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Alteration of Mn exchange coupling by oxygen interstitials in ZnO:Mn thin films

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ABSTRACT

The un-doped and Mn doped ZnO thin films, with oxygen rich stoichiometry, were deposited onto Si (1 0 0) substrate using spin coating technique. The structural analysis revealed the hexagonal wurtzite structure without any impurity phase formation. A consistent increase in cell volume with the increase in Mn doping concentration confirmed the successful incorporation of bigger sized tetrahedral Mn^{2+} ions (0.83 Å) in ZnO host matrix that was also endorsed by the presence of Mn $2p_{3/2}$ core level XPS spectroscopic peak. Extended deep level emission (DLE) spectra centered at ~627 nm confirmed the presence of oxygen interstitials. Moreover, the magnetic measurements of field dependent *M–H* curves revealed the origin of ferromagnetic ordering from Mn-defect pair exchange coupling with oxygen interstitials in ZnO host matrix.

1. Introduction

Dilute magnetic semiconductors (DMS) have recently attracted tremendous attention due to their possible applications in spintronic devices as the charge and spin of electrons are accommodated into single material for interesting magneto-optical and magneto-electric properties [1,2]. Soon after Dietl's prediction about the room temperature ferromagnetism (RTFM) in ZnO:Mn thin films heavily doped with holes[3], a lot of research work was started on ZnO based DMS. Wide band gap wurtzite phase ZnO is a strong piezoelectric and electro-optic material which with transition metal doping can be used as a multifunctional material in optoelectronics and spintronics [4,5]. There has been a considerable interest in the fabrication of transition metal doped ZnO thin films with RTFM for its implementation in spintronic devices [6]. Numerous studies have therefore been carried out to grow ZnO:Mn thin films due to large magnetic moment exhibited by manganese (Mn) [7,8]. However, one of the main obstacles in creating high quality ZnO-based optoelectronic and spintronic devices, is the unavailability of ferromagnetic ZnO:Mn thin films with significant hole carriers concentration. The main reason behind the difficulty in achieving the p-type conductivity is the presence of structural defects like oxygen vacancies and zinc interstitials which are unintentionally introduced during thin film growth, making ZnO inherently an n-type material. The RTFM in n-type ZnO:Mn thin films is reported to be limited at lower temperatures [9]. Some researchers have addressed this issue by reporting defect mediated RTFM due to zinc and oxygen vacancies [10,11]. In spite of RTFM in ZnO:Mn thin films reported by several groups [12–14], a non ferromagnetic behavior has also been reported in polycrystalline ZnO:Mn thin films at room temperature [15,16]. Subsequently, some researchers reported the origin of ferromagnetism due to impurity phases such as oxides of Mn and spinal phases ($ZnMn_2O_4$) [17]. Due to the controversial results indicated in literature, the origin of ferromagnetism is still in debate and is a matter of great concern. In addition, the lack of reproducibility of ferromagnetic signal in ZnO:Mn thin films prepared with the same manganese content and growth conditions put the question mark on the origin of the ferromagnetism.

In view of controversial results about the origin of RTFM in transition metal doped ZnO, the present paper aims to shed some light on the origin of ferromagnetism in Mn doped ZnO thin films grown by spin coating method. In view of Dietl's prediction [3] about the importance of holes in ZnO:Mn thin films, we report the origin of ferromagnetism in oxygen rich ZnO:Mn thin films to be due to Mn-defect pair ferromagnetic exchange coupling with acceptors (oxygen interstitials). The investigation of ZnO:Mn based DMS to optimize the synthesis and growth parameters of Mn doped ZnO nanocrystalline thin films is useful for spintronic applications.

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2. Experimentation

Mn doped ZnO thin films with wurtzite structure were synthesized using spin coating technique. The Mn-doped ZnO thin films were prepared for four different Mn doping concentrations of 0, 2, 5 and 10 at.% hereinafter referred as SG0%, SG2%, SG5% and SG10%, respectively. Zinc acetate dihydrate (90 mMol) and manganese acetate tetrahydrate (2.9 mMol) were mixed along with potassium hydroxide (280 mMol) at room temperature in an environment of methanol (50 ml) for the preparation of SG2% sample. The solution was continuously stirred using a magnetic stirrer for 3 h at 52 °C to get homogeneous mixing in solution. It was then cooled to room temperature and was allowed to age for 24 h. Similar coating solutions for thin films of SG5% and SG10% were prepared by the same procedure using suitable quantities of acetates and solvents. The thin films of these solutions were coated on Si (1 0 0) substrate at 3000 rev/min for 30 s using 6708D Desk-Top Precision Spin Coating System. After deposition with spin coater, the thin films were dried at 100 °C for 5 min. The procedure from coating to drying was repeated 5–8 times to reach the desired thickness of ~150 nm. The thin films were then annealed in air at 550 °C for 2 h to improve their crystalline quality.

The structural properties regarding the crystallinity of the thin films were analyzed using SIEMENS D5005 Cu K_α (1.504 Å) X-ray Diffractometer (XRD). Near band edge (NBE) and deep level emission (DLE) energy transitions in photoluminescence (PL) spectra, obtained using Hd–Cd (325 nm, 10 mW) laser as an excitation source, were used to study the variations in optical band gap and structural defects with varying Mn doping concentration. Kratos Axis-Ultra Spectrometer equipped with a focused monochromatic Al-K_α (1486.6 eV) X-ray beam (15 kV and 10 mA) was employed for X-ray photoelectron spectroscopy (XPS) to identify the surface stoichiometry and elemental oxidation states in Mn doped ZnO thin films. Surface morphology of the thin films along with the quantitative analysis of elements was characterized using a JEOL JSM 6700 field emission scanning electron microscope (FESEM) coupled with Oxford Instrument's energy dispersive X-ray (EDX) System. Furthermore, the field dependent magnetic characterization was performed using Lakeshore 7404 vibrating sample magnetometer (VSM) at room temperature to study the ferromagnetic ordering in ZnO:Mn thin films.

3. Results and discussion

3.1. XRD analysis

The XRD spectra of $Zn_{1-x}Mn_xO$ thin films for different Mn doping concentrations (x = 0.00, 0.02, 0.05 and 0.10) are shown in Fig. 1. The XRD profiles, showing hexagonal wurtzite structure, were matched well with space group $P6_3mc$ (no. 186) (ICSD # 82028) of wurtzite ZnO and no signatures of any impurity or binary zinc-manganese phase (including oxides of Mn and spinal phases) were observed. So the occurrence of impurity phases such as the oxides of Mn and spinal phase is ruled out in any of the doped samples. The texture coefficient of ZnO:Mn thin films was estimated to determine the preferred orientation of polycrystalline thin films using the formula proposed by Barret and Massalski [18]. The (1 0 1) peak was found

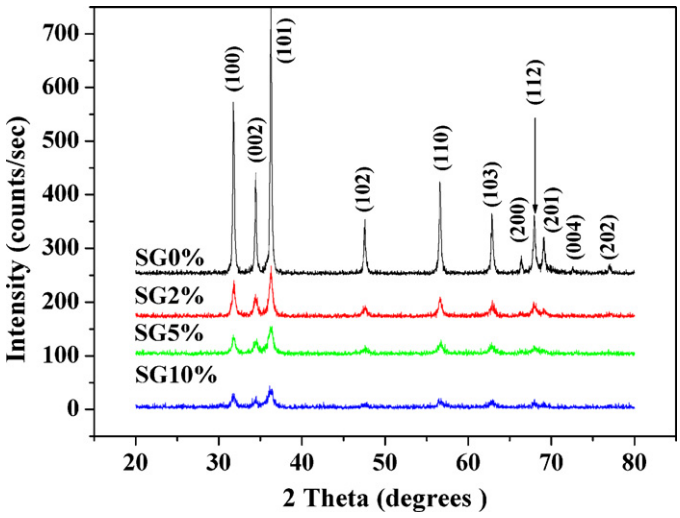

Fig. 1. XRD spectral profiles of un-doped and Mn-doped ZnO thin films.

to have higher texture coefficient indicating the preferred orientation of the thin films along this plane. Hence, the parameters such as diffraction peak shift, lattice parameters and lattice volume of ZnO:Mn thin films have been estimated for this peak. The lattice parameters, listed in Table 1, were estimated using the plane-spacing equation for hexagonal wurtzite structure of ZnO and the Bragg's equation. Highly textured peak centered at ~36.2° (characterizing the hexagonal wurtzite structure) was shifted toward smaller angles (indicating increasing d-spacing) with the increase in Mn doping content (refer Table 1). This peak shift suggests the incorporation of larger sized (0.83 Å) tetrahedral Mn^{2+} ions at the substitutional lattice sites of Zn^{2+} (0.74 Å) ions [19] resulting in increased interlayer spacing (d-spacing). In addition, the diffraction peak broadening (increase in FWHM) with increase in Mn content can be attributed to the decrease in average crystallite size and/or to the strain induced from the incorporation of Mn ions at Zn ion sites (size mismatching). The average crystallite sizes of the samples, determined from the FWHM of the diffraction peak centered at ~36.2° using Scherer formula, were estimated to be 17.01, 8.81, 7.01 and 6.17 nm for SG0%, SG2%, SG5% and SG10%, respectively. The lattice parameter 'a' and cell volume increased consistently with the increase in Mn content, as seen in Table 1, while the trend in variation of lattice parameter 'c' was inconsistent. The cell expansion reflects the incorporation of larger Mn^{2+} cations (0.83 Å) at the substitutional sites of Zn^{2+} (0.74 Å), without any degradation in the wurtzite crystal structure of host ZnO matrix.

3.2. PL analysis

PL spectra of un-doped and Mn doped ZnO thin films exhibit two emission bands in UV and visible (mostly in yellow spectral region) regions, as shown in Fig. 2. The UV emission peak, centered at ~376–384 nm (3.24–3.30 eV) for different Mn doping concentrations, originates from the radiative exciton recombination corresponding to the NBE exciton emission of the wide band gap ZnO. The intensity of the UV emission peak (refer Fig. 2) strongly

Table 1
FWHM and cell volume of ZnO:Mn thin films.

Sample name	Center of peak	FWHM	d-Spacing (Å)	Lattice parameter a (Å)	Lattice parameter c (Å)	Cell volume (Å^3)
SG0%	36.264	0.008554	2.4752	3.2489	5.2049	47.579
SG2%	36.261	0.016541	2.4754	3.2493	5.2047	47.588
SG5%	36.248	0.020784	2.4763	3.2509	5.2018	47.609
SG10%	36.209	0.023618	2.4788	3.2534	5.2062	47.722