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Research Paper

Structural Properties of ZnO - Mn Films Synthesised by Spray Pyrolysis Method

Physics

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ABSTRACT

This Paper emphasizes the detail study of synthesis and characterization of Mn doped ZnO thin film. Undoped and ZnO: Mn thin films with different Mn content (5, 10 and 15 mol %) were grown on glass substrates by spray pyrolysis technique. Here we have doped Mn in 5, 10 and 15 mol% in for undoped, 5, 10 and 15 mol% of Mn in ZnO respectively. Characterization technique of XRD measurement was done to investigate the effect of Mn doping on the structural properties of Mn: ZnO thin films.

1.1 Introduction

ZnO, a wide band gap (Eg = 3.3 eV) semiconductor is a potential candidate for opto - electronics devices [1]. Large exciton binding energy (60 meV), strong room temperature luminescence, high electron mobility, good transparency etc. are some of the advantages of ZnO [2]. Accordingly it has immense potential in different applications in photo thermal conversion systems, heat mirrors, hetro-junction solar cells, transparent electrodes, blue/UV light emitter device, solid state sensor, transducer etc. [3]. Pure zinc oxide thin films have certain limitations in their application. In order to widen the potential areas where ZnO thin films can be applied, dopant ions have to be incorporated into them to obtain certain desired properties like wider or narrower band gap, higher optical absorbance, lower or higher melting point etc. Mn doped ZnO (Zn1-xMnxO) has also been found as one of the most promising material for spintronic devices retained at room temperature [4]. There are continuous efforts to detect the origin of the observed FM in Mn doped ZnO systems. But like origin of magnetism, another debatable issue is the nature of variation of Eg with Mn concentration.

In the spray pyrolysis technique, the raw materials which are usually a chloride or acetates compounds are dissolved in water. Then, the droplets of the aqueous solution decomposed after falling on the hot surface and consequently formed the thin film. The spray pyrolysis has the advantages such as cheapness, safeness, simplicity and possibility to use in industry.In this work, ZnO and ZnO: Mn thin films have been prepared on the glass substrate using spray pyrolysis method [5]. We put the emphasis on Mn concentration influence on the structural as well as optical parameters for opto-electronic application.

1.2 Experimental

To synthesize Zn1-xMnxO (x = 0.00, 0.05, 0.10, 0.15) thin films by sol-gel technique stoichiometric amount of zinc acetate Di-hydrate and manganese acetate Di-hydrate [Mn(CH3COO)2.2H2O] was added to a solution containing 2-propanol and Di-ethanolamine (DEA). DEA was used as the solution stabilizer. All the chemicals used in this paper are of sigma-aldrich having purity more than 99.99 %. The resultant solution was mixed thoroughly with a magnetic stirrer at room temperature for 3 hours and kept for 48 hours. Glass substrate was used for film deposition. The substrate was cleaned, before deposition , by ultrasonic cleaner in equi-volume acetone and alcohol and through rinsing in de-ionized water. The cleaned substrate was alternatively dipped in zinc chloride solution and hot NaOH solution. One complete set of dipping cycle involves dipping in zinc chloride bath for 2 seconds and dipping in sodium hydroxide bath for 2 seconds. The total concentration of the solution was kept at 0.5 mol. The substrate temperature was maintained at 500°C during the deposition. Compressed air was used as a carrier gas with an air flow rate of 40 lbs/in^2. The solution was sprayed onto the substrate in several spraying cycles of 3 sec, followed by an interval of no spray for 1 min, which avoided the strong cooling of the substrate due to the continuous spray. The films were sprayed for 3 h with the above systematic steps.

The x-ray diffraction profiles of the pure and doped samples were recorded using Ni-filtered Cu-Kα radiation from a highly stabilized and automated (Bruker D8 diffractometer) operated at 40 kV and 20 mA. The experimental peak positions were compared with the standard JCPDS files and the Miller indices were indexed to the peaks.

1.3 Results and Discussions

1.3.1 X-Ray Diffraction

Fig. (a) shows the XRD patterns of the undoped and ZnO thin films with 5, 10 and 15 mol % of manganese concentration grown at 500°C on glass substrate. The major peaks in XRD patterns are in close agreement with JCPDS data file (file No 36-1451) for ZnO powder corresponding to the reflection peaks of the Wurtzite structure which are indexed in Fig.(a). All four films exhibit random orientations, because glass substrates allowed the films to crystallize in {002} orientation. While, decreasing {002} peak intensity with the presence of Mn atoms in structure is evident. The preferencial c-axis orientation has been also observed in undoped ZnO thin films grown by other deposition techniques [6]. In this case, Mn ions prevent the crystallization from orienting {002} reflection plane.

The shifting of the peak position to lower angle with increase in Mn doping concentration indicates the expansion of the lattice parameter.Increase in c axis lattice parameter with increasing Mn concentration in Zn1-xMnxO thin films. The ionic radii of Mn^2+ ions (0.66 A°) are larger than that of Zn^2+ ions (0.60 A°) [1]. Thus, such increase of lattice parameter and hence the corresponding expansion of the unit cell volume of the Zn1-xMnxO samples with increasing Mn doping is expected. Moreover, crystalline quality of Mn doped ZnO films decreases with increasing Mn doping. Actually, the XRD in Fig. (a) shows that when Mn concentration is increased, intensity of the XRD peak decreases monotonously. Also width of the obtained XRD peaks shows a systematic broadening with increasing doping concentration. These two concurrent observations signify the degradation of the crystalline quality. It is probably associated to the lattice disorder and strain induced in the ZnO lattice due to the substitution of Zn^2+ ions by comparatively higher ionic radius of Mn^2+ ions .

Utilizing the X-ray diffraction data, the average particle size was estimated from Williamson-Hall equation :

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\epsilon Sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.1)$$

Where λ is the wavelength of radiation used (1.524 A° for Cu-Kα radiation used), k is the Scherer constant, β is the full width at half maximum (FWHM) intensity of the diffraction peak for which the particle size is to be calculated, Θ is the diffraction angle of the concerned diffraction peak, D is the crystallite dimension (or particle size) and € is the micro-strain. The lattice constants determined from XRD data, the average crystalline size calculated from Scherer's formula are summarized in table 1.1.

1.3 Result and Discussion

The primary aim of the present investigation was to explore the possibility of doping ZnO with manganese by spray pyrolysis method. Mn doped ZnO films with different percentage of Mn content (0 %, 5 %, 10 % and 15 %) could be successfully synthesized through this technique. The films had good adherence to the substrate. The XRD revealed that despite the Wurtzite single phase structure, Mn ions prevent the crystallization from c-orienting. The lattice parameters and unit cell volume increases with increasing Mn concentration. It indicates increase in Mn incorporation with increasing Mn doping. The thin films were characterized by X-Ray diffraction (XRD) which indicate that sol-gel ZnO films have potential applications such as catalyst and transparent electrodes in optoelectronic devices.

Table 1.1: Structural Studies for Zn Films by using XRD analysis

Mn Content (mol%)	0.0	5.0	10.0	15.0
[002] Peak Position (°)	36.64	34.40	34.52	34.48
Lattice Const. a (A°)	3.2400	3.2425	3.2420	3.2390
Lattice Const. c (A°)	5.1750	5.1768	5.1760	5.1765
Crystalline size (nm)	29.25	24.07	24.72	25.36

Table 1.2: Thickness of Sprayed Undoped ZnO and ZnO thin films with different Mn content

Mn Content (mol%)	0.0	5.0	10.0	15.0
Film Thickness	440	400	370	370

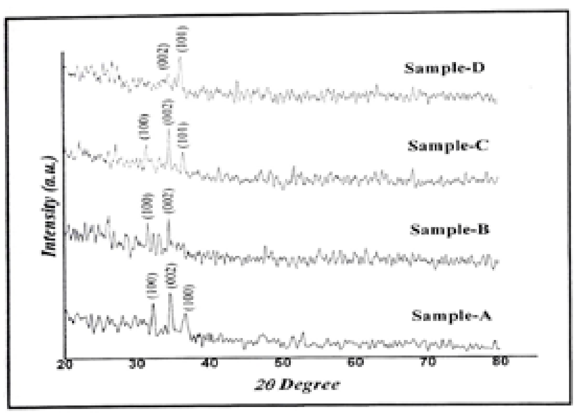

Fig. a : XRD Spectra for Zn1-xMnxO thin films

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