CHAPTER 4

ROOM TEMPERATURE FERROMAGNETISM IN Mn, N CODOPED ZnO THIN FILMS

4.1 INTRODUCTION

Semiconductor materials are always of great interest in materials science due to their interesting electronic and optical properties and have the potential for extensive applications. There has been considerable interest in ZnO semiconductor material because of its wide prospect in optoelectronic applications owing to its wide bandgap (3.37eV) and large binding energy (60meV) at room temperature. Diluted magnetic semiconductors are formed by partial replacement of the cations of the non-magnetic semiconductors by magnetic transition metal ions (Ohno 1998). Dietl et al (2000) first predicted that p-type Mn doped ZnO will show ferromagnetism with Curie temperature ($T_c$) well above room temperature. Wang et al (2004) have shown that the ferromagnetism is hole mediated in Mn, N codoped ZnO thin films and nitrogen could be a p-type dopant. Based on the theoretical investigations, many efforts have been made to investigate ferromagnetism in ZnO/Mn systems experimentally. Some groups have reported ferromagnetism but have reported different $T_c$ in p-type and n-type ZnO/Mn systems, whereas others have observed paramagnetic or ferromagnetic behaviours (Kittistveed et al. 2005, Xu et al 2005, Wan 2006, Alaria et al 2006).

One-dimensional Mn doped ZnO nanostructure such as nanowires, nanobelts and nanorods have been successfully synthesized due to
their potential application as building blocks for optoelectronic devices. ZnO nanostructures in the form of quantum dots along with natural biodegradable polymers such as dextran and chitosan have been considered for targeted drug delivery (Zhang et al 2007, Yuan 2008). For spintronic applications, dilute magnetic semiconductor has to be a p type semiconductor. However, it is not easy to obtain p type ZnO because undoped ZnO can always has some defects, which act as donors. So, addition of appropriate acceptor impurities is necessary to obtain p type ZnO suitable for dilute magnetic semiconductor applications. Group I and V elements are the possible dopant materials to obtain p type ZnO. Among all the elements, Mn and nitrogen are found to be suitable candidates to be added to ZnO to obtain p type ZnO because of their much smaller acceptor ionisation energy and formation energy than other elements. Nitrogen has been considered as a possible good candidate for realising p-ZnO because the radius of nitrogen atoms are close to that of oxygen atoms, and nitrogen atoms can substitute for oxygen lattice positions by the formation of acceptor. N\(^3\) can occupy a lattice position of O\(^2\) forming an acceptor. By doping nitrogen during the deposition of ZnO, it is possible to compensate oxygen vacancies and decrease the density of defects and the concentration of conduction electrons. Therefore, ZnO codoped with Mn and nitrogen can be expected to be a transparent ferromagnetic material with a high Curie temperature. Among the different methods used to prepare undoped and doped ZnO, hydrothermal synthesis route is an important method in wet chemistry which has been attracting material chemists’ attention. ZnO has been prepared by different research groups using various physical and chemical methods (Yan et al 2007). The solution based synthesis method when compared to the vapour phase method is simple and has the advantage of room temperature reaction process. In this chapter, we report about the structure and magnetic properties of ZnO and Mn, N codoped ZnO nanorods synthesized by hydrothermal method.
4.2 EXPERIMENT

All chemicals were purchased and used as received without further purification. The ZnO seed layer was formed by sol-gel method. Zinc acetate (0.1 mol) was dissolved in 10mL ethanol. Then, 0.25ml of deionised water was introduced drop by drop and on constant stirring, the solution transformed into a clear homogeneous solution. The solution was stirred continuously for 2h at room temperature. The resulting solution was used as the solution to deposit seed layer onto well cleaned sapphire substrates by spin coating method. Then, the coated films were annealed in a hot air oven at the temperature of 200°C for 1h. ZnO seed layer coated sapphire was used as substrate. Zinc nitrate hexahydrate was used as the starting material, and it is the source for zinc and nitrogen.

The dopant source for manganese is manganese chloride. In a typical synthesis process, 50 mL of 0.02M ZnNO$_3$6H$_2$O aqueous solution with MnCl$_2$ was mixed with 50ml of ammonia acetate aqueous solution at room temperature. The mixture solution was magnetically stirred and transferred into a Teflon lined stainless steel autoclave. The ZnO seed layer coated substrates were vertically immersed into the reaction solution, which was maintained at 80°C for 10h. Subsequently, the substrates with the film were washed with distilled water and ethanol and dried at 65°C in air. The prepared Mn,N codoped ZnO films were annealed at 900°C. The structure and composition of the Mn,N codoped ZnO films have been studied by X-ray diffraction method and X-ray photoelectron spectroscopy(XPS) respectively. Magnetic measurement was carried out using a superconducting quantum
interference device magnetometer at room temperature. The films were observed to be stable and had good adherence to the substrate.

4.3 RESULTS AND DISCUSSION

Figure 4.1 shows the X-ray diffraction pattern of the ZnO and Mn, N codoped ZnO nanorod based thin films. The strong and narrow diffraction peaks indicate that the material is a well crystallized material, and the result indicates that the nanorods possess hexagonal wurtzite structure. X-ray diffraction pattern shows peaks corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) planes of hexagonal ZnO in ZnO thin film and peaks corresponding to (100), (002) and (004) planes in Mn,N codoped ZnO thin film respectively.

When compared to pure ZnO, the (002) peak in the Mn, N codoped ZnO is very sharp and highly intense. In the Mn, N codoped ZnO films, only the peaks corresponding to ZnO is observed. This indicates that no secondary phases have been formed, and Mn and N substitute for Zn and O respectively. Because of Mn and nitrogen doping, there is a small shift in the 2θ value to lower angles. This is because the radius of Mn and N is larger than the radius of Zn ions. It is understandable since both the ionic radii of Mn$^{2+}$ (80pm) and N$^{3-}$ (146pm) are relatively large than those of Zn$^{2+}$ (74pm) and O$^{2-}$ (138pm).
Figure 4.1 X-ray diffraction pattern of (a) ZnO nanorod based film and (b) Mn,N codoped ZnO thin film

According to Bragg’s formula: $2d \sin \theta = n\lambda$, after the addition of Mn and N the interplanar distance of the (002) plane becomes larger, so the
value of 2θ is shifted to the lower angle. The lattice constant ‘c’ value increased from 5.169Å for undoped ZnO films to 5.180Å for Mn, N codoped ZnO films. The X-ray diffraction data show that the prepared Mn, N codoped ZnO thin films have mainly a c-axis oriented ZnO structure on the sapphire substrate.

In order to analyse the chemical states of constituent elements, XPS measurements were carried out with an emphasis to identify the peaks corresponding to Mn 2p, N 1s, Zn 2p and O1s. Figure 4.2 shows the XPS spectra of the Mn, N codoped ZnO films. The core level peaks of O 1s, Mn 2p, Zn 2p and N 1s are observed. Zn 2p$_{3/2}$ peak is observed at 1022eV. For O1s state, the peak obtained at 530.902eV can be attributed to O$^{2-}$ ions in Zn-O and Mn-O bonds. In the N1s spectrum, the peak obtained at 399.644eV indicates the formation of Zn-N bonds as a result of N$^{3-}$ ion acting as substitute ion in the film.

![Figure 4.2 (Continued)](image-url)
Figure 4.2 (Continued)
Figure 4.2 X-ray photoelectron spectra of the Mn, N codoped ZnO films
X-ray photoelectron spectroscopy results reveal the presence of Zn-N chemical bonding in the films. It can be said that nitrogen ions substituted at some of the oxygen sites of the ZnO films and mediated the ferromagnetic properties of the films. The chemical constituents present in the film are 45.23 at% Zn, 48.76 at% O, 4.13 at% Mn and 1.88 at% N respectively. In general, the higher the oxidation state the higher the value of Mn 2p\textsubscript{3/2}.

The peak at around 640eV in the Mn 2p\textsubscript{3/2} is attributed to Mn\textsuperscript{2+} cations, whereas peaks at 641.0eV and 642.695eV are assigned to Mn\textsuperscript{3+} and Mn\textsuperscript{4+} cations respectively. The strong peak obtained at 642.69eV can be attributed to Mn\textsuperscript{2+} and Mn\textsuperscript{4+} cations where Mn\textsuperscript{2+} cations may come from those substituting in ZnO nanorods at Zn\textsuperscript{2+} site and Mn\textsuperscript{4+} cations are from the impurity (Oxidation state of Mn). The Mn2p\textsubscript{3/2} main peaks have satellite structure on the higher binding energy side, indicating a divalent state of the Mn ions and they are in good agreement with the previous report by Xu et al (2006).

Figure 4.3 shows the scanning electron microscope image of the ZnO seed layer, undoped ZnO and Mn, N codoped ZnO nano rod arrays grown on ZnO seed layer coated sapphire substrates. The seed layer image shows the presence of small particles. It is found that the ZnO nanorods are well separated from each other, and the average diameter of the nanorods is 504±5nm. It can be clearly seen that the as grown nanorods are well aligned, oriented in a perpendicular fashion to the substrate. The nanorods are found to cover the substrate uniformly.
Figure 4.3  SEM images of (a) ZnO seed layer (b) ZnO nanorod based film and (c) Mn, N codoped ZnO film
The room temperature Raman spectra of the ZnO and Mn, N codoped ZnO nanocrystalline thin films are shown in Figure 4.4. The wurtzite ZnO structure belongs to the space group $C_{6v}^4$ with two formula units per primitive cell. Therefore, group theory predicts that the zone centre optical phonons are described by

$$
\Gamma_{\text{opt}} = A_1 + 2B_1 + E_1 + 2E_2
$$

Figure 4.4 Raman spectrum of (a) ZnO nanorod based film and (b) Mn, N codoped ZnO films
The \( A_1 \) and \( E_1 \) modes represent Raman and infrared polar phonons, showing frequencies for transverse optical to and longitudinal optical \( \text{Lo} \) modes. The \( E_2 \) mode is non-polar and Raman active in two frequencies: the \( E_2 \) (high) associated to the oxygen anions and the \( E_2 \) (low) associated to the Zn cations in the lattice, whereas the \( B_1 \) mode is Raman inactive. The Raman peak centered at 330\,\text{cm}^{-1} \) (Wang et al 2009) is described through a multiphonon process associated to three different modes; the domain \( A_1 \) mode plus a weak \( E_2 \) component and an even weaker \( E_1 \) component. The earlier reports describe the frequency of this mode as the difference between the \( E_2 \) (high) and the \( E_2 \) (low) modes. This mode shows an obvious red shift to 321\,\text{cm}^{-1}. Several normal phonon modes of ZnO have been observed: the peak at 441\,\text{cm}^{-1} is attributed to the \( E_2 \) (H) mode and shows a slight shift to high frequency compared to the normal value of 437\,\text{cm}^{-1}. The peaks at 581, 1165, 1741, 2316, and 2892\,\text{cm}^{-1} are ascribed to \( A_1 \) 1 (Lo), \( A_1 \) 2 (Lo), \( A_1 \) 3 (Lo), \( A_1 \) 4 (Lo) and \( A_1 \) 5 (Lo) modes.

The small peaks at 216, 645, 1006 and 1567\,\text{cm}^{-1} are ascribed to 2\( E_2 \) low or 2\( T_A, [E_1 \, E_2 \, (T_A + \text{Lo})] \), \( A_1 \) 2To and (\( A_1 \) 2To+ 1Lo) modes.\( A_1 \) 2A+To mode is not present in (Mn, N) doped ZnO. Compared to Raman modes of ZnO, the \( E_2 \) (H) phonon frequency and \( A_1 \) 2To mode exhibits a slight blue shift to 450 and 1022\,\text{cm}^{-1} for (Mn, N) codoped ZnO nanorods. The peaks at 578, 1152, 1736, 2320, 2894 and 3466\,\text{cm}^{-1} in Mn, N codoped ZnO nanorods are ascribed to 1Lo, 2Lo, 3Lo, 4Lo, 5Lo and 6Lo mode. The peaks are highly intense when compared to pure ZnO nanorods. The peak at 684\,\text{cm}^{-1} is related to \( E_1 \) Lo+\( E_2 \) low mode. This is due to compressive strain induced by Mn incorporation.

The field dependent magnetization of Mn, N codoped ZnO film was measured at 300K and is shown in the Figure 4.5. The M-H curves for the films were obtained after the contribution from the sapphire substrate had
been subtracted from the raw data. A hysteresis loop has been observed for Mn, N codoped ZnO films with a saturation magnetization of 0.12 and 0.17 kA m$^{-1}$ when the magnetic field is applied perpendicular and parallel to the sample plane respectively. The coercive field $H_c$ is the same for both. A high value of magnetization is obtained when the magnetic field is applied parallel to the sample. This suggests that the easy axis of the magnetization lies along the direction parallel to the applied field.

It is found that the prepared Mn, N codoped ZnO film shows ferromagnetic behavior. Yan et al (2007) have discussed in their result that the room temperature ferromagnetism should be intrinsic. The p type conduction is necessary to realize room temperature ferromagnetism ordering. Both manganese and nitrogen incorporated into ZnO prefer to exist as the nearest neighbours in ZnO. The N atoms replace some of the O sites, and there is an interaction between N2p and Mn 3d states. Hence, the total energy is lowered so that the ferromagnetic state is stabilized by the double exchange mechanism (Mn-O-Mn is changed into Mn,N-Mn). Co doping of both Mn and N in ZnO changes the Mn-Mn antiferromagnetic interaction to ferromagnetic coupling. The magnetic moment of Mn polarizes the spins at the neighbouring N sites antiferromagnetically, which results in ferromagnetic coupling between the Mn atoms. The spin alignment can be Mn↑-N↓-Mn(↑), indicating that ferromagnetic nature is mediated through the p-d exchange interaction between the carriers and Mn atom. The origin of ferromagnetism in oxide dilute magnetic semiconductors remains a very controversial topic: vacancies have been proposed to play a vital role in the magnetic origin for oxide DMSs in addition to the magnetic doping effect.

During synthesis, Zn interstitials and oxygen vacancies can be easily introduced into the sample. As the vacancy density increases, the overall volume occupied by bound magnetic polarons also increases. The
impurities (defects) in the doped film are located throughout the lattice at arbitrary distances with respect to the Mn sites. The spins of the localized defects align those of the nearby Mn ion, activating ferromagnetic interaction among the Mn ions. We suggest that large amount of holes have been introduced by N doping, so consequently, the magnetic properties of the films are greatly improved compared to hole mediated ferromagnetic interactions among magnetic impurities.

Figure 4.5 Hysteresis curve for Mn and N doped ZnO

This result is consistent with the theoretical prediction that hole might be necessary in order to mediate ferromagnetism for high Curie temperature dilute magnetic semiconductor (Dietl et al 2000).