

COMPOSITION, OPTICAL AND PL PROPERTIES OF Mn DOPED ZnO NANO CRYSTALLINE THIN FILMS PREPARED BY SOL-GEL METHOD

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Abstract: In recent years dilute magnetic semiconductors have paid much attention due to their complementary properties of semiconductors and ferromagnetic behavior. There are many techniques used to deposit high-quality ZnO thin films. One of these based on chemical method for the production of ZnO thin films is the Sol-Gel. ZnO:Mn nano films doped with different manganese concentrations were deposited on glass substrates by the spin-coating method. The precursors for the synthesis of ZnO:Mn are: Zinc acetate dehydrate, manganese acetate tetrahydrate, 2-methoxyethanol and monoethanolamine as zinc and manganese source, solvent and stabilizer respectively. Characterization techniques of XPS and UV-Vis-NIR measurements were done to investigate the effect of doping concentration on the composition and optical properties of ZnO:Mn nano films. X-ray photoelectron spectroscopy (XPS) pattern suggest that Mn²⁺ ions were successfully incorporated into the lattice position of Zn²⁺ ions in ZnO lattice. The optical absorption studies revealed that the energy band gap of the films followed the Vegard's law. The optical band gap of the Mn-substituted ZnO samples increases with increase in doping concentration of manganese. Room temperature photoluminescence is observed for the Mn doped ZnO thin films. The electrical resistivity of ZnO films varied with Mn-doping.

Keywords: Zinc oxide, Sol-gel, Spintronics, DMS and Optical band gap

1. Introduction

Diluted magnetic semiconductors (DMSs) are [1] formed by substitutional introduction of a small percentage of transition metal (TM) magnetic ions into a compound semiconductor. Due to the host sp-TM d interactions in the DMSs, ferromagnetism can be produced [2]. Diluted magnetic semiconductors (DMSs) have attracted much attention recently because in these materials new function can be added by transporting and controlling various types of spin states [3]. In recent years, ZnO has become a particularly interesting metal oxide material because of the unique properties. ZnO has a semiconductor with a wide band gap (3.3eV), large exciton binding energy, abundant in nature and environmentally friendly. These characteristics make this material attractive for many applications such as solar cells, optical coatings, photo catalysts, anti-bacterial activities, electrical devices, active medium in UV semiconductor lasers and in gas sensors [4]. The theoretical prediction which were carried out by Dietl et al. [5] showed that ZnO can exhibit ferromagnetism at room temperature with a manganese doping concentration of 5% and this has increased the attention on oxide based magnetic semiconductors. In recent times, a number of transition metal ions such as Mn²⁺, Co²⁺, Ni²⁺, V³⁺ and Fe³⁺ have been introduced into the ZnO lattice to form the required dilute magnetic semiconductors. Among these ions, the incorporation of Mn²⁺ into the ZnO lattice promises to lead to very interesting and novel magnetic, electrical and optical properties. Owing to its half-filled 3d shell having the largest ionic moment [6].

There are a number of reporters on the growth of Mn doped ZnO thin films using pulsed laser deposition (PLD), RF magnetron sputtering, molecular beam epitaxy (MBE), chemical vapor deposition (CVD), spray pyrolysis, electro chemical deposition and sol-gel process. The sol-gel process is simple and inexpensive in fabrication, capable of producing a large number of samples, has easier composition control and an accurately controlled mole ratio, has high solubility, better homogeneity, a lower processing temperature, and has a general advantage for large area deposition and thickness of the films. Hence in the present study, an attempt has been made to prepare Zn_{1-x}Mn_xO films using a simple and cost effective process, sol-gel process with different 'Mn' compositions. The composition, optical and PL properties of the grown layers were investigated and discussed.

II. Experiments

The Mn-doped ZnO (Zn_{1-x}Mn_xO) precursor solutions were prepared as follows. Zinc acetate dehydrate (Zn(CH₃COO)₂·2 H₂O, 99.9%) and manganese acetate tetrahydrate (Mn(CH₃COO)₂·4 H₂O, 99.9%) were dissolved in 2-methoxyethanol and this solution was stirred for 1h at 65°C, and then 3h at RT. We added monoethanolamine (NH₂CH₂CH₂OH) as a stabilizer to the solution. Mn doping was achieved by the introduction of appropriate amount of manganese acetate tetrahydrate. In the process of doping, Mn content was varied from 0 to 20% of molar weight. Mn-doped ZnO films were deposited on corning glass substrates by spin coating at RT, with a spinning rate of 3000 rpm for 30s. Wet films were heated in air at 300°C for 5 min to remove organic materials in the film. This procedure was repeated 10 times to achieve desired film thickness. The elemental composition and its uniformity across the layer thickness was measured using AXIS Ultra Instruments X-ray photoelectron spectroscopy. The surface morphological studies of the films were carried out using Veeco atomic force microscope. Hitachi U:3400 UV-Vis-NIR spectrophotometer was employed for obtaining optical data and evaluating different optical parameters. The FLUOROLOG Fluorimeter was used to study the photoluminescence of the experimental films. Studies on the electrical behavior of the films was carried out using four probe method with silver contacts.

III. Results and discussion

The XPS spectra were measured for studying the chemical bond configuration and composition of doped thin films. Fig.1 shows the wide scan XPS spectrum of $Zn_{0.85}Mn_{0.15}O$ film revealed two strong peaks at the binding energies 1021.7 eV and 1047.4 eV that respectively correspond to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ lines, in addition to other normal and Auger reflections. Reflections corresponding to Mn $2p_{1/2}$ and Mn $2p_{3/2}$ states were also observed at 654.4 eV and 641.6 eV respectively, which confirms the presence of manganese in Mn^{2+} state. The O 1s peak located at an energy of 529.79 eV corresponds to Zn-O bonding rather than pure oxygen. Chen et al. [7] reported on the XPS study of ZnO:Mn thin films prepared by sol-gel method. The XPS spectra of ZnO:Mn films with the Mn-doping concentration varying from 0.8 to 5 at. % indicated that peaks located at about 640.2 eV correspond to the Mn $2p_{2/3}$ peak. This implies that the layers had uniform oxidation state of Mn^{2+} rather than Mn^{3+} or Mn^{4+} . The binding energy of Mn^{2+} hardly changed with the increase of doping concentration. The intensity of Mn $2p_{2/3}$ peak in the spectra increases with the increase of doping concentration. Also the position of O 1s peak moved slightly to higher binding energy side with the increase of doping concentration. This might be attributed to the lattice distortion due to the replacement of Zn^{2+} by Mn^{2+} and the development of ferromagnetism because of Mn ions. A similar observation was reported by Wang et al. [8] in Mn-doped ZnO films prepared by sol-gel method where the O 1s peak was slightly shifted towards lower binding energy side after 1% Mn doping. This was considered to be due to the lattice distortion in the layers with doping.

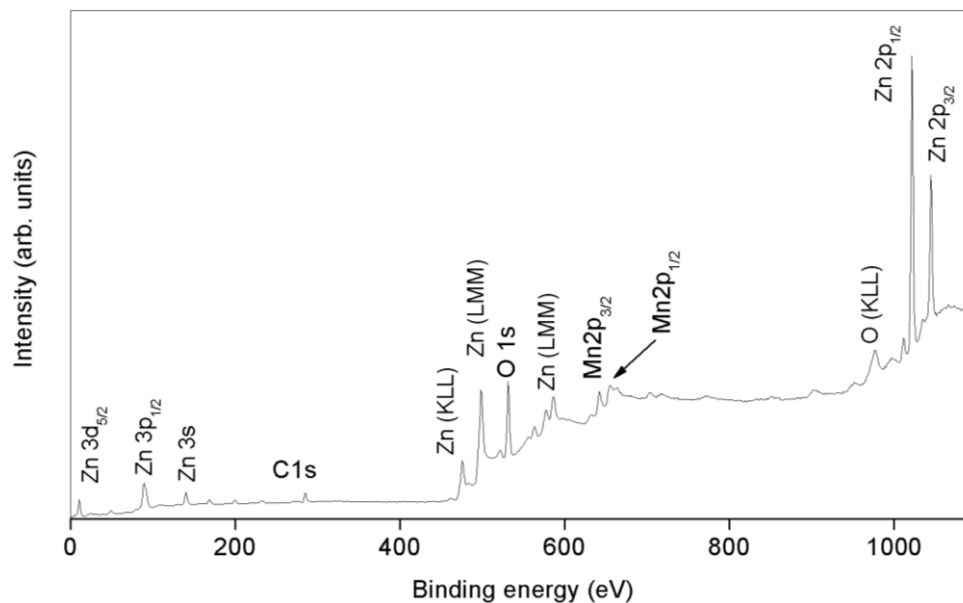


Fig. 1. XPS spectrum of $Zn_{1-x}Mn_xO$ film ($x=0.15$)

The absorption coefficient, α in the strong absorption region was evaluated from the optical transmittance data using Lambert's principle,

$$\alpha = -(1/t) \ln T \quad (3.1)$$

where T is the transmittance and ' t ' is the thickness of the film. The absorption coefficient α in the low energy range follows the well known exponential law, that is, the Urbach tail expressed by

$$\alpha = \alpha_0 \exp (hv/E_0) \quad (3.2)$$

where E_0 and α_0 are characteristic parameters of the material, represented as the Urbach energy width of the exponential tail and Urbach absorption energy. The type of optical transition and the energy band gap of the films can be determined from the dependence of absorption coefficient, α on the photon energy, $h\nu$. The direct or indirect nature of optical transition between parabolic bands can be studied using the relation,

$$(\alpha h\nu) = A(h\nu - E_g)^x \quad (3.3)$$

where E_g is the optical band gap, $h\nu$ is the photon energy and A is a constant. In the present study, the variation of absorption coefficient with photon energy followed the relation when $x=1/2$, indicating that the transition corresponds to a directly allowed transition.

The energy band gap was determined from the plots of $(\alpha h\nu)^2$ versus $h\nu$ in which the extension of linear portion of the plot onto the energy axis gives the energy band gap of the material. Fig. 2. shows the change of $(\alpha h\nu)^2$ with the incident photon energy, $h\nu$. The variation of energy band gap of $Zn_{1-x}Mn_xO$ films with 'Mn' composition was found to be linear, which is due to the fact that the band gap of MnO (4.2 eV) is greater than that of ZnO (3.3 eV) [9]. The optical band gap of the films varied in the range, 3.23 - 3.41 eV when the composition of 'Mn' varied from 0.0 to 0.20. The increase in band gap from bulk ZnO with dopants can be attributed to the sp-d spin exchange interaction between the band electrons and localized spin of the transition metal ions. At higher 'Mn' doping composition ($x \geq 0.15$), the variation of energy band gap, E_g was found to be nonlinear (Fig. 3). This nonlinearity in the energy band gap was explained by Avrutin et al. in $Zn_{1-x}Mn_xO$ layers grown by molecular beam epitaxy. According to him, at higher Mn-doping concentrations, majority of the Mn atoms do not substitute Zn lattice sites, and

part of them are incorporated into Mn-rich precipitates so that only a fraction of substituted Mn determines the fundamental absorption edge in these layers [10].

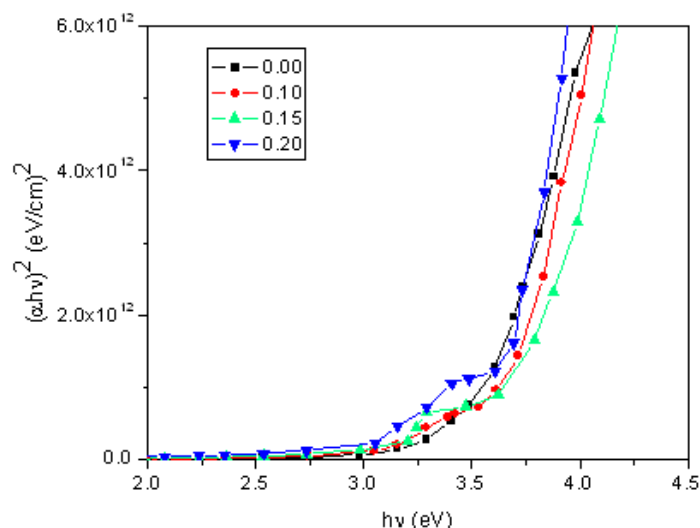


Fig. 2. $(\alpha hv)^2$ vs $h\nu$ plots of $Zn_{1-x}Mn_xO$ films.

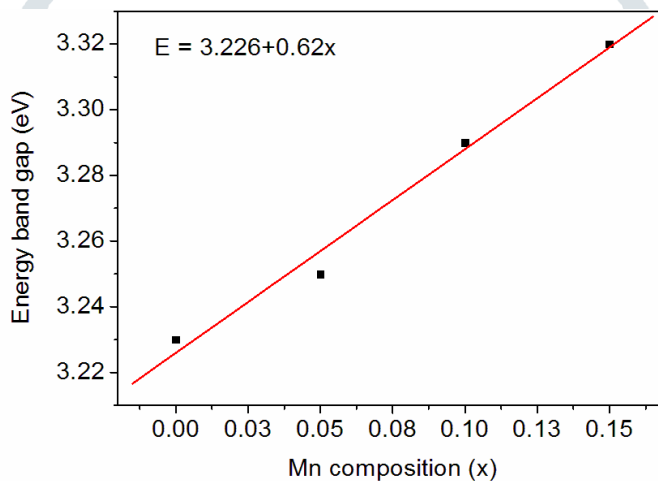


Fig. 3. Change of energy band gap with Mn-content in $Zn_{1-x}Mn_xO$ films.

Fig. 4. shows the room temperature photoluminescence spectra of $Zn_{1-x}Mn_xO$ layers prepared at three typical Mn-doping concentrations using the excitation light of 325 nm wavelength. The films showed two emission bands, one is in the UV region and the other in the visible region. The observed UV band can be assigned to the near band edge emission in the ZnO host material and the visible emission in the green band due to the emission from oxygen defect states [11].

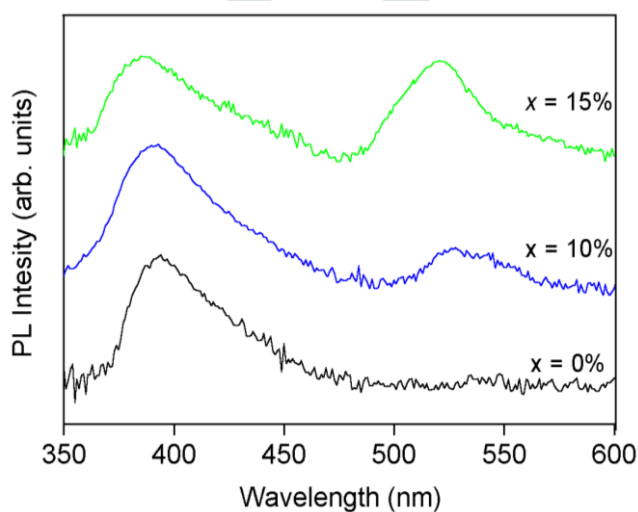


Fig. 4. Photoluminescence spectra of $Zn_{1-x}Mn_xO$ films

The electrical properties of a semiconductor can be highly affected by doping. Fig. 5 shows the resistivities of $Zn_{1-x}Mn_xO$ films deposited with different Mn composition. All the as-grown layers exhibited n-type electrical conductivity. It is clear that the electrical resistivity varied in the range, 10^4 - 10^7 Ω cm with increase of dopant concentration from 0 at. % to 20 at. %.

know that the valence of Zn^{2+} and Mn^{2+} are the same and the substitution of Mn^{2+} for the group II cation of Zn could not generate or consume carriers in ZnO. However, the electrical properties of ZnO films change so much after doping with Mn. The increase of the resistivity should not be related with the charged carriers formed from the substitution of Mn for Zn. It has been reported [12] that Mn is a deep donor in ZnO with ionization energy around ~ 2.0 eV at room temperature, which significantly decreased the concentration of charged carriers (intrinsic donors, interstitial zinc or oxygen vacancy). Deep donors may modify the concentration of the intrinsic defects at the grain boundaries, thereby decreasing the donor concentration and increasing the acceptor density. This may be the reason for an increase in electrical resistivity. Besides this, there is also a possibility that Mn at the grain boundaries may produce electrical barriers, which increases scattering of the carriers, and thus increasing the resistivity. For Mn-compositions > 20 at. %, the electrical resistivity could not be measured.

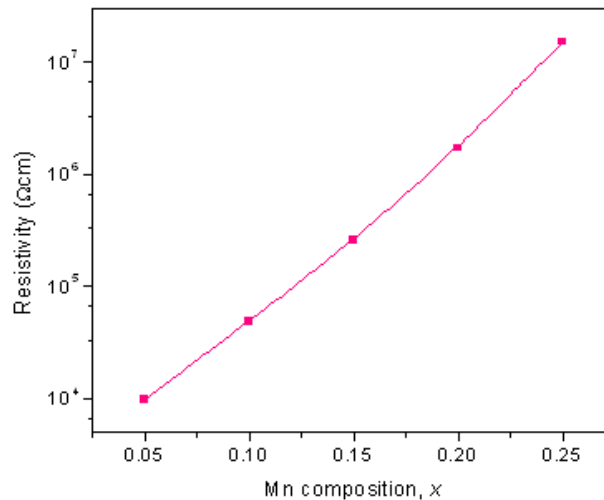


Fig. 5. Variation of electrical resistivity with Mn-composition.

IV. Conclusions

Mn doped ZnO thin films were deposited on glass substrate by sol-gel method. XPS results reveal that the films are free from the formation of secondary phase and indicate Mn^{2+} substitute for Zn^{2+} of ZnO host. Optical properties indicate that band gap of the Mn doped ZnO thin films were blue shifted compared with the undoped ZnO thin films band gap. PL spectra were investigated at room temperature. A broad UV peak ascribed to the free exciton emission was observed in the doped ZnO thin films. The electrical resistivity of ZnO films increases with Mn-doping.

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