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Temperature-dependent stoichiometric alteration in ZnO:Mn nanostructured thin films for enhanced ferromagnetic response

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ABSTRACT

The study investigates the effect of in-situ substrate temperature and argon-oxygen ambient gas pressure of pulsed laser deposition facility on material composition, optical quality and magnetic response of ZnO:Mn thin films. Structural and optical analyses revealed the existence of an optimal in-situ substrate temperature (450 °C) at which thin films showed relatively better texture and optical quality with minimum concentration of structural defects. The detailed analysis of Zn $2p_{3/2}$ and O 1s core level XPS spectra revealed that the structural disorder was considerably reduced in thin films after being annealed (in-situ) at substrate temperature of 450 °C. Magnetic measurements revealed the stronger p-d hybridization between oxygen 2p and Mn 3d orbitals in ZnO:Mn thin films being annealed in-situ at 450 °C under Ar:O_2 admixture of 2.5 mbar subsequently leading to improved ferromagnetic response.

1. Introduction

Wurtzite phase ZnO, with wide band gap, is a strong electro-optic and piezoelectric material which can be used as a multifunctional material in optoelectronics and spintronics [1,2] when doped with transition metals. One of the problems in ZnO thin films synthesis is the instability of its functional properties due to its tendency to change the stoichiometry (Zn-rich or O-rich) with temperature and ambient atmosphere in the deposition chamber [3]. This problem becomes more pronounced in the case of depositions being done at elevated operational temperatures [4,5] which provides the intensification of surface/bulk processes consequently leading to the deterioration in functional properties. According to Zhu et al. [6], the oxygen ambience in the deposition chamber affects not only the crystalline structure but also alters the optical and electrical properties along with the variations in surface morphologies. It is well known that as-grown ZnO as well as ZnO:Mn thin films [7] usually contain a certain number of intrinsic defects like oxygen vacancies and zinc interstitials due to the deviation from stoichiometry and cause intrinsic charge carriers. The relative concentration of structural defects in Mn doped ZnO (ZnO:Mn), estimated through deep level emissions (DLE) in room temperature photoluminescence (PL) spectra, influence the exchange coupling of Mn in ZnO host matrix [8] making the origin of ferromagnetism controversial. The control and stability of structural defects in thin films of ZnO:Mn, to achieve room temperature ferromagnetism (RTFM) [9] through indirect ferromagnetic p-d exchange coupling, are a pre-requisite for spintronics device applications. Therefore, an investigation about the effects of deposition parameters on the stoichiometry of ZnO:Mn thin films is of strong fundamental and practical interest.

This study investigates the influence of substrate temperature and ambient gas pressure on the material composition and optical quality of ZnO:Mn thin films to minimize the contribution of structural defects towards the ferrromagnetic response, a pre-rquisite for spinronics device applications. The direct correlation between the oxygen partial pressure in pulsed laser deposition (PLD) chamber and oxygen defeciency in thin films of ZnO:Mn, which is altered with in-situ annealing, is observed and discussed.

2. Experimentation

The ZnO:Mn thin films were grown on Si(100) substrate by pulsed laser deposition (PLD) using 2nd harmonic Nd:YAG laser

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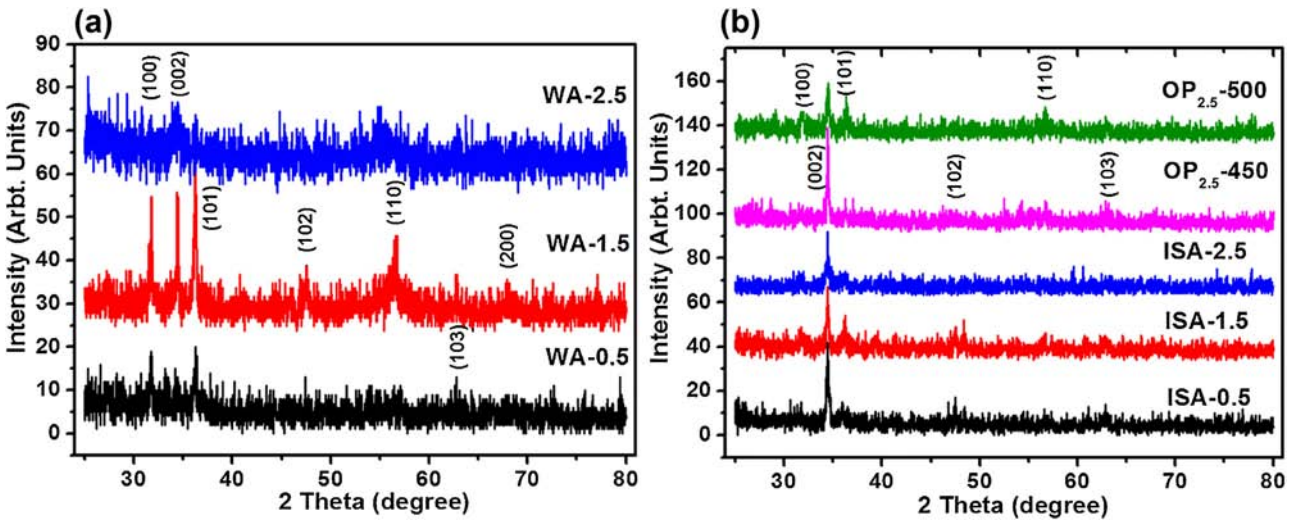

Fig. 1. XRD spectral profiles of ZnO:Mn thin films grown under different Ar:O_2 admixture gas pressures (a) as-grown and (b) with in-situ annealing.

(532 nm, 30 mJ). Pelletized PLD targets of ZnO:Mn (with 5% Mn concentration) were synthesized through wet chemical method with the processing conditions reported elsewhere [10–12] in our previous studies. The PLD chamber was evacuated to a base pressure of the order of $\sim 10^{-6}$ mbar prior to thin film deposition. All thin films were deposited on n-type Si(100) substrate, having target to substrate distance of ~5.5 cm, under different argon-oxygen admixture (with Ar:O_2 = 9:1) gas pressures for 30 min. The thin films grown at argon-oxygen admixture ambient pressures of 0.5, 1.5 and 2.5 mbar without any in-situ annealing are herein after referred as WA-0.5, WA-1.5 and WA-2.5, respectively. The thin films were then deposited with in-situ annealing of substrate at 400 °C under the similar conditions of ambient gas pressures and PLD parameters. The corresponding depositions are herein after referred as ISA-0.5, ISA-1.5 and ISA-2.5, respectively. To further study the effect of substrate temperature the thin films were also deposited at fixed argon-oxygen admixture gas pressure of 2.5 mbar at in-situ annealing temperatures of 450 and 500 °C and the corresponding depositions are referred as $OP_{2.5}$-450 and $OP_{2.5}$-500 in the text, respectively.

The structural analysis of ZnO:Mn thin films was performed using SIEMENS D5005 Cu Kα (1.5406 Å) X-ray Diffractometer (XRD). The activation of structural defects and the transitions related to near band edge (NBE) and deep level emission (DLE) were studied from photoluminescence (PL) spectra, measured using He-Cd (325 nm, 10 mW) laser. Elemental oxidation states and surface stoichiometry were identified using X-ray photoelectron spectroscopy (XPS) with Kratos axis-ultra spectrometer equipped with a focused monochromatic Al-Kα (1486.6 eV) X-ray beam (15 kV, 10 mA). The morphological analysis of thin films was carried out using Jeol JSM 6700 field emission scanning electron microscope (FESEM) coupled with energy dispersive X-ray (EDX) system. Moreover, room temperature ferromagnetic response of ZnO:Mn thin films was studied by using Lakeshore 7404 vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. XRD analysis

Structural analysis was performed to study the dependence of the crystalline quality of thin films on ambient gas pressures and in-situ annealing temperatures. Fig. 1 shows the XRD spectral plots of Mn doped ZnO thin films (without and with in-situ annealing).

There are distinct differences between XRD spectral profiles of non-annealed and annealed thin films. Fig. 1(a) reveals the spectral profiles of non-annealed (WA samples) thin films with relatively poor crystalline quality while those grown under different ambient gas pressures along with in-situ annealing (ISA and OP samples) reveal better texture with c-axis (002) orientation as shown in Fig. 1(b). In general, the crystalline quality is closely related to the partial pressure of the ambient gas. Inconsistent variations in diffraction peak intensities were observed for thin films grown without in-situ annealing (non-annealed) which might be attributed to different concentrations of structural defects for these samples; discussed in later sections. While a consistent decrease in diffraction peak intensity was observed, with increasing Ar:O_2 partial pressure, for thin films grown with in-situ annealing at 400 °C (samples ISA-0.5 to ISA-2.5) as is evident in Fig. 1(b). However, in both cases (with and without in-situ annealing), the higher oxygen partial pressure (WA-2.5 and ISA-2.5) led to reduced diffraction peak intensity indicating deterioration in crystallinity, similar to the one observed by Gopalakrishnan et al. [13]. In PLD, the kinetic energy of plasma species impinging on the substrate is controlled by energy density of laser beam at target, target to substrate distance and the ambient gas pressure. An increase in ambient gas pressure will enhance the interaction with background gas leading to reduced energy of impinging plasma species. The enhanced interaction with background gas will also result in greater scattering of the plasma plume species leading to lesser amount of material being deposited on the substrate surface. The lower energies of impinging plasma and reduced amount of material at the substrate surface at higher background gas pressure will lead to less crystalline structure.

It is worth to mention that the crystalline quality is also dependent on the diffusion path length of adatoms on substrate surface before settling down during the thin film growth. The adatoms in thin films grown with in-situ annealing take larger diffusion path to settle down which is considered to be the cause of improved crystalline quality, under similar ambient gas pressures, in ISA/OP thin films in comparison to non-annealed (WA) ones [14]. This indicates the importance of substrate temperature on the crystalline quality of the thin film samples which is evident from Fig. 1(b) in which $OP_{2.5}$-450 shows relatively better crystallinity.

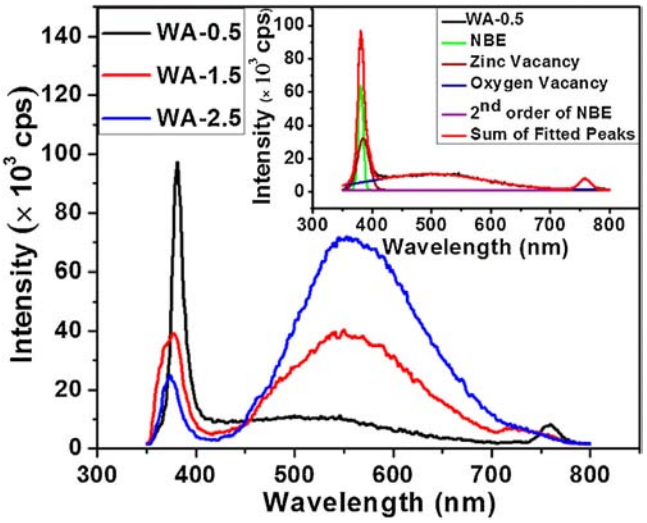

Fig. 2. Room temperature PL spectra of as-grown ZnO:Mn thin films, comprising two emission bands regarding NBE and DLE spectral regions(Inset shows the deconvoluted PL spectra of WA-0.5 revealing the presence of intrinsic defects).

3.2. PL analysis

Room temperature photoluminescence spectra of non-annealed (WA) ZnO:Mn thin films, comprising two peaks regarding near band edge (NBE) in UV and deep level emissions (DLE) in the visible spectral regions, are shown in Fig. 2. The NBE of ZnO is attributed to the direct recombination of electrons in the conduction band of Zn 4p with the holes in valence band of O 2p and is strongly dependent on the crystalline quality and material stoichiometry [15,16]. During Mn doping, part of the Mn ions will be incorporated into the lattice of ZnO and introduce inhomogeneous broadening, which is reflected by the broadening of the NBE emission shown in Fig. 2. Meanwhile, the incorporations will generate defects such as interstitials and vacancies which result in large re-organization of local charge distributions, change the equilibrium bond lengths and shift the NBE peak related to the optical band gap of ZnO. The DLE spectra in ZnO are attributed to the transitions from the intrinsic structural defects, like oxygen vacancy (V_o), oxygen interstitial (O_i), zinc vacancy (V_{Zn}) and zinc interstitial (Zn_i), present in the optical band gap of ZnO [11]. The native structural defects play a very important role in the conductivity, crystallinity and magneto-optical properties of ZnO:Mn thin films.

The concentration and distribution of structural defects was estimated by deconvoluting the DLE spectral profiles individually using Gaussian peak fitting as shown in the inset of Fig. 2. The main contribution in the DLE spectra was estimated from the peak centered at ~530–570 nm in the green spectral region which is attributed to the electrons trapped in oxygen vacancies (V_o) with photo generated holes [16,17]. For as-grown ZnO:Mn thin film prepared by PLD the chemical component is generally non-stoichiometric with the zinc rich stoichiometry. Therefore, many surface and lattice defects are contained in the thin films (refer Fig. 2) which reduce ionic diffusion at the lattice sites and inhibit the grain growth [18]. These defects produce some non-radiative centers and reduce the PL emission intensity from as-grown ZnO:Mn thin films. A consistent increase in the radiative emission from the structural defects in DLE spectra reveals the increased concentration of oxygen vacancies in the lattice with increasing Ar:O_2 ambience. It was observed that the concentration of oxygen vacancies increased from 8.72% in WA-0.5 to 39.70% in WA-2.5. The increased concentration of oxygen vacancies will increase the concentration of residual electrons in the ZnO host matrix and result in systematic decrease in ferromagnetic exchange interaction as ferromagnetism in n-type ZnO is limited to lower temperatures [19].

The in-situ heat treatment of the thin films at suitable substrate temperatures, revealed the consistent decrease in the concentration of structural defects. Fig. 3 shows the room temperature PL spectra of ISA thin films having relatively stronger near band edge emission (NBE) in ZnO:Mn thin films in comparison to non-annealed ones (WA) which is attributed to the improved material composition with reduced concentration of structural defects. With increasing ambient pressure for ISA samples, the oxygen supply is increased which will result more oxygen in ZnO host matrix reducing the vacant sites of oxygen in the lattice.

The relative concentration of oxygen vacancies was reduced from 19.4 (for ISA-0.5) to 8.0% (for ISA-2.5) with increasing ambient gas pressure revealing the inverse relation with the ambient pressure. Beside this, small signatures of zinc vacancies were also observed in ISA-2.5 (refer inset of Fig. 3).

In order to fine tune the results, thin films of ZnO:Mn were grown at in-situ substrate temperatures of 450 °C ($OP_{2.5}$-450) and 500 °C ($OP_{2.5}$-500) at Ar:O_2 ambient pressure of 2.5 mbar. The strongest NBE emission for $OP_{2.5}$-450 with minimum deep level emissions from structural defects in the visible region (refer Fig. 3) was observed which in turn points to improved optical quality and material composition. Lower or higher temperatures (ISA-2.5 and $OP_{2.5}$-500) were found to activate the defect states (like vacancies and interstitials of oxygen) in deep level emission spectra and effect the PL emission. In other words, one can say that residual electrons, which can contribute towards the n-type conductivity and suppress the p-d hybridization of Mn in ZnO host matrix, were effectively reduced after the thin film growth under Ar:O_2 pressure of 2.5 mbar with in-situ substrate temperature of 450 °C.

3.3. FESEM analysis

Fig. 4 shows the FESEM images of non-annealed and in-situ annealed samples. Morphological studies in as-deposited thin film samples (film thickness 90 ± 15 nm) reveal that the particle shape and size were non-uniform and resulted in increased surface roughness as is evident from Fig. 4(a, b). The WA-0.5 sample shows a mixed surface morphology with smaller sized nanoparticles (at background), bigger-sized agglomerated particles (formed from coalescence of smaller sized nanoparticles) and nano-plates or nano-sheets. The nano-plates disappeared in WA-2.5 sample and only nanoparticle and particle agglomerates were found to decorate the surface as seen in Fig. 4(b).

The micrographs in Fig. 4(c, d) show the uniform distribution of well-defined nano-sized particles at the surface of ZnO:Mn thin films (film thickness 80 ± 10 nm) grown with in-situ annealing. The ISA-0.5 sample, shown in Fig. 4(c), is seen to have individual particles as well as particle agglomerates with average particle size of ~26 nm estimated using image processing (image J®) software. With increasing ambient gas pressure the concentration of agglomerated particles decreased and finally disappeared in ISA-2.5. Fig. 4(d) reveals uniform particle size distribution (with no agglomeration) in ISA-2.5 with average nanoparticle size of ~13 nm. With increasing argon-oxygen partial pressure, the ablated species from the target would face more collisions and loose energy to the background gas. The greater loss in energy of the plasma species arriving at the substrate surface for higher ambient gas pressure will lead to lower adatom mobility and hence the smaller grain growth or the particle size.

Moreover, temperature-dependent variation in the surface morphology in ISA thin films was also studied at temperatures of 450 and 500 °C. Thin film samples of $OP_{2.5}$-450 and $OP_{2.5}$-500 reveal the formation of nano-sized particles and nanoplate-like morphology

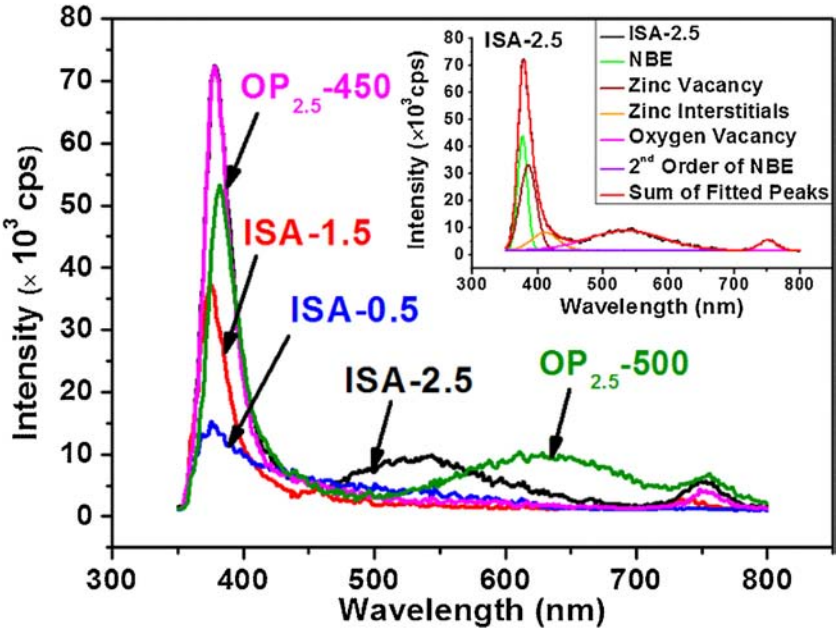

Fig. 3. Room temperature PL spectra of ZnO:Mn thin films with in-situ annealing (ISA), comprising two emission bands regarding NBE and DLE spectral regions(Inset shows the deconvoluted PL spectra of ISA-2.5 indicating the concentration of different structural defects).

with their well-defined facets along the surface of nanocrystalline ZnO:Mn thin films. The average particle size was found to be ~22 nm for $OP_{2.5}$-450 with narrow size distribution as particles were quite uniform in shape and size. The increase in average particle size from ~13 nm (ISA-2.5) to ~22 nm ($OP_{2.5}$-450) with increase in-situ annealing temperature is attributed to enhanced adatom mobility. The sample grown at 500 ($OP_{2.5}$-500) has wider distribution in shape and size of nano-sized features. There are smaller sized nanoparticles and bigger sized flat shaped nanoplates. The average size of nanoplate-like structures in $OP_{2.5}$-500 is estimated to be ~38 nm. The higher in-situ substrate temperature of 500 °C seems to cause Oswald ripening whereby the bigger sized nanoplates-like structures grow at the expense of smaller sized nanoparticles.

3.4. XPS analysis

Compositional analysis was carried out to study the surface stoichiometry and elemental oxidation states in ZnO:Mn thin films by analyzing the Zn $2p_{3/2}$ and O 1s core level XPS spectra shown in Figs. 5 and 6. The core level XPS spectra of Zn $2p_{3/2}$ exhibited the asymmetrical features and therefore, was deconvoluted using Gaussian peak fitting. Fig. 5(a) shows the core level XPS spectrum of WA-2.5 deconvoluted with three Gaussian peaks centerd at ~1020.0, 1021.0 and 1022.9 eV, respectively. The relative contributions of these peaks were estimated to be 2.0, 82.6 and 15.3%, respectively. The small peak centered at ~1020.0 eV is attributed to the presence of zinc with a broken bond while the peak centerd at ~1022.9 eV is attributed to the presence of zinc in its elemental form or zinc being surrounded by oxygen vacancies. As these zinc atoms are not occupied at the lattice sites, they may be termed as zinc interstitials [20]. The presence of zinc interstials, though in small percentage, can be attributed to the fact that the atoms at the substrate surface (with the increasing ambient gas pressure) did not have sufficient energy to diffuse at the lattice sites and remain resident non-uniformly in the structure. The peaks centered at ~1021.0 eV can be attributed to the presence of Zn^{2+}. Normally, the peak regarding the Zn in its +2 oxidation state appears at 1021.5 eV [20], which in our case, has been shifted towards lower binding energy side possibly due to the incorporation of Mn in ZnO.

Inset of Fig. 5 shows the core level XPS spectra of O 1s exhibiting the presence of multi-component oxygen in the samples. The core level XPS peak of O 1s in WA-2.5, shown in inset of Fig. 5(a), was deconvoluted by two peaks centered at ~531.2 and ~532.6 eV. The peak centered at ~531.2 eV is associated with the presence of oxygen vacanceis [21]. The relative concentration of oxygen vacancies was estimated to decrease from 66.2% (WA-0.5) to 30.3% (WA-2.5) with increasing $Ar:O_2$ pressure. However, the crystalline quality of WA-2.5 observed to be minimum (weak diffraction peak intensities in XRD) which reveals the enhanced structural disorder. It might be attributed to the presence of oxygen related species at the interstitial sites in the form of hydroxyl species which were estimated to be 69.6% in WA-2.5. The maximum concentration of chemisorbed oxygen in WA-2.5, refer Fig. 5(a), will increase the non-homogeniety and degrade the crystalline and magneto-optical properties of thin films deposited under higher ambient gas pressures.

Fig. 5(b) shows the deconvoluted XPS core level peaks of Zn $2p_{3/2}$ in ISA-2.5 centered at ~1020.6 and 1021.6 eV. The peak centred at ~1021.6 eV is related to the presence of zinc surrounded by oxygen vacancies [20], which can possibly be attributed to the imcoplete reaction of oxygen and zinc host lattice. As the zinc atoms at this binding energy are not residing at the lattice sites as regular zinc ions, they might be termed as zinc interstitials [20]. The relative contribution of this peak, estimated by using the relative area under the deconvoluted peaks, was estimated to be 82% (ISA-0.5), 18% (ISA-1.5) and (93%) in ISA-2.5, respectively. The peak centered at ~1020.6 eV is attributed to the presence of Zn in Zn—O bonds (or the presence of Zn in its +2 oxidation state). The relative contribution of this peak was estimated to be maximum (94.8%) in $OP_{2.5}$-450 which in turn indicates the improved material composition as is evident from Fig. 6.

Inset of Fig. 5(b) shows the XPS core level spectra of O 1s exhibiting the presence of multi-component oxygen in the samples. Mainly, the oxygen peak was deconvoluted by three peaks (for ISA samples) centered at ~529.8, 531.0 and 532.6 eV, respectively as is evident from Fig. 5(b). The peak centered at ~529.8 eV is attributed to the presence of oxygen in oxide form (Zn—O bonding) [22] and is related to material stoichiometry. The concentration of oxygen in oxide form varies from 37.9% (ISA-0.5) to 67.4% (ISA-2.5)

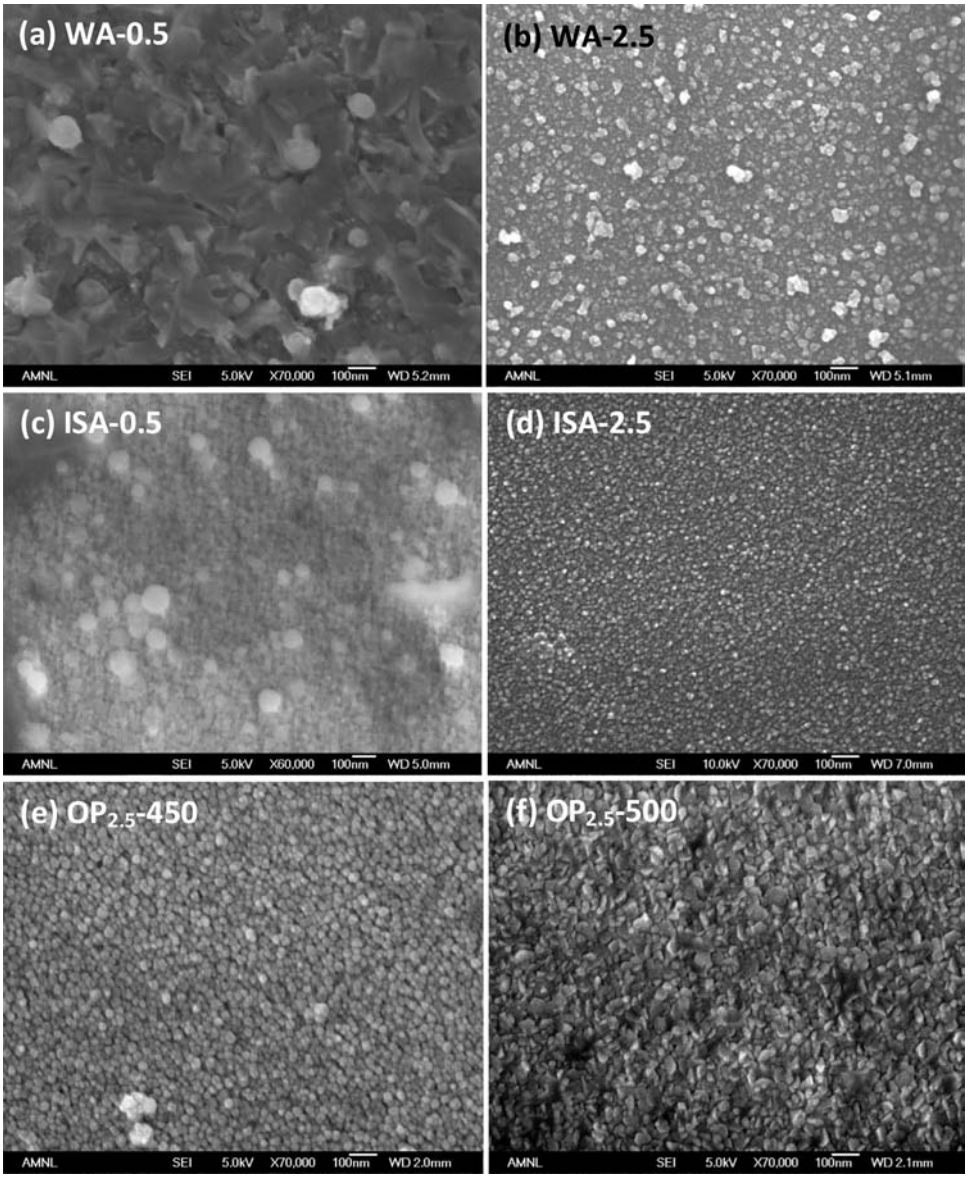

Fig. 4. FESEM micrographs of (a)WA-0.5, (b) WA-2.5, (c) ISA-0.5, (d) ISA-2.5, (e) $OP_{2.5}$-450 and (f) $OP_{2.5}$-500 thin films revealing the distribution of nanoparticles and nanoplates in the ZnO:Mn thin films.

with increasing ambient gas pressure. The relative concentration of oxygen vacancies (estimated from 531.0 eV peak) is varied from 62.0% (ISA-0.5) to 20.1% (ISA-2.5). The increased concentration of zinc in oxide form of zinc and oxygen in ISA-2.5 in turn favors the coupling mechanisms of Mn in ZnO host matrix in turn, improving the ferromagentic response, discussed in later section.

In order to further study the rate of oxygen diffusion in the ZnO host matrix, the ratio of Zn—O bonding to the concentration of chemisorbed oxygen was estimated. A cross-comparison of Zn—O bonding and interstitial oxygen O_i shows that the rate of diffusion of oxygen at the lattice sites is less in ISA-0.5 in comparison to oxygen vacancy formation due to in-situ annealing. It might be attributed to the fact that at argon-oxygen pressure of 0.5 mbar, there might not be enough oxygen to be diffused in the lattice resulting in oxygen vacancy formation. Greater rate of oxygen vacancy formation will result in incomplete reaction of Zn and oxygen leading to non-stoichiometric material composition affecting crystallinity and ferromagnetic ordering of the sample.

Temperature-dependent variation in material composition in ZnO:Mn thin films was also studied. The typical core level XPS spectra of Mn 2p, Zn $2p_{3/2}$ and O 1s of $OP_{2.5}$-450 are shown in Fig. 6. The relative contribution of the peak related to oxide form of zinc (~1020.5 eV) was maximum (94.8%) in $OP_{2.5}$-450 in comparison to the sample ISA-2.5 (93%) grown at 400 °C, which indicates the better material composition for $OP_{2.5}$-450. Moreover, the enhanced contribution from the peak regarding the oxide form of oxygen (~530.5 eV) compliments the better material composition in this sample. The better material composition in $OP_{2.5}$-450 favors the strong indirect sp-d exchange coupling in ZnO:Mn thin films resulting in enhanced ferromagnetic response.

Fig. 6(inset) shows the core level XPS peaks of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ (spin-orbit doublet) centered at ~640.8 eV and 656.2 eV which, in turn reveals the presence of Mn^{2+} and rules out the possibility of nanoclustering of Mn. It is believed that the short range ferromagnetic/anti-ferromagnetic exchange interaction of Mn is strongly dependent on the concentration of structural defects. Therefore, the optimum concentration of structural defects with improved stoichiometry (Zn—O bonding) and better homogeneity of Mn is favorable to enhance the room temperature ferromagnetic response in $OP_{2.5}$-450.

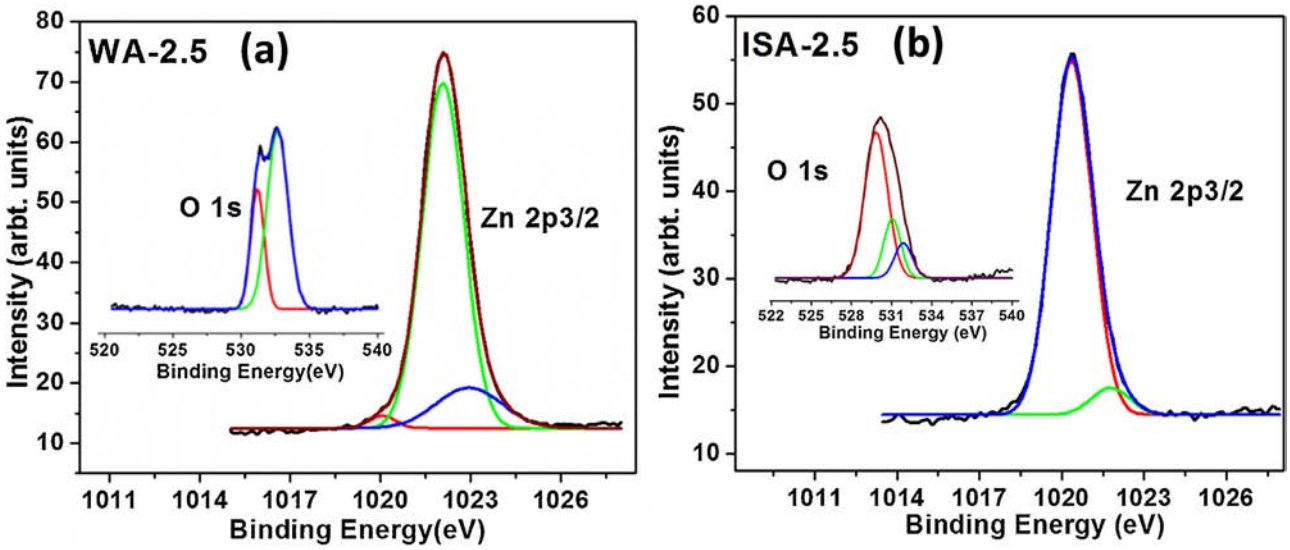

Fig. 5. Zn $2p_{3/2}$ and O 1s core level XPS spectra of ZnO:Mn thin films grown under ambient Ar:O_2 pressure of 2.5 mbar.

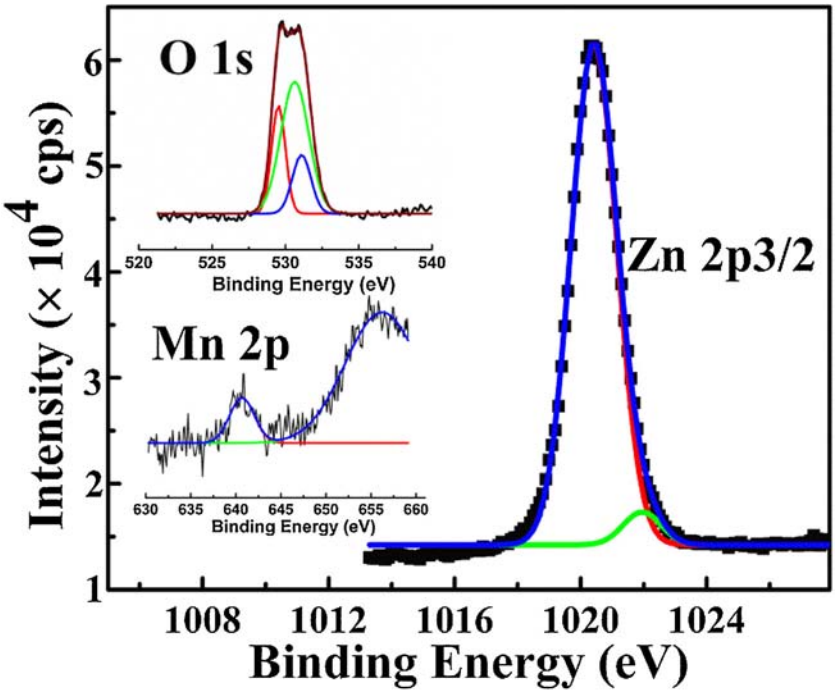

Fig. 6. Core level XPS spectra of Zn $2p_{3/2}$, O 1s and Mn 2p of $OP_{2.5}$-450.

From above discussion, we can infer that in-situ annealing provides sufficient thermal energy and diffusion path length for the ionic species to settle down at the lattice sites in ZnO host matrix for better material composition and improved oxygen stoichiometry.

3.5. VSM analysis

Room temperature ferromagnetic behavior of ISA and WA samples was investigated using the vibrating sample magnetometer (VSM) in the magnetic field range of 0–6000 G. The actual magnetic signal of all the thin film samples was obtained after subtracting the diamagnetic contribution from the silicon substrate. In-situ annealing seems to have a considerable effect on the ferromagnetic response of ZnO:Mn thin films in which the magnetic moment varies as a function of ambient gas pressure and substrate temperature.

The M-H curves, shown in Fig. 7, exhibit obvious hysteresis loops for ISA samples with a consistent increase in saturation magnetization with increasing ambient gas pressure (from 0.5 to 2.5 mbar). The values of saturation magnetization and field were estimated to be 18.83 μemu and 116.08 G, 34.07 μemu and 106.4 G, 37.63 μemu and 96.56 G, and 13.68 μemu and 128.39 G for ISA-1.5, ISA-2.5, $OP_{2.5}$-450 and $OP_{2.5}$-500, respectively. Hence, the temperature dependent variation in saturation magnetization was observed to be maximum for $OP_{2.5}$-450. Values of saturation magnetization and coercivity along with the shape of M-H curves suggest the presence of soft magnetic phase (weak ferromagnetism) in all the thin film samples. Ferromagnetic ordering is strongly correlated with the oxygen concentration and material composition (Zn—O bonding)

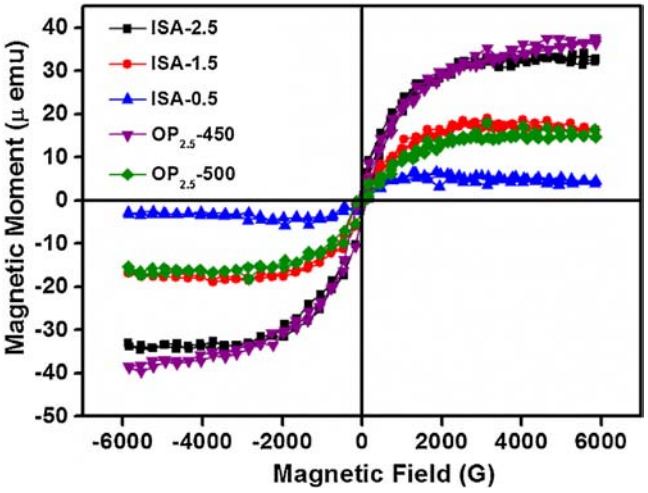

Fig. 7. M-H curves of ZnO:Mn thin films, with in-situ annealing temperature under different ambient Ar:O_2 gas pressures exhibiting RTFM.

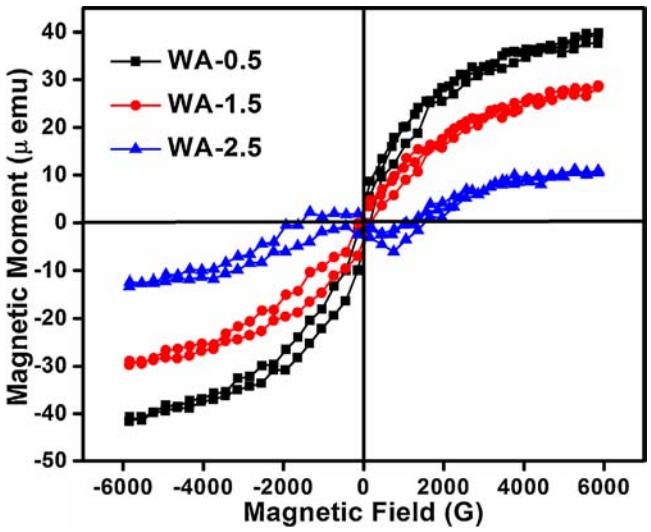

Fig. 8. M-H curves of as-deposited ZnO:Mn thin films under different ambient Ar:O_2 admixture gas pressures.

of the samples which leads to carrier mediated or defect-mediated ferromagnetism [23]. The combination of defect analyses based on XPS and PL results provides a good opportunity to clarify the physical nature of local magnetic moment. It seems that substrate temperature favors the room temperature ferromagnetism in samples with in-situ annealing with enhanced material composition. The better material composition (Zn—O bonding) and improved optical quality of ISA-2.5, among the other samples annealed at different pressures, can be cited as the possible reasons for better ferromagnetic response in this sample. However, the optical measurements show the presence of zinc vacancies (refer Fig. 3) which might be considered as the possible reason for better ferromagnetic response in this sample. In samples having zinc vacancies, Mn d level moves down in energy with the increase in zinc vacancies causing better hybridization between p orbital of oxygen and Mn d orbital in ZnO. This is very important for p-d exchange mechanism and yields spontaneous nearest-neighbor ferromagnetic exchange coupling [24]. Moreover, the location of oxygen vacancy (V_o) in ZnO host matrix alters the magnetic moment by the unpaired electrons whose wave function overlaps with that of magnetic ions in an anti-ferromagnetic way and plays an important role towards the net magnetic moment [25]. When the defect site (like V_o) is formed near the magnetic ion, more electrons will be transferred to 3d orbital as impurity spins and distributed in anti-ferromagnetic way. This will result in reduction of net magnetic moment. While for defect sites, formed relatively farther apart from the magnetic ions, relatively fewer electrons are transferred to the 3d orbitals of transition metals and act anti-ferromagnetically. Therefore, the net magnetic moment in ZnO:Mn thin film sample with oxygen vacancies far apart is more in comparison to those with nearer defect sites. The presence of defect sites like vacancies of oxygen and zinc and their role in ferromagnetic response lead to the defect mediated ferromagnetism.

However, in analyzing the temperature dependent variation of ferromagnetic response in thin films of $OP_{2.5}$-450 and $OP_{2.5}$-500, better ferromagnetic response, enhanced material composition and improved optical quality (without DLE spectra) was observed in $OP_{2.5}$-450. At this temperature, it seems that more oxygen diffused in ZnO is increasing the concentration of Zn—O bonding which, in turn favors stable ferromagnetic ordering. Moreover, the absence of DLE spectra in this sample rules out the contribution of oxygen or zinc vacancies towards the ferromagnetic response. Therefore, improved material composition, with enhanced Zn—O bonding, is possibly considered as the main source of p-d exchange interaction of Mn in ZnO. On the contrary, structural defects (vacancies and interstitials of oxygen) are activated at lower or higher temperatures which alter the functional properties of thin films.

Conversely, for non-annealed WA samples, a consistent deviation from stoichiometric material composition was observed which resulted in the presence of defect sites at nearer distance to magnetic impurities ultimately leading to reduced magnetic moment with increasing oxygen partial pressure. Fig. 8 shows that non-annealed thin films grown in relatively oxygen deficient environment (WA-0.5) has more ferromagnetic fraction at room temperature in comparison to those with oxygen rich environment (WA-2.5). The sp-d exchange interaction, when d-states of incorporated transition metals carry magnetization, gives a sizeable spin splitting of bands in the conduction (s-state) as well as in the valence (p-state) bands. The s-d interaction (follows from the spin-dependent Coulomb interaction) provides ferromagnetic exchange coupling between the delocalized s-state and the localized d-state and stabilizes the forming of oxygen vacancy-induced magnetic cluster [26] which can be the possible reason of ferromagnetic signal in WA-0.5. The sample with in-situ annealing at 400 °C (ISA-0.5) reduces the net magnetic moment which might be attributed to the insufficient oxygen diffusion from the ambience leading to more oxygen vacanceis. While for WA-2.5, a considerable increase in ferromagnetic response was observed after being deposited with in-situ annealing (ISA-2.5). It can be attributed to the better material composition and homogeneity of Mn in ZnO host matrix. In non-annealed WA-2.5 thin film, relatively larger concentration of chemisorbed oxygen in the form of hydroxyl species was observed which is validated by O 1s core level XPS spectra. Moreover, the enlarged concentration of defect sites like V_o, consistently reduces their distance from the magnetic ions which, in turn gives the opportunity to the corresponding electrons from oxygen vacancy to move in the d orbital of Mn ions as minority spins. These electrons will act anti-ferromagnetically and reduce the net magnetic moment. It might also be attributed to the fact that the magnetic interactions becomes weaker with increasing distance of defect sites from magnetic impurities (with increasing ambient gas pressure) as expected from the exchange interactions from the magnetic elements in semiconducting host matrix. To account for the small ferromagnetism in WA-2.5 samples, we have to consider the existence of relatively larger concentration of chemisorbed oxygen (hydroxyl species) in the form of O—H bonding or OH^- in ZnO host matrix which is validated by photoemission

analysis of O 1s core level XPS spectra. An isolated interstitial H^+ is stable in its +1 oxidation state while oxygen is in −2 state giving rise to O—H bonding with oxygen in ZnO host matrix or remaining at the interstitial position in the form of OH^-. The existence of H at the interstitial sites can mediate a strong short-ranged ferromagnetic spin-spin interaction between neighboring magnetic impurities through the formation of a bridge bond [27] which can be cited as the possible reason for the weak ferromagnetic signal observed in this sample (refer Fig. 8). In addition, small signatures of diamagnetic signal along with weak ferromagnetic response in WA-2.5 reveal the presence of higher concentration of zinc in its elemental form (refer XPS analysis) which has diamagnetic behavior. It can therefore, be inferred that the activation and concentration of a particular type of defect in PLD grown ZnO:Mn is sensitive to ambient gas pressure used and can be effectively reduced by in-situ annealing at 450 °C which can also alter the ferromagnetic exchange interactions, subsequently leading to change the origin of ferromagnetism.

4. Conclusions

Mn doped ZnO thin films were grown under different processing conditions on Si(100) substrate using PLD. The in-situ substrate temperature and argon-oxygen ambient gas pressure were found to affect the structural, compositional, optical, morphological and magnetic properties of ZnO:Mn thin films. The compositional and structural analyses revealed improved material composition, stronger texture and better crystallinity for thin film sample annealed at substrate temperature of 450 °C due to sufficient thermal energy provided to adatoms to settle down at appropriate lattice sites of ZnO host matrix. The detailed analysis of Zn $2p_{3/2}$ and O 1s core level XPS spectra revealed systematic increase in Zn—O bonding (material stoichiometry) in in-situ annealed (ISA) thin films which lead to reduction in oxygen vacancies in contrary to non-annealed (WA) thin films, in which the stoichiometry of the material was observed to be degraded with increasing ambient gas pressure. The magnetic measurements revealed that p-d hybridization between oxygen 2p and Mn 3d orbitals is stronger in in-situ annealed thin films with improved material composition and minimum structural defects under $Ar:O_2$ pressure of 2.5 mbar which is favorable for the better ferromagnetic response in ZnO-based spintronic materials.

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