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Effect of thickness on structural, optical and electrical properties of nanostructured ZnO thin films by spray pyrolysis

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ABSTRACT

Transparent conducting zinc oxide thin films were prepared by spray pyrolytic decomposition of zinc acetate onto glass substrates with different thickness. The crystallographic structure of the films was studied by X-ray diffraction (XRD). XRD measurement showed that the films were crystallized in the wurtzite phase type. The grain size, lattice constants and strain in films were calculated. The grain size increases with thickness. The studies on the optical properties show that the direct band gap value increases from 3.15 to 3.24 eV when the thickness varies from 600 to 2350 nm. The temperature dependence of the electrical conductivity during the heat treatment was studied. It was observed that heat treatment improve the electrical conductivity of the ZnO thin films. The conductivity was found to increase with film thickness.

1. Introduction

Zinc oxide (ZnO) is one of the most important group II–VI semiconductor materials. It is a wide-band gap oxide semiconductor with a direct energy gap of about 3.37 eV. ZnO has high chemical and mechanical stability, together with nontoxic in nature and high abundance. Recently, transparent conducting oxides (TCOs) have been widely studied. ZnO is one of the most promising materials for the fabrication of the next generation of optoelectronic devices in the UV region and optical or display devices. 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 mirrors used in gas stoves, conducting coatings in aircrafts glasses to avoid surface icing, and thin film electrodes in amorphous silicon solar cells. ZnO is a member of the hexagonal wurtzite class; it is a semiconducting, piezoelectric and optical waveguide material and has a variety of potential applications such as sensors [1], surface acoustic devices [2], transparent electrodes [3], and solar cells [4,5]. Some of these applications are based on the simultaneous occurrence of low resistivity and high transmittance in the visible spectrum, when ZnO is manufactured in the form of thin solid films. For many of these applications, it is very important to control the ZnO physical properties by doping. Usually, n-type doping is obtained by Al, Ga and In. An important disadvantage of ZnO is that fabrication of p-type layers is difficult. While, the existence of both (n and p) types conduction is of fundamental importance for a material to be used in light-emitting devices.

Various deposition techniques have been widely used to produce ZnO thin films. However, seeking the most reliable and economic deposition technique is the main goal. The most intensively studied techniques include, RF magnetron sputtering [6], chemical vapor deposition (CVD) [7], sol–gel method [8], thermal evaporation [9] and spray pyrolysis [10]. The chemical bath deposition [11] and sol–gel technique [12] are also well known methods of preparation of ZnO thin films. Among these methods, spray pyrolysis is useful for large area applications. This method is cheaper, simpler and permits to obtain films with the required properties for optoelectronic applications. Thickness dependent on structural, electrical and optical properties of the ZnO films have been carried out.

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2. Experimental

The spray pyrolysis is an excellent method for the deposition of thin films of metallic oxides, as is the case for the ZnO material. In this deposition technique, a starting solution, containing Zn precursors, is sprayed by means of a nozzle, assisted by a carrier gas, over a hot substrate. When the fine droplets arrive at the substrate, the solid compounds react to become a new chemical compound. ZnO thin films of various thickness were deposited onto ultrasonically cleaned glass substrates using the spray pyrolysis method at 723 K. A solution of 0.1 M Zn $(CH_3COO)_2$ was used as a precursor, prepared by dissolving in deionized water. The nozzle was at a distance of 20 cm from the substrate during deposition. The solution flow rate was held constant at 3 ml/min. Air was used as the carrier gas, at the pressure of 1.5 bar. When aerosol droplets come close to the substrates, a pyrolytic process occurs and highly adherent ZnO films were produced. The possible reaction proposed by Paraguay et al. [10] is as follows:

$$\begin{aligned} &Zn(CH_3COO)_{2(\text{solid near substrate})} \xrightarrow{\text{heat}} 4Zn(CH_3COO)_{2(\text{gas near substrate})} \\ &+H_2O \xrightarrow{\text{adsorption}} Zn_4O(CH_3COO)_{6(\text{adsorbed/substrate})} \\ &+2CH_3COOH_{(\text{gas near substrate})} \text{ and} \uparrow Zn_4O(CH_3COO)_{6(\text{adsorbed/substrate})} \\ &+3H_2O \rightarrow 4ZnO_{(\text{film/substrate})} + 6CH_3COOH_{(\text{gas})} \uparrow \end{aligned} \quad (1)$$

Samples with different thickness were fabricated under the same spray conditions, varying only the deposition time. The r.m.s. (root-mean-square) value of roughness and thickness was measured using Stylus profile meter. The structural properties were studied by X-ray diffraction measurements (XRD) using Rigaku D/Max ULTIMA III diffractometer with Cu Kα radiation (λ = 1.5406 Å). The average dimensions of crystallites were determined by the Scherrer method from the broadening of the diffraction peaks. The optical measurements of the ZnO thin films were carried out at room temperature using Shimadzu UV-1700 Spectrophotometer in the wavelength range 300–1100 nm. Electrical conductivity measurements were carried out using four probe methods with Keithley Electrometer – 6517A in the temperature range of 300–450 K. The film composition of the zinc oxide was determined using energy dispersive X-ray analysis (EDX, JEOL Model JED-2300) attached with SEM (BJEOL Model JSM-6390LV).

3. Results and discussion

3.1. Structural characteristics

The structural characterization is very important in explaining optical and electrical properties of thin ZnO films. The X-ray diffraction patterns were recorded from 20° to 80° as shown in Fig. 1. The XRD results show that all the films are polycrystalline in nature and randomly oriented. The random orientation however, is contradiction to the *c*-axis orientation of previously reported, ZnO thin films by spray pyrolysis [13]. This is probably due to the difference in the precursor chemistry and heat treatment temperature [14]. Van Heerden et al. [15] reported that if the substrate temperature is above 693 K, then the structure degrades towards randomly oriented structure. It is observed from Fig. 1 the intensity of the peaks increases with film thickness. It is not the result of structural changes in the films, but the result of increase in the film thickness [15]. The peaks were identified to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) plane of reflections for a single phase wurtzite structure of ZnO. The lattice constants '*a*' and '*c*' were calculated using the following equation [16]:

$$\frac{1}{d^2_{(hkl)}} = \frac{4}{3}\left[\frac{h^2+hk+k^2}{a^2}\right] + \frac{l^2}{c^2} \quad (2)$$

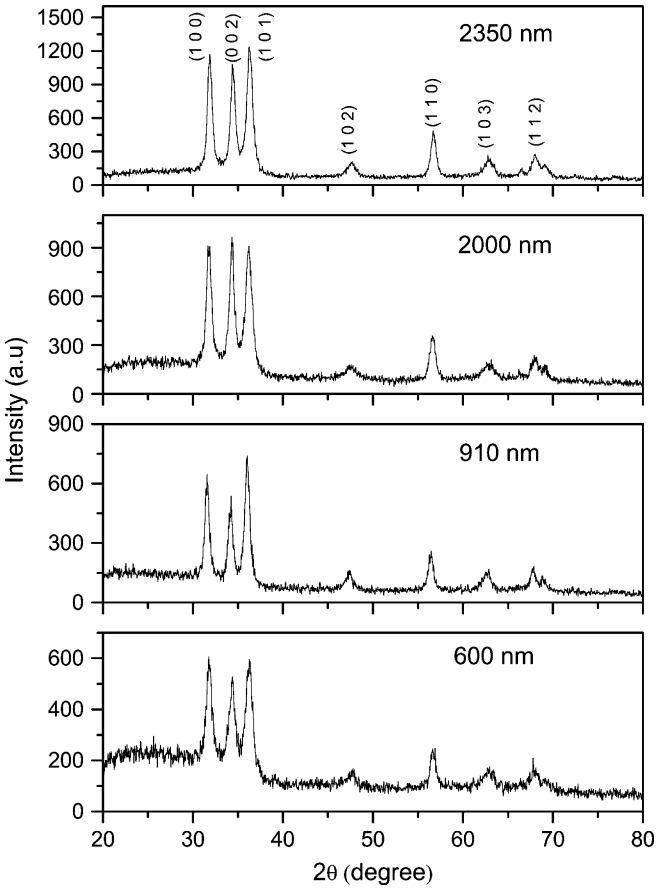

Fig. 1. XRD patterns of ZnO thin films with different thickness.

The observed '*c*' and '*a*' values are in good agreement with the standard values taken from the Joint Committee of Powder Diffraction Standards (JCPDS) card 75-0576. An estimation of the average crystallite size has been done using the well known formula of Scherrer:

$$L = \frac{0.9\lambda}{\beta\cos\theta} \quad (3)$$

where 'β' is the observed angular width at half maximum intensity (FWHM) of the peak.'λ' is the X-ray wavelength (1.5406 Å for Cu $K\alpha_1$) and 'θ' is the Bragg's angle. Fig. 2 shows the full width at half maximum values of the films with the variation of thickness. The FWHM value decreases quasi linearly as the thickness increases, indicating a better crystallinity of the films with higher thickness. The XRD data shows that the positions of (1 0 1) diffraction peak shifts towards higher angle indicating that the *c*-axis value of the ZnO thin films decreases with increase in the thickness. The *c*-axis strain (ε_{zz}) values have been calculated using the following equation [12]:

$$\varepsilon_{zz}\,(\%) = \frac{c - c_0}{c_0} \times 100 \quad (4)$$

where '*c*' is the lattice parameters of the strained films calculated from the X-ray diffraction data and 'c_0 'is the unstrained lattice parameter of bulk ZnO. Table 1 gives the variation of lattice parameters, grain size, roughness and strain with film thickness. From the data, it can be understood that strain (ε_{zz}) in the film is tensile. It decreases with increase in thickness, indicating existence of more relaxed films for higher thickness. Fig. 3 shows the variation of strain with film thickness. This means that the crystallinity becomes better in higher thickness films. The average