Spectral Investigations of Chemical Bath Deposited Zinc Oxide Thin Films – Ammonia Gas Sensor

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Zinc oxide thin films have been deposited on glass substrates at various bath temperatures (40ºC, 60 ºC and 80 ºC) by simple chemical bath deposition technique. The structure of the deposited ZnO films was determined by powder X-ray diffraction and it exhibits hexagonal structure along with c-axis orientation. The optical absorbance of the deposited films was characterized by UV-VIS-NIR spectrometry. The optical band gap of deposited films was found to be 2.9eV, 2.72eV and 2.4eV respectively. The photoluminescence and gas sensing properties along with micro structural quantities were studied and reported.

Keywords: Zinc oxide film, Ammonia gas sensor, Chemical bath deposition

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1. Introduction

ZnO is a technologically important material whose electronic and optical properties are size and shape dependant [1]. ZnO-based materials have been used in solar cells, chemical sensors, laser diodes, etc [2, 3]. ZnO thin films have been studied as the active channel material in thin film transistors development because of its exhibiting n-type semi conductive characteristic with band gap of 3.3eV and excellent thermal stability and can be well oriented crystalline on various substrates [4, 5].

Over the past few years, many methods to synthesize nano and micro Zno thin films have been developed. Among the fabrication methods chemical bath deposition was used for the preparation of semi conducting oxide films [6]. In chemical bath deposition technique, deposition of metal oxide semi conducting thin films occurs due to substrate maintained in contact with chemical bath containing metal ions. The film formation on substrate takes place when the ionic product exceeds the solubility product [7]. The CBD method is based on the controlled precipitation of the material to be prepared, so as to produce a film upon the substrate surface.

Although the precipitation can be controlled by adjusting the experimental conditions (chemical composition and process temperature), nucleation in the solution and on the reactor wall cannot be avoided. Hence only a small amount of the reagents in the solutions are used for film growth and a larger amount of material produces colloidal particles in the solution. Only 2% of the reagents in the solution is used during CdS film growth on the substrate [8].

This paper reports the deposition of ZnO thin films on glass substrates using chemical bath deposition with the structural, optical, photo luminescent and gas sensing properties along with micro structural quantities.

2. Experimental Evidence

The deposition solutions were formed by first dissolving weighed amounts of $Zn(CH_3COO)_2.2H_2O$, $N(CH_2CH_2OH)_3$ and NaOH in water to the volume of 50ml. In order to minimize the temperature fluctuation during deposition, a water bath was used. (In this case temperature was 40°C, 60°C and 80°C). The micro corning glass was used as a substrate. 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.

$$Zn(CH_3COO)_2.2H_2O+TEA \rightleftharpoons [Zn(TEA)]^{2+}+2CH_3COO^-$$

$$[Zn(TEA)]^{2+} \rightleftharpoons Zn^{2+}+TEA \quad (1)$$

$$2NaOH \rightleftharpoons 2Na^{+}+2OH^-$$

$$Zn^{2+}+2OH^- \rightleftharpoons Zn(OH)_2\downarrow \quad (2)$$

$$Zn(OH)_2 \rightleftharpoons ZnO+H_2O\uparrow \quad (3)$$

The color of the deposited ZnO thin films was milky white. In the present work the deposition time was 3 hours. 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 photoluminescence study was done by using high sensitive spectrophotometer and gas sensitivity response also studied and reported.

3. Result and discussion

3.1. Structural characterization

The crystallographic structure of the ZnO films was examined by powder X-ray diffraction technique. The figure (1a, 1b and 1c) shows the XRD pattern of ZnO films which was deposited on glass substrates at different bath temperatures (40°C, 60°C and 80°C). The film deposited at 40°C was annealed at 573K for 15 minutes because the solid ZnO particles may form in aqueous solution only when the temperature is above 50°C.

The diffraction peaks (100), (002), (101) indicate that the produced ZnO crystals have hexagonal structure. In addition, the prominent peak (002) indicates preferential c – axis orientation of the crystals [10]. The grain size for the three different samples was calculated from the X-ray diffraction data by using Scherer's formula.

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \quad (5)$$

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

The dislocation density was calculated by the relation:

$$\delta = 1 / D^2 \quad (6)$$

where D is the grain size
The micro strain was calculated by the formula

$$\varepsilon = \beta \cos\theta / 4 \quad (7)$$

In other words, the grains are mainly grown with c-axis vertical to the substrate. Moreover, from the recorded patterns (Fig.1(b) and 1(c)) the minor diffraction peaks of (102), (110), (103) and (112) are approved of randomly oriented ZnO films [11]. The appearance of the small peaks may be due to the formation of new crystallites with random orientations.

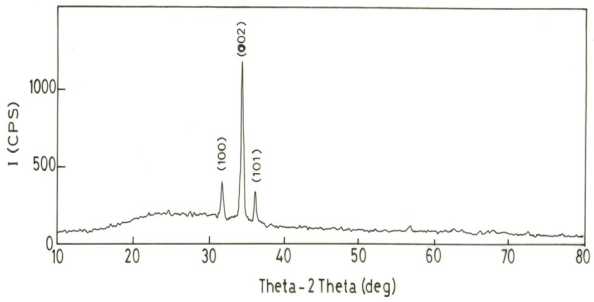

Figure 1. (a) XRD pattern of 40°C ZnO thin films annealed at 573K

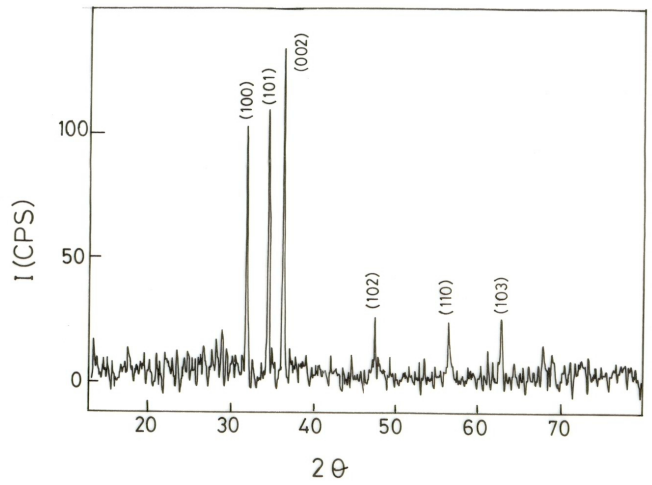

Figure1. (b) XRD pattern of ZnO thin film deposited at 60°C

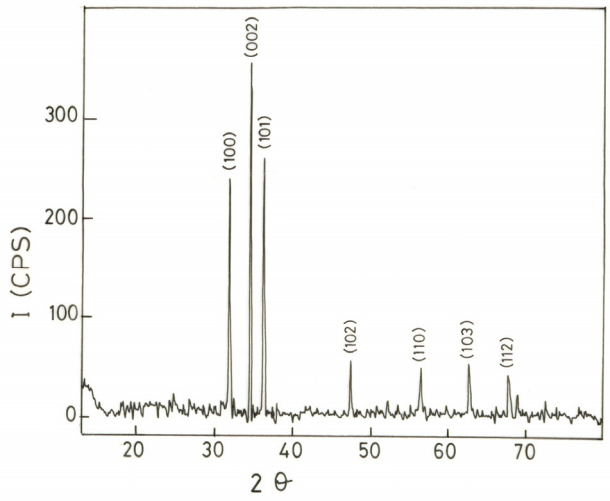

Figure 1. (c) XRD pattern of ZnO thin film deposited at 80°C

From equations (5, 6 and 7), the average grain size, dislocation density and micro strain of ZnO thin films deposited at 40°C, 60°C and 80°C were calculated as reported in the Table 1.

Table 1. Micro structural quantities of ZnO thin films

Bath temperature	Grain size(nm) D	Dislocation density(δ)line^2/m^2	Micro strain(ε) 10^{-3}	Thickness(Å)
40° C	22.72	1.937 x 10^{15}	1.525	2350
60° C	26.28	1.447 x 10^{15}	1.317	3860
80° C	27.60	1.312 x 10^{15}	1.254	6340

As the bath temperature increases the grain size increases but the dislocation density and micro strain decrease. From the observed data one can understand that the degree of crystallinity improves with temperature [5]. The formation of new crystallites decreases the dislocation density (imperfection of crystallites) and micro strain.

3.2 Optical characterization

The variance of absorbance (A) of ZnO films deposited at various bath temperatures 40°C, 60°C and 80°C is shown in Fig.2.(a).

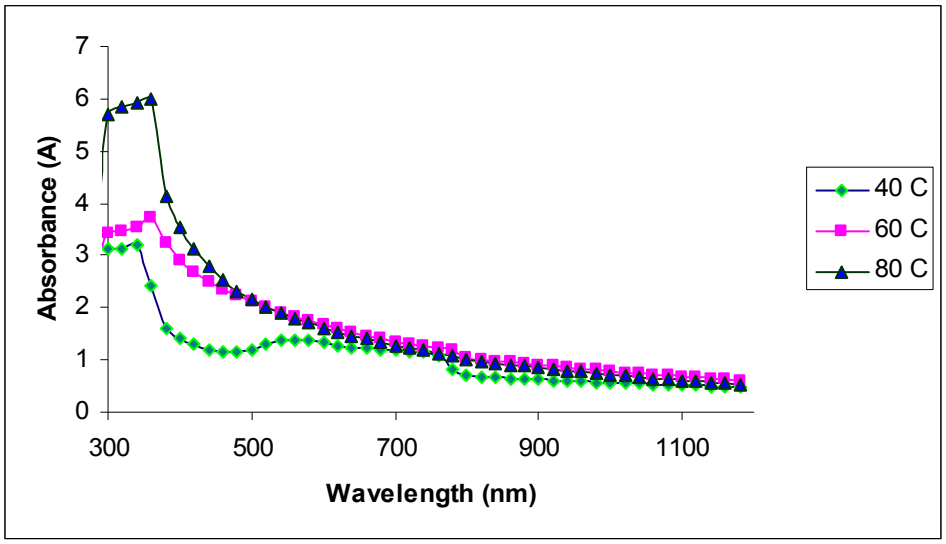

Figure 2. (a) Variation of absorbance of ZnO thin films for different wavelength

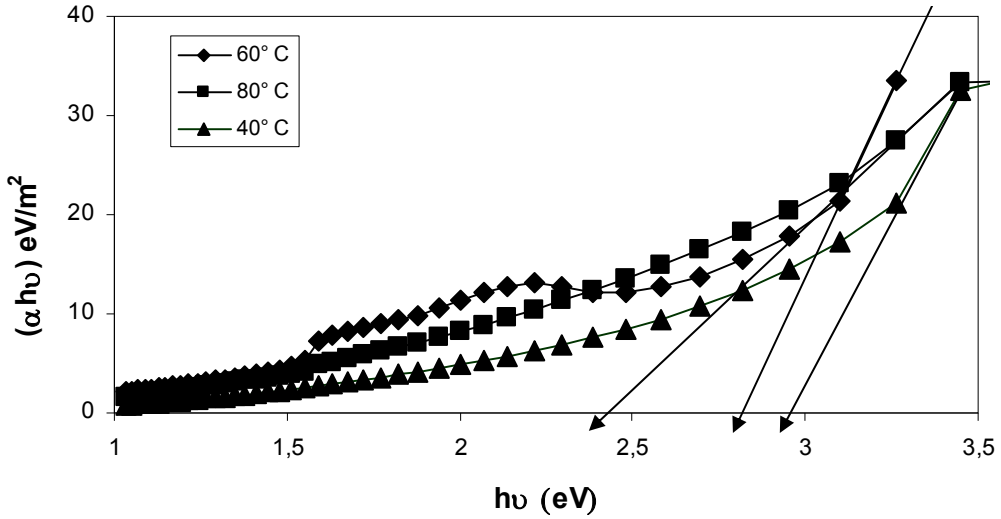

Figure 2. (b) Plot of $(\alpha h\upsilon)^2$ Vs hυ for ZnO thin films

This spectrum reveals that deposited ZnO films have low absorbance in visible region, which is a characteristic of ZnO. The absorbance decreased as the bath temperature increased. This may be due to decrease in the hydroxide ion accumulation along the grain boundaries. From the theory of optical absorption, the relation between the absorption coefficient (α) and photon energy (hυ) for direct allowed transition is

$$\alpha\, h\upsilon = (h\upsilon - E_g)^{1/2} \quad (4)$$

This equation (4) gives the band gap (E_g). When straight portion of (αhυ) is extrapolated to the point α = 0, the intercept in the X-axis gives the band gap (E_g). From the Fig.2 (b) the band gap of ZnO films was found to be 2.9 eV (40°C), 2.72 eV (60°C), 2.4 eV (80°C) respectively. The higher band gap may be due to the presence of zinc hydroxide. The band gap decreased to 2.4 eV as the bath temperature increased to 80°C, which is common phenomenon in chemical bath deposition [9].

3.3. Photoluminescence

Fig.3 shows the photoluminescence spectra of Zinc Oxide thin films deposited on glass substrate at bath temperature of 80°C under the excitation of 318 nm. The films exhibit very similar emission properties throughout the investigated wavelength range, indicating good consistency of the structure of the films. A strong and sharp emission peak localized at around 2.65eV corresponds to the band to band transmission.

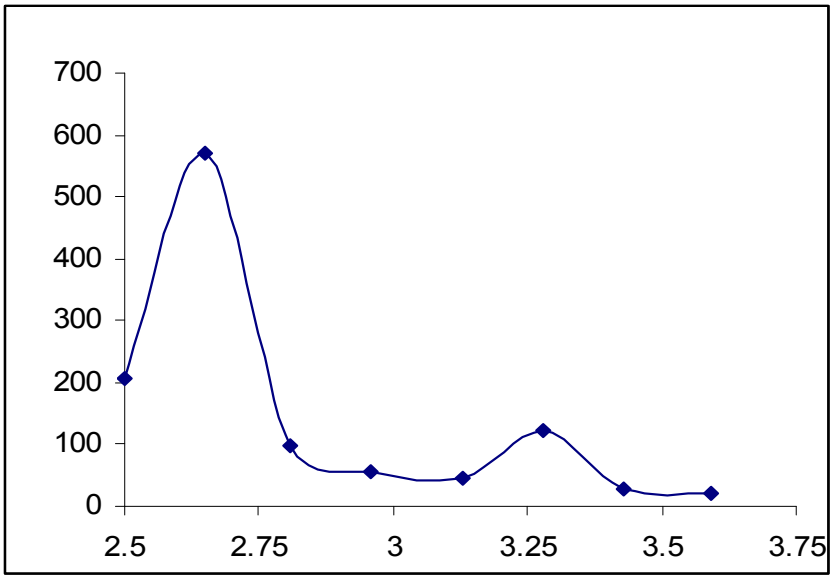

Figure 3. PL Spectra of ZnO thin film deposited at 80°C

The second peak is a sub band transition located at around 3.3eV. The deep level emission corresponds to the Zinc vacancy (V_{Zn}) and anti site defect (O_{Zn}) as suggested by J.Wang et al [12]. It has been proposed that the violet green emission in the material might be associated to a transition with a self activated center formed by a doubly-ionized Zinc vacancy V_{Zn}^{2-} and the single-ionized interstitial Zn^{+} at the one end [13]. The stronger intensity of violet emission shows that there is a great fraction of Oxygen vacancies [14]. The PL spectra reveal that the ZnO thin films exhibit better quality as the band edge transition peak is intense and the sub-band transition peak is suppressed and gets diffused.

3.4. Gas sensitivity

Gas sensitivity is defined as the ratio of resistance in ambient atmosphere to the resistance in gas atmosphere. Mathematically it can be related as

$$S_g = R_a / R_g$$

Where

R_a - Resistance in ambient atmosphere (2 MΩ)

R_g - Resistance in gas atmosphere

The Fig.4 shows the variation in resistance of ZnO thin films for ammonia gas. One observes that gas sensitivity increases as bath temperature increases. The characteristic behavior of decrease in resistance of the films upon detecting ammonia vapor is typical of n-type semiconductor oxide gas sensors. The calibration curve indicates that the relation between gas sensitivity and bath temperature is linear, which benefits an actuator by enabling it to detect ammonia gas.

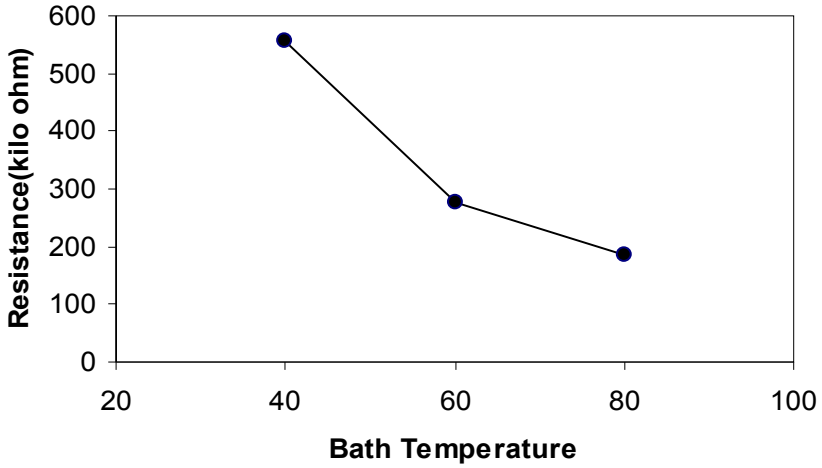

Figure 4. Variation in the resistance of ZnO thin films for ammonia gas

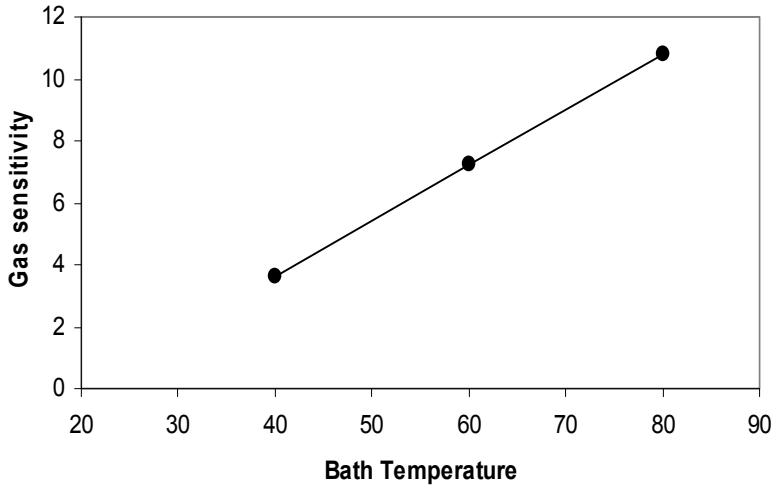

Figure 5. Variation in gas sensitivity of ZnO thin films for ammonia gas

The gas sensing mechanism normally accepted for semiconductor sensors assume that the oxygen adsorbed on the surface removes some of the electron density. When the gas molecules come into contact with this surface, they may interact with this oxygen leading to increase in conductivity [15]. This utilizes the gas-induced resistance variations in potential barrier height at grain boundaries to detect the gas in the air. Fig.5 shows the Variation in gas sensitivity of ZnO thin films for ammonia gas. In this study, the gas exposing time 1 minute was kept as constant. The decrease in resistance for ammonia may be due to the oxidation of gases coming in contact with ZnO surface at room temperature, the film exhibit good sensitivity with quick time-recovery of 45 seconds and it was found that the sensitivity for ammonia was 10.81 at pressure of 1 N/m^2.

4. Conclusions

Zinc oxide thin films have been successfully deposited on glass substrates by the chemical bath deposition technique. A deep level PL emission from the film was absorbed at room temperature in addition to the band edge emission. It suggests that it can be used as an alternative for luminescent material. From the X-ray diffraction analysis all the films show hexagonal structure along with c-axis oriented (002) plane. The gas sensing property of the film shows that they can be used as ammonia gas sensor at the room temperature with quick recovery time of 45 seconds.

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