution TEM and selected area diffraction pattern (SADP) reveal the existence of non-room-temperature-ferromagnetic secondary phases such as MnO$_2$, ZnMn$_2$O$_4$, ZnMn$_3$O$_7$, Mn$_3$O$_4$, ZnMnO$_3$, and MnO in both as-deposited and annealed samples. Magnetization value of Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films increased with increasing temperatures and reached maximum value at 700$^0$C. Mn$^{3+}$ and Mn$^{4+}$ co-existed in annealed and as-deposited samples, proving that the enhancement of magnetization value is not solely come from double exchange interactions but majority contribution is probably come from oxygen vacancies whose existence can be proved by Raman spectra. UV-Vis spectra shows shrinkage of band-gap of nanocluster assembled films due to temperature-induced enlargement of nanocluster size at high temperatures.

The magnetization value of ZnO:Mn-SiO$_2$ nanocomposite were decreased from 4.99 emu/cc to 0.75 emu/cc when the volume fraction of ZnO:Mn was increased from 4 vol. % to 50 vol. % due to the decrease of distance between Mn-Mn atoms and increasing antiferromagnetic interactions among them. TEM analysis revealed bivalent Mn secondary phases existed in both as-deposited and annealed nanocomposites. Raman spectra shows contribution of oxygen vacancies dominate over contribution of Mn$^{3+}$-Mn$^{4+}$ double exchange interactions in enhancing the ferromagnetism of nanocomposites. UV-Vis absorption spectra shows band gap shrinkage with increasing volume fraction of ZnO:Mn nanoclusters.
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<th>Description</th>
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<tr>
<td>1-D</td>
<td>1-dimensional</td>
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<tr>
<td>2-D</td>
<td>2-dimensional</td>
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<tr>
<td>3-D</td>
<td>3-dimensional</td>
</tr>
<tr>
<td>AGM</td>
<td>alternating gradient field magnetometer</td>
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<tr>
<td>BF</td>
<td>bright field</td>
</tr>
<tr>
<td>DF</td>
<td>dark field</td>
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<tr>
<td>DSI</td>
<td>Data Storage Institute</td>
</tr>
<tr>
<td>DMSO</td>
<td>diluted magnetic semiconductor oxide</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EM</td>
<td>electron microscope</td>
</tr>
<tr>
<td>Eqn</td>
<td>equation</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast-Fourier Transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>Hcp</td>
<td>hexagonal closed-packed</td>
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<tr>
<td>HR</td>
<td>high-resolution</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high-resolution transmission electron microscope/microscopy</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SADP</td>
<td>selected area diffraction pattern</td>
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SGC  sputtering gas condensation
TEM  transmission electron microscope/microscopy
UV-Vis ultraviolet-visible
XPS  x-ray photoelectron spectroscopy
XRD  x-ray diffractometer/diffractometry

List of Symbols
°C  degree Celsius
λ  wavelength
θ  incidence angle
a  lattice parameter of unit cell
Ar  argon
β  full width at half maximum of the broadening of peak in radians
Cu  copper
d-spacing  interplanar spacing
emu  elementary magnetic unit
(hkl)  Miller index in reciprocal space to designate plane
{hkl}  Family of (hkl) plane
H  applied magnetic field
He  helium
I  intensity
kB  Boltzmann constant
kBT  thermal energy
K  Kelvin
Ku  magnetocrystalline anisotropy energy/constant
KuV  anisotropy energy barrier
M   magnetization (magnetic moments per unit volume)
Mr  remanent magnetization
Mₘ   saturation magnetization
M-H  loop hysteresis loop
nm   nanometer
Oe   Oesterd
sccm standard cubic centimeter per minute
Si   silicon
SiO₂  silicon dioxide
T   temperature
Tm   melting temperature
Torr measurement units of pressure
t   thickness of sample
[UVW] zone axis UVW
Chapter 1 Introduction

1.1 Background

The novel class of materials known as diluted magnetic semiconductor oxides (DMSOs) which is applicable in spintronic devices has a lot of advantages as compared to traditional charge based electronics devices in terms of power consumption, coherence times and reading/writing speed. This class of materials attracted great interests of numerous researchers due to the fact that physical properties of such solids can be adjusted in wide circumstances by controlling the volume fractions and shape of dopants, as well as the dopant and matrix materials. The chemical properties of nanostructured DMSO can be controlled by the manipulating Ar/He ratio, pressure and sputtering power to adjust the shape, size and coordination numbers of surface atoms which are significantly influence the chemical potential and thermodynamic properties of their surfaces. High-temperature semiconductors with wide band gaps such as GaMnN\textsuperscript{1} and ZnMnO\textsuperscript{2,3} are the potential materials for application in modern nanoelectronics. The ultimate goal of research in DMSO is to achieve room temperature or high temperature magnetic semiconductors with magnetic and optical properties controllable by manipulation of charges and spins which are attractive properties for applications in non-volatile switching elements. The limited availability of DMSO materials with high Curie temperatures leads to a rapid exploitation of various potential materials. These materials are expected to be processable on a single substrate in nanodevices which offer multi-purpose functionality in magnetic (information storage), photonic (laser and light-emitting diodes) and electronic (field-effect and bipolar transistors).

The embedment of nanoclusters in the wide-bandgap oxide semiconductors such as ZnO by using sputtering gas aggregation techniques combined with r.f. (radio frequency) sputtering are considered as a promising DMSO system for exhibiting interesting RT (room
temperature) ferromagnetism and optical properties. The most widely studied matrix for DMSO is ZnO which has well-studied characteristics and properties and processable by using conventional r.f. sputtering techniques, thus providing a good basis for research in this area.

1.2 Research status and problem statements of ZnO nanocluster assembled films and nanocomposites

ZnO is a promising candidate for room temperature (RT) DMSO which has tunable magnetic and optical properties when it is doped with transition metals. Most of the ferromagnetism mechanism requires presence of ferromagnetic phases or carriers in the materials in order to have long range magnetic interactions for occurrence of significant ferromagnetism in whole sample. DMSO has unique feature which is differ from conventional DMS materials such as GaMnAs, InMnAs and GaMnSb, in such the way that its carrier population (electron or hole) is quite low compared to conventional DMSs. Its system is normally comprised of oxide matrix and transition metal dopants. The nanocluster can be assembled into two forms of DMSO system, i.e. nanocluster assembled films (nanocluster film without matrix) and nanocomposite (nanocluster-matrix system). Both systems have been successfully proved to be possessed room temperature (RT) ferromagnetism and interesting optical properties\textsuperscript{4-7}.

For search of origin of ferromagnetism in DMSO system, the insulating and non-ferromagnetic matrix and dopant materials must be used to exclude the possibility presence of ferromagnetic phases in the system in the first place. The nanocluster beam deposition technique used in these experiments can also ensure the avoidance of structural damage done on the surface of thin films as experienced by other ZnO thin films fabricated by physical
vapor deposition such as pulsed laser deposition (PLD) and ion implantation method. Such structural damages will create point defects and switch on the RT ferromagnetism of films\(^8\). The ferromagnetism seems to be impossible to be induced in the films without the aid of carriers. Although many researchers had successfully induced RT ferromagnetism in such insulating and non-ferromagnetic DMSO system\(^9\)-\(^14\), however some research areas still remain vague and unclear, as follows:

(1) Various researches have shown that nonmetallic materials like polymer\(^15\), oxides\(^16\), carbon\(^17\) and nitrides\(^18\) can show ferromagnetism behavior with or without dopants. Various ferromagnetism mechanisms such as carrier-mediated ferromagnetism\(^{19,20}\), defect-mediated ferromagnetism\(^{21,22}\), superexchange\(^{23,24}\), double exchange\(^{11,25}\) and bound magnetic polarons model\(^26\) have been proposed to explain the origin of ferromagnetism of DMSO system. However, origin of DMSO is still remains unclear since the mechanism which satisfied the corresponding ferromagnetism in one experiment can’t be used to explain ferromagnetism phenomena in other experiments which involved different materials and growth conditions. In other words, a universal ferromagnetism mechanism is required to fully explain the various ferromagnetism phenomena presented in the materials which thought to be impossible for occurrence of ferromagnetism.

(2) For ZnO-Cu system, there still exists a debate on whether the magnetic behavior is an intrinsic property of thin film or due to the presence of nanoclusters of magnetic phase or both due to the difficulty of the microstructure characterization in large scale. Due to the difficulty in the observation of the small amount of CuO nanometer scale inclusions/precipitate, the debate on the origin of ferromagnetism of ZnO:Cu films either from the Cu ions substituted in Zn cation sites or some Cu/CuO nanoclusters or both still exists\(^{27,28}\).
(3) For ZnO-Mn system, the debate on the origin of ferromagnetism of ZnO:Mn films either from the double exchange interactions as a consequence of presence of bivalent Mn$^{3+}$ and Mn$^{4+}$ in the films or from free-carrier mediated mechanism still exists. This is due to the fact that difficulty of the observation of the small amount of Mn-related nanometer scale inclusions/precipitate and the presence of many carriers in the films due to their growth condition and fabrication methods.$^{29}$

The study of nanoclusters-assembled films and supported nanoclusters (nanocomposite system) enable us to understand the fundamentals behavior of matter related to magnetic and optical properties which is situated in the grey area between the atom and bulk through the combination of technology of deposited mass-selected nanoclusters and surface science techniques.

1.3 Objectives

There were three main objectives in this project: (1) To fabricate and study the structural, magnetic and optical properties of Cu nanocluster embedded in ZnO thin film (2) To produce Zn$^{0.94}$Cu$^{0.06}$O nanocluster assembled films and ZnO:Cu-SiO$_2$ nanocomposite and study their unique magnetic and optical properties (3) To produce Zn$^{0.94}$Mn$^{0.06}$O nanocluster assembled films and ZnO:Mn-SiO$_2$ nanocomposite and study their unique magnetic and optical properties
1.4 Methodologies and approaches

Most of the researchers try to avoid the formation of metal clustering or transition metal related nanocrystals in the investigation of origin of ferromagnetism of thin films because they are considered as secondary phases which will contribute ferromagnetism in the homogenous thin films. However, in our research, we deliberately assembled the transition metal nanoclusters to form nanocluster assembled films and nanoclusters embedded-matrix films which were solely comprised of non-ferromagnetic nanoclusters or nanocluster and matrix only. The fabrication approach is different from the conventional sputtering i.e. pulsed laser deposition, ion beam deposition, reactive sputtering, molecular beam epitaxy, etc. where sputtered atoms are epitaxially grown on the substrate. In nanocluster beam deposition, the shape and cluster size of the nanoclusters were formed before they soft-landed on the substrate. The bonding between clusters-clusters and nanoclusters-substrate is so weak that a sweep by fingers could destroy their bondings. The pre-form nanoclusters have preserved their characteristic sizes and shapes before landing on the substrate where certain degree of coalescences and diffusions occurred among stacked clusters and neighbouring clusters based on DDA model (deposition diffusion aggregation) \(^{30}\). After the non-ferromagnetic nanoclusters were fabricated in thin films form, the magnetic properties examined by characterization tools are purely come from the transition metal nanoclusters themselves or interactions of nanocluster-matrix. Hence the measured magnetic results can be used to distinguish whether the induced ferromagnetism is intrinsic or extrinsic.

All samples were stored in the dry cabinet in cleanroom before they were used for various measurement and characterization purposes to avoid oxidation from air and also contaminations from surroundings affecting the actual saturation magnetization (\(M_s\)) value of samples. The resistivity test has been done on the pure ZnO and SiO\(_2\) matrices as well as nanocluster assembled films and nanocomposites by using multimeter. The results showed
that all samples have resistivity >10^{-6} \Omega m. Thus both ZnO and SiO\textsubscript{2} are the insulating matrices and the nanoclusters deposited in the films also lack of free carriers.

Experimental parameters such as sputtering time and annealing temperatures were varied to explore the possibility of obtaining ferromagnetism in oxide semiconductors which are non-ferromagnetic in bulk form. Magnetic properties were investigated by alternating gradient force magnetometer (AGM). The microstructures of the nanoclusters assembled films and nanocomposites were studied by x-ray diffractometer (XRD) and transmission electron microscope (TEM). The chemical state was probed by x-ray photoelectron spectroscopy (XPS). Photoluminescence (PL) and Raman spectroscopy were used to examine the presence of defects in the films. UV-Vis spectroscopy was used as investigation tools for optical properties of nanocluster assembled films and nanocomposites.

1.5 Novelties

The novelties of the research work were listed out as follows:

(1) Cu nanoclusters, and ZnO:Cu and ZnO:Mn alloy nanoclusters were deliberately embedded in the ZnO and SiO\textsubscript{2} matrices respectively. Since the nanoclusters were softly landed on the ZnO or SiO\textsubscript{2} films and it was unlikely to cause the large-scale diffusion of Cu atoms or ZnO:Cu and ZnO:Mn alloy nanoclusters into the ZnO or SiO\textsubscript{2} lattices during deposition. Thus the effects of transition metal atoms substitution with host lattices can be neglected and only nanocluster effects on ferromagnetism can be investigated.

(2) Detailed examinations on microstructures, magnetic and optical properties of Cu nanocluster-embedded ZnO thin film, ZnO:Cu and ZnO:Mn nanoclusters assembled
films and nanocomposites with different volume fraction of nanoclusters and annealing temperatures were carried out.

(3) The influence of nanocluster-matrix interactions on the ferromagnetism of films was discussed in this study.

(4) The influence of defects on the ferromagnetism of films was investigated in this research.

(5) A unique optical property, surface plasmon resonance of vacuum-annealed ZnO:Cu-SiO₂ nanocomposites was discovered.

1.6 Organization of the thesis

Seven chapters were written to report all experiments during my master’s study. A brief introduction on this project was given in chapter 1. Chapter 2 focuses on literature review of ZnO thin film, diluted magnetic semiconductors oxides, magnetic and optical properties of nanostructured DMSO. In chapter 3, fabrication technique such as nanocluster beam deposition and RF sputtering techniques and material characterization techniques such as XRD, TEM, AGM, XPS, SEM, SQUIDS, Raman spectroscopy, UV-Vis and PL spectroscopy were discussed. Magnetic and optical properties of Cu nanoclusters embedded in ZnO thin film was discussed in chapter 4. The content of chapter 5 included the the microstructure, magnetic and optical properties of ZnO:Cu nanoclusters assembled films and the ZnO:Cu –SiO₂ nanocomposite. The microstructure, magnetic and optical properties of ZnO:Mn nanoclusters assembled films and the ZnO:Mn –SiO₂ nanocomposite were discussed in chapter 6. The summary of the project concluded all experiments and results in the end of thesis.
Chapter 2 Literature review

2.1 ZnO as candidate for DMSO

2.1.1 Properties of ZnO thin film

ZnO also called as zincite. It has a lot of interesting properties which attract the interest of researchers. These properties included large direct band-gap (3.3 eV), large exciton binding energy (60 meV), high efficient excitonic emission above room temperature, unusually high exciton oscillator strength and other properties. Generally almost all semiconducting chalcogenides (Group VI elements) of divalent main groups elements (II-VI compounds) and pnictides (Group V elements) of trivalent main group elements (III-V compounds) have great tendency to crystallize in tetrahedral structures. ZnO also included in this trend of structures. The covalent congenors tend to adopt cubic F4 3m zinc blende structure while the more polar compounds are favor the structure of hexagonal P63mc wurtzite. Since ZnO is the polar compound so the most stable structure in the ambient conditions is wurtzite. Wurtzite structure has the arrangement of hexagonal closed packed (HCP) as shown in Figure 2.1. The ratio of lattice parameters, a and c is related by c/a = 1.633. The length of the bond parallel to the c axis, in units of c, u= 0.375. Coordination numbers of Zn atoms inside the wurtzite structure is 4 and O atoms also have the same number as Zn. Only 50 % tetrahedral sites are occupied by the Zn atoms while none of the octahedral sites are occupied. Both anions (O^{2-}) and cations (Zn^{2+}) are tetrahedrally coordinated and linked to each other by corner sharing. This tetrahedral coordination is typical of sp3 covalent bonding as showed in the figure 1. From the view of (0001) planes there are triangularly arranged alternating biatomic along the (0001) direction causing the stacking sequence AaBbAaBb.... Since the wurtzite structure has good polar symmetry it is sensitive to piezoelectricity and spontaneous polarization, crystal growth, etching and the
defect. There are two types of face termination can be found on the wurtzite ZnO. Polar faces consisted of Zn (0001) and O (0001\textbar) c-axis while nonpolar faces consisted of a-axis (112\textbar0) and (101\textbar0) and has equal number of Zn and O. Zn (0001) is a basal plane and O (0001\textbar) c-axis has slightly different electronic structure. On the hand, O (0001\textbar) c-axis is the less stable surfaces and has higher surface toughness\textsuperscript{32}.

ZnO is chosen as candidate for the matrix of DMSO due to the fact that wider band gap semiconductors tend to have smaller spin-orbit interactions, larger p-d hybridization and smaller lattice constants which are the requirements for the materials with higher Curie temperature\textsuperscript{33}. ZnO can be used to study the phenomenon of quantum confinement in the semiconductor because it is possible to experimentally produce ZnO particle size smaller than 7 nm which is the range for observable quantum size effects\textsuperscript{34}. ZnO in bulk and thin film form possessed stable wurtzite structure with tetrahedrally coordinated Zn-O atoms. ZnO is belonged to space group P\textit{6}_3\textit{mc} with lattice constant \(a = 3.2595\) Å, \(c = 5.2070\) Å and internal coordinate, \(u = 0.3820\). The electronic structure of bulk ZnO mostly involved sp\textsuperscript{3}d\textsuperscript{5} orbitals of zinc and p\textsuperscript{3} orbitals of oxygen which are major portions of valence and conduction bands. The hopping interactions between the nearest neighbor Zn-Zn and O-O interactions are important interactions describing the band structure of ZnO. The observed band gap shift in the quantum size effect phenomenon is contributed by the major shift of conduction band edge. This is due to the fact that effective electron mass is lighter than effective hole mass and hence the have larger energy difference from the bulk band gap\textsuperscript{34}.
2.1.2 Properties of low-dimensional ZnO nanostructures

The properties and structure of ZnO nanoclusters are quite different from their bulk counterparts due to the size, surface and shape factors of nanoclusters. When ZnO are fabricated in low dimensional structures such as two-dimensional (2D) nanofilms, one-dimensional (1D) nanowires and nanorods and zero-dimensional (0D) nanoclusters, as shown in Figure 2.2 (a)-(c), physical properties such as structural relaxations, stiffness and cohesive energy are expected to be different from their bulk counterpart. According to C. Li et. al. simulation, structural relaxations on Zn- and O-terminated surfaces of 2D ZnO ultra thin film will cause compression of distance between the two outmost Zn-O double layer.
2.2 ZnO-based DMSO

2.2.1 Diluted magnetic semiconductor oxide (DMSO)

Diluted magnetic semiconductor oxide (DMSO) is an oxide semiconductor doped with transition metal to achieve many degree of freedom in controlling spins and charges in the materials. Through manipulation of magnetic and electrical properties of DMSO, various applications involved semiconductor and ferromagnetism can be realized. DMSOs are usually deposited in the form of thin films or nanoparticles and may be semiconducting.
insulating or metallic. Most of them have high Curie temperature when they were deposited on a substrate or synthesized as nanoparticles and nanocrystallites. The oxides are usually n-type and may be partially compensated d-orbital. The emergence of DMSO is boosted by current advancement of synthesis or fabrication of high quality size/shape-controllable nanomaterials, metal oxide films, and interface systems. It is a special class of doped metal oxides which involved oxides with general formula \((M_{1-x}T_x)_nO\) where \(n\) is an integer or rational fraction and \(x < 0.1\), for instance, ZnO, TiO\(_2\), SnO\(_2\), Cu\(_2\)O, La\(_{1-x}\)Sr\(_x\)TiO\(_3\). It has different bonding, natures of defect states, ordering phenomena, structural properties, special role of oxygen non-stoichiometry, carrier-related properties, magnetic anisotropies, and mechanisms of exchange coupling compared to the conventional compound and elemental semiconductors. The early works of DMSO systems showed discovery of ferromagnetism in Co-doped TiO\(_2\)\(^{37}\) and Mn doped ZnO\(^{38}\). However, the research area of DMSO is not mature enough as compared to III-V semiconductor based DMS. The main problems of investigation of DMSO ferromagnetism origin are the uniformity of dopants and clustering of dopants in the samples which are sensitively depended on the growth conditions and post-deposition treatments.

Figure 2.3: Common positions of incorporated transition metals inside the ZnO wurtzite structure.
As indicated in the Figure 2.3, the transition metals are the most common dopants used in the synthesis because of the interesting ferromagnetism properties showed after transition metal-doped ZnO become diluted magnetic semiconductors (DMS) materials. Normally after doping process occurred, the transition metals will replace the Zn atoms in the tetrahedral coordination. Zinc atomic radius is about 1.35 Å and the atomic radius of transition metals are in the range 1.25 Å -1.6 Å. So the incorporation of transition metals inside the wurtzite structure wouldn’t cause so much lattice distortion. However there’re difficulties in ZnO p-type doping since long times ago until recently some researchers succeed to incorporate nitrogen and phosphorous as p-type dopants inside the ZnO. The difficulties of achieving bipolar (n-type or p-type) doping is the common occurrence in wide band gap semiconductors fabrication. This is due to the compensation of substitutional impurity levels by the native point defects or dopant atoms that locate on interstitial sites and the formation of deep level traps. The strong lattice relaxation also occurred to drive dopant energy level deeper within gap. Sometimes the accessibility of extrinsic carrier density also limited by the low solubility of chosen dopants39.

2.2.2 ZnO:Co DMSO system

Most of the results cannot consistently indicate appropriate magnetic interactions mechanism for the induced ferromagnetism in DMSO samples. Co$^{2+}$ and Ni$^{2+}$ ions doped ZnO quantum dots fabricated by wet chemical route proved that nucleation and growth of nanocrystals influenced by the coordination chemistry of dopant ion or distribution of dopants in the host materials. Subsequently, defect states will be influenced by the growth condition and fabrication method leading to the alteration of magnetism of whole samples16. A few Zn$_{1-x}$Co$_x$O thin films which were produced by pulsed laser deposition (PLD) showed ferromagnetic behavior while others showed spin glass-like behavior. Magnetization value of
Zn$_{1-x}$Co$_x$O thin films fabricated by Ney et. al.$^{40}$ is very low due to antiferromagnetic coupling of Co-O-Co pairs in the samples. However, some researchers discovered that contribution of secondary phases CoZn should not be neglected since it is ferromagnetic phase.$^{41}$ Later several mechanisms have been proposed to explain the ferromagnetism origins which are different from conventional carrier-mediated ferromagnetism mechanism. In Schwartz and Gamelin’s works, they found out that zinc interstitial is playing important role in switching “on” or “off” the ferromagnetism of Co:ZnO system$^{42}$. In addition, the presence of grain boundary and other extended structural defects also perceived as primary source of ferromagnetism in the samples which showed ferromagnetism behavior but lack of magneto-transport properties$^{43}$. Lattice defects at film-substrate interface seem suited for the mechanism if the thickness or dopant concentration do not systematically proportional to the magnetic moment value$^{44}$. Another mechanism proposed also related to the introduction of additional dopant by co-doping with other pre-existed dopants or defects such as two-electron defects F$_t$ centers will “switch on” the ferromagnetism favorable condition$^{45}$. Most of the research concentrated on the correlation between magnetic properties and the charge transport, however some researchers succeeded to use magneto-optical phenomenon explain the source of ferromagnetism in their Co-ZnO system. Involvement of photo-induced carriers and the interactions in charge-transfer (CT) excited states between conduction band and valence band caused the exchange interactions between additional defect-bound or free charge carriers and the magnetic dopants will stabilize ferromagnetic ordering in the samples$^{46}$.

2.2.3 ZnO:Cu DMSO system

Although less research works done on Cu-ZnO system as compared to Co-ZnO system, the ferromagnetism origin of ZnO doped with Cu also becomes disputable issue in
the DMSO research area. For Cu-ZnO DMSO system, Buchholz et al. found out that p-type thin films were ferromagnetic while n-type samples were nonmagnetic\(^{10}\). Contrastly, Cu-ZnO thin films fabricated by Hou et al. disproved the previous claims by showing that n-type Cu-doped ZnO were ferromagnetic\(^{47}\). Later, p-type carriers were indicated are not necessity for the occurrence of ferromagnetism in the system\(^{48}\). Antiferromagnetic interactions were perceived to be existed among neighboring pairs of Cu ions since the magnetic moment per Cu atom of Cu doped ZnO films was decreased with increasing Cu concentration in the films. The most discouraging result was obtained by Keavney et al. group, where XAS and MCD analysis showed no magnetic signal from Zn and O and only paramagnetic signal from Cu\(^{49}\). Besides, ferromagnetism origin was reported as contribution of Cu-related secondary phase such as CuO planar nanophase inclusions based on the microstructural analysis\(^{28}\). Defect-mediated ferromagnetism was reported by Ran et al. to be responsible for the high temperature ferromagnetism behavior of Cu-ZnO system which have low magnetic moment\(^{50}\).

Another defect–mediated ferromagnetism was discovered by Straumal et al. linked the ratio of grain boundary area to grain volume to the occurrence of ferromagnetism in ZnO-based DMSO system\(^{51}\).

### 2.2.4 ZnO:Mn DMSO system

Besides Cu-ZnO system, another ZnO-based DMSO system, Mn-doped ZnO seems to be intriguing DMSO for the exploration of ferromagnetism origin. In the synthesis of Mn doped ZnO colloid, p type nitrogen defects were reported to be introduced into the ZnO lattice by the calcination of amines during fabrication process\(^{14}\). Magnetism results of Mn doped ZnO thin films produced by Droubay and co-workers give hints about the possibility of non-stochastic doping may stabilize ferromagnetic ground state in p-type Mn-ZnO
system. Existence of secondary phases once again was thought as source of ferromagnetism in high-temperature processed samples due to clustering of Mn-related phases. However, low-temperature processed samples also found to be possessed ferromagnetic behavior due to interaction of metastable ferromagnetic phase $\text{Mn}_{2-x} \text{Zn}_x\text{O}_{3-\delta}$ formed by the diffusion of Zn into Mn oxide and the oxygen vacancies in the Mn-ZnO system.

Most of fabricated DMSO have nonuniform distribution of dopants in the samples which is not qualified enough to be classified under DMS material category. Furthermore, the non-reproducibility of magnetism results from different researchers due to high sensitivity of DMSO ferromagnetism to the growth conditions. The disconnection between magnetic and magneto-transport properties evidenced by the insulating nature of the ZnO-based DMSO having ferromagnetism behaviors. Non-ferromagnetic impurities or constituents in metal oxides could induce ferromagnetism in DMSO system. Only spin is existed but no charge transport observed (i.e. low carriers regime) in the samples, making the system more puzzling and difficult to fit into the current available ferromagnetism mechanisms. Hence emergence of research area of defect ferromagnetism becomes one of the best explanations for the observed ferromagnetism in the samples which have low quantity of carriers and non-ferromagnetic constituents.

2.3 Low dimensional DMSO system

2.3.1 Nanostructured DMSO system

Nanocluster has semicrystalline or amorphous nanostructures with size smaller than 10nm and narrow size distribution. A nanocluster shows only some regions of crystallinity
and other regions might be amorphous. On the other hand, for single crystalline nanomaterials with ordered arrays and typical size smaller than 10nm, the nanostructures can be termed as nanocrystal. Nanocluster is a particle comprised of two or more atoms in a cluster. It has unique physical and chemical properties and its structure and crystal symmetry are not the same as its corresponding bulk material. In other words, its physical or chemical properties are discontinuous with size and shape. For example, Au$_{55}$ (gold clusters comprised of 55 atoms) is thermodynamically more stable than Au$_{56}$ even if the difference between them is only one atom. When the number of atoms clustered together is small, their atomic and electronic is well defined. When the nanoclusters were assembled into thicker films they are inhomogenous due to the non-uniform distribution of nanoclusters upon landing on the surface of substrate after pressure-driven nanoclusters travelled from nanocluster source chamber to deposition chamber. The nanoclusters were randomly landed on the surface of substrate, causing some nanoclusters agglomerated to become islands while some of them are isolated from others. Low dimensional DMSO with nanostructured form offers many advantages for the spintronic and optoelectronic applications such as high surface-to-volume ratio, unique chemical and electrical properties due to surface modifications, and tunable shape and size distribution.

Most of the non-doped nanostructured thin films and nanoparticles which reported as positive to ferromagnetic response explained as originated from different sources. Among the researches, point defects such as oxygen vacancies, zinc interstitials, zinc vacancies which resided in the interior or surface of the nanostructured materials were the most widely reported source of ferromagnetism. However, J. Osorio- Guillen et. al. researchers showed that concentration of point defects is not large enough to induce macroscopic magnetization since the exchange interactions of these defects are expected to be short range. The calculation of non-doped ZnO nanostructures by A. L. Schoenhalz and coworkers indicate
the importance of extended defects such as grain boundaries and dislocations to induce ferromagnetism in undoped ZnO system\textsuperscript{59}. Coey et. al. works suggested charge transfer mechanism to explain ferromagnetism in oxide nanoparticles where the electrons are transferred from the core of nanoparticles to their surfaces\textsuperscript{60}. The extended defects have larger and wider surface areas or volumes to mediate long range magnetic interactions. In addition, the magnetization is always strongly localized at the surface of low dimensional nanostructured materials and the magnetic behavior of surface also can be altered by capping molecules\textsuperscript{61}. Due to the unique surface properties of nanostructured materials, the magnetization value per surface atom will increase with the decreasing size of nanoparticles. The enhanced ferromagnetism of nanostructured materials contributed by extended defects which existed on the surfaces of nanoparticles. The surface defect states were created and exchange-splitted in the band gap of nanoparticles, leading to the delocalization on whole surfaces of nanoparticles. Thus the net macroscopic ferromagnetism is observed when the population of surface states is large enough. On the other hand, in d\textsuperscript{0} ferromagnetism mechanism, the point defects were assumed as majority impurities in the samples with population large enough to initiate the defect-related hybridization at Fermi level. Pure ZnO nanowires and nanorods synthesized by CVD\textsuperscript{62} and wet chemical route\textsuperscript{63} respectively were reported possessed ferromagnetism with small saturation magnetization. Both group of researchers, G. Z. Xing et. al. and B. Panigraphy et. al. agreed that oxygen vacancies play important role in enhancing ferromagnetism of samples. In their assumptions, the oxygen vacancies were formed anionic vacancy clusters and induced sizable magnetic moment in whole sample.
2.3.2 Nanostructured ZnO:Cu system

Cu-doped ZnO DMSOs were synthesized by chemical vapor deposition (CVD), radio-frequency (RF) plasma sputtering and wet chemical route. All samples produced by those researchers possessed Curie temperature higher than room temperature. However, most of the samples possessed small coercivities and the value of saturation magnetization is quite low in which the magnetic moment per Cu atom is lower than theoretical value of a single atom which is 1 $\mu_B$/Cu. The low magnetic moment per Cu atom was reported due to the weaker interparticle exchange and nanostructured nature of the material $^{13,64}$. All magnetism results showed similar trend of saturation magnetization vs. concentration of Cu in the samples, i.e. decrease of magnetic moment with increasing Cu concentration. The magnetism trend can be explained by the decrease of distance between Cu-Cu atoms leads to the increase of occurrence of antiferromagnetic coupling between adjacent Cu pairs $^{65}$.

2.3.3 Nanostructured ZnO:Mn system

Most of the Mn-doped ZnO nanostructured materials were deposited via CVD and wet chemical route. Magnetization value obtained by all works are much smaller than 5 $\mu_B$/Mn for a free Mn$^{2+}$ ion with S = 5/2 and g =2. Some researchers suggested the reduction of magnetization value was attributed to the AFM coupling between neighboring Mn-Mn ions $^{66}$ and some results implied the existence of secondary phase (Zn, Mn) Mn$_2$O$_4$ $^{67}$. Various explanations based on different mechanisms have been given for their own fabricated Mn-doped ZnO nanostructured materials. V. A. L. Roy and co-workers suggested presence of defects at the surface of tetrapod structures contributed to the occurrence of ferromagnetism phenomenon in the materials $^{66}$. Z. F. Wu et. al. reported the induced ferromagnetism in Mn-doped ZnO nanorods was originated from aid of oxygen vacancies which aligned with Mn$^{2+}$ level to create effective dopant-defect hybridization as described in the bound magnetic polarons (BMP) model $^{68}$. Importance of intrinsic atomic exchange such as sp-d and d-d
exchange interactions among Zn and Mn orbitals and the existence of impurities or defects such as oxygen vacancies which served as trap center for electrons or holes were underlined in the J. Iqbal et al. research for explanation of ferromagnetism in the samples\textsuperscript{69}. Contrastly, the carrier-mediated ferromagnetism was thought as main contributor to the ferromagnetism due to exchange coupling between ionized spins of Mn in Mn-ZnO nanoparticle system fabricated via wet chemical route and the magnetism results showed that the increase of Mn concentration activates the conversion from paramagnetic behavior to ferromagnetic behavior\textsuperscript{70}. Ferromagnetism of Mn-doped ZnO nanostructured materials also attributed to the homogenous distribution of Mn ions substituting Zn cation sites and the overlap of unoccupied 3d states of Mn with impurity bands contributed by oxygen vacancies\textsuperscript{71,72}.

2.4 Optical properties of ZnO thin films

ZnO is n-type semiconductor with band gap 3.3 eV. It has high excitonic binding energy 60eV. ZnO thin film posses high transmittance in the visible region and sharp absorption edge near 380 nm. Typical photoluminescence spectrum of ZnO thin film exhibits strong UV emission and strong or weak deep-level emission (normally green luminescence) depends on the intrinsic and extrinsic defects existed in the samples. Single crystal ZnO has band gap around 3.37 eV\textsuperscript{73}. Hexagonal wurtzite ZnO has non-central symmetry structure which creates normal pole moment and spontaneous polarization along the c-axis due to the presence of negatively charged (0001)-$\text{O}^{2-}$ and positively charged (0001)-$\text{Zn}^{2+}$ polar surfaces. Hence there are two independent refractive indices, $n_0$ and $n_e$ in ZnO. Intrinsic properties of bulk ZnO normally take place between electrons from conduction band and the holes from valence band. Bulk ZnO with low impurities level would have free excitons which have ground-state transitions and excited states. Excitonic effects induced by Coulombic
interactions enable existence of free and bound excitons in the band structures. Existence of impurities and defects will influence the extrinsic optical properties of ZnO by creating discrete electronic states in the band gap. Absorption and emission processes of ZnO were affected by impurities and defects. Conduction band of ZnO formed by majority s-like state with $\Gamma_7^c$ symmetry while p-like state forms valence band which split into three bands under the influence of spin-orbit interactions and crystal-field effects. Three bands splitted in valence band and thus transition from these bands dominated near-band-gap intrinsic absorption and emission\textsuperscript{74}. A (heavy hole), B (light hole) and C (crystal-field split band) are given to free-exciton related transitions from the conduction band to three valence bands or vice versa. However, the valence-band symmetry ordering has been a subject of controversy due to different interpretation of the spectral line\textsuperscript{75,76}.

2.5 **Optical properties of low dimensional ZnO**

The photoluminescence and photo absorption of nanoclusters are affected by their intrinsic electronic properties and effect of doping of nanoclusters. The semiconductor nanocluster optical properties are depend on the nanocluster radius or size. The quantum-size effect will modifies the energy spectra of three dimensionally confined quasiparticles and hence their luminescence and absorption spectra. The transition between hole and electron quantum-size levels can be observed in linear and nonlinear optical spectra. For instances, Figure 2.4 (a) shows the PL spectra for the ZnO nanocluster film and the annealed nanocluster films at 600 °C. A relatively sharp and strong ultraviolet and a broad weak emission are observed in the UV emission and visible range respectively. The visible emission at 2.43 eV originates from the transition in defect states associated with oxygen vacancies or Zn interstitials. Figure 2.4 (b) indicates the UV emission of pure ZnO, 1 at.%
and 2 at.% Ga-doped ZnO nanowires. Doped ZnO have broader UV peak at the longer wavelength region revealing the decrease of band gap. When dopants are existed in ZnO, the excess carriers supplied by the impurities to the conduction band will increase electrical conductivity of ZnO and thus leads to a red-shift of the UV peak. Figure 2.4 (c) displays the green emission spectra of pure ZnO and doped ZnO samples measured at room temperature. As compared to pure ZnO, the doping effect caused smaller FWHM of peaks and the enhanced green emission which are useful in photodiode applications. On the other hand, in UV-Vis absorption spectra, the shift of total energy of band edge implies that the decreasing nanoclusters size can increase the energy of lowest electron and hole quantum-size levels. Therefore, ratio of the nanocluster radius, a to the Bohr radius of bulk exciton, $a_B$ is the important factor that affect optical properties of nanoclusters. The exciton Bohr radius in bulk ZnO is 0.9 nm$^7$, while our fabricated nanoclusters have the size ~10 times larger than $a_B$. Hence optical properties of nanoclusters is categorized in weak confinement regime where $a \gg a_B$. In other words, the quantization energy of electrons and holes is smaller than the binding energy of an exciton, $E_{ex}$ and the quantum confinement of the exciton center of mass will affect the optical spectra of the nanoclusters. In considering the nanocluster optical spectra, the Coulomb interaction between the optically created electron and hole shall not be ignored although this interaction can affect the results by reducing the transition energies in a relatively small amount. This is due to the fact that Coulomb energy increases with decreasing size as $1/a$ while the quantization energy scales with size as $1/a^2$. However, the Coulomb interaction is more important than the quantization energies of the electrons and holes in the large nanoclusters$^7$. When the particle size is reduced, the energy level spacing will increase due to the quantum size confinement effect. The effective band gap of a spherical nanoparticle is related to particle radius and effective mass of hole and electron by equation $E_g(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\epsilon R}$, where $E_g(\infty)$ is bulk band gap, $R$ is
particle radius, $\varepsilon$ is bulk dielectric constant, $m_e$ and $m_h$ is effective mass of electron and holes respectively. The effective band gap is inversely proportionally to the particle radius. When the particle radius is small, the second term (quantum size effect) has greater influence than third term (Coulomb effect). However, when the particle size is too large compared to the Bohr exciton radius, the second term is negligible compared to Coulomb effect and thus bigger particle’s band gap is depends on the Coulomb effect. The quantum size confinement effect is expected to occur at much bigger sizes for semiconductors than for metal nanoparticles. The smaller size of nanoparticles have totally different density of states function compared to 3D bulk material and the function will varies depends on the number dimensional constraints. The changes of density of state (DOS) will affects the electronic, vibrational, dynamic and equilibrium properties of nanomaterials. The band structure of nanomaterials is not as well characterized as with bulk materials. Intensive debates still focused on the true source of luminescence detected and whether the nanoparticle is direct or indirect band gap material. The determination of electronic band structure of nanomaterials is complicated by the surface effect of nanoscale materials. The surface phonons are involved in the electron-phonon interaction tends to have lower frequency compared to the bulk phonon. The surface of nanomaterials will introduce electronic traps states and change the electron-phonon interaction and electron-surface interaction in the system and consequently the charges carrier lifetimes will be affected. The absorption spectrum can be obtained by measure the transmission or absorbance as the function of wavelength of light. The nanoscale materials will show blueshift of absorption spectra with decreasing of size. Sometimes, the absorption spectroscopy will conducted at low temperature to reduce the inhomogenous broadening due to the thermal effect. The surface and shape are crucial factors that will affect the electronic relaxation in the nanoparticles. When the shape of nanoparticle changes the ground state electronic absorption spectrum will changes significantly.$^{79}$
Figure 2.4 PL spectra of the (a) ZnO nanocluster film and the film after annealed at 600 °C. (b) UV emission spectra of pure ZnO, 1 at.% Ga-doped ZnO, and 2 at.% Ga-doped ZnO nanowires at 300 K. (c) Green emission of pure ZnO, 1 at.% Ga-doped ZnO, and 2 at.% Ga-doped ZnO nanowires at 300 K.
Chapter 3 Experimental Methodologies

3.1 Nanocluster beam deposition

The size of nanoparticles can be controlled by adjusting sputtering parameters: magnetron powers, inert gas flow (Ar to He flux ratio), aggregation length, gas-aggregation tube temperature and the condensation length in which the clusters aggregate. Due to the strong relationship between cluster size and their structural, magnetic, optical and electronic properties, it is possible to produce nanoclusters with various properties by tuning those sputtering parameters. The advantage of sputtering gas condensation system is the narrow size distribution of produced nanoclusters. The schematic setup of sputtering gas aggregation system is shown in Fig. 3.1. The main chambers of this system are nanocluster source chamber containing a liquid nitrogen cooled aggregation tube with a magnetron sputter discharge and the main deposition chamber with a R.F. plasma sputtering gun and a substrate holder. ZnO:Cu and ZnO:Mn nanocluster assembled films were fabricated by using sputtering gas aggregation while ZnO:Cu-SiO$_2$ and ZnO:Mn-SiO$_2$ were prepared by depositing ZnO:Cu and ZnO:Mn with sputtering gas aggregation technique and SiO$_2$ by RF sputtering alternatively into multilayered films.

Figure 3.1 Schematic diagram of nanocluster beam deposition system.
At the discharge voltage around 250 V, when a few percent of diatomic molecules and small clusters are sputtered from metal surfaces they are dissociated by the intense magnetron discharges. Only some of the atoms will be ionized and some of them managed to leave sputter discharge. Argon gas plays important role as carrier gas and introduced directly over the sputter target while He gas was fed from the back to control the cluster size. The existence of argon or helium gas reduced the velocity of sputtered atoms and cools the atoms, leading to redeposition of some atoms onto sputter target while others swept by the viscous gas stream into a condensation cell cooled with liquid nitrogen. Increasing the He to Ar flux ratio will decrease the cluster size. The clusters will grow larger and larger if they stay very long in the condensation region. Since almost only atoms are exist at first in the condensation region, the cluster formation start with the metal dimer formation. Two-body collision is not possible for the formation of dimer due to the energy and momentum conservation laws. Hence the three-body collisions best suit the process. First step of dimer clustering involved the process: $\text{M} + \text{M} + \text{Ar} \rightarrow \text{M}_2 + \text{Ar}$ where M is metal atom and Ar is argon gas. Next, the cooling of newly formed dimer by collision with argon gas leads to formation of trimer: $\text{M}_2 + \text{M} + \text{Ar} \rightarrow \text{M}_3 + \text{Ar}$. The clusters will continue to grow by cluster-cluster coagulation if the monomer density has been effectively reduced by this process. The sputter discharge operated at pressure of 0.1-1.0 Torr while deposition chamber has lower pressure around $10^{-4}$-10$^{-5}$ Torr. Consequently, the difference of pressure caused the clusters fly to the deposition chamber and softly landed on the surface of substrate.\textsuperscript{81,82}
3.2 Characterization methods

3.2.1 X-ray diffraction (XRD)

In X-ray analysis, the source used in Bruker AXS: D8 Advance machine is 2.2 kW Cu anode in long fine focus ceramic X-ray tube running at 40 kV and 40 mA. The X-ray machine is comprised of several parts which included x-ray source, x-ray beam shaping optics, goniometer, reflectometry sample stage, and the detector. Collimated beam can be compressed and frequency filtered by a Göbel mirror and V-Groove. They served as monochromator and beam collimator so that only Cu-K$_{\alpha1}$ (wavelength 1.541837 Å) is present in the controlled beam. The installed goniometer is served as adjustor for Theta and 2Theta measurement with smallest angular step size 0.0001° while detector part is comprised of NaI dynamic scintillation detector.

\[
\text{Incident rays} \quad \text{Scattered rays}
\]

\[
\begin{align*}
\text{d} & \quad \text{\theta} \\
\end{align*}
\]

\[2\theta
\]

Figure 3.2 Illustration of x-ray diffraction.

In Fig. 3.2, the distance between two adjacent planes is given by the interplanar spacing $d_{\text{hkl}}$ with the indices indicating the Miller indices of the specific lattice planes. The simple geometric consideration is given when considering a simple cubic crystal case where distance...
between two planes is given by \( d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \). To observe a maximum intensity in the
diffraction pattern of a simple cubic crystal, the Bragg equation has to be obeyed, \( 2d_{hkl}\sin\theta_B = \lambda \) where \( d \) is the interplanar spacing of atomic planes, \( \theta \) is the angle of incidence and \( \lambda \) is the
wavelength of x-ray. When certain crystallographic lattice planes impinged by plane wave x-rays at angle \( \theta \), the x-rays will be scattered by the atomic planes. The relative phase shift of
the wave is depends on the configuration of middle atoms which located at top plane and one
plane beneath. Only when the phase shift \( 2d_{hkl}\sin\theta \) is a multiple of the wavelength, then the
constructive interference for the reflected wave can be obtained. The relation of interplanar
spacing and the unit cell parameters of crystal system other than simple cubic can be
represented by Table 3.1. These formulas can be used to estimate corresponding
crystallography planes for that particular XRD peaks after interplanar spacing \( d_{hkl} \) obtained
from XRD measurement.

Table 3.1 Interplanar spacings \( d_{hkl} \) for different crystal systems and their dependency on Miller indices

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Constraints</th>
<th>[ \frac{1}{d^2_{hkl}} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>( a = b = c ) &lt;br&gt;( \alpha = \beta = \gamma = 90^0 )</td>
<td>( \frac{h^2 + k^2 + l^2}{a^2} )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( a = b ) &lt;br&gt;( \alpha = \beta = \gamma = 90^0 )</td>
<td>( \frac{h^2 + k^2 + l^2}{a^2} + \frac{l^2}{c^2} )</td>
</tr>
<tr>
<td>Orthorombic</td>
<td>( \alpha = \beta = \gamma = 90^0 )</td>
<td>( \frac{h}{a} + \frac{k^2}{b^2} + \frac{l^2}{c^2} )</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Conditions</td>
<td>Equations</td>
</tr>
<tr>
<td>----------------</td>
<td>------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b$, $\alpha = \beta = 90^0$, $\gamma = 120^0$</td>
<td>$\begin{align*} 4h^2 + 2h + k^2 + l^2 &amp; = \frac{4}{3} \frac{a^2}{c^2} + \frac{l^2}{c^2} \end{align*}$</td>
</tr>
<tr>
<td>Trigonal/Rhombohedral</td>
<td>$a = b = c$, $\alpha = \beta = \gamma$</td>
<td>$\begin{align*} (h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + hl + kl)(\cos^2 \alpha - \cos \alpha) &amp; = \frac{a^2(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)}{a^2 \sin^2 \beta + \frac{k^2}{b^2} + \frac{l^2}{c^2} \sin^2 \beta - \frac{2hl\cos \beta}{a \sin^2 \beta}} \end{align*}$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$\alpha = \gamma = 90^0$</td>
<td>$\begin{align*} \frac{h^2}{a^2 \sin^2 \beta} &amp; + \frac{k^2}{b^2} + \frac{l^2}{c^2} \sin^2 \beta - \frac{2hl\cos \beta}{a \sin^2 \beta} \end{align*}$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>None</td>
<td>$\begin{align*} \begin{bmatrix} \frac{h}{a} &amp; \cos \gamma \cos \beta &amp; 1 \ \frac{k}{a} &amp; 0 &amp; \frac{k}{b} \cos \alpha \end{bmatrix} \begin{bmatrix} 1 \ + \frac{l}{c} \cos \gamma \cos \alpha \cos \beta \cos \alpha \end{bmatrix} &amp; = \begin{bmatrix} 1 \cos \gamma \cos \beta \ \cos \gamma \cos \alpha \end{bmatrix}^{-1} \end{align*}$</td>
</tr>
</tbody>
</table>

After the detector collected diffracted x-ray beam at angle $2\theta$ which obeyed Bragg’s law, the diffraction peaks will be indexed by comparing $d_{hkl}$ value obtained from the scan with $d_{hkl}$ value provided in powder diffraction file (PDF) database from International Center for Diffraction Data (ICDD).
3.3 Transmission electron microscopy (TEM)

All TEM micrographs and high resolution TEM images, selected pattern diffraction patterns and bright-field and dark-field TEM images were taken using JEOL 2010 and JEOL 3010 operating at 200 kV and 300 kV respectively. As can be seen in Fig. 3.3 the illustration system, specimen stage, objective lens system, magnification lens system, data recording system and the chemical analysis system are the basic components for a TEM analysis system.

Figure 3.3 Components in TEM.
After the electron beams were focused with the objective lens the atomic potential form
diffraction spots on the back focal plane will scatter the diffracted waves. Then the image will
formed on the image plane by recombined diffracted waves. The electromagnetic lenses can
be used to control diffracted electrons to be focused into a regular arrangement of diffraction
spots that are projected and recorded as the electron diffraction pattern. A magnified image of
the sample can be observed if the diffracted and transmitted beams interfere on the image
plane. Real space is the space at the image plane or at a specimen while the reciprocal space
is a space where the diffraction forms. Fourier transform can be used to represent the
transformation from the real space to reciprocal space.

Diffraction pattern can be obtained in a specific area as small as 100 nm in diameter
by inserting a selected area aperture and using the parallel incident beam illumination.
Conical beam is used in convergent beam electron diffraction (CBED) to produce diffraction
disks. Thus the intensity distribution inside the disks enables determination of all the point
groups and most space groups. The relationship between reciprocal lattice and mutual crystal
orientation in the polycrystalline materials can be obtained since the selected area diffraction
pattern can be easily recorded from almost every grain. The first thing to do in investigation
of TEM images is to obtain electron diffraction pattern. When the transmitted beam is
directed through a small objective aperture and the lenses is changed to the imaging mode,
the bright-field mode can be used, as shown in Fig. 3.4 (a). Dark-field mode can be used
when the diffracted beam is selected, as shown in Fig. 3.4 (b). The change of the amplitude of
diffracted beam or transmitted beam due to the absorption and dynamic scattering in the
specimens will create contrast in the images. Thus absorption-diffraction or amplitude
contrast is termed for the image contrast and the technique is suitable for the study of
mesoscopic microstructures such as interfaces, lattice defects and precipitates. High-
resolution mode can be used when more than two beams are selected on the back focal plane
by using a large objective aperture, as shown in Fig. 3.4 (c). Multiple beam interference due to differences of phase of the diffracted and transmitted beams can be used to form phase contrast image. Determination of an approximate structure model is possible by using HRTEM with aid of high resolution powder x-ray or neutron diffraction. HRTEM is also a powerful tool for the investigation of disordered and defect structures.

Figure 3.4 (a) Bright-field method (b) dark-field method and (c) high-resolution electron microscopy observation mode in electron microscope using an objective aperture which has center located on the optical axis.

3.4  X-ray photoelectron spectroscopy (XPS)

All samples compatible with ultra-high vacuum can be analyzed for the determination of the surface chemical composition, thickness measurement and the concentration profiling and imaging. Atoms of a solid will emit electrons upon the irradiation by x-ray photon due to the photoelectron effect. XPS characterization involved analysis of kinetic energy of the
photo-emitted electrons at the time of irradiation by a monoenergetic beam of x-ray photons. Binding energy, $E_B$ can be used to characterize an electron of a given electronic level: $E_B = h_i - E_k$ where $E_k$ is the measured kinetic energy of the photoelectron and $h_i$ is the incident energy of an x-ray photon. In order to analyze the samples the binding energy of all core or valence electrons must be lower than $h_i$. The atomic identification and quantification is possible since the binding energy of a core electron is specific to an atom. A photoelectron can undergo a wide range of interactions that limit its access to the surface during its transfer from core to surface. The photoelectron kinetic energy and the nature of crossed medium (atomic density) will influence the photoelectron mean free path. XPS is a very weakly and non-destructive method due to the low dosage of incident photon and the negligibly small induced damages in sample surface. For element identification, the detected photoelectron spectra give information of electron intensity versus their binding energy. The peaks in the spectrum can be indexed according to their electron levels from where the photoelectrons are coming by using quanta numbers n, l, j. For chemical analysis, the chemical shift is observed when there are orbital energy variations of a fraction to several eV due to reorganization of core levels when an atom is inserted in a chemical component. This chemical shift is characteristic of the nature and the number of the atoms surrounding the emitter atom. The chemical bonding structure can be determined by peak deconvolution of the corresponding peak in XPS spectrum. The operation of XPS required ultra high vacuum ($<10^{-9}$ Torr) condition so the electrons diffusion by the residual atmosphere molecules can be avoided during their residual transfer to the detector and the reactions or contaminations of sample surfaces also can be avoided. The basic components of a photoelectron spectrometer are x-ray source, electron energy analyzer, Ar ion gun, neutralizer, vacuum system, electronic controls and computer system. An anode with its surface coated with the element emitting the required $K_a$ radiation is used as the x-ray source. Electron beams of high energy used to
irradiate the anode to emit x-ray. Elimination of the satellite rays and reduction of principal x-ray width can be done by using monochromator. The electron energy analyzer is a hemispherical sector which acts as filter and photoelectron spectrum scanner with constant resolution. The electron multiplier (channeltron or channel plate) linked with a CCD camera are used to detect electron at analyzer exit slit. In electron spectroscopy, there are three main processes can be happened, X-ray photoemission spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and the Auger electron spectroscopy (AES). XPS analysis involved emission of a core electron after absorbing a photon, UPS analysis involved emission of a valence electron after absorbing a photon while AES analysis involved core electron excitation by a photon. The two common phenomena commonly occurred in the process of electron spectroscopy are photoemission and Auger effect, as shown in Fig. 3.5.

![Diagram](image.png)

Figure 3.5 Two common phenomena in electron spectroscopy: (a) photoemission process (b) Auger effect.
3.5 Raman spectroscopy

Raman system used in this project is Renishaw System 2000 Raman Spectrometer which is equipped with both laser beam of 514 nm (Ar green laser) and laser beam of 632 nm (HeNe red laser). Raman system is typically consists of excitation source, sample illumination system and light collection optics, wavelength selector (filter or spectrophotometer), and the detector (photodiode array, CCD or PMT), as shown in Fig. (The CCD detector can provide direct 2-D Raman imaging and Raman spectroscopy for the study of contamination analysis, carbon overcoat property test, solid thin film monitoring and the nanomaterial related study. The spectral resolution is 1 cm\(^{-1}\) and the spectral range is 100-9000 cm\(^{-1}\).

Raman spectroscopy is a characterization technique based on inelastic scattering of monochromatic light such as laser source. The photons in incident laser light are absorbed by the sample and the reemitted. The shift-up or down of the reemitted photons frequency compared to the original monochromatic frequency is called the Raman effect. The Raman shift provides information about rotational, vibrational and other low frequency transitions in molecules of solid, liquid and gaseous samples. The Raman effect is based on the molecular deformations in electric field \(E\) determined by the molecular polarizability \(\alpha\). The laser beam can be perceived as an oscillating electromagnetic wave with electrical vector \(E\). Electric dipole moment \(P = \alpha E\) which can be induced upon interaction with the sample. The molecules start vibrating with characterization frequency \(\nu_m\) due to periodical deformation. Nuclear displacement is given to describe amplitude of vibration. Molecules are excited by monochromatic laser light with frequency \(\nu_0\) and transformed into oscillating dipoles. Light with three different frequencies will create three type of scattering depends on the oscillating dipoles, Rayleigh scattering, Stokes Raman scattering and Anti-stoke Raman scattering.
About 99.999% of all incident photons in spontaneous Raman undergo elastic Rayleigh scattering which is useless for practical purposes of molecular characterization. Only 0.001% of the incident light produces weak inelastic Raman signal with frequencies $\nu_0 \pm \nu_m$ which is useful for the analysis. Laser beam is used to illuminate sample in the ultraviolet, visible or near infrared range. A lens is used to collect the scattered light and sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Notch filter is used to reduce Rayleigh scattering and obtain high-quality Raman spectra. Stray light generated in the spectrometer upon light dispersion on gratings and strongly depends on the grating quality. Charge-Coupled Devices (CCD) camera is used to reduce detection time and improve the sensitivity and performance of detection of Raman scattered light. The laser beam spot can be reduced to $\sim 1 \mu m$ diameter with the aid of high-magnification microscope objectives to enable analysis of Raman scattering in micro-scale.

Figure 3.6 Schematics of Raman system.
3.6 Photoluminescence (PL) analysis

PL system used in the experiment is luminescence spectrometer Perkin Elmer LS 55 with laser source Xenon discharge lamp which is equivalent to 20 kW for 8 μs duration. The sample detector is made of gated photomultiplier with modified S5 response for operation up to around 650 nm and another reference detector is consisted of photodiode for operation up to around 900 nm. The monochromators used in this machine is Monk-Gillieson type monochromators cover the following ranges: excitation 200-800 nm and emission 200-650 nm with standard photomultiplier with zero order. The scan result has wavelength accuracy +1.0 nm.

Photoluminescence is a non-destructive technique in which excess electron-hole pairs are created and excited by absorption of an external optical source whose energy is $hν > E_1 – E_0$, where $h$ is Planck’s constant, $ν$ is frequency of incident light, $E_0$ is energy level of valence band and $E_1$ is energy level of conduction band. Subsequently the relaxation of electrons to bottom of conduction band and holes to top of valence band will occur. Finally the radiative recombination of electron-hole pairs released photons with energy $hν = E_1 – E_0$. The resultant luminescence signal will be detected for further analysis. Nonradiative recombination will produce no photon in the process and affect the overall photoluminescence efficiency. The laser source is used to excite the samples while sharp plasma lines from the laser source can be blocked by bandpass filter. The luminescence is collected and dispersed by a spectrometer. Then the luminescence will be detected by photomultiplier tube (PMT) and received information will be transformed into electrical current signal. Conversion of analog signal into digital data will be carried out by Data ACQ so that the resultant signal can be recognized and accepted by computer. The computer is used to control the spectrometer via the spectrometer controller and to collect the data. Signal-to-noise ratio can be improved by using optical chopper combined with lock-in amplifier technique.
3.7 **UV-Vis absorption spectroscopy**

Varian 5000 Cary UV-Vis-NIR Spectrophotometer is used for UV-Vis absorption analysis in the project. Scanning wavelength range spans from 175 to 3300 nm. The limiting resolution for UV-Vis range is <0.05 nm and <0.2 nm for near-infrared (NIR) range. The bandwidth of spectrum is 0.01 nm to 5.00 nm in UV range and 0.04 to 20 nm in near-infrared range. The detector part is equipped with R928 photomultiplier tube for UV-Vis range and equipped with electrothermally controlled lead sulfide (PbS) photocell for detection in NIR range.

The absorption of radiation in the UV-VIS region of the spectrum is dependent on the electronic structure of the absorbing species such as ions, molecules, atoms or complexes. If the energy of a photon matches with the difference in the energies of electronic energy levels,
a transition amongst the electronic energy levels may occur when a photon with certain wavelength interacts with the molecule. The spectrum of transitions in the gaseous or vapor phase will have a number of closely spaced lines, forming the band spectrum. For solution phase, the solvent molecules surrounded the absorbing molecules and constant collision occurred among them. Consequently, the energies of quantum states will spread out and the sample absorbs photon spread over a range of wavelength. Continuous and smooth absorption peak will be obtained in the solution phase. For inorganic species such as ZnO and transition metal dopants, they mostly give weak absorption bands in the visible range. Some ions and complexes of transition metals are colored due to transitions amongst d-orbitals. The relationship between the light absorption capacity of the sample and the thickness of absorbing medium can be explained by Lambert’s law while the relationship between the light absorption capacity of the sample and its concentration can be explained by Beer’s law. The absorbance can be related to transmittance by equation $A = -\log T = \varepsilon bc$ where $\varepsilon$ is molar absorptivity, $b$ is path length of cuvette and $c$ is concentration of solution.

The basic components of UV-Vis spectroscopy are consisted of a stable radiation source, wavelength selector, sample holder, radiation detector or transducer, and the signal processing and output device. The common radiation source for UV region is electric discharge sources like hydrogen or deuterium lamp while tungsten-halogen lamp is used for visible region. The absorption filter is used to cut off undesirable wavelength and to isolate the radiant energy from source. There are two types of monochromators available for the selectively emission of radiation at a desired wavelength but out of the range of wavelength emitted by the source; the prism and grating monochromators. Common detectors used in the machine for conversion of a light signal to an electrical signal which can be suitably measured and transformed into an output are phototube, photomultiplier tube and diode array.
detector. The electrical signal from transducer is suitably amplified or processed before it is sent to recorder to give an output.

![Diagram of UV-Vis spectrometer]

Figure 3.8 Principle of UV-Vis spectrometer.

### 3.8 Alternating Gradient Force Magnetometer (AGM)

AGM has higher magnetic moment sensitivity (~$10^{-8}$ emu) which is 1000 times more sensitive than a conventional VSM and faster applied field sweep rate (2500-5000 Oe/second) compared to SQUIDS magnetometer. AGM is suitable for the characterization of ultrathin films and nanostructure thin film which are sensitive to the size of magnetic particles. The sample size is limited to 3 x 3 mm for the optimum measurement condition.

The working principle is almost same as vibrating sample magnetometer (VSM), except that the changing flux of AGM originated from alternating applied magnetic field in
spite of from the vibrating samples. The end of a cantilevered rod which incorporated with a
piezoelectric element is the place for sample mounting. Then the sample will be
simultaneously subjected to a small alternating field gradient when it is magnetized by a dc
field (variable in magnitude). An alternating force will be exerted on the sample which is
proportional to the magnitude of the magnetic moment and field gradient of the samples.
Subsequently, the voltage output of the piezoelectric element is measured based on the
deflection of cantilever rod. Then the output signal is amplified by operating at or near a
mechanical resonance frequency of the cantilever. The typical value of mechanical Q value is
25-250 while 100-1000 Hz is the range for operating frequency of machine. The only
shortcoming of AGM measurement is the sensitivity of measurement is limited by
mechanical and acoustic noise in the environment.\textsuperscript{84}
Chapter 4 Ferromagnetism of Cu nanoclusters embedded in ZnO Thin Films

4.1 Introduction

As reviewed in Chapter 2, Cu nanoclusters can be embedded in ZnO thin film by using nanocluster beam deposition combined with RF sputtering techniques. It is important to investigate the origin of ferromagnetism in DMSO due to the prospects of integrating intrinsic magnetic and electronic functionalities into a single material for the application of spintronics. Among the semiconductor matrices, ZnO is of particular interest because it holds the possibility of a DMSO with a Curie temperature above the room temperature $^{33}$. ZnO doped with various transition metals such as Mn, Co, Cr, Ni, V or Fe were reported to show ferromagnetism at room temperature $^{85,86}$. There still exists a debate on whether the magnetic behavior is an intrinsic property of thin film or due to the presence of nanoclusters of magnetic phase or both due to the difficulty of the microstructure characterization in large scale. In order to exclude the contribution of ferromagnetic nanoclusters, Cu doped ZnO thin films were investigated since neither metallic Cu nor Cu$_2$O or CuO in the bulk is ferromagnetic. Room temperature ferromagnetism of ZnO:Cu films were found by many researchers $^{9,10,48,87}$. Various mechanisms of the origin of ferromagnetism in ZnO:Cu films such as free-carrier and defects mediated mechanism, bound magnetic polarons model, indirect double-exchange model, etc. $^{9,48,88,89}$ were proposed to interpret their wide range of experimental observations. However, nanometer sized CuO nanoparticles have been reported to show ferromagnetic behavior as size was below 10 nm $^{90}$. Especially, planar nanoscale CuO inclusions in Cu-doped ZnO films were found by HRTEM which was considered as the origin of ferromagnetism $^{28}$. Due to the difficulty in the observation of the small amount of CuO nanometer scale inclusions/precipitate, the debate on the origin of ferromagnetism of
ZnO:Cu films either from the Cu ions substituted in Zn cation sites or some Cu/CuO nanoclusters or both still exists. In this work, we deliberately fabricate Cu nanoclusters embedded ZnO and SiO₂ films by combination of nanocluster beam deposition technique and radio frequency (RF) - magnetron sputtering. The ferromagnetism and microstructure of Cu nanocluster embedded ZnO films were investigated. Since the nanoclusters were softly landed on the ZnO films and it was unlikely to cause the large-scale diffusion of Cu atoms into the ZnO lattice during deposition the effects of Cu substitution with Zn can be neglected and only nanocluster effects on ferromagnetism can be investigated.

4.2 Experimental details

Cu-embedded ZnO were prepared by combining nanocluster beam deposition and RF sputtering. ZnO thin films were deposited on the glass substrate by RF sputtering prior to the embedment of Cu nanoclusters while Cu nanoclusters were formed by gas-aggregation technique. The details of this nanocluster deposition technique was described in our previous report⁹¹. After the Cu nanoclusters were softly landed on the surface of 50 nm ZnO thin film, another 50nm coverlayer ZnO were deposited ontop of the nanoclusters to completely surround Cu nanoclusters within ZnO thin films. The nanocluster deposition time was tuned between 2 seconds to 200 seconds to produce volume fraction of Cu in ZnO from 0.1 vol. % to 10 vol. %. Another three sets of samples which are comprised of Cu embedded ZnO and Cu and Cu-oxides embedded SiO₂ multilayer with Cu nanocluster volume fraction ranging from 4 vol. % to 50 vol. % were fabricated for comparison of hybridization effect between nanoclusters and matrixes. Notice that the volume fraction was calculated based on the deposition rate of nanocluster assembly film. Since the nanocluster assembly films were very porous the actual volume fraction should be less than those stated in the present work. The
crystal structures, microstructures and the chemical state of Cu embedded ZnO thin film were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) respectively. Room temperature magnetic properties were examined by AGM. Optical properties of the films were probed by UV-Vis spectroscopy and PL (photoluminescence).

4.3 Results and discussions

Figure 4.1 (a) shows the XRD patterns of Cu nanoclusters-embedded ZnO films with different volume fractions of Cu nanoclusters. It was found that the ZnO (002) peak intensity decreased with the increase of Cu nanocluster volume fractions in ZnO and ZnO (103) diffraction peak became more observable. This may be explained that the increase of porous Cu nanoclusters in the ZnO caused the interruption of ZnO (002) grain growth in film normal direction and promoted the growth of grains with other orientation. XRD pattern don’t show any peak related to Cu or Cu oxides in the film due to the small quantities of nanoclusters in films or amorphous nature of nanoclusters. In addition, it is worth noting that the lattice constant $c$ of pure ZnO film was larger than $c$ value of bulk ZnO (5.205 Å). Upon insertion of Cu nanocluster in ZnO film the lattice constant $c$ was sharply decreased to 5.200 Å and then decreased slightly with further increase of the Cu contents as shown in Figure 4.1 (b). Since the Cu nanoclusters were deposited by low energy deposition which utilized differential pressure-driven techniques to transfer sputtered nanoclusters from target to sample surface. The nanoclusters were softly landed on ZnO, thus possibility of change in lattice constant caused by Cu substitution of Zn can be ruled out. The larger lattice constant in the sputtered ZnO films than the value of bulk ZnO were attributed to the existence of tensile stress in the thin film$^{92,93}$. The addition of Cu nanoclusters in ZnO thin film caused ZnO grown on non-
epitaxial layers due to discontinuous layers formed by nanoclusters. Hence the stress state of ZnO film were changed and subsequently caused the relief of the stress and the decrease of the lattice constant $c$.

Figure 4.1 (a) XRD patterns of the Cu-embedded ZnO films with various Cu volume fraction.

(b) Change of d-spacing at c-axis of wurtzite ZnO with Cu nanocluster concentration.
Figure 4.2 (a) Plan view TEM image of Cu nanoclusters deposited on carbon grid with sputtering time 30s. Inset shows particle size distribution of corresponding nanoclusters. (b) HRTEM image shows lattice fringes of a Cu nanocluster which has facet in (111) plane. (c) HRTEM image of an agglomerated Cu$_2$O nanocluster in as-deposited Cu-embedded ZnO. Inset shows SADP of ZnO-Cu thin film.

The plan-view TEM image of Cu nanoclusters softly landed on carbon covered with Cu grid is showed in Figure 4.2 (a). The Cu nanoclusters were randomly distributed on the Cu grid surface with particle size ranging from 6 nm to 12 nm. It is interesting to note that some
nanoclusters were agglomerated with neighboring nanoclusters. Nanocluster has semicrystalline or amorphous nanostructure, hence a nanocluster might be crystalline but the assemblies of nanoclusters might not in this case as indicated in Fig. 4.2 (a)-(c)\textsuperscript{54}. The assemblies of nanoclusters just formed discontinuous and porous layers of films. High resolution TEM (HRTEM) image (Figure 4.1 (b)) revealed Cu nanoclusters were crystallized with hexagonal or icosahedra shape. When the Cu nanoclusters were embedded in ZnO films, it was found that the Cu nanoclusters existed in pure Cu and oxidized Cu form, i.e. Cu\textsubscript{2}O phase which were proved by the selected area diffraction and HRTEM as shown in Figure 4.2 (c). From the selected area diffraction pattern shown in inset Figure 4.2 (c), only ZnO phases, pure Cu and Cu\textsubscript{2}O were found on the Cu nanoclusters embedded-ZnO thin films.

UV-Vis absorption spectrum of pure ZnO thin film and Cu nanocluster-embedded ZnO is shown in Figure 4.3. As-grown ZnO had absorption edge at 370 nm and the corresponding band gap 3.35 eV determined from wavelength $\lambda_{1/2}$ based on E. A. Meulenkamp method\textsuperscript{94}. As the nanocluster volume fraction increases, the absorption edge showed a slight redshift. The band gap slightly reduced to 3.31 eV at 0.1 vol. % Cu and further reduced to minimum band gap 3.30 eV at 0.4 vol. % Cu. The band gap remained constant with further increase of the Cu content. The small changes in band gap with Cu nanocluster were consistent with the change of lattice constant with different Cu nanocluster volume fractions. Therefore the addition of Cu nanoclusters hardly modified optical properties of ZnO film. It has been reported that the relaxation of compressed lattice led to the formation of narrower band gap (redshift) due to decrease of repulsion between the oxygen 2p and the zinc 4s bands\textsuperscript{95}. This further confirmed that the decrease of lattice constant of ZnO thin films with the addition of Cu nanocluster was due to the release of the stress.

AGM measurement was carefully conducted on Cu-embedded ZnO thin film deposited on the glass substrate to investigate ferromagnetism of the Cu nanoclusters
embedded ZnO films. Field-dependent magnetization curves of ZnO film, Cu nanocluster assembled film and ZnO embedded with different contents of Cu nanoclusters are shown in Figure 4.4 (a). Both the magnetization curves of pure ZnO film and Cu nanocluster assembled film showed anhysteresis behavior. However, both films revealed a small magnetization. For pure ZnO film, its saturated magnetization is about 0.49 emu/cc. Since the ZnO film was deposited by RF sputtering without feeding oxygen at room temperature, some defects such as oxygen vacancies etc. were existed in films. These defects might be origin of the weak magnetization of ZnO film. A weak magnetization of about 0.5 emu/cc also observed in Cu nanoclusters assembled film. Since the Cu nanocluster assembled film was porous film, real magnetization should be larger than this value. The nanoclusters are very reactive due to large surface to volume ratio and the oxidation of Cu nanoclusters were observed. The uncompensation of surface spin Cu$^{2+}$ might be attributed to the weak

![Figure 4.3 UV-Vis absorbance spectra of pure ZnO and Cu-embedded ZnO films.](image-url)
magnetization of surface oxidized Cu nanocluster assembled film\textsuperscript{27}. Cu oxide nanoclusters assembled fabricated by feeding oxygen when nanoclusters were softly landed on the substrate showed increased magnetization as shown in Figure 4.4 (b). After the Cu nanoclusters were embedded in ZnO thin film, the total magnetization values were increased and small coercivities were observed in the hysteresis loops, which indicated these films were ferromagnetic at room temperature. The film with 0.4 vol. \% Cu showed maximum magnetization. With the increase of Cu nanoclusters content, the magnetization decreased toward that of Cu nanoclusters assembled films. These may be associated with the microstructure change of the films. With the increase of their volume fraction, the Cu nanoclusters become closer to each other and finally formed a continuous layer of Cu nanoclusters in the ZnO films. Based on the above results, it can be deduced that the room temperature ferromagnetism and increase of magnetization were not due to the intrinsic properties of ZnO film and Cu nanoclusters but may be originated from the reaction between Cu nanoclusters with ZnO matrix.

In order to clarify the effect of ZnO matrix, various volume fractions of Cu nanoclusters were embedded in SiO\textsubscript{2} matrix where the films fabrication procedure were same as that of Cu nanoclusters embedded ZnO films. The field dependent magnetization curves of Cu embedded SiO\textsubscript{2} and Cu-oxides-embedded SiO\textsubscript{2} films with various volume fractions are shown in Figure 4.4 (b). It was indeed observed that Cu oxidization can slightly increase the magnetization. However, all samples showed anhysteresis behavior. Therefore, the local environment of Cu nanoclusters played an important role in the room temperature ferromagnetism of Cu nanocluster embedded ZnO films. It was reported that the p-d hybridization effect between O 2p orbital in ZnO and Cu 3d orbital was possible mechanism for the induced ferromagnetism in the Cu-ZnO system due to their close energy level\textsuperscript{97-101}.  

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Figure 4.4 (a) The field dependent magnetization curve of pure ZnO, pure Cu nanoclusters assembled films and Cu-embedded ZnO films deposited at various Cu volume fractions. (b) The field dependent magnetization curve of pure Cu and pure Cu oxide nanoclusters assembled films and Cu and Cu oxide nanoclusters embedded SiO$_2$ films deposited at various Cu volume fractions.

In order to investigate the interaction between ZnO matrix-Cu nanoclusters the chemical state of the Cu in ZnO thin films was examined by XPS spectra. Cu 2p spectra of
0.4 vol. % Cu and 10 vol. % Cu in ZnO matrix are shown in Figure 4.5. In 0.4 vol. % Cu nanocluster embedded ZnO film, Cu 2p$_{3/2}$ peak was detected at 931.5 eV corresponding to existence of Cu$^{+102}$. After the volume fraction of Cu nanoclusters has been increased to 10 vol. %, the Cu 2p$_{3/2}$ peak shifted to higher oxidation state at 932.2 eV to become Cu$(1+x)^+$ where 0<$x$<1. The Zn 2p$_{3/2}$ peak in pure ZnO thin film is located at 1020.84 eV. Its binding energy decreased to 1020.6 eV after Cu were embedded in ZnO with volume fraction 0.4 vol. % and the binding energy remained at same position even though volume fraction increased to 10 vol.%. For O 1s peak, O 1s in as-grown ZnO had binding energy 529.7 eV and decreased to 529.5 eV after 0.4 vol. % Cu were embedded in ZnO. When the Cu nanoclusters content increased to 10 vol. %, O 1s peak was maintained at same position. Zn 2p, Cu 2p and O 1s XPS spectra suggest that there were charge transfers between Cu cluster and the neighboring atoms once Cu nanoclusters were embedded in ZnO. The interface effect was induced between the surface atoms of nanoclusters and the ZnO where the Cu cluster impurities energy levels were accommodated within ZnO surface bands$^{103}$.

The presence of defects in the samples can be detected in photoluminescence spectra of pure ZnO thin film and Cu-embedded ZnO films with nanocluster volume fraction 0.4 vol. %, 1 vol. % and 10 vol. %. As can be seen in Figure 4.6, as-grown ZnO thin film has UV emission centered at 390 nm which is attributed to near band-edge transition (recombination of free excitons through an exciton-exciton collision process)$^{104}$. The position of UV emission redshift to emissions centered around 406-414 nm as the Cu nanocluster concentration is increased, indicating narrowing of band gap of matrix ZnO which is matched with UV-Vis absorption results. The intensity of emission are strong and near to UV emission of pure ZnO film (390 nm), thus those emission peaks can be deduced as near-band-edge transitions. The FWHM (full-width at half-maximum) of UV emission peak increased with the increment of Cu nanocluster volume fraction. This is due to the decrease of crystallinity$^{105,106}$ with
increasing porous nanocluster content inside ZnO, as evidenced by XRD patterns shown in Figure 4.1. When the Cu was embedded in ZnO in very low concentration < 0.4 vol. % the valence state of Cu is between 0 and +1 and no green luminescence was detected at PL spectra. However, when 0.4 vol. % Cu volume fraction was achieved, Cu valence state becomes +1 and a weak green luminescence emission was detected at 588nm which is attributed to the presence of oxygen vacancies\textsuperscript{107}. Consequently, electron donated by Cu will compensate the defects such as oxygen vacancies whose presence was proved by photoluminescence spectra and the resulting compensated charged oxygen vacancies will be in a more ferromagnetic energetically favorable state. The roles of electrons, oxygen vacancies and Cu ions in enhancing the ferromagnetism of Cu-ZnO system can be explained by “indirect double-exchange” mechanism\textsuperscript{89}. 

Figure 4.5 (a) Cu 2p XPS spectra of Cu-embedded ZnO thin film with various nanocluster concentrations.
Figure 4.6 Room temperature PL spectra of pure ZnO thin film and Cu nanocluster embedded ZnO films.

4.4 Summary

In summary, Cu nanoclusters were softly landed and embedded in ZnO thin film by using nanocluster beam deposition and RF sputtering. Both XRD and UV-Vis absorption results suggest the addition of Cu nanoclusters will relax the stress pre-existed in ZnO. The secondary phases Cu$_2$O and CuO were detected by using HRTEM and SADP analysis. However, AGM measurement showed anhysteresis loops of pure Cu nanoclusters, Cu oxides nanoclusters and pure ZnO thin film, ruling out the possibility of intrinsic ferromagnetism. The as-grown Cu-embedded ZnO thin films can exhibit room temperature ferromagnetism due to the interface effect between nanoclusters and the matrix. The oxidation of Cu species and reduction of Zn and O species were detected in XPS spectra. These results suggest that nanocluster-matrix charge transfer and the existence of defects as indicated in PL spectra
could leads to possible interaction between defects and the Cu species and hence created favorable ferromagnetism environment for the Cu embedded ZnO films.
Chapter 5 Microstructural, magnetic and optical properties of ZnO:Cu nanocluster assembled films and ZnO:Cu-SiO$_2$ nanocomposite

5.1 ZnO:Cu Nanocluster Assembled Films

5.1.1 Introduction

Among the semiconductor matrices, ZnO is of particular interest because it holds the possibility of a DMSO with a Curie temperature above the room temperature$^{33}$. ZnO doped with various transition metals such as Mn, Co, Cr, Ni, V or Fe were reported to show ferromagnetism at room temperature$^{85,86}$. There still exists a debate on whether the magnetic behavior is an intrinsic property of thin film or due to the presence of nanoclusters of magnetic phase or both due to the difficulty of the microstructure characterization in large scale. In order to exclude the contribution of ferromagnetic nanoclusters, Cu doped ZnO thin films were investigated since neither metallic Cu nor Cu$_2$O or CuO in the bulk is ferromagnetic. Room temperature ferromagnetism of ZnO:Cu films deposited by pulsed laser deposition (PLD), filtered cathodic vacuum arc and magnetron sputtering were found$^{9,10,48,87}$. Nanocluster-beam deposition, as a promising technique, has been attracted to synthesize low dimensional materials, such as zero-dimensional nanoparticles (quantum dots) and cluster-assembled nanomaterials. Using this technique, the obtained materials could exhibit novel properties induced by the small particle size$^5$. In present work, Zn$_{0.94}$Cu$_{0.06}$O nanocluster assembled films were fabricated by nanocluster beam deposition technique. The magnetic and optical properties of the Zn$_{0.94}$Cu$_{0.06}$O nanocluster assembled films and the effects of the post-annealing were investigated.
5.1.2 Experimental details

\( \text{Zn}_{0.94}\text{Cu}_{0.06}\text{O} \) nanocluster assembled films were grown by nanoclusters beam deposition technique as described in our previous report. The \( \text{Zn}_{0.94}\text{Cu}_{0.06} \) nanoclusters were formed by sputtering the ZnCu alloy target in gas aggregation chamber and flew through to the deposition chamber where the oxygen gas was fed. The oxidized ZnCu nanoclusters were then deposited on the thermally grown \( \text{SiO}_2/\text{Si} \) substrate. The sputtering power was fixed at 100 W and the gas flows of argon and helium were fixed at 200 and 100 SCCM (standard cubic centimeters per minute) respectively. The samples were post-annealed in vacuum at the temperature from 400 \(^{0}\text{C}\) to 700 \(^{0}\text{C}\). The crystallographic structures, microstructures and the chemical state of ZnO and Cu nanoclusters were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM) (JEOL 2010) and X-ray photoelectron spectroscopy (XPS), respectively. Room temperature magnetic properties were examined by alternating gradient magnetometer (AGM). Optical properties were studied by photoluminescence (PL) spectroscopy Raman spectroscopy and ultraviolet-visible (UV-Vis) spectroscopy.

5.1.3 Results and discussions

Figure 5.1 shows the XRD \( \theta-2\theta \) scans of \( \text{Zn}_{0.94}\text{Cu}_{0.06}\text{O} \) nanoclusters assembled films with various annealing temperature. No diffraction peak can be observed for the as-deposited sample. This implied that the sample was amorphous or the grain size was too small. When the annealing temperatures were increased, the ZnO (100), ZnO (002) and ZnO (101) phases began to appear at 400 \(^{0}\text{C}\). No XRD peak related to Cu was detected due to low quantity of Cu in samples. The intensities of those three phases were gradually increased as the temperature was increased. This is the sign of the improvement of crystal quality of nanocluster assembled films under annealing treatment. In addition, full-width-at-half-maximum (FWHM) of the peaks decreased with the increment of annealing temperatures which implies the
enlargement of grain size of nanoclusters. Upon annealing at higher temperature, ZnO (002) peak position shifted to higher value and lattice constant, c was decreased due to temperature-induced stress relaxation and subsequently followed by the reduction of d-spacing of films.

Figure 5.1 XRD patterns of the as-deposited and vacuum-annealed $\text{Zn}_0.94\text{Cu}_{0.06}\text{O}$ nanoclusters assembled films.

The plan-view TEM image of as-deposited ZnCuO nanoclusters softly landed on carbon covered with Cu grid is showed in Figure 5.2 (a). The ZnCuO nanoclusters were deliberately deposited at sputtering time 30s for ease of TEM analysis. Actual nanoclusters were sputtered 6 minutes to achieve assembled film thickness around 500 nm. As can be seen in Figure 5.2 (a), those nanoclusters were randomly distributed on the Cu grid surface with average particle size 9 nm. Selected area diffraction in the inset of Figure 5.2(b) show existence of additional phase Cu$_2$O in the sample. Upon annealing at temperature 700°C, the nanoclusters grew bigger with average particle size 21 nm. It was found that the Cu nanoclusters existed in oxidized Cu form such as Cu$_2$O and CuO phases which were proved by the selected area diffraction and HRTEM as shown in Figure 5.2 (d). It seems that Cu$_2$O
Figure 5.2 TEM image of (a) as-deposited ZnO:Cu nanoclusters deposited on a Cu grid with sputtering time 30s. The inset shows the size distribution of the corresponding nanoclusters. (b) High resolution TEM image of the as-deposited ZnO:Cu nanoclusters with multi-domain structures. The inset of the electron diffraction pattern indicates wurtzite ZnO and copper oxides structures. (c) 500°C vacuum-annealed ZnO:Cu nanoclusters deposited on a Cu grid. The inset shows the size distribution of the corresponding nanoclusters. (d) Isolated 500°C vacuum-annealed ZnO:Cu nanoclusters with enlarged size. The inset of the electron diffraction pattern indicates wurtzite ZnO and copper oxides structures.
and ZnO phases co-existed within a nanocluster, thus it is proven that Cu went into the crystal structure of ZnO.

Field-dependent magnetization curves of ZnCuO films treated with different post-annealing temperatures are shown in Figure 5.3 (a). The as-deposited Zn$_{0.94}$Cu$_{0.06}$O nanoclusters assembled films showed small saturation magnetization around 1.22 emu/cc with small coercivity. After the films were annealed at higher temperatures, the total magnetization values were increased and small coercivities also observed in the hysteresis loops, which indicated these films were ferromagnetic at room temperature. The film treated with annealing temperature 700$^\circ$C showed maximum magnetization. The increment of $M_s$ value with increasing annealing temperatures may be associated with the existence of defects and change of Cu valence states in the films under different post-annealing temperatures, which will be explained in the XPS and Raman results.

In order to investigate the effect of magnetic anisotropy, the magnetic field was applied in the direction of perpendicular and parallel to the sample plane to investigate the preferred easy axis of assembled films. As can be seen in inset of Figure 5.3 (b), the measured saturation magnetization in direction of in-plane and out-of-plane showed gradual increase with the increasing annealing temperatures. Zn$_{0.94}$Cu$_{0.06}$O nanocluster assembled film was porous film and the real magnetization should be larger than this value. One can also observe that the in-plane magnetization values of sample annealed at various temperatures are larger than the out-of-plane magnetization values. For further confirmation of preferred easy axis of assembled film, hysteresis loops of in-plane magnetization and out-of-plane magnetization of 700$^\circ$C annealed sample was compared. The measured saturation magnetization in parallel direction is 1.88 emu/cm$^3$ while 0.88 emu/cm$^3$ was obtained in perpendicular direction. Due to the lower value of saturation field of parallel magnetization compared to perpendicular magnetization, the annealed film has preferred magnetization.
Figure 5.3 (a) Field dependent magnetic hysteresis loops of as-grown and annealed Zn$_{0.94}$Cu$_{0.06}$O nanocluster films for in-plane magnetization. (b) Comparison between out-of-plane and in-plane magnetization of 400°C annealed Zn$_{0.94}$Cu$_{0.06}$O nanocluster films. Inset shows comparison between out-of-plane and in-plane magnetization of Zn$_{0.94}$Cu$_{0.06}$O nanocluster films annealed at various temperature.
orientation in-plane direction. This phenomenon was found to be existed in all samples because there was certain degree of flattening possessed by nanoclusters upon landing on the substrate and subsequently increased the contribution of shape and surface anisotropy constants of nanoclusters in the direction perpendicular to the film.109

Typical XPS survey scan of as-deposited Zn_{0.94}Cu_{0.06}O nanocluster assembled films is shown in Figure 5.4. No trace of ferromagnetic contamination was detected within the sensitivity of XPS. Cu 2p peaks of as-deposited and annealed samples were examined and compared in the inset of Fig. 4. The dominant species of Cu in as-grown samples is Cu^+ where their peak is centered at 931.2 eV. This can be account for the formation Cu_2O as observed in the TEM micrograph. After the film was annealed at 700°C, the peak position of Cu 2p_{3/2} peaks shifted to slightly higher valence state at 932.2 eV and became mixed valence state between +1 and +2, Cu^{(1+x)} where 0<x<1. The coexistence of CuO and Cu_2O phases in the annealed films is expected as can be seen in high resolution TEM and selected area diffraction patterns in Figure 5.2 (d). The valence state between +1 and +2 is the favourable condition for the occurrence of room temperature ferromagnetism according the various ZnO-Cu systems’ simulation works.

In order to investigate possible contribution of defects on the ferromagnetism of films, Raman spectra of as-deposited and annealed nanocluster assembled films were examined. As can be seen in Figure 5.5, only one phonon mode was observed at 580 cm^{-1} for as-deposited sample which is assigned to A_1 (LO) and can be associated with presence of the defects such as oxygen vacancies or zinc interstitial.110 After post-deposition annealing from 400°C to 700°C was applied on the samples, the position of A_1 (LO) peak remained at same position 580 cm^{-1} but the intensity of peak was increased, indicating the increment of concentration of oxygen vacancies. The increase of M_s value at higher annealing temperature might be related to the increase of oxygen vacancies concentration, whose formation energy favored the
Figure 5.4 XPS spectrum of as-deposited Zn$_{0.94}$Cu$_{0.06}$O nanoclusters assembled films. Inset shows the Cu 2p$_{3/2}$ XPS spectra of as-deposited and 400°C vacuum-annealed ZnO:Cu nanoclusters assembled films.

The condition of vacuum annealing\textsuperscript{111}. The vacuum annealing tends to create oxygen vacancies within the samples as the intensity of A$_1$ (LO) mode become higher at high temperature due to the increase numbers of diffused oxygen atoms from interior part of films to the surface. The magnetism results matched the Raman results which proved the relationship between oxygen vacancies and the ferromagnetism of the films. Due to highly insulating nature of nanocluster assembled films, the carrier mediated ferromagnetism is not suitable for explanation of origin of ferromagnetism. From the XPS patterns and Raman spectra results, we know that at elevated temperatures, the concentration of defects was increased and the chemical state of Cu became mixed valence state between +1 and +2. These conditions fulfilled the requirements of favorable ferromagnetism environment in which oxygen vacancies were located throughout the lattice at arbitrary distances with respect to Cu sites and thus the ferromagnetic interactions can be mediated by shallow donor electrons and the
empty transition metal 3d states at Fermi level, as described by indirect double exchange mechanism\textsuperscript{89}. 

The absorption spectra of as-deposited and post-annealed Zn\textsubscript{0.94}Cu\textsubscript{0.06}O nanocluster assembled films are shown in Figure 5.6. All samples have similar spectra with shoulders located in UV range, which is attributed to the transitions from optical to exciton state. The wavelength $\lambda_{1/2}$ at which the absorption is 50\% of shoulder was used to evaluate their band-gap energy\textsuperscript{94}. As-deposited sample has band gap 3.54 eV which is bigger than typical bulk ZnO band gap 3.37 eV. The blue-shifted band gap is anticipated for nanoclusters since their size is small and the quantum size confinement effect is valid within the samples. When the annealing temperature was increased from room temperature to 700\textdegree C, the slopes of shoulders became steeper and the band gap increased towards the value of bulk ZnO band gap. The red-shift of band gap from 3.54 eV (350 nm) to 3.30 eV (376 nm) implies the enlargement of grain size in the samples with the increasing annealing temperatures which were proved by the narrowing FWHM of XRD peaks at higher annealing temperatures.
5.1.4 Summary

In summary, Zn$_{0.94}$Cu$_{0.06}$O nanoclusters assembled films were fabricated in porous film form by using nanocluster beam deposition. XRD patterns show the existence of ZnO phases (100), (002) and (101) at elevated temperatures due to improved crystal quality of the films. All secondary phases were detected by TEM are non-ferromagnetic. Vacuum annealing up to 700°C leads to increase of $M_s$ value from 1.22 emu/cm$^3$ to 1.88 emu/cm$^3$. Raman results suggest oxygen vacancies concentration was increased with increasing annealing temperatures. XPS spectra reveals the Cu oxidation changed from +1 to mixed valence state +1 and +2. These results indicate vacuum annealing can create favourable ferromagnetism environment for indirect double exchange and subsequently leads to the increase of magnetization value. The optical properties of films were altered by annealing in which the absorption edge of UV-Vis absorption was red-shifted due to the quantum size confinement effect.
5.2 ZnO:Cu-SiO₂ Nanocomposite

5.2.1 Introduction

DMSO materials can be fabricated in the form of nanocomposite films which were comprised of metal or alloy nanoclusters embedded in insulating matrices such as glasses, ceramics or polymers have attracted numerous interests due to their unique magnetic, optical and electrical properties. The properties of nanoclusters embedded in insulating or conducting, magnetic or non-magnetic matrices are more technologically important than those of nanocluster assembled films for various novel functional applications in magnetic, optics and electronics. Most nanocomposites were prepared by wet chemical route or by physical vapor deposition (PVD) and subjected to thermal annealing to form nanoclusters in the matrices. Recently, the sputtering gas aggregation technique combined with radio frequency (RF) sputtering were utilized to prepare nanocluster-assembled nanocomposites which consisted of controllable ferromagnetic cluster size and shape in the non-magnetic host matrices such as Fe-embedded Ag, CoPt-embedded Ag, FePt-embedded C, FePt-embedded B₂O₃ and FePt-embedded Ag. However, not much works focused on the magnetic and optical properties of non-magnetic nanoclusters embedded in a matrix which is non-magnetic and insulating. Cu nanoclusters-embedded SiO₂ or Cu nanocluster-embedded ZnO is an intriguing nanocomposite system which possess interesting magnetic and optical properties such as ferromagnetism, photoluminescence and surface plasmon resonance (SPR). It would be interesting to investigate the magnetic and optical properties of the nanocomposites due to their interactions between nanoclusters and matrix and unique surface properties.
5.2.2 Experimental details

In the present work, ZnO:Cu nanoclusters were embedded in SiO$_2$ nanocomposite films by using nanocluster beam deposition combined with RF sputtering. The fabricated multilayers were consisted of SiO$_2$(5nm)-[ZnO:Cu nanoclusters(t nm)- SiO$_2$(5nm)]$_{5}$times where t is the average thickness of ZnO:Cu nanoclusters. ZnO:Cu nanoclusters and SiO$_2$ were deposited alternatively by nanocluster beam deposition and RF sputtering respectively on the thermally grown SiO$_2$/Si substrates. The volume fraction of ZnO:Cu nanoclusters was adjusted by varying the thickness of ZnO:Cu and t varied from 1-35 nm. The corresponding volume fraction of ZnO:Cu in the films is ranged from 20%-85%. ZnO:Cu nanoclusters were deposited at sputtering power 100W while the gas flow of argon and helium were maintained at 200 and 100 s.c.c.m. respectively. The nanocomposites were fabricated and The crystal structures, morphology of nanocluster surfaces and the chemical state of ZnO and Cu nanoclusters were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM) (JEOL 2010), and X-ray photoelectron spectroscopy (XPS) respectively. Room temperature magnetic properties were examined by alternating gradient magnetometer (AGM). Optical properties were studied by using He-Cd laser (325 nm) for photoluminescence (PL) measurement, Raman spectroscopy, and UV-Vis spectroscopy.

5.2.3 Results and discussions

Field dependent magnetization curve of ZnO:Cu-SiO$_2$ nanocomposites with varying ZnO:Cu volume fractions were shown in Figure 5.7 (a). All M-H curves show ferromagnetic hysteresis loop with small coercivities. With the increase of content of ZnO nanocluster internally doped with Cu, the saturation magnetization of nanocomposite was increased until the maximum value was achieved at 6.98 emu/cc for 50 vol% ZnO:Cu in SiO$_2$ (sample ZCS3). Further increase of volume fraction of ZnO:Cu nanoclusters will reduced
magnetization value. This magnetism trend can be associated with the microstructure change of the films. The increase of their volume fraction will caused the Cu nanoclusters become closer to each other and finally formed a continuous layer of Cu nanoclusters in the ZnO films. The nanoclusters were no longer isolated in the SiO$_2$ matrix and they were allowed for further agglomeration upon deposition on the substrate. In order to observe change of magnetization value under the influence of temperature, another set of samples were subjected to the vacuum annealing treatment at various temperatures as shown in Figure 5.7 (b). All annealed samples show higher magnetization value compared to as-deposited nanocomposites. The increment is due to the magnetism contribution of oxygen vacancies which were created during vacuum annealing$^{122,123}$. In vacuum state, higher annealing temperature provides more thermal energy for oxygen atoms to migrate from inner part of film to the surface. The interaction between oxygen vacancies and the Cu atoms will create favorable condition for the occurrence of ferromagnetism. The magnetization value increases with the annealing temperature until it achieved highest $M_s$ value 8.68 emu/cm$^3$ at temperature 600$^0$ C. The saturation magnetization values of ZnO:Cu-SiO$_2$ nanocomposite films is higher as compared to Cu-embedded ZnO films because SiO$_2$ effectively isolate and prevent further agglomeration of ZnO:Cu nanoclusters in the film. This condition helps to decrease too much overlapping between O 2s and Cu 2p bands and thus increases their exchange coupling.

No phase was detected by XRD analysis for both as-deposited and annealed samples due to the amorphous nature of nanoclusters or their crystallite size is too small leading to the lack of scattering domain in the samples. When the ZnO:Cu nanoclusters were deposited inside the SiO$_2$ matrix, the nanoclusters were isolated and prevented from agglomeration or coalescence. At high annealing temperature, SiO$_2$ matrix will also act as diffusion barrier for the mass transport of nanoclusters. However, the retardation of nanocluster growth can be
Figure 5.7 (a) Field dependent magnetization curve of ZnO:Cu-SiO$_2$ nanocomposite with different volume fraction of ZnO:Cu nanoclusters. (b) Field dependent magnetization curve of ZnO:Cu-SiO$_2$ nanocomposite which were annealed at different temperatures.
Figure 5.8 (a) TEM image of as-deposited ZnO:Cu nanoclusters deposited in SiO$_2$ matrix with sputtering time 30s. The inset shows the size distribution of the corresponding nanoclusters. (b) High resolution TEM image of the 600°C post-annealed ZnO:Cu nanoclusters. The inset of the electron diffraction pattern indicates wurtzite ZnO and copper oxides structures.
evidenced by TEM micrograph in Figure 5.8(a). The average size of ZnO:Cu nanoclusters embedded in annealed nanocomposite is 11.48 nm and is slightly bigger than as-deposited ZnO:Cu nanoclusters in nanocomposite which have size 10.6 nm. On the other hand for ZnO:Cu nanoclusters without matrix, the same annealing treatment will yield bigger-sized nanoclusters as compared their as-deposited nanoclusters, as reported in our previous work. The improvement of the crystal quality of nanocomposites by vacuum annealing can be proved by the change of broad halo rings to narrower halo rings in selected area diffraction pattern of as-deposited and annealed samples, as shown in inset of Figure 5.8(a) and 8(b). In an as-deposited ZnO:Cu nanocluster, some Cu atoms will occupied Zn cation lattices since the nanoclusters were produced from the alloy binary Zn\(_{0.94}\)Cu\(_{0.06}\) cluster source. As can be seen in Fig. 2(b), after vacuum annealing treatment, the Zn and Cu atoms start to diffuse out from their ideal lattice sites and the possibilities of diffuse Cu atoms being trapped by various sorts of defects also increased. Hence there is possibility that formation of pure Cu element nanoclusters is allowed in high temperature-annealed samples, as reported in the U. Wahl et. al. work\(^{124}\). None of the secondary phases will contribute to the induced ferromagnetism in the film.

Chemical state of Cu and Si were examined in XPS spectra as shown in Figure 5.9 (a) and (b). The formation of pure copper metal in the as-deposited nanocomposite can be observed in Fig. 3(a) where the Cu 2p\(_{3/2}\) peaks was centered at 932.5 eV\(^2\). Another small satellite peak was found at higher binding energy side 935.05 eV and it can be related to the presence of Cu\(^{2+}\) ions in the sample. The XPS results match the observations found in TEM micrograph where the divalent copper and pure copper metal was found co-existed in the as-deposited samples. After post-annealed at 600° C, the oxidized copper phases (CuO) were reduced to lower oxidation state and formed the pure copper clusters when the thermal energy was high enough to enable thermal reduction process. Consequently, the amount of pure Cu
Figure 5.9 The Cu 2p₃/₂ XPS spectra of (a) as-deposited ZnO:Cu-SiO₂ nanocomposite and (b) 600°C post-annealed ZnO:Cu-SiO₂ nanocomposite. The Si 2p₃/₂ XPS spectra of (c) as-deposited ZnO:Cu-SiO₂ nanocomposite and (d) 600°C post-annealed ZnO:Cu-SiO₂ nanocomposite.

metal nanoclusters in the annealed nanocomposite was increased. Similar thermal reduction process was also reported in S. Y. Lee et. al. works for reduction of the bulk copper oxide
thin film to pure Cu metal thin film by using vacuum annealing process. As can be seen in Fig. 3(c), the Si 2p\textsubscript{3/2} peaks centered at 102.48 eV is attributed to the presence of oxidized Si\textsuperscript{3+} ions\textsuperscript{126} in the samples and responsible for the formation of zinc silicate (ZnSiO\textsubscript{3}). The formation of insulating ilmenite ZnSiO\textsubscript{3} is the product of interaction between Zn and SiO\textsubscript{2} at the interface of Zn-SiO\textsubscript{2} nanocomposite. Annealing at 600\textdegree C caused Si 2p\textsubscript{3/2} peaks of nanocomposite shifted to 102.93 eV which can be assigned to the existence of Si\textsuperscript{4+}. This Si in +4 valence state was responsible for the formation of SiO\textsubscript{2} or Zn\textsubscript{2}SiO\textsubscript{4} in the samples.

Figure 5.10 (a) and (b) show the UV-vis absorption spectra of as-deposited and annealed ZnO:Cu-SiO\textsubscript{2} nanocomposite. Band gap of the nanocomposite were measured from the corresponding \(\lambda_{1/2}\) by using Meulenkamp’s method\textsuperscript{94}. However, the estimated band-gap energy seems to be much bigger than that of ZnO:Cu nanocluster assembled films as reported in previous paper. The absorption edge of nanocomposites clearly blue-shifted with respect to their bulk counterpart because of the quantum confinement effect obtained for the samples with effective embedment of nanoclusters in the matrix\textsuperscript{127,128}. When the volume fraction of ZnO:Cu nanoclusters in SiO\textsubscript{2} matrix was increased, the absorption edge tends to red-shifted, as shown in Figure 5.10 (a). The estimated band gap decreased from 4.23 eV to 3.4 eV, towards the band gap value of ZnO:Cu nanocluster assembled film. The reduction of band gap may be due to the crystal lattice distortion caused by the altered optical properties of nanocomposites which strongly depend on their microstructures or the enhanced carrier-carrier interactions induced by the increased carrier concentration in conduction and valence bands \textsuperscript{129-131}. In Figure 5.10 (b) it is interesting to observe the appearance of optical absorption peaks due to the weak surface plasmon resonance (SPR) of Cu particles in UV-Vis absorption spectra of as-deposited and annealed ZnO:Cu-SiO\textsubscript{2} samples. The most prominent SPR effect is observable at 600\textdegree C annealed sample, indicating the formation of pure Cu nanoclusters in the sample. This result can be proved by the existence of pure copper phase.
found in selected area diffraction patterns of 600°C annealed ZnO:Cu-SiO2 nanocomposite. Before vacuum annealing provides sufficient diffusion energy to Cu atoms, the SPR effect is very weak and not observable in the spectra due to low quantity of pure Cu particles in the nanocomposite. However after annealing temperature was achieved at 600°C, Cu atoms started to diffuse from substituted ideal Zn site and formed Cu nanoclusters. The increased interactions between Cu nanoclusters and the SiO2 matrix lead to the observation of SPR phenomenon in the visible light wavelength around 589 nm. Similar SPR effect was observed by C. C. Zhao and R. Kibar and co-workers in the wavelength range of 550-600 nm for the Cu-SiO2 nanocomposites. According to Mie scattering theory, the dipolar oscillations of the free electrons in the conduction band that occupy energy states near Fermi level are involved in the plasmon band of metal particles.

In order to examine the presence of defects in the samples PL analysis was carried out as shown in Figure 5.11 (a) and (b). The low temperature PL analysis reveals UV luminescence peaks at 366 nm, 376 nm and 380 nm in both as-deposited and post-annealed samples. PL peaks at 366 nm, 376 nm and 380 nm can be attributed to the existence of FX(\(n=1\)), ground-state free excitation transition, two electron satellite (TES) transition and the first longitudinal optical (LO) phonons of neutral-donor-bound exciton (D\(^0\)X-1LO) emission. Another common feature in which both samples have was presence of mobile intrinsic defects such as interstitial zinc in violet wavelength 413 nm. In green luminescence region, PL peaks at 515 nm and 489 nm were detected in as-deposited and annealed samples respectively which are related to the existence of singly ionized oxygen vacancies or other point defects and the recombination of the electrons in single occupied oxygen vacancy with the photoexcited holes in the valence band. On the other hand, room temperature PL analysis shows that both as-deposited and annealed samples have UV emission peak at 376 nm and green luminescence peak at 413 nm which can be attributed to
Figure 5.10 (a) UV-Vis spectra of ZnO:Cu-SiO$_2$ nanocomposite with different volume fraction of ZnO:Cu nanoclusters. (b) UV-Vis spectra of ZnO:Cu-SiO$_2$ nanocomposite which were annealed at different annealing temperatures.

the first longitudinal optical phonons of the FX (FX-1LO$^{138}$) and the mobile intrinsic defects such as interstitial zinc. Comparison of low temperature PL spectra of as-deposited and
annealed samples, both as-deposited and annealed samples have UV peaks intensity higher than green luminescence peak intensity. On the other hand, examination at room temperature indicates that the ratio of green luminescence peak intensity to UV region peak intensity is higher in the annealed samples as compared to the as-deposited sample; therefore the defect level of 600°C post-annealed nanocomposite at room temperature is higher than other samples. The PL results match the magnetism results in which increased amount of defects enhance the magnetization value of the sample.

![Figure 5.11 Comparison of low temperature and room temperature PL spectra of as-deposited and 600°C post-annealed ZnO:Cu 50%-SiO₂ nanocomposite.](image)

5.2.4 Summary

In conclusion, ZnO:Cu-SiO₂ nanocomposite were produced by nanocluster beam deposition combined with RF sputtering. Existence of non-ferromagnetic secondary phases such as ZnSiO₃, Cu₂O, CuO and pure Cu are detected by HRTEM and XPS analysis. The
most prominent surface phonon resonance feature was found in 600°C annealed sample due
to outdiffusion of Cu atoms from nanocomposite to form pure Cu nanocluster. PL analysis
suggests the maximum room temperature Ms obtained in 600°C annealed nanocomposite was
caused by the existence of larger defects concentration in the samples. For annealed samples,
enhanced ferromagnetism is mediated by oxygen vacancies as described by bound magnetic
polarons model.
Chapter 6 Microstructural, Magnetic and Optical Properties of ZnO:Mn Nanocluster Assembled Films and ZnO:Mn-SiO$_2$ Nanocomposite

6.1 ZnO:Mn Nanocluster Assembled Films

6.1.1 Introduction

Among various II-VI DMS materials, Mn-doped ZnO material is an intriguing diluted magnetic semiconductors system so far due to the skepticism whether antiferromagnetic nature of Mn can induce ferromagnetism in ZnO system. Diverse experimental results seem to be contrary to each other and can’t clarify the above question. For instance, Mn-doped ZnO was reported to posses spin-glass behavior$^{139}$, paramagnetism$^{140}$, antiferromagnetism$^{141}$, low temperature ferromagnetism$^{12}$ and room temperature ferromagnetism$^{142}$ or even not posses any ferromagnetism at all$^{143}$. From the origin of ferromagnetism point of view, different mechanisms also have been suggested as the possible source for the enhancement of ferromagnetism in the system. Sharma et. al. suggested carrier-mediated ferromagnetism in their works$^{29}$ while Kundaliya et. al. proposed oxygen vacancies as origin of ferromagnetism in the film$^{53}$. Besides, the combination of bound magnetic polarons (BMP) model and indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) also used to explain ferromagnetism in samples with different conductivities$^{144}$. Furthermore, double exchange mechanism between Mn$^{3+}$ and Mn$^{4+}$ also was reported as possible driving force for the induced ferromagnetism$^{11}$. Magnetic properties of the fabricated samples are very sensitive to the growth conditions and the post-annealing treatment. The growth conditions of DMSO will be n-type or p-type depend on whether fabricated samples were fabricated in O-rich or O-poor environment. The
samples grown in O-poor condition will have a majority donor defects such as oxygen vacancies and zinc interstitial while samples grown in O-rich condition have acceptor defects such as zinc vacancies\(^{145,146}\). The type of dominant carriers existed in the samples will determine whether ferromagnetism can be mediated by electron or hole. The structure of nanocluster assembled films is totally different from typical thin film. The structural, magnetic and optical properties of the nanoclusters are very sensitive to nanocluster size (number atoms in a unit of nanocluster), shape, symmetry and surface of nanoclusters.

### 6.1.2 Experimental details

Since the sputtering alloy target ZnMn (Zn 94 at%, Mn 6 at%) was used as nanocluster source, the atomic percentage of Mn in fabricated nanocluster assembled films was fixed at 6 at%. The sputtering power of DC magnetron of nanocluster target was fixed at 100W. Ar and He carrier gasses were tuned at 200 sccm and 100 sccm respectively while oxygen gas was continuously fed to the films at 10 sccm. ZnMn binary nanoclusters were swept from the nanocluster source chamber to main deposition chamber where they were constantly oxidized by the oxygen gas. The magnetic properties of nanocluster films was measured by alternating gradient field magnetometer (AGM) while optical properties were probed by using photoluminescence fluorescence spectrometer, micro-Raman and UV-Vis NIR spectroscopy. XRD and TEM were also used for investigation of structural properties of nanoclusters.

### 6.1.3 Results and discussions

In order to investigate whether ferromagnetism can be observed in as-deposited and annealed nanocluster assembled films, their magnetic properties were carefully measured by
AGM in applied magnetic field up to 5000 Oe in the direction parallel to the surface of samples. Field-dependent magnetization curve of as-deposited and annealed Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films is shown in Figure 6.1(a). The magnetization value of Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films was increased with increasing annealing temperatures until highest M$_s$ value was achieved at 700°C for 7.91 emu/cc or 0.07 $\mu_B$/Mn. However, this value is lower than 0.16 $\mu_B$/Mn achieved by Mn-doped ZnO bulk and thin film as reported by P. Sharma and coworkers$^{29}$ and the value is also much smaller than $\sim$5 $\mu_B$/Mn for a free Mn$^{2+}$ ion with S= 5/2 and g =2. These magnetism results suggest possible existence of antiferromagnetism in all samples and subsequently caused partial reduction of net magnetic moment. In order to investigate magnetic anisotropy of 700°C annealed Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films, the comparison between in-plane and out-of-plane field-dependent magnetization have been made in Figure 6.1 (b). Obviously, in-plane magnetization is an easy axis for the films due to small contribution from magnetocrystalline term and significant contribution from shape anisotropy which were caused by certain degree of ‘ flattening’ of the nanoclusters upon landing on the substrate$^{108}$.

Figure 6.2 shows XRD pattern of as-deposited and annealed Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films. For as-deposited sample, no phase was detected due to random orientation of nanoclusters in the assembled films upon soft-landing on the substrate during deposition process. Upon thermal annealing, ZnO-related phases were detected in the films which were comprised of ZnO (100), ZnO (002) and ZnO (101). No Mn-related phase was detected due to low quantity of Mn in films. The value of full width at half maximum (FWHM) were reduced with the annealing temperature, indicating the enlargement of grain size at higher temperatures. The position of ZnO (002) peak slightly shifted to higher value at higher temperature, indicating the reduction of d-spacing caused by the stress relaxation Zn$_{0.94}$Mn$_{0.06}$O nanoclusters$^{92,93}$.  

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Figure 6.1 Field dependent magnetization curve of as-deposited and annealed Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films. (b) Comparison between out-of-plane and in-plane magnetization of 700°C annealed Zn$_{0.94}$Mn$_{0.06}$O nanocluster films.
As can be seen in Figure 6.3 (a) and 3 (b) the phases existed in the films were Mn$_2$O$_3$, ZnO, ZnMn$_2$O$_4$ and Mn$_3$O$_4$. MnO$_2$ is an antiferromagnetic material with low temperature $T_c$ = 17 K$^{147}$ or 84K$^{148}$ while ZnMn$_2$O$_4$ is an antiferromagnetic phase with $T_N$=42 K$^{149}$. Mn$_2$O$_3$ is an antiferromagnetic phase with $T_N$ = 80-100K$^{150}$. Mn atoms from ZnMn binary nanoclusters formed Mn-oxides and ZnMn$_2$O$_4$ spinel after oxidization was occurred in the deposition chamber. After the samples were annealed at 700°C, the enlarged nanoclusters were found to have size around 30-60 nm. From HRTEM and SADP (selected area diffraction pattern) shown in Fig. 3 (c) and 3 (d), the secondary phases existed in the annealed samples are Mn$_3$O$_4$, ZnMn$_2$O$_3$ and MnO. ZnMn$_2$O$_3$ is a spin-glass phase which has freezing temperature around 15K$^{151}$ while Mn$_3$O$_4$ is a ferromagnetic phase with $T_c$ = 42K which will not contribute to room temperature ferromagnetism. MnO is an antiferromagnetic phase with $T_N$ = 122K$^{148}$. Therefore room temperature observed FM cannot be due to any one of them. The
coexistence of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ in the nanoclusters increase the possibility of involvement of double exchange mechanism in the ferromagnetism of samples.\textsuperscript{152} However, since $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ coexisted in both as-deposited and annealed samples, the significant difference of
magnetization value between 700°C annealed sample and the other samples should not be contributed by the double exchange interactions of bivalent Mn ions. The results imply that origin of ferromagnetism is not solely come from Mn\(^{3+}\) and Mn\(^{4+}\) double exchange interactions which is contrary to the result of other researchers who supporting double exchange interactions in Mn-doped ZnO as the main origin of ferromagnetism\(^{11,153,154}\).

The chemical state of Mn in Zn\(_{0.94}\)Mn\(_{0.06}\)O nanocluster assembled films can be probed by using XPS analysis. As can be seen in Figure 6.4 (a), Mn 2p\(_{3/2}\) peak can be deconvoluted into two components at 640.5 eV and 642.5 eV. The lower binding energy side can be attributed to the presence of Mn\(^{2+}\) in the samples while the higher binding energy side can be attributed to the presence of Mn\(^{3+}\). After the films were annealed at 700°C, the Mn 2p\(_{3/2}\) peak can be deconvoluted into three components which are located at 640.1 eV, 642.7 eV and 644.1 eV, as shown in Figure 6.4 (b). Those three components can be attributed to the valence state +2, +3 and +4 of Mn respectively from lower to higher binding energy components. This results proved the co-exist of bivalent Mn in both as-deposited and annealed samples.

From Figure 6.5 we know that A\(_1\) (LO) phonon mode was detected at 579 cm\(^{-1}\) in the as-deposited sample and this phonon mode remained at same position when the thermal annealing was applied on the samples. It can be associated with presence of the defects such as oxygen vacancies or zinc interstitial\(^{110}\). Based on the first principle calculations, oxygen vacancies can alter the band structure of a host oxide and subsequently caused shifting of Fermi level of 3d transition metal, making spin polarization become more favorable for the occurrence of ferromagnetism\(^{155}\). As the temperature was increased, the intensity of A\(_1\) (LO) peak was gradually increased and the concentration of oxygen vacancies in the samples was increased. The increment of oxygen vacancies in the annealed samples was matched with the magnetization trend of Zn\(_{0.94}\)Mn\(_{0.06}\)O nanocluster assembled films at elevated vacuum.
annealing treatment. Raman results suggest that the presence of defects seem to play an important role in influencing the magnetic behavior of the samples.

Optical properties of Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films were examined by UV-Vis spectra as shown in Figure 6.6. The absorption edge of as-deposited film was located at 338 nm which is corresponding to band-gap 3.67 eV. The band gap of nanocluster films is bigger than pure ZnO thin film due to the quantum confinement effect in the nano-sized particles. As the annealing temperature was increased, the absorption edge of the films red-shifted to 370 nm at 700$^0$C and band gap shrunk to 3.35 eV. The band gap shrinkage at elevated temperatures can be explained by the temperature-induced band gap shrinkage which is applicable for nanoclusters obeying quantum confinement effect$^{156}$. It is interesting to note that the slope of absorption edge become steeper as the annealing
Figure 6.5: Raman spectra of as-deposited and annealed Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films.

Figure 6.6: UV-Vis absorption spectra of as-deposited and annealed Zn$_{0.94}$Mn$_{0.06}$O nanocluster assembled films.
temperature was increased. In the interface of nanoclusters-nanoclusters and nanoclusters-matrix the formation of defect states will alter the electronic structure of films. Contrary to the Cu doped-ZnO system, Mn atoms in the ZnO lattice environment will have the tendency to form clustering around oxygen atoms which caused the system to have inclination towards the nature of intrinsic antiferromagnetism\(^97\). The hybridization between O 2p orbital from ZnO and Mn 3d orbital will produce magnetic moment lower than free Mn atom. This result indicates the atomic moment of Mn itself is stronger than the magnetic moment induced by the hybridization between O 2p orbital and Mn 3d orbital\(^157\). Measurement of conductivity of the films by Hall effect measurement system suggests the samples were highly insulating in nature due to their high resistivity \(> 10^6 \, \Omega\text{cm}\). This electrical behavior rules out the charge carrier mediated ferromagnetism based on the Ruderman-Kittel-Kasuya-Yoshida (RKKY) mechanism or Zener-based models.

### 6.1.4 Summary

In conclusion, \(\text{Zn}_{0.94}\text{Mn}_{0.06}\text{O}\) nanocluster-assembled films were fabricated by nanocluster-beam deposition. XRD analysis indicates improvement of crystallinity of films and stress relaxation upon vacuum annealing. The secondary phases were detected in both as-deposited and annealed samples in the form of \(\text{Mn}^{3+}\) and \(\text{Mn}^{4+}\). The double exchange mechanism enhanced the RT ferromagnetism of all samples. However, the significant contributor to the magnetic moment of annealed samples is oxygen vacancies which can be proved by the increase of \(A_1(\text{LO})\) phonon mode in Raman spectra with increasing thermal annealing temperatures. UV-Vis absorption edge showed red-shift as the annealing temperature was increased, implying the occurrence of temperature-induced band gap shrinkage in the samples.
6.2 ZnO:Mn-SiO₂ Nanocomposite

6.2.1 Introduction

Embedment of transition metal nanoclusters in insulating dielectric matrix is another choice for fabrication of DMSO due to the intriguing magnetic and optical properties of nanocomposites which can be applied in sensors¹⁵⁸, microelectronics components¹⁵⁹, catalysis¹⁶⁰, and ceramic products¹⁶¹. Many researchers used various techniques such as impregnation, molecular capping, target-attached RF co-sputtering, and sol-gel to disperse ZnO nanoparticles in the insulating matrix such as silicon dioxide or polymeric matrix. Nano-sized ZnO can exhibit interesting magnetic and optical properties which are different from bulk ZnO due to their high surface-to-volume ratio and reactive interaction with surrounding materials in the host matrix. On the other hand, SiO₂ serve as perfect matrix prevent the interactions among nanocluster, thus providing ideal condition to examine the intrinsic magnetic properties of nanoclusters. Recently, there were many reports showed either paramagnetism¹⁶² or ferromagnetism²⁹ or non-ferromagnetism¹⁴³ characteristics in the Zn₁₋ₓMnₓO materials. Since those films were grown by different deposition techniques the experimental results tends to vary and even contradictory to each others. Thus the reported origin of the ferromagnetism still remains disputable. Insufficient microstructural studies can cause discrepant results, therefore a variety of characterizations of these complex materials must be conducted to find reliable origin of ferromagnetism. In addition to the interesting magnetic properties, SiO₂ embedded with transition metal nanoclusters also have unique optical properties. Most of ZnO:Mn-SiO₂ nanocomposite were synthesized by wet chemical route and the resultants have strong PL bands in visible wavelength range and surface plasmon resonance in UV wavelength range¹⁶³,¹⁶⁴. Through the control of nanocluster size, wavelength of the fundamental transitions can be easily manipulated for optical purposes,
especially optoelectronic and photonic devices$^{165}$ due to their large third-order optical susceptibility. To our knowledge, not much report done on the detailed investigation of the microstructural, magnetic and optical properties of Mn-doped ZnO nanoclusters embedded in SiO$_2$ matrix as well as the correlation between those properties.

### 6.2.2 Experimental details

In this experiment, ZnO:Mn-SiO$_2$ nanocomposites were prepared by using nanocluster beam deposition combined with RF (radio frequency) sputtering. Binary alloy target $\text{Zn}_{0.94}\text{Mn}_{0.06}$ has been used as nanocluster source and oxide target SiO$_2$ served as matrix to the nanoclusters. The fabricated multilayers were consisted of SiO$_2$(5nm)-[ZnO:Mn nanoclusters(t nm)- SiO$_2$(5nm)]$_5$ times where t is the average thickness of ZnO:Mn nanoclusters. ZnO:Mn nanoclusters and SiO$_2$ were deposited alternatively by nanocluster beam deposition and RF sputtering respectively on the thermally grown SiO$_2$/Si substrates. The volume fraction of ZnO:Cu nanoclusters was adjusted by varying the thickness of ZnO:Cu and t varied from 1-35 nm. The corresponding volume fraction of ZnO:Cu in the films is ranged from 4%-50%. Notice that the volume fraction was calculated based on the deposition rate of nanocluster assembly film. Since the nanocluster assembly films were very porous the actual volume fraction should be less than those stated in the present work. Another set of samples with 4 vol. % ZnO:Mn were selected to underwent vacuum annealing from 400 $^\circ$C to 700 $^\circ$C for the investigation of thermal annealing effect on the magnetic and optical properties of the nanocomposites. In this experiment, ZnO:Mn nanoclusters were deposited at sputtering power 100W while the gas flow of argon and helium were maintained at 200 and 100 s.c.c.m. respectively. The crystal structures, morphology of cluster surfaces and the chemical state of ZnO:Mn-SiO$_2$ nanoclusters were studied by using X-ray diffraction (XRD), transmission electron microscopy (TEM) (JEOL 2010), atomic force microscopy (AFM) and X-ray
6.2.3 Results and discussions

Figure 6.7 (a) shows field-dependent magnetization curve of ZnO:Mn-SiO$_2$ nanocomposite with various ZnO:Mn nanocluster concentration from 4 vol. % to 50 vol. %. The nanocomposites were cut into 3 x 3 mm samples and measured carefully by using AGM. The saturation magnetization value of 4 vol. % ZnO:Mn-SiO$_2$ was dropped from 4.99 emu/cc to 0.75 emu/cc when the volume concentration of ZnO:Mn was increased to 50 vol. %. At low cluster concentration Mn atoms in each nanocluster were far from each other and no interaction among nanocluster was occurred. When the cluster concentration was increased, the $M_s$ value tends to decrease. This is because when the nanoclusters were agglomerated and contacted each other, the distance between Mn atoms will be decreased. Hence the antiferromagnetic interaction between Mn atoms will be became stronger, leading to the reduction of $M_s$ value$^{166}$. According to first principal calculations, when the distance between Mn atoms was increased, AFM and FM interactions tend to be degenerate and compete each other, the system will tend to posse paramagnetic or spin glass behavior$^{167}$.

Nanocomposites with 4 vol. % ZnO:Mn nanoclusters embedded in SiO$_2$ were selected for investigation of thermal annealing effect on their magnetic properties. As can be seen in Figure 6.7 (b), $M_s$ value was increased with annealing temperature and subsequently
Figure 6.7 (a) Field dependent magnetization of ZnO:Mn-SiO$_2$ nanocomposite with various ZnO:Mn nanocluster volume fraction from 4 vol. % to 50 vol. %. (b) Field dependent magnetization of as-deposited and annealed 4 vol. % ZnO:Mn-SiO$_2$ nanocomposite treated with temperature from 400$^\circ$C to 700$^\circ$C.
reached maximum $M_s$ value at 500 °C before decreased again to lower value at higher temperatures. Notice that the $M_s$ value of 500 °C annealed sample is significantly larger than other samples. These results were matched with the magnetism results of Mn-doped ZnO thin films done by other researchers\textsuperscript{168,169}, where 500 °C was reported as optimized annealing temperature. The coexistence of bivalent state of Mn such as Mn$^{2+}$ and Mn$^{3+}$ in the samples might causing occurrence of double-exchange interactions among 3d orbitals of Mn and the host matrix p bands\textsuperscript{11,154,168} and subsequently enhance ferromagnetism of the samples. Further increase of annealing temperature may destroy such double exchange interactions among Mn orbitals which might related to decrease of Mn$^{3+}$ species in samples. Further investigation on the microstructural and chemical state of Mn in as-deposited and annealed samples would prove the contributors of ferromagnetism in the films.

XRD θ-20 scans of ZnO:Mn-SiO$_2$ nanocomposites showed no peak in the XRD patterns. This implied that the sample was amorphous or the grain size was too small. As can be seen in high resolution TEM (HRTEM) image and selected area diffraction pattern (SADP) in Figure 6.8 (a) and 6.8 (b), ZnO, Mn$_2$O$_3$, Mn$_3$O$_4$ and ZnMn$_2$O$_4$ phases were detected in both as-deposited and 500°C annealed ZnO:Mn-SiO$_2$ nanocomposites. These results indicate that both as-deposited and annealed samples have bivalence Mn state in the form of +2 and +3. The coexistence of bivalence state in both as-deposited and 500°C annealed samples enable the occurrence of ferromagnetism in samples as proved by hysteresis loops in M-H curves. However, there was remarkable difference of magnetization value between 500°C annealed and the as-deposited and annealed samples, implying that there was other factor which dominated the magnetic interactions in 500°C annealed sample and enhanced its $M_s$ value significantly.
In order to investigate the change of chemical state of nanocluster with the annealing temperature, XPS spectra of as-deposited and annealed ZnO:Mn-SiO$_2$ nanocomposite were examined. As can be seen in Figure 6.9, the Mn 2p XPS spectra has two Gaussian-fitted

![Image](image_url)

Figure 6.8 (a) Plan view TEM image of as-deposited ZnO:Mn-SiO$_2$ nanocomposite deposited on carbon grid. Inset shows selected area diffraction pattern of corresponding sample. (b) HRTEM image of ZnO:Mn nanocluster embedded in SiO$_2$ matrix. (c) Plan view TEM image of 500$^\circ$C annealed ZnO:Mn-SiO$_2$ nanocomposite. Inset shows selected area diffraction pattern of corresponding sample. (c) HRTEM image of the 500$^\circ$C annealed 4 vol. % ZnO:Mn-SiO$_2$ nanocomposite.
peaks which are centered at 641.07 eV and 644.09 eV. The lower component is attributed to presence of Mn$^{2+}$ while the higher component is attributed to the occurrence of Mn$^{3+}$\textsuperscript{170,171}. After the nanocomposite was annealed at 500$^\circ$C, Mn 2p spectra shifted to lower binding energy positions which are centered at 640.66 eV and 642.59 eV, indicating the reduction of Mn valence state. The lower component of Mn 2p spectra indicates the presence Mn$^{2+}$ while the higher component of the spectra showed presence of Mn mixed valence state between +2 and +3 in the samples. As can be seen in both spectra, the area under peak corresponding to Mn$^{2+}$ is larger as compared to Mn$^{3+}$ state, indicating a favorable condition for occurrence of ferromagnetism in ZnO-Mn system\textsuperscript{172}. The prevalence of bivalence Mn states in both as-deposited and annealed samples was once again proved by XPS analysis. However, when nanocomposite samples were annealed in vacuum at higher 700$^\circ$C, the Mn$^{3+}$ peak disappeared.
The absence of Mn$^{3+}$ in 700°C annealed samples may reduce double exchange interactions since only one species Mn$^{2+}$ remained in samples and thus magnetization value will be reduced as shown in Figure 6.7 (b).

In order to determine the role of defects in influencing the magnetic properties of nanocomposite, the as-deposited and annealed samples were examined by using room temperature PL analysis. As can be seen in Figure 6.10 both as-deposited and annealed samples have weak UV emissions and violet emissions which are centered at 380 nm and 412 nm respectively. The weak UV emission can be attributed to the free exciton$^{173}$ or bound excitation recombination$^{174}$ which was occurred near band edge of ZnO while the violet emission can be attributed to the presence of oxygen vacancies or zinc interstitial defect$^{136,175,176}$. Upon vacuum annealing, the UV and violet emission peaks were remained at same position 380 nm and 412 respectively. However, only violet emission intensity was significantly increased under the effect of vacuum annealing. The increased concentration of oxygen vacancies in the 500°C annealed samples might be explained the larger saturation magnetization value of 500°C annealed sample as compared to as-deposited sample. Oxygen vacancies are capable of mediating long range magnetic coupling in ZnO-Mn system$^{177,178}$.

Optical properties of ZnO:Mn-SiO$_2$ nanocomposite was examined by UV-Vis absorption spectra. As-deposited sample has absorption edge at wavelength 297 nm corresponding to band gap 4.18 eV which is larger than typical ZnO thin film, as shown in Figure 6.11 (a). When the volume fraction of ZnO:Mn nanocluster in nanocomposite was increased, the absorption edge position was red-shifted until it reached 440 nm at 50 vol. % of ZnO:Mn. Such band gap shrinkage can be related to the crystal lattice distortion caused by the altered optical properties of nanocomposites which strongly depend on their microstructures or the enhanced carrier-carrier interactions induced by the increased carrier concentration in their conduction and valence bands$^{129-131}$. The vacuum annealing has similar
effect on the optical absorption spectra of nanocomposite as volume fraction of nanoclusters did on the absorbance spectra of nanocomposites, as shown in Figure 6.11 (b). The absorption edge of the nanocomposites red-shifted as the annealing temperature was increased. The enlargement of nanocluster size is expected since annealing promoted growth of nanoclusters and thus the band gap will be increased. Contrary to the UV-Vis absorption results of ZnO:Cu-SiO$_2$ nanocomposite as described in our previous report, none of surface plasmon resonance was detected in ZnO:Mn-SiO$_2$ nanocomposites.
Figure 6.11 UV-Vis absorption spectra of (a) as-deposited and (b) 500°C annealed 4 vol. % ZnO:Mn-SiO₂ nanocomposite.
6.2.4 Summary

In conclusion, ZnO:Mn-SiO$_2$ nanocomposites embedded with various volume fraction of ZnO:Mn nanoclusters were fabricated by nanocluster beam deposition combined with RF sputtering. XRD analysis showed no detection of phases in the samples due to lack of scattering domain inside the nanocomposite. High resolution TEM images and selected area diffraction pattern revealed the coexistence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ in both as-deposited and annealed samples. Due to the prevalence of bivalence Mn states in the all samples, PL analysis further clarify that the oxygen vacancies made majority contribution to the magnetization value of nanocomposites. Optical properties of nanocluster ZnO:Mn were altered by SiO$_2$ matrix since their band gap significantly enlarged and the band gap was drastically reduced with increasing volume fraction of nanoclusters.
Chapter 7 Conclusions

Transition metals Cu and Mn were embedded in ZnO in different forms of films i.e. nanocluster assembled films and nanocomposites by using nanocluster beam deposition combined with RF sputtering technique. Preliminary investigation started with the embedment of Cu nanoclusters in ZnO thin films to observe interactions between nanoclusters and ZnO thin film. The microstructures and magnetic of embedded nanocluster system were affected by the volume fraction of Cu nanoclusters in the ZnO thin films. While optical properties Both XRD and UV-Vis absorption results suggest the addition of Cu nanoclusters will relax the stress pre-existing in ZnO. The secondary phases Cu$_2$O were detected by using HRTEM and SADP analysis. However, AGM measurement showed anhysteresis loops of pure Cu nanoclusters, Cu oxides nanoclusters and pure ZnO thin film, ruling out the possibility of intrinsic ferromagnetism. The as-grown Cu-embedded ZnO thin films can exhibit room temperature ferromagnetism due to the interface effect between nanoclusters and the matrix. The oxidation of Cu species and reduction of Zn and O species were detected in XPS spectra. These results suggest that nanocluster-matrix charge transfer and the existence of defects as indicated in PL spectra could leads to possible interaction between defects and the Cu species and hence created favorable ferromagnetism environment for the Cu embedded ZnO films.

Next experiment was involved fabrication of Zn$_{0.94}$Cu$_{0.06}$O nanoclusters assembled films in porous nanocluster film form by using nanocluster beam deposition. XRD patterns show the existence of ZnO phases (100), (002) and (101) at elevated temperatures due to improved crystal quality of the films. All secondary phases were detected by TEM are non-ferromagnetic. Vacuum annealing up to 700$^0$C leads to increase of $M_s$ value from 1.22
emu/cm$^3$ to 1.88 emu/cm$^3$. Raman results suggest oxygen vacancies concentration was increased with increasing annealing temperatures. XPS spectra reveals the Cu oxidation changed from +1 to mixed valence state +1 and +2. These results indicate vacuum annealing can create favourable ferromagnetism environment for indirect double exchange and subsequently leads to the increase of magnetization value. The optical properties of films were altered by annealing in which the absorption edge of UV-Vis absorption was red-shifted due to the quantum size confinement effect.

ZnO:Cu-SiO$_2$ nanocomposite were produced by nanocluster beam deposition combined with RF sputtering. Existence of non-ferromagnetic secondary phases such as ZnSiO$_3$, Cu$_2$O, CuO and pure Cu are detected by HRTEM and XPS analysis. The most prominent surface phonon resonance feature was found in 600$^\circ$C annealed sample due to outdiffusion of Cu atoms from nanocomposite to form pure Cu nanocluster. PL analysis suggests the maximum room temperature Ms obtained in 600$^\circ$C annealed nanocomposite was caused by the existence of larger defects concentration in the samples. For annealed samples, enhanced ferromagnetism is mediated by oxygen vacancies as described by bound magnetic polarons model.

Zn$_{0.94}$Mn$_{0.06}$O nanocluster-assembled films were fabricated by nanocluster-beam deposition. XRD analysis indicates improvement of crystallinity of films and stress relaxation upon vacuum annealing. The secondary phases were detected in both as-deposited and annealed samples in the form of Mn$^{3+}$ and Mn$^{4+}$. The double exchange mechanism enhanced the RT ferromagnetism of all samples. However, the significant contributor to the magnetic moment of annealed samples is oxygen vacancies which can be proved by the increase of A$_1$(LO) phonon mode in Raman spectra with increasing thermal annealing temperatures. UV-Vis absorption edge showed red-shift as the annealing temperature was increased, implying the occurrence of temperature-induced band gap shrinkage in the samples.
Lastly, ZnO:Mn-SiO$_2$ nanocomposites embedded with various volume fraction of ZnO:Mn nanoclusters were fabricated by nanocluster beam deposition combined with RF sputtering. XRD analysis showed no detection of phases in the samples due to lack of scattering domain inside the nanocomposite. High resolution TEM images and selected area diffraction pattern revealed the coexistence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ in both as-deposited and annealed samples. Due to the prevalence of bivalence Mn states in the all samples, PL analysis further clarify that the oxygen vacancies made majority contribution to the magnetization value of nanocomposites. Optical properties of nanocluster ZnO:Mn were altered by SiO$_2$ matrix since their band gap significantly enlarged and the band gap was drastically reduced with increasing volume fraction of nanoclusters. Cu and Mn embedded ZnO nanocluster assembled films and nanocomposites have unique and interesting magnetic and optical properties. Ferromagnetism of all samples seems to be associated with existence of vacancies (especially oxygen vacancies) or other defects. Further investigation of nanoscale ferromagnetic properties and surface plasmon resonance properties of nanocluster assembled films and nanocomposites should be done in the future by using X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectroscopy (XAS) to precisely locate the ferromagnetism source from single atoms/molecules.
Publication

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