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Quenching of surface traps in Mn doped ZnO thin films for enhanced optical transparency

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ABSTRACT

The structural and photoluminescence analyses were performed on un-doped and Mn doped ZnO thin films grown on Si (1 0 0) substrate by pulsed laser deposition (PLD) and annealed at different post-deposition temperatures (500–800 °C). X-ray diffraction (XRD), employed to study the structural properties, showed an improved crystallinity at elevated temperatures with a consistent decrease in the lattice parameter 'c'. The peak broadening in XRD spectra and the presence of Mn 2p3/2 peak at ~640 eV in X-ray Photoelectron Spectroscopic (XPS) spectra of the doped thin films confirmed the successful incorporation of Mn in ZnO host matrix. Extended near band edge emission (NBE) spectra indicated the reduction in the concentration of the intrinsic surface traps in comparison to the doped ones resulting in improved optical transparency. Reduced deep level emission (DLE) spectra in doped thin films with declined PL ratio validated the quenching of the intrinsic surface traps thereby improving the optical transparency and the band gap, essential for optoelectronic and spintronic applications. Furthermore, the formation and uniform distribution of nano-sized grains with improved surface features of Mn-doped ZnO thin films were observed in Field Emission Scanning Electron Microscopy (FESEM) images.

1. Introduction

Dilute magnetic semiconductors (DMS) have attracted great research interest due to their promising applications in spintronics. In these materials, the charge and the spin state of electrons are accommodated into a single material leading to interesting magnetic, magneto-optical and magneto-electric properties [1,2]. There has been a considerable interest in the fabrication of semiconducting ZnO for a variety of applications because of their fascinating properties. ZnO, with a direct band gap of 3.37 eV [3], has been found to be a useful candidate material for blue ultraviolet light emitters/detectors, transparent high power electronics and piezoelectric transducers. The low threshold for optical pumping and large exciton binding energy (60 meV) [4,5] allow lasing action in ZnO with extremely low pumping power at room temperature [6] and has been recognized as a promising photonic material in the UV region [7]. The wide band gap of ZnO makes it transparent in the visible range, which is maintained even at higher carrier concentrations, making ZnO a promising material to be used as a transparent conductor. These favorable optical and electrical properties allow ZnO to have wide applications such as transparent electrodes in flat panel displays and solar cells, thin film gas sensors and ultraviolet detectors [8]. Additionally, the high solubility of various 3d transition elements in ZnO makes it suitable for spintronic applications [9,10]. The biggest roadblock in processing of a fully ZnO based device is the unavailability of highly p-type conducting ZnO. The main reason behind the difficulty in achieving p-type conductivity is the presence of surface traps (native defects) such as oxygen vacancies and Zn interstitials which are unintentionally introduced during thin film growth process, making un-doped ZnO inherently an n-type material. So, quenching of surface traps by the incorporation of 3d transition element is essential for ZnO thin films to be used in optoelectronic and spintronic applications.

In this paper, we report the preparation and characterization of un-doped and Mn doped ZnO thin films with enhanced optical transparency due to the quenching of intrinsic surface traps. The wet chemical method [11] was used to synthesize nano-crystalline Mn-doped ZnO powders, which were later pelletized and sintered for making PLD targets. To the best of our knowledge, this method

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has not been used to prepare doped ZnO PLD pellets as the extensive literature search shows the use of solid-state reaction as the main method of preparation of doped PLD pellets. The powder obtained from wet chemical method offers homogeneous doping as compared to the powder obtained by solid-state reaction method. The influence of post-deposition annealing and the dopant concentration on the structural, compositional, photoluminescence and morphological properties of the thin films is investigated and presented.

2. Experimental details

2.1. Preparation of nanocrystalline Mn doped ZnO powder

Nano-crystalline Mn doped ZnO powder with wurtzite structure was synthesized through a wet chemical method. The Mn-doped ZnO powders were prepared for two different Mn doping concentrations of 2 and 5 at.%, hereinafter referred as SP-2% and SP-5%, respectively. The procedure for the preparation of SP-2% powder is as follows: zinc acetate dihydrate (15.79 g), manganese acetate tetrahydrate (0.52 g) and potassium hydroxide (12.96 g) were mixed in 800 ml of methanol. The solution was continuously stirred, using a magnetic stirrer, for 3 h at 52 °C. The solution was then cooled to room temperature and was allowed to age for 24 h to get precipitates. The fine precipitates were removed by centrifugation and washed repeatedly with distilled water to remove unreacted materials. The product was dried in an oven at 50 °C for 1 day. The zinc acetate dihydrate (Aldrich), manganese acetate tetrahydrate (Aldrich), potassium hydroxide (Baker), and methanol (Aldrich), in above mentioned preparation procedure, were used as received. The SP-5% powder was also prepared following the same procedure using suitable quantities of acetates and solvents. The un-doped and Mn dope powders of ZnO were then pelletized under a pressure of 10.5 metric tons and sintered at ~1000 °C for 12 h in air to get PLD targets.

2.2. Pulsed laser deposition (PLD) of thin films

The sintered pellets of Mn doped ZnO were fixed on the gyrating target holder and ablated by second harmonic Nd:YAG laser (532 nm, 26 mJ) at a pulse repetition rate of 10 Hz. The substrate holder was set to rotate at a speed of about 33 rpm to ensure uniform thin film deposition. The thin films were deposited on Si substrate for a constant ablation period of 90 min in ultra high vacuum (10^{-6} Torr). The Si (1 0 0) substrates were sequentially cleaned in ultrasonic bath with ethanol, acetone and de-ionized water, separately, at a temperature of 45 °C for 15 min each, before being mounted to the substrate holder in the PLD chamber. Deposited thin films were annealed at different temperatures (500, 600, 700 and 800 °C) for 4 h in air.

The crystalline phase of thin films was analyzed using a SIEMENS D5005 Cu Kα (1.504 Å) X-ray Diffractometer (XRD). Near band edge (NBE) energy transitions in Photoluminescence (PL) spectra, measured using Hd–Cd (325 nm, 10 mW) laser, were used to study the variation in surface traps (intrinsic defects) and optical band gap with dopant concentration. 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 and 10 mA), was used to identify the surface stoichiometry and elemental oxidation states of thin film samples. The morphology of thin films was characterized using a Joel JSM 6700 Field Emission Scanning Electron Microscope (FESEM).

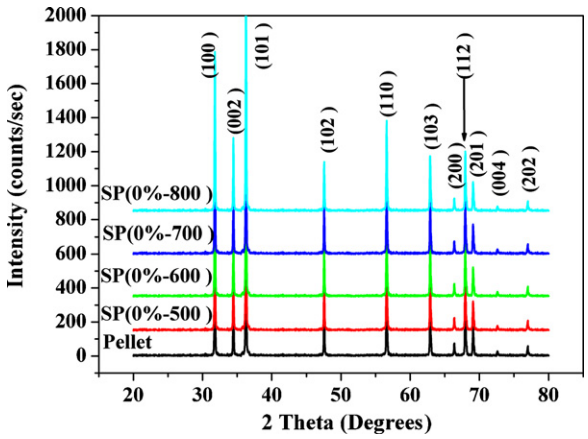

Fig. 1. XRD spectra of polycrystalline SP-0% ZnO thin films annealed at different temperatures (500–800 °C).

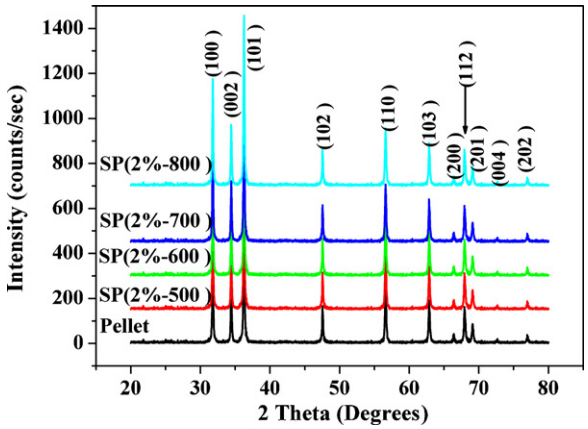

Fig. 2. XRD spectra of SP-2% ZnO thin films annealed at different temperatures (500–800 °C).

3. Results and discussion

3.1. Structural analysis

The XRD spectra of ZnO thin films doped with different Mn concentrations and annealed at 500–800 °C are shown in Figs. 1–3. The XRD peaks corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0),

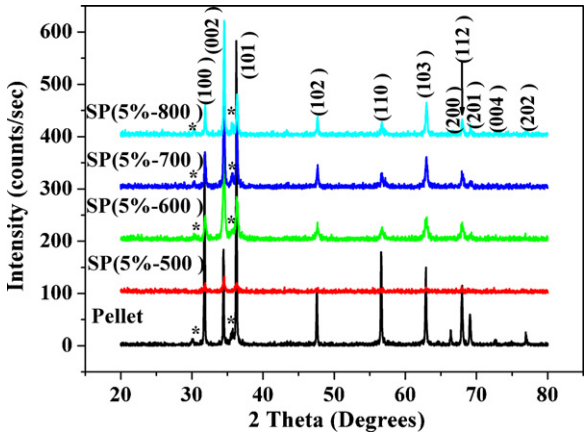

Fig. 3. XRD spectral profiles of SP-5% ZnO thin films annealed at different post-deposition annealing temperatures (500–800 °C) showing the formation of $Zn_2Mn_3O_8$ impurity phases.