Enhanced ferromagnetic response in ZnO:Mn thin films by tailoring composition and defect concentration

Usman Ilyas a,b, T.L. Tan a, P. Lee a, R.V. Ramanujan c, Fengji Li d, Sam Zhang d, R. Chen e, H.D. Sun e, R.S. Rawat a,*

a NSSE, NIE, Nanyang Technological University, 1 Nanyang Walk, Singapore 637516
b Department of Physics, University of Engineering & Technology, Lahore 54890, Pakistan
c School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798
d School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798
e Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

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The presence of structural defects degrade the crystalline quality of ZnO:Mn thin films and affects the magneto-optical properties of ZnO:Mn thin films. The donor defects in ZnO, which are known to be the source of n-type conductivity in ZnO host matrix, play an important role in limiting the ferromagnetism to lower temperatures. A systematic study of structural, optical and magnetic properties was carried out with the primary focus on understanding the relationship between the defect concentration, material composition and ferromagnetic properties. Single phase ZnO:Mn thin films with wurtzite structure were grown under ambient argon–oxygen admixture to investigate the effect of stoichiometry and interstitial oxygen on magnetic properties. A consistent increase in crystallinity of ZnO:Mn thin films (without precipitation of Mn) with increasing argon–oxygen admixture gas pressure was observed. Extended near band edge (NBE) emission spectra with marked decrease in photoluminescence (PL) ratio in optical characterization revealed improved optical quality of ZnO:Mn thin films. Magnetic measurements revealed enhanced room temperature ferromagnetism (RTFM) in sample grown at optimum argon–oxygen ambient pressure. The enhancement was directly related to maximal core level X-ray photoelectron spectroscopic peak of stoichiometric ZnO which, in turn, favors strong hybridization of Mn in the ZnO host matrix.

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1. Introduction

The emerging field of spintronics has generated a wide spread interest because of its potential to provide new functionalities and enhanced performance in conventional electronic devices [1]. Transition metal doped dilute magnetic semiconductors (DMS), exhibiting room temperature ferromagnetism (RTFM) have attracted wide-spread interest for their promising applications in spintronics. In these materials, the charge and spin state of electrons are accommodated into a single material leading to interesting magnetic, magneto-optical and magneto-electric properties [1,2]. The most well studied systems are the II–VI systems doped with Mn [3]. The magnetic properties of II–VI-based DMS have attracted much attention following Dietl’s prediction [4] of RTFM in Mn-doped ZnO as well as its high Curie temperature due to strong p-d hybridization [5]. To realize the practical spintronic devices, RTFM should be an intrinsic property of the semiconducting host matrix. There has been considerable interest in the fabrication of transition metal doped ZnO to implement spintronic devices [6]. Ferromagnetism can be induced by incorporation of transition metal atoms at substitutional sites in the host semiconductor. Among transition metals (TM), Mn can be easily substituted in Zn sites due to its close ionic radius to that of Zn2+ and having exactly half-filled d-shell giving rise to highest magnetic moment (5 μB) [7]. Additionally, the high solubility of various 3d transition elements in ZnO makes it suitable for spintronic applications [8,9]. The resulting magnetic behavior is strongly dependent on different parameters including the concentration of TM ions in the host matrix, carrier concentration, crystalline quality and defect density [5,10].

However, controversial reports [11–14] on the origin of ferromagnetism in Mn doped ZnO and the unavailability of highly p-type ZnO are among the main obstacles in creating high quality ZnO-based spintronic devices. So far, the major focus of ZnO:Mn thin films is on tailoring the doping concentration to realize RTFM [15,16]. Another important consideration in ZnO based systems is the role of oxygen vacancies (Vo) on the magnetic properties [17].
The role of these vacancies on magnetic behavior is unclear. Optimization of oxygen concentration and its effects on the material stoichiometry and RTFM in Mn doped ZnO thin films needs to be addressed in detail for high quality ferromagnetic thin films. Therefore, it is important to study the correlation between material composition, structural defects (due to deep level emissions) and RTFM by optimizing the concentration of oxygen in Mn doped ZnO thin films.

Hence, this paper aims to determine the correlation between material stoichiometry, oxygen related structural defects, and the ferromagnetic response in Mn doped ZnO thin films grown under different ambient gas pressures. We find that RTFM is due to enhanced Zn−O bonding (material stoichiometry) which favors strong p−d exchange coupling in the ZnO host matrix. The role of oxygen interstitials and the marked decrease in photoluminescence (PL) ratio for enhanced optical transparency in ZnO:Mn thin films is also discussed.

2. Experimental details

Nano-crystalline Mn doped ZnO powder (having 5 at% Mn concentration) with wurtzite structure was synthesized by a wet chemical method to prepare the PLD pellets. The growth parameters and processing conditions of ZnO:Mn nanocrystalline powder were similar to those reported by us elsewhere [18]. For the growth of ZnO:Mn thin films, ZnO:Mn targets (pelletized and sintered from ZnO:Mn nanocrystalline powder) were ablated by a second harmonic Nd:YAG laser (532 nm, 26 mJ) at a pulse repetition rate of 10 Hz. Before deposition the vacuum chamber was evacuated to a base pressure of 10−6 mbar. The substrate holder was set to rotate at a speed of 33 rev/min to ensure uniform thin film deposition. Thin film samples were deposited on rotating Si (100) substrate for an ablation period of 90 min under argon-oxygen (9:1 admixture) partial pressure of 1, 2 and 5 mbar herein after referred to as $P_{O_2}$-1, $P_{O_2}$-2 and $P_{O_2}$-5 respectively.

X-ray diffraction of ZnO:Mn thin films was carried out using a SIEMENS D5005 Cu Ka (1,5406 Å) X-ray diffractometer (XRD). Near band edge (NBE) and deep level emission (DLE) energy transitions in photoluminescence (PL) spectra, measured using a He−Cd (325 nm, 10 mW) laser, were used to study the defects, quality and optical transparency of thin film samples. X-ray photoelectron spectroscopy (XPS) with a focused monochromatic Al-Kα (1486.6 eV) X-ray beam (15 kV and 10 mA), equipped with Kratos Axis-Ultra spectrometer, was used to identify the surface stoichiometry and elemental oxidation states of thin film samples. Furthermore, magnetic characterization for the ferromagnetic ordering in ZnO:Mn thin films was done using a Lakeshore 7400 vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns corresponding to the single phase wurtzite structure ZnO:Mn thin films, exhibiting its polycrystalline nature. It is important to note that the as-deposited thin films were polycrystalline without any in-situ or post-deposition annealing. The XRD patterns matched well with the space group P63mc (186) (No. 36-1451) of the wurtzite ZnO structure. No signatures of Zn−Mn binary phases or oxides of Mn (within the detection limit of XRD) were observed in any of the thin films, as is evident from Fig. 1.

The texture coefficient of the thin films was estimated to determine the preferred orientation of the polycrystalline thin films, using the formula proposed by Barrett and Massalski [19]. A consistent increase in diffraction peak intensity (Fig. 1) of the highly textured (002) diffraction peak in turn indicates the improved crystalline quality of ZnO:Mn thin films with increase in argon−oxygen partial pressure. The lower diffraction peak intensity at lower argon−oxygen partial pressure is attributed to the incomplete reaction of Zn and oxygen in non-stoichiometric ZnO due to relatively larger amount of oxygen vacancies as native defects which deteriorate the crystalline quality. With increasing oxygen partial pressure, the oxygen vacancies are being filled by substitutional oxygen at the lattice sites. This results in enhanced material stoichiometry (Zn−O bonding) and higher diffraction peak intensity in ZnO:Mn thin films.

3.2. PL analysis

Room temperature PL analysis was carried out to investigate the possible effects of argon−oxygen partial pressure on the band gap energy, optical quality and optical transparency of Mn doped ZnO thin films. Fig. 2 shows the room temperature PL spectra, with two prominent emission bands in the UV and visible regions, of thin film samples grown under different argon-oxygen partial pressures. The UV band emission (at~380 nm) originated from exciton recombination corresponding to near band edge (NBE) transitions in photoluminescence (PL) spectra, measured using a SIEMENS D5005 Cu Ka (1,5406 Å) X-ray diffractometer (XRD). Near band edge (NBE) and deep level emission (DLE) energy transitions in photoluminescence (PL) spectra, measured using a He−Cd (325 nm, 10 mW) laser, were used to study the defects, quality and optical transparency of thin film samples. X-ray photoelectron spectroscopy (XPS) with a focused monochromatic Al-Kα (1486.6 eV) X-ray beam (15 kV and 10 mA), equipped with Kratos Axis-Ultra spectrometer, was used to identify the surface stoichiometry and elemental oxidation states of thin film samples. Furthermore, magnetic characterization for the ferromagnetic ordering in ZnO:Mn thin films was done using a Lakeshore 7400 vibrating sample magnetometer (VSM).

Fig. 1. XRD spectra of as-deposited ZnO:Mn polycrystalline thin films grown under different argon−oxygen partial pressures.

Fig. 2. Room temperature PL spectra of Mn doped ZnO thin films under different argon−oxygen partial pressures.
emission taking place through an exciton–exciton collision process [20]. A slight red shift in UV emission band (Fig. 2), with increasing argon–oxygen partial pressure, suggests a reduction in band gap energy, possibly due to the inclusion of oxygen within the ZnO host matrix. The deep level emission (DLE) spectrum in the visible region, which strongly manifests a polycrystalline structure [21] of ZnO, is due to energy transitions of native defects such as zinc vacancies ($V_{\text{Zn}}$), oxygen vacancies ($V_{\text{O}}$), interstitial zinc ($Z_{\text{n}}$) and interstitial oxygen ($O_{\text{i}}$) within the optical band gap of ZnO.

The contribution of native defects to the DLE spectra can be evaluated by estimating the relative intensities of the deconvoluted peaks. All the DLE spectra were deconvoluted with two peaks, centered at 550 and 620 nm, using Gaussian peak fitting (not shown here). The photoemission peak centered at 550 and 620 nm were related to structural defects due to oxygen vacancies ($V_{\text{O}}$) and oxygen interstitials ($O_{\text{i}}$), respectively. A consistent increase in the concentration of $O_{\text{i}}$ (from 16% to 23%) and reduced concentration of $V_{\text{O}}$ (38% to 15%) with increasing argon–oxygen partial pressure was observed. This increase in concentration of $O_{\text{i}}$ (acceptors) can be the result of oxygen incorporation within the ZnO host matrix which adds to its advantage to stabilize hole (acceptors) mediated RTFM in Mn doped ZnO thin films [4].

Normally, the luminescent properties are closely related to the quality and crystallinity of ZnO:Mn thin films. The crystalline and optical quality of ZnO:Mn thin films is enhanced by a reduction in defect density. A marked decrease in PL ratio (ratio of DLE/UV peaks) from 1.26 ($P_{\text{O}_{2}-10}$) to 0.64 ($P_{\text{O}_{2}-5}$) with increasing argon–oxygen partial pressure reveals the quenching of surface traps [22] leading to improved optical transparency of the thin films. The strong dependence of PL emission (UV and visible) on ambient gas pressure suggests the alteration of the electronic structure close to the surface. These results can be understood by assuming that the oxygen content in the thin films controls the recombination centers, or provides alternative non-radiative paths, resulting in reduced PL ratio. Moreover, the increased intensity of the second order diffraction (at ~750 nm) of UV emission peak with increasing argon–oxygen partial pressure, (Fig. 2), further justifies the enhanced optical quality of Mn doped ZnO thin films [23].

3.3. XPS analysis

Surface stoichiometry and elemental oxidation states of ZnO: Mn thin films were studied using XPS by investigating the Zn2p, Mn2p and O1s core level spectra. The binding energies of all the spectra were calibrated by the adventitious carbon C1s peak (~284.6 eV). All the samples showed oxygen rich stoichiometry with $\text{Zn}/\text{O} < 1$. Fig. 3 shows the XPS core level spectra of Zn 2p, Zn 2p1/2, Mn 2p, and O 1 s of $P_{\text{O}_{2}-2}$ sample. The XPS core level spectra were deconvoluted (using Gaussian peak fitting) with similar spectral features exhibited for other samples. Fig. 3(a) shows that Zn 2p spectra have shown strong shift toward higher binding energies with increasing ambient gas pressure. This shift in binding energy can be attributed to the presence of Zn in its different charge states. Moreover, the Zn 2p3/2 (Fig. 3(b)) spectrum exhibited slightly asymmetrical features indicating the existence of zinc in its different elemental states. The asymmetrical Zn 2p3/2 peak in elemental and oxide form usually consists of two peaks centered at ~1022.4 and 1021.5 eV, respectively [24]. The main core level XPS spectrum of Zn 2p3/2 of $P_{\text{O}_{2}-2}$ was deconvoluted with two peaks centered at ~1020.6 and 1022.1 eV (Fig. 3(b)). The deconvoluted peak centered at higher binding energy side (1022.1 eV) is related to metallic zinc [25].

The main core level XPS peak centered at 1020.6 eV in Zn2p3/2 is attributed to the Zn–O bonding (stoichiometric ZnO) which is the dominant peak in all the samples. The contribution from the peak centered at ~1020.6 eV was estimated to be 45%, 81% and 48% for $P_{\text{O}_{2}-1}$, $P_{\text{O}_{2}-2}$ and $P_{\text{O}_{2}-5}$, respectively, exhibiting highest contribution of Zn–O bonding in $P_{\text{O}_{2}-2}$ sample. This enhanced Zn–O bonding favors improved material stoichiometry in $P_{\text{O}_{2}-2}$ sample. The peak corresponding to oxide form of zinc, normally observed at ~1021.5 eV, is shifted to the lower binding energy of about 1020.6 eV which is attributed to the partial substitution of Zn in ZnO lattice by Mn2+ ions in Zn–Mn bonding structure [26]. The Mn has lesser tendency to attract electrons (due to its smaller electron negativity) in comparison to oxygen in ZnO host matrix. Therefore, the substitutional Mn atoms will result in shift in binding energy towards lower energy side [27]. Fig. 3(c) reveals the Mn 2p core level XPS spectra of $P_{\text{O}_{2}-2}$ deconvoluted with two prominent peaks centered at ~640.8 eV and ~655.7 eV which corresponds to Mn 2p1/2 and Mn 2p3/2, respectively. The peak centered at ~640.8 eV is attributed to the presence of Mn in its Mn2+ oxidation state which is consistent with the value reported in the literature [27]. The concentration of Mn in the thin films was estimated by calculating the relative area under Mn 2p peaks after Shirley background subtraction by non-linear least square fitting using mixed Gauss–Lorentz function. The values of Mn concentration are estimated to be 3.72, 3.17 and 3.04 at% for $P_{\text{O}_{2}-1}$, $P_{\text{O}_{2}-2}$ and $P_{\text{O}_{2}-5}$, respectively.

The deconvoluted peak in Fig. 3(d) shows the XPS peak of O 1s core level spectrum of $P_{\text{O}_{2}-2}$ implying the presence of oxygen in its different oxidation states. Due to asymmetrical feature of this peak, it was deconvoluted into three peaks, centered at ~529.9, 531.0 and 532.1 eV. The peak centered at the lower binding energy side is associated with the presence of oxygen in the wurzite structure of hexagonal ZnO ion array which is attributed to Zn–O bonding [28]. The contribution of oxygen in Zn–O bonds, estimated from the relative area under curve of the peak at ~529.9 eV, was observed to be 2%, 4% and 22% for $P_{\text{O}_{2}-1}$, $P_{\text{O}_{2}-2}$ and $P_{\text{O}_{2}-5}$, respectively. The deconvoluted peak with binding energy centered at ~531.0 eV is associated with the O2– ions in oxygen deficient regions within the ZnO matrix. The presence as well as the changes in the intensity of this component can be related to the variation in the concentration of oxygen vacancies [29]. By calculating the relative area under the curves of deconvoluted peaks, the concentration of oxygen vacancies was estimated to be 30%, 2% and 71% for $P_{\text{O}_{2}-1}$, $P_{\text{O}_{2}-2}$ and $P_{\text{O}_{2}-5}$, respectively. The reduced concentration of oxygen vacancies for $P_{\text{O}_{2}-2}$ is consistent with enhanced Zn–O bonding. This enhanced bonding favors the strong hybridization of Mn in ZnO host matrix resulting in enhanced ferromagnetic properties, discussed later, for this sample. The deconvoluted peak centered toward the higher binding energy side (~532.1 eV) is associated with the presence of chemisorbed oxygen within the ZnO host matrix [30] which in turn reveals the presence of oxygen interstitials. This result is consistent with our optical measurements.

3.4. VSM analysis

The magnetic characterizations of Mn doped ZnO thin films were performed using VSM in the magnetic field range of 0–4000 G at room temperature. All the $M–H$ curves were obtained after subtracting the raw data from the background signal taken from bare silicon substrate to obtain the signal from thin films only. All the $M–H$ curves reveal the strong dependence of magnetization on the ambient gas pressure. Fig. 4 shows an increase in saturation magnetization from 16.3 µemu to 115.8 µemu with an increase in argon–oxygen partial pressure from 1 to 2 mbar, respectively and subsequently it decreases to 52.1 µemu for 5 mbar deposition. According to Dietl's [4] prediction, RTFM is possible in Mn-doped ZnO which is heavily doped with holes, while the carrier mediated ferromagnetism in n-type material should be limited to lower temperatures [31]. A strong direct
correlation between material stoichiometry (Zn−O bonding) and saturation magnetization has been observed in our thin films. The oxygen rich stoichiometry resulting from increased Zn−O bonding reduces oxygen vacancies (refer XPS analysis) and favors p–d exchange coupling of Mn in ZnO host matrix. This coupling is responsible for enhanced RTFM.

In the case of ferromagnetic ordering in thin films, the magnetic spins align to yield minimum resistivity [32] which is the result of strong Zn−O bonding and the presence of minimum structural defects. In the case of \(P_{O2}^{-2}\), we have strong Zn−O bonding with the optimum concentration of oxygen interstitials. The enhanced ferromagnetic signal in this sample therefore can be attributed to the dominant effect of correlated spins in strongly coupled Mn−O−Mn exchange interaction. These interactions act ferromagnetically in the stoichiometric ZnO. The presence of greater amount of oxygen interstitials in the ZnO host matrix will increase the distance between the magnetic ions (Mn\(^{2+}\)), reducing the coupling and thus the ferromagnetism. In this situation, the paramagnetic phase of isolated Mn\(^{2+}\) ions and uncorrelated spins reduce the net magnetic moment and the ferromagnetic ordering. Previous studies [10] report the importance of oxygen interstitials in mediating Mn−O−Mn indirect ferromagnetic exchange coupling, however, the presence of oxygen interstitials at concentrations greater than the optimum value, thereby result in reduction of Coulombic forces giving rise to un-correlated spins of magnetic ions.

In accordance with the bound magnetic polaron (BMP) model, the magnetization arising from correlated spins is ferromagnetic whereas for un-correlated spins it is paramagnetic [12]. The competition between correlated and uncorrelated spins might suppress the Mn−O−Mn indirect p−d exchange coupling, resulting in a reduction in the ferromagnetic signal. Moreover, the oxygen rich stoichiometry (with maximum O\(_i\)) can reduce the magnetic moment of \(P_{O2}^{-3}\). In this sample, the thin films, with isolated Mn atoms in the ZnO host matrix behave paramagnetically [33,34]. Therefore, the maximum value of saturation magnetization in \(P_{O2}^{-2}\) can be attributed to the strong hybridization of Mn in ZnO host matrix in good quality ZnO: Mn thin films with enhanced material stoichiometry.

4. Conclusions

In summary, we have investigated the effect of ambient argon−oxygen gas pressure on the structural, optical and magnetic

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Fig. 3. XPS core level spectra of (a) Zn 2p peaks shift under different ambient pressures and deconvoluted spectra of (b) Zn 2p\(_{3/2}\), (c) Mn 2p and (d) O 1 s of \(P_{O2}^{-2}\).

Fig. 4. Field dependent \(M-H\) curves of Mn doped ZnO thin films grown under different argon−oxygen partial pressures.
properties ZnO:Mn thin films. All the thin film samples show an inconsistent variation in concentration of oxygen at the lattice sites with corresponding variations in Zn–O bonding and gradual decrease in oxygen vacancies with increasing ambient gas pressure. Extended near band edge emission in room temperature photoluminescence spectra along with reduced PL ratio (DLE/NBE) revealed the improved optical quality of the thin films. Structural analyses based on X-ray diffraction and X-ray photoelectron spectroscopy convincingly excluded the existence of any impurity phase and revealed enhanced Zn–O bonding under controlled argon–oxygen partial pressure. The enhanced Zn–O bonding, which is related to the incorporation of substitutional oxygen at the lattice sites in ZnO host matrix, was directly correlated with an increase in ferromagnetic ordering. Thus Mn doped ZnO thin films grown under optimal argon–oxygen partial pressure exhibit enhanced Zn–O bonding, resulting in enhanced ferromagnetic ordering.

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