

SYNTHESIS AND STRUCTURAL PROPERTIES OF ZNO:MN NANO FILMS GROWN 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. ZnO:Mn nano films doped with manganese different concentrations were deposited on glass substrates by the spin-coating method. The precursors for the synthesis ZnO:Mn are: Zinc acetate dehydrate, manganese acetate dehydrate, 2-methoxyethanol and monoethanolamine as zinc and manganese source, solvent and stabilizer respectively. Characterization techniques of XRD and EDX measurements were done to investigate the effects of Mn doping concentration on the structural properties of ZnO:Mn nano films. The XRD patterns of all nano films show the crystallization behavior and are hexagonal wurtzite structure for different x, without existing other phases. The average crystallite size was also estimated by measuring fullwidth at half maxima of the intense diffraction peaks in all the compositions using Scherrer formula. Our results reveal that with high percent manganese not only the degree of crystalline decreases but also peak broadening occurs.

Keywords: Zinc oxide, Sol-gel, Semiconductors, Spintronics, DMS

1. Introduction

The diluted magnetic semiconductors (DMSs) have attracted much attention recently because in these materials new functions can be added by transporting and controlling various types of spin states. In DMS materials, a non-magnetic semiconductor is doped with magnetic ions. These materials have resulted in the emergence of a new field of semiconductor spin-electronics involving the use of spin states inside semiconductor materials. Among these materials Mn doped II–VI and III–V semiconductors have been extensively studied [2, 3]. However, the Curie temperatures (T_c) of these materials have been limited to 140 K, which is far too low for practical device applications [1-4]. A theoretical prediction, by Dietl et al. [5], that hole-mediated Mn-doped ZnO and GaN can achieve Curie temperatures well above the room temperature initiated intense experimental work on a variety of doped diluted magnetic semiconductors. Subsequently, the values of T_c above room temperature were reported in Co-doped TiO₂ [6, 7], ZnO [8, 9] and Mn-doped GaN.

ZnO, an II-VI compound semiconductor with a wide band gap of about 3.4 eV, is an attractive material for applications in optical devices such as blue-, violet, and UV- light emitting diodes (LEDs) and laser diodes (LDs). ZnO is also a strong piezoelectric material. Thus, transition metal doped ZnO has the potential to be a highly multifunctional material with coexisting magnetic, semiconducting, electromechanical and optical properties. A number of workers have therefore investigated the ferromagnetic properties of Mn-doped ZnO in the last few years. The samples have been synthesized in the bulk and thin film forms and a wide range of magnetic properties including room temperature ferromagnetism have been reported [10-14]. Similar, widely varying results have been reported on bulk samples also. Recently, Chen et al. [15] have studied the effect of sintering temperature and atmosphere on the magnetic properties of Mn-doped ZnO. 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 structural and compositional behaviour of the grown layers were investigated and discussed.

II. Experiments

The Mn-doped ZnO(Zn_{1-x}Mn_xO) x=0.00, 0.01, 0.03, 0.05,0.07 precursor solutions were prepared as follows. Zinc acetate dihydrate (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 mono ethanolamine (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 0to10% 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 at300°C for 5 min to remove organic materials in the film.This procedure was repeated 10 times to achieve desired film thickness. The structural properties of the films were carried out using Siemens X-ray diffractometer and Veeco atomic force microscope.

III. Results and discussion

The XRD results reveal that all the films are single crystalline with a hexagonal wurtzite structure and have (002) preferred orientation along the c-axis. Within the XRD detection limit, no extra diffraction peak from Mn-related second phases

was observed. This indicates that Mn²⁺ substituted for Zn²⁺ of ZnO host without changing the wurtzite structure. As the Mn content increase, the diffraction intensity from ZnO (002) peaks of the samples is getting weaker, which indicates that the film crystallinity is deteriorated with more Mn incorporation. The full-width at half-maximum (FWHM) of (002) peaks are increased for the Zn_{1-x}Mn_xO films with Mn doping content $x = 0.00, 0.10, 0.15, 0.20,$ and $0.25,$ respectively. Small peak broadening occurs with an increase of the Mn content. This small degree of broadening occurs as a result of increasing strain in the film due to Mn incorporation in the Zn lattice site [16]. This indicates that the crystal quality decreases with an increase of Mn content in the films. In addition, a slight shift of (002) peak positions related to the change of lattice spacing was observed. This is probably due to the substitution of the relatively large ionic radii Mn²⁺ (0.080 nm) ions at the smaller radii Zn²⁺ (0.074 nm) sites expands the lattice parameter, leading to a small increase in the c-axis lattice constant with the Mn content. The weaker (002) peak intensity and the slight shift of (002) peak positions may imply that Mn²⁺ incorporates in to the ZnO lattice and substitutes the Zn²⁺ site.

The crystallite size (D) of Zn_{1-x}Mn_xO films prepared with different Mn-doping contents, x were calculated using the Scherrer's formula. The crystallite size decreased with increasing Mn doping content.

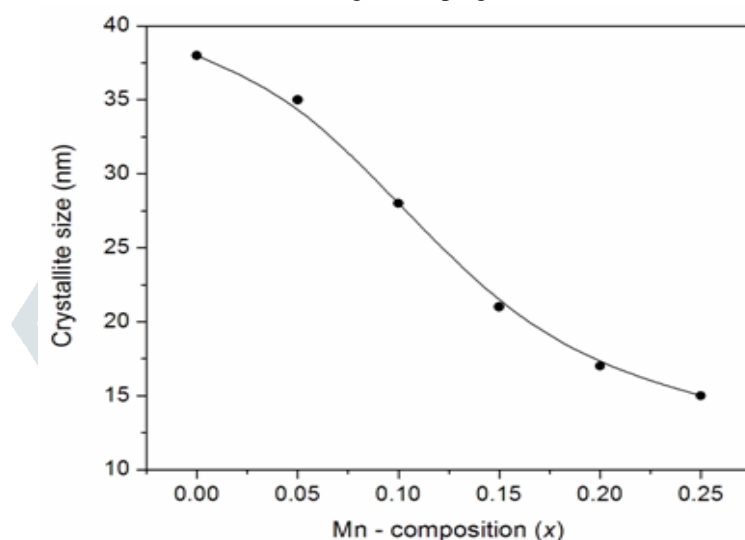


Fig.2. Variation of Crystallite size with Mn-composition.

The surface morphology of Zn_{1-x}Mn_xO films was examined by the atomic force microscope (AFM). Fig. 3 shows the typical AFM images of the Zn_{1-x}Mn_xO ($x=0.10, 0.20$) film. It can be seen from Fig. 3 that the surface of the films seems to be uniform without any cracks with fine grains. The average grain size was found to be 30 and 22 nm for Mn doping content $x=0.10$ and $x=0.20,$ respectively.

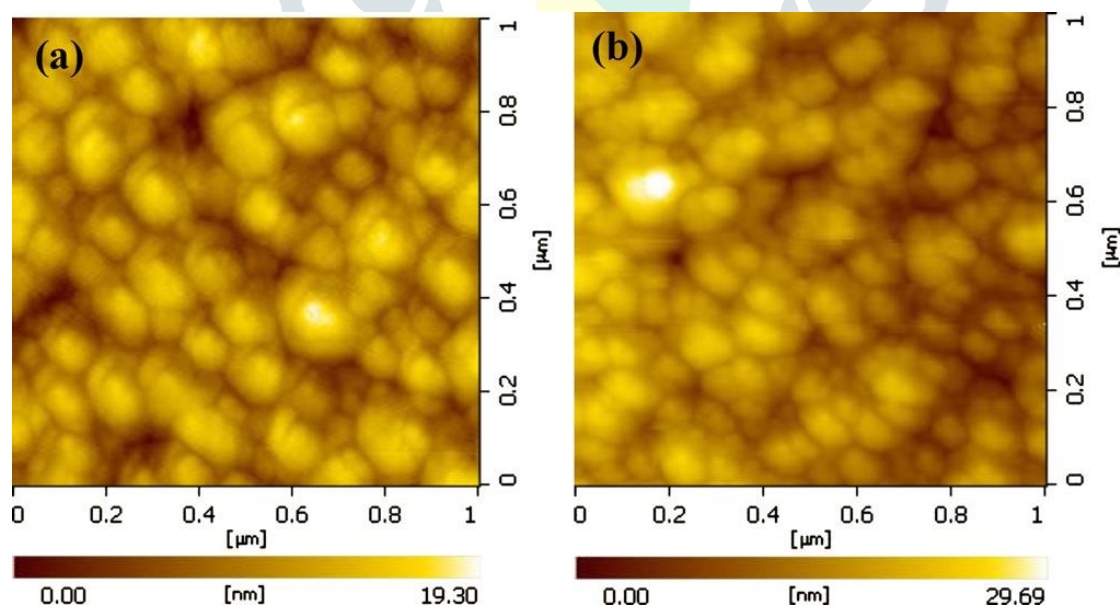


Fig. 3. The AFM images of the Zn_{1-x}Mn_xO films. (a) $x=0.10,$ (b) $x=0.20.$

IV. Conclusion

Mn-doped ZnO thin films were deposited on glass substrate by the sol-gel method. XRD, SEM and AFM characterization reveals that all of the samples have a polycrystalline hexagonal wurtzite structure and the high quality thin films are obtained with high crystallinity and low surface roughness.

V. Acknowledgements

This work was supported by UGC-SERO in the form of a Minor research project.

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