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Growth and characterization of nano-structured Sn doped ZnO

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HIGHLIGHTS

- Sn–ZnO films fabricated by a chemical spray pyrolysis method.
- The reducing of the band gap is induced by the introduction of deep states in the band gap.
- The optical property of Sn–ZnO system in terms of the band structure has been tentatively discussed.
- The more interesting and relevant observations are obtained from variable range hoping mechanism.

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ABSTRACT

In the present investigation, we report the transparent and conducting Sn doped ZnO (Sn–ZnO) films fabricated by a chemical spray pyrolysis technique (CSPT). The effect of Sn concentration on the structural, morphological, electrical and optical properties has been studied. Contrary to the common observation, the optical band gap of Sn–ZnO is red-shifted from 3.26 to 2.98 eV as the dopant concentration was increased to 5 wt.% but remained at this value with a further increase in Sn percentage to 10 wt.% (2.96 eV). The red-shift of the optical band gap is due to the deep states in the band gap. The increase in density of states has been confirmed by variable range hoping (VRH) mechanism. The activation energy was found to be decreased when Sn concentration increased. The low temperature conduction has been explained by VRH mechanism, which fits very well in the temperature range 100–300 K. The optical property of Sn–ZnO system in terms of the band structure has been tentatively discussed.

1. Introduction

For a decade, there has been a great interest in functional materials which play an important role in the field of science and technology because of their unique properties in response to a change in their environment. Among these materials, much attention has been paid to ZnO owing to its wide band gap energy of 3.37 eV and a large exciton binding energy of 60 meV. Also as an *n*-type direct band gap II–IV semiconductor with a wurtzite structure, ZnO is attractive for high efficiency short wavelength optoelectronic devices such as transparent electronics and nanodevices [1,2]. As a matter of fact, simultaneous occurrence of both high optical transmittance in the visible range, and low resistivity make ZnO an important material in the manufacture of heat mirror used in gas stoves, conductive coating in aircrafts glass avoiding surface icing. Thin films of ZnO have favorable electrical and optical properties that make them popular in photoelectric devices, information storage, gas sensors, catalyser, etc. [3–7]. In order to develop material for special applications, doped ZnO films have been fabricated and investigated by many researchers. It was reported that tin is one of the most efficient elements utilized to improve the optical and electrical properties [8].

Reports in the field of Sn doped ZnO point out that small amounts of tin substituting zinc atoms in ZnO lattice appear to cause a strong donor effect [9]; it act as a doubly ionized donor impurity that providing carriers will lead to a good quality ZnO based semiconductor. Consequently, the present contribution is mainly focused on the physical properties of the Sn–ZnO films when low amounts of Sn dopant are employed.

Sn as a cation dopant can substitute for Zn. Sn can be applied as an impurity that changes the band gap of ZnO. By alloying ZnO with another material of a different band gap, the band gap of ZnO can be fine tuned, thus affecting the wavelength of exciton emission. Whereby, the alloying of ZnO with SnO_2 creates a ZnO/SnO_2 structure, a potential candidate for future optoelectronic devices.

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As well known, transport and optical properties of semiconductors are dominated by the electronic states in the neighborhood of the bandgap [10–13]. Thus, it is necessary to understand the nature of the electronic states near the gap.

Many techniques have been used to deposit ZnO films on different substrates, including chemical vapor deposition [14], sol–gel [15], evaporation [16], sputtering [17], pulsed laser deposition [18] and spray pyrolysis [19]. Among these methods spray pyrolysis, is an excellent, simple, versatile and economical method. Besides the high growth rates with uniformity, this is a simple method for large area coating applications such as window panels, automotive glass and solar cells.

In the following, we describe the results for ZnO thin films prepared by spray pyrolysis technique, focusing on the crystalline quality, electro-optical properties and impurity incorporation.

2. Preparation of Sn–ZnO films

The Sn–ZnO thin films with different concentrations viz 0, 0.25, 1, 5, 10 wt.% have been prepared by using a spray pyrolysis experimental set up. The films are prepared by using aqueous solution of (0.2 M), zinc nitrate [$Zn(NO_3)_2$]. Tin doping was achieved by the addition of tin chloride ($SnCl_2$) to the precursor solution [11]. The following chemical reaction took place:

$$2Zn(NO_3)_2 \cdot 6H_2O + O_2 \rightarrow 2ZnO \downarrow + 4NO_2 \uparrow + 2O_2 \uparrow + 12H_2O$$

The films have been deposited on the microscopic glass substrates which were chemically and ultrasonically cleaned. At first step the substrates were washed with detergent solution 'Labolene' and then washed with water. In the next step these substrates were kept in nitric acid for 15 min. The substrates were dipped in 4 M NaOH solutions for 15 min to remove the acidic contamination. After that the substrates were washed with distilled water and then kept in acetone for 10 min. Finally the substrates were cleaned ultrasonically, and after drying it was ready for use. Several initial trials were made to optimize the deposition conditions before real sample preparation. The optimization was done by preparing the films at different temperatures ranging from 200 °C to 400 °C. A 2 KW heater was employed for heating the glass substrates. It has been found after several trials that smooth and good adherent pinhole free films were obtained at a temperature 400 °C. Thus during the deposition the substrate temperature was maintained at 400 °C. The temperature was measured by using chromel–alumel thermocouple fixed on the hot plate. The solution flow rate was maintained at 1 ml/min. The distance between the tip of the nozzle and the substrate was kept at 28 cm. The atomization of the solution in the fine droplets was affected by spray nozzle with the help of compressed air, during the course of spray.

3. Characterization

Films thicknesses calculated with the help of gravimetric method were found approximately 280–300 nm. The samples were weighed before and after spraying operation to determine the mass of the films. Knowing the dimension of the substrates used, one can determine the thicknesses considering the following equation:

$$t = \frac{\Delta_m}{\rho_m l L},$$

where Δ_m is the difference between the mass after and before the spray operation, L the length, l the width and ρ_m is the density. The structural studies of the prepared Sn–ZnO thin films were carried out by means of X-ray diffractometer employing Bruker D8 ADVANCE with CuKα radiation having the wavelength of 1.5418 Å. XRD patterns were recorded in the 2θ ranging from 25° to 75°. The experimental peak positions were compared with the standard JCPDS files (PDF # 891397). The elemental analysis of the films was performed by an energy dispersive X-ray spectrometer (EDX) JEOL JSM-5600. The surface morphology of the films was done by using atomic force microscopy (AFM) (Digital instruments Nanoscope E with Si3N4 100 μm cantilever, 0.58 N/m force constant) in contact mode at room temperature and scanning electron micrographs (SEM) (JEOL JSM-5600). The resistivity measurement was done by using two probe resistivity method in a home built apparatus with Teflon insulated coaxial cables. The whole unit was kept in the cryostat, the resistance was measured by the Keithley 616 digital electrometer connected to DC-power supply. Optical transmittance measurements were carried out using UV–Vis spectrophotometer (Perkin Elmer Lambda 950) for the wavelength region 300–900 nm.

4. Results and discussion

4.1. Microstructure and surface studies

The crystal structure of representative thin films was carried out by XRD as shown in Fig. 1a. Figure depicts the X-ray diffraction (XRD) patterns of ZnO films with various Sn doping concentrations. All diffraction peaks can be attributed to polycrystalline with hex-

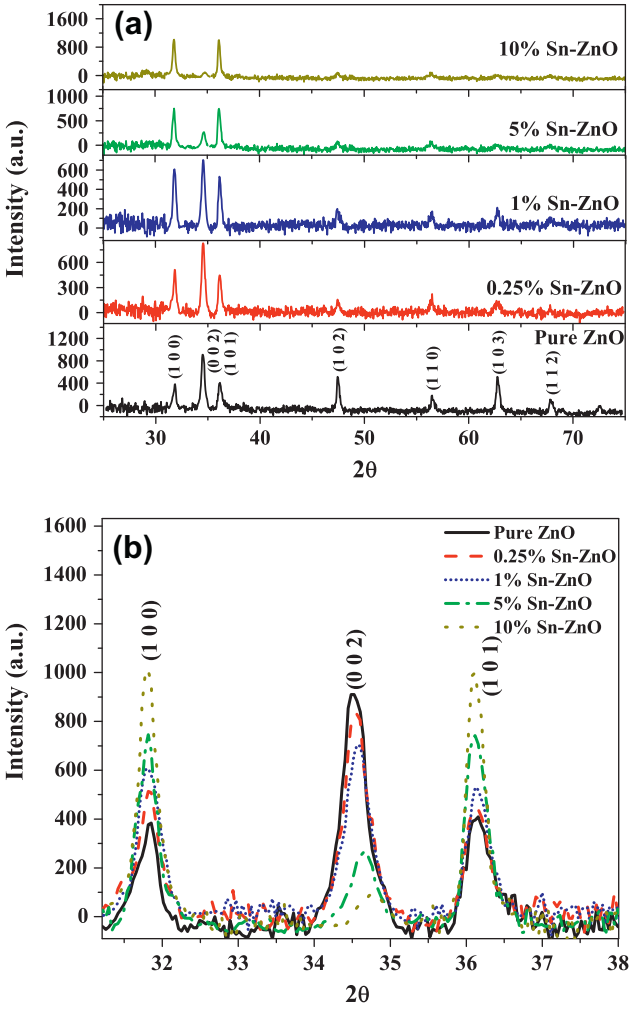

Fig. 1. (a) XRD patterns; (b) X-ray ω-rocking curve performed for (100), (002) and (101) peak of Sn–ZnO thin films.