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The effect of deposition time on the optical, structural and morphological properties of deposited ZnO films by CBD method for solar energy applications

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ABSTRACT

Zinc oxide thin films have been deposited on glass substrates at various deposition times (150mins, 160mins and 170mins) by simple Chemical Bath Deposition technique. The structure of the deposited ZnO films was determined by powder X-ray diffraction and it shows several peaks. The film has high transmittance at the visible region. This high transmittance and wide band gap of film suggests its usefulness as host materials in optoelectronics The reflectance of the deposited ZnO increases with deposition time. The optical band gap of deposited films was found to be 2.4eV, 2.55eV and 2.8eV respectively which show decrease of band gap with deposition time. The EDS result revealed that the required phase has both Zn and O present.

KEYWORDS

Deposition time;
ZnO;
Band gap;
XRD.

INTRODUCTION

Zinc oxide (ZnO) as an important semiconducting material occupies an enviable place, having a wide range of potential applications[1-3]. ZnO is an important electronic and photonic material because of its wide direct band gap of 3.37eV. Recently, ZnO nanocrystals have been used for solar cell applications[4], ultraviolet lasing action at room temperature[5] and gas sensors[6].

Nanocrystals of ZnO have been prepared using both physical and chemical methods[3]. Among these are spray pyrolysis, sputtering, sol-gel spin coating, pulsed laser deposition (PLD), chemical vapor deposition (CVD)[7–11]. Generally, most of these methods of synthesis require relatively high temperatures or involve the use of expensive chemicals or apparatus.

It is therefore advisable to find simple method to produce ZnO nanocrystals using commonly available chemicals[3].

EXPERIMENTAL PROCEDURE

The deposition solutions were formed by first dissolving weighed amounts of Zinc nitrate in water to the volume of 200ml with molar concentration of 0.1M. To make the solution alkaline, aqueous ammonia solution was added with constant stirring. Firstly, the solution became milky – turbid due to the formation of $Zn(OH)_2$.

Further addition of excess ammonia dissolved the turbidity and made the solution clear and transparent. The pH value of the resultant solution was ~ 12.0. In order to minimize the temperature fluctuation during deposition, a water bath was used. The glass substrates were used in this work. Prior to the deposition, the beaker containing the deposition solution was placed in the water bath and maintained at a constant temperature for about 5 minutes to stabilize the temperature of the solution. The beaker was kept in the water bath throughout the deposition process while heating and stirring.

The ZnO coated substrates were removed at different deposition time ranging from 150–170mins from the bath, washed with distilled water, dried in air and preserved in an air-tight container.

For the deposition of ZnO films, $Zn(NO_3)_2$ was used as a source of zinc. When ammonia was added to it, white precipitate of $Zn(OH)_2$ occurred, which was dissolved by addition. This can be represented by the following equations[12]:

$$Zn(NO_3)_2 + 2NH_4OH \rightarrow Zn(OH)_2 + 2NH_4NO_3$$

$$Zn(OH)_2 + NH_4OH\ (NH_4)ZnO_2^- + H_2O + H^+$$

When the solution was heated, the ionic product exceeded the solubility product and precipitation occurred on the substrate and in the solution to form ZnO nuclei and this was adherent and uniform ZnO film formed on the substrate by the following reaction[12]:

$$(NH4)\ ZnO_2^- + H^+ \rightarrow ZnO + NH4OH$$

The deposited ZnO thin films were milky white. In the present work the deposition temperature was 70°C. The optical absorbance measurements were made on ZnO thin films by UV-VIS-NIR spectrophotometer. The structure of the ZnO thin films was investigated by powder X-ray diffraction technique. The morphology of the ZnO thin film was also ascertained using Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

Structural characterization

The crystallographic structure of the ZnO films was examined by powder X-ray diffraction technique. The Figure 1 shows the XRD pattern of ZnO films which was deposited on glass substrates at different deposition time (150mins, 160mins, and 170mins). The film deposited the different time was annealed at 673K for 15 minutes because the solid ZnO particles may form in aqueous solution only when the temperature is above 70°C. Several diffraction peaks were noticed. From Figure 3.1(a and b) the minor diffraction peaks of (102), (110), (103) and (112) are approved of randomly oriented ZnO films[13]. The appearance of the small peaks may be due to the formation of new crystallites with random orientations. The grain size for the three different samples was calculated from the X-ray diffraction data by using Scherer's formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ = wavelength of the X- rays (1.5406ï), β = FWHM of the peak with highest intensity and θ = diffraction angle

The dislocation density was calculated by the relation:

$$\delta = 1/D^2 \quad (2)$$

Where D is the grain size

The micro strain was calculated by the formula

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (3)$$

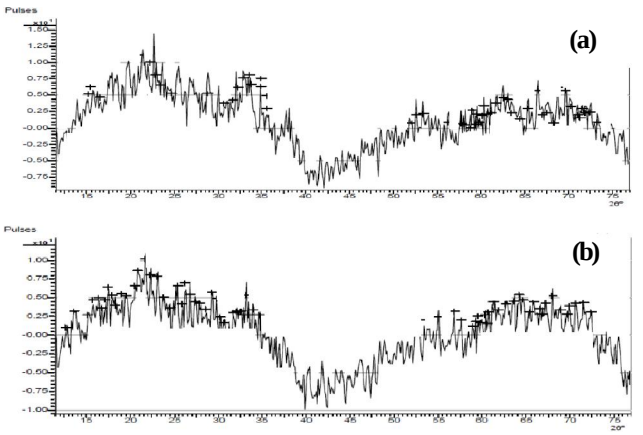

Figure 1: The XRD pattern of the deposited ZnO for the deposition time of (a) 150mins and (b) 170mins

From TABLE 1 below, as the deposition time increases the grain size increases but the dislocation density and micro strain decrease. One can understand that the degree of crystallinity improves with increase in deposition time, and would conclude that the formation of new crystallites decreases the dislocation density (imperfection of crystallites) and micro strain.

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TABLE 1: Micro structural properties of deposited ZnO thin films

Deposition Time	Grain size (nm) D	Dislocation density(δ) line^2/m^2	Micro strain(ε) 10^{-3}	Thickness (Å)
150mins	22.71	1.94×10^{15}	1.50	890
160mins	26.43	1.43×10^{15}	1.31	960
170mins	27.43	1.33×10^{15}	1.26	1130

Optical properties of deposited ZnO

The optical transmittance of the thin films in the UV–Vis-NIR wavelength range is presented in Figure 2a. It can be seen that the film has high transparency (>50%) for the films with deposition time of 150mins at the Visible region. Also noticed is higher transparency of film at lower deposition time. The films deposition time of 150mins and 160mins have relatively high transmittance at the NIR region and could possibly be used as material for poultry roofs and walls which is more advantageous than using the conventional methods of heating[14].

Figure 2b shows the reflectance of ZnO film deposited at different deposition time (150mins, 160mins and 170mins). All the films show low reflectance in the UV-VIS-NIR region. The sample deposited with the deposition time of 150mins exhibited the least reflectance, and the highest deposition time having the greatest reflectance.

The ZnO thin film with deposition time 150mins has wider band gap when compared with those 160mins and 170mins as shown in Figure 2c. The band gaps of the deposited ZnO thin film decreases with increase in deposition time, the theory behind this is called the quantum size effect. The optical band gap of deposited films was found to be 2.4eV, 2.55eV and 2.8eV for films of 150mins, 160mins and170mins respectively. This wide band gap and the high transmittance exhibited by this film suggest that the film can also be used as host material in optoelectronics applications as reported in literature[15].

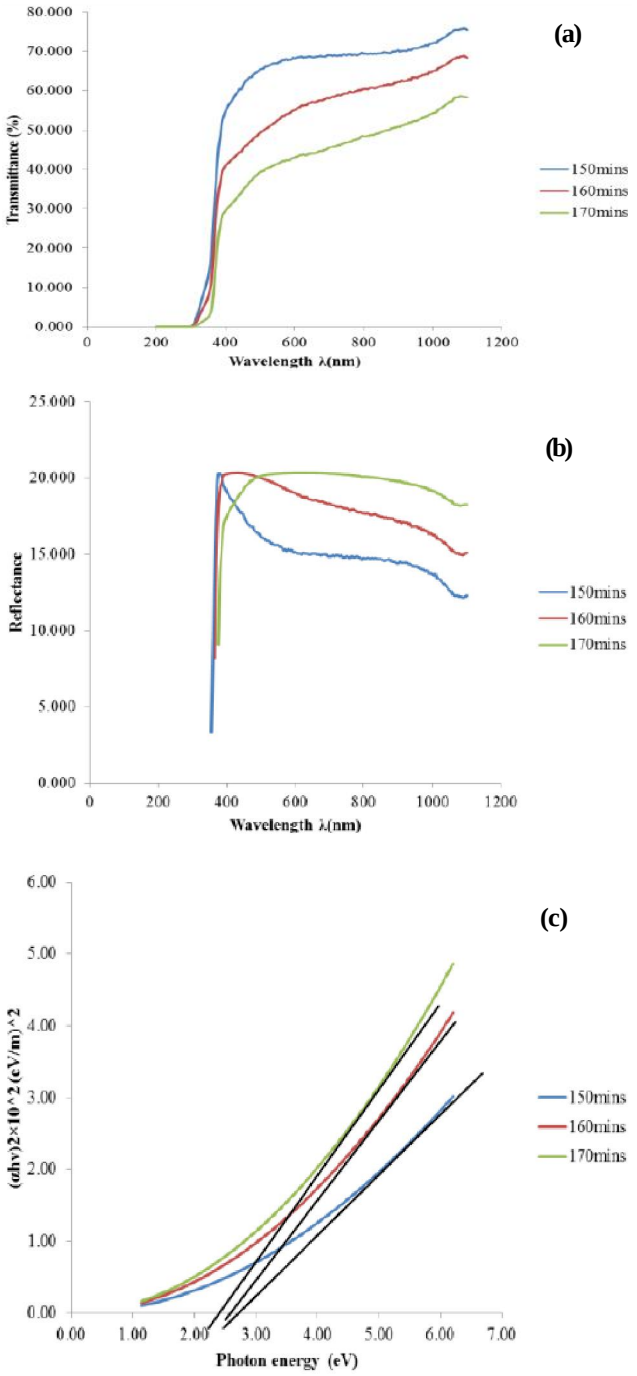

Figure 2 : A plot of (a) transmittance (b) reflectance and (c) band gap of the deposited ZnO films

Energy dispersive spectroscopy

Energy dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. The EDS result in Figure 3 is for the sample with the deposition time of 150mins. The EDS of the ZnO sample was done by the SEM (JEOL-JSM 5800) machine.

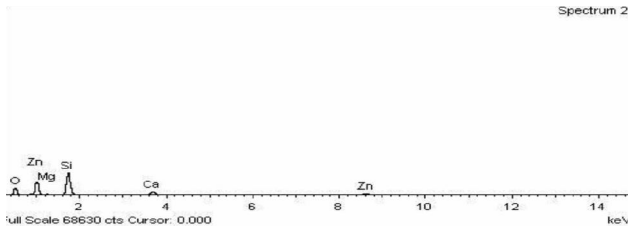

Figure 3 : EDS result of the deposited ZnO

The EDS results reveal that the required phase has both Zinc (Zn) and Oxygen (O) present in the sample. Also observable on the graph are the presence of Mg, Si and Ca, probably from the glass substrate used for the deposition of ZnO thin films.

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