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Effect of substrate temperature on the nebulizer sprayed zinc oxide thin films

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ABSTRACT

Zinc oxide (ZnO) thin films deposited on glass substrates at various temperatures 300, 400 and 500 °C by the nebulizer spray pyrolysis technique. X-ray diffraction results indicate that the films are polycrystalline in nature having hexagonal crystal structure with preferred grain growth orientation along (002) plane. The crystallite size increases along (002) plane with temperature increase from 350 to 500 °C and attains a maximum 109 nm at 500 °C. High resolution scanning electron microscopy (HR-SEM) study shows the formation of good quality film on total substrate surface with uniformly distributed tiny spherical shaped grains at 350 °C. The UV–Vis–NIR spectroscopy confirms the possibility of good transparent ZnO thin films deposited with an average transmission of ~85% in the visible region. Optical band gap energy increases from 3.19 to 3.27 eV with the substrate temperature 350–500 °C. The depression of NBE emission and DL emission of the films were estimated through PL measurements. As the substrate temperature increases, the peak of NBE emission is found to have a blue shift towards lower wavelength side and the same result is also found from the band gap energy determination of optical transmittance measurement. The complex impedance shows two distinguished semicircles and the diameter of the arcs got decreased in diameter as the temperature increases from 350 to 500 °C and thereafter slightly increased.

1. Introduction

Zinc oxide (ZnO) is a very interesting material for many different applications in optoelectronic and microelectronic devices. It is a wide band gap oxide semiconductor with direct band gap energy of about 3.32 eV [1]. These characteristics have generated a wide serried of applications such as gas sensors, liquid crystal displays, heat mirrors, photovoltaic devices, surface acoustic wave (SAW) devices [2–6] among others. It is a near-stoichiometric n-type semiconductor with a low resistivity and high transmittance in the visible region in the form of thin film [7]. The one-dimensional (1D) ZnO nanomaterials, such as nanowires or nanorods, are especially attractive due to their tunable electronic and opto-electronic properties and the potential applications in the nanoscale electronic and opto-electronic devices. ZnO thin films have been deposited using various techniques, such as RF sputtering, pulsed laser deposition, molecular beam epitaxy, thermal evaporation, sol–gel spin coating, sol–gel dip coating, electrochemical deposition, and spray pyrolysis [8]. Among these methods, spray pyrolysis is the simple, low cost and reliable process to produce uniform and well adherence films.

In this work focuses on ZnO thin films deposited on glass substrates by nebulizer spray pyrolysis technique. The effect of temperature on the structural and optical properties of ZnO thin films using water was investigated. A detailed study of strain and dislocation density in the film has been done to provide useful information related with the defect evolution, which is very important for better understanding the quality improvement of the films. The results are discussed and reported.

2. Experimental details

Thin films of ZnO were deposited on glass substrates by nebulizer spray pyrolysis technique with various substrate temperatures. The precursor solution used was 0.1 M concentration of high purity zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$; Sigma–Aldrich] dissolved in deionized water. The substrates were ultrasonically cleaned in isopropyl alcohol and then hydrochloric acid for 15 min,

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in order to remove the organic matter and metal ions absorbed on the substrate surface. Then the substrates were washed with deionized water again and finally dried in air. The nebulizer spray pyrolysis experimental setup and the details of the procedure for the deposition ZnO thin films have been described elsewhere [9]. The spray nozzle was at a distance of 5 cm from the substrate during deposition and solution flow rate was held constant at 0.5 ml/min. Air was used as the carrier gas, at the pressure 30 psi and substrate temperature varied from 350 to 500 °C in steps of 50 °C.

When the substrate temperature is below 350 °C, the spray falling on the substrate undergoes incomplete thermal decomposition (oxidation) giving rise to a foggy film whose transparency as well as electrical conductivity is very poor. If the substrate temperature is above 500 °C, the spray gets vaporized before reaching the substrate, whereas at optimum substrate temperature in the range 350–500 °C, the spray reaches the substrate surface in the semi-vapor state and complete oxidation will take place to give a clear ZnO film.

X-ray diffraction, high resolution scanning electron microscopy, UV–Vis–NIR spectroscopy and photoluminescence were used to study the formed ZnO thin films.

3. Results and discussion

3.1. Structural properties of ZnO films

X-ray diffraction patterns recorded in the range 20–80° of ZnO thin films deposited at different substrate temperatures by nebulizer spray pyrolysis technique are shown in Fig. 1. The X-ray diffraction studies revealed that all films exhibit polycrystalline nature with hexagonal structure, irrespective of the deposition conditions. It is found that film growth is along (100), (002), (101), (110), (103), (200), (112), (201) and (004) panes. It is further observed that the grain growth is random having preferential orientation along (002) and (101) planes to some extent. The observed and standard '*d*' values (JCPDS Card No. 897102) compares well with each other. Fig. 1 shows that when the substrate temperature increases the diffraction peaks become sharper and the intensity is increased. For substrate temperature increases to 500 °C, the intensity of peak is decreased.

The variation lattice constants (*a*,*c*) with substrate temperature for the ZnO thin films are listed in Table 1. It is observed that Table 1 the lattice constants of the films nearly match with the standard

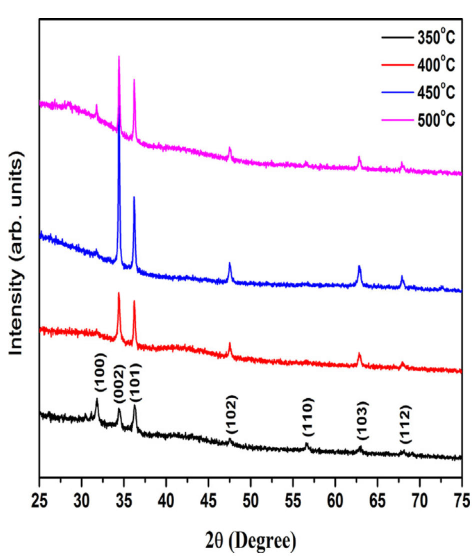

Fig. 1. XRD patterns of ZnO thin films.

JCPDS values. The lattice constants value slightly increases with substrate temperatures from 300 to 400 °C. The crystallite size of ZnO thin films was calculated using Scherrer's formula [10]. The variation of crystallite size with temperature for the ZnO films is listed in Table 1. From Table 1, it is observed that the crystallite size increases with substrate temperature and the film deposited at 500 °C is found to have the maximum crystallite size value 95 nm at 450 °C. In addition, to get more information on the defects in the films, the dislocation density (δ) was calculated using the simple approach of Williamson and Smallman [10]. The variation of dislocation density (δ) and microstrain (σ) with substrate temperature for the ZnO thin films are listed in Table 1. An increase in crystallite size (D) and decrease in dislocation density (δ) and microstrain (σ) values with increase in substrate temperature imply the better crystallization of the films.

3.2. Morphological analysis of ZnO films

The substrate temperature dependence of crystallinity and crystallite size for the ZnO films were brought out through high resolution SEM micrographs. Fig. 2 shows the high resolution SEM morphologies of ZnO films deposited at 350, 400, 450 and 500 °C, respectively. The microstructure of the ZnO films consists of many tiny edge-like grains distributed uniformly throughout the surface. The surface morphology of the ZnO films deposited at low substrate temperature (350 °C) show small size grain but dense grains. The increase of substrate temperature up to 400 °C apparent mixed nano-flakes net-like structure and spherical grains with grains ~78 nm is observed (Fig. 2b). When the substrate temperature increases to 500 °C (Fig. 2c), the number of nuclei increases and the nuclei grow over the whole surface area of the substrate with uniform grains. The grain size became smaller with increase of substrate temperature up to 500 °C. This is mainly due to the increase of migration ability of atoms and molecules on the surface during the growth at higher substrate temperature.

3.3. Elemental analysis of ZnO films

The EDAX spectra of ZnO thin films deposited at various temperatures 350, 400, 450 and 500 °C is shown in Fig. 3. EDAX indicates presence of zinc and oxygen elements. The Si and Ca elements are due to the glass substrates. Table 2 gives the atomic percentage of Zn:O elemental composition. EDAX analysis showed that the amount of O element in the sample increases with temperature increase. These spectra show that the expected elements exist in the solid films. The substrate temperature has a strong effect on the structural, morphological and optical properties of ZnO thin films have been proved.

3.4. Optical properties of ZnO films

Fig. 4 shows optical transmittance spectra of ZnO thin films obtained in the range of 300–2500 nm. The films deposited at a substrate temperature of 350 °C showed the maximum transmittance (~78%), while the films formed at a still higher substrate temperature 500 °C exhibit the highest optical transmittance 93% in the visible region. The decrease of transmittances at lower substrate temperature may be attributed to the increased scattering of photons by rough surface morphology and crystal defects. All the samples show sharp absorption edge near to 396 nm in the UV region and these absorption edges shifts to longer wavelength sides with temperature. The optical band gap is determined from the transmittance spectra by applying the Tauc model [11]. The nature of transition and bandgap of the ZnO thin films have been determined by plotting $(\alpha h\nu)^p$ against the photon energy, $h\nu$. The plots