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Chemical bath deposition and characterization of nanocrystalline ZnO thin films

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The subject of this paper is the wet chemical synthesis and characterization of nanocrystalline ZnO thin films. ZnO thin film was deposited on a zinc plate using a chemical bath of zinc acetate ($Zn(O_2CCH_3)_2$) and ethylenediamine ($C_2N_2H_8$) at various temperatures. Different substrates were used and their effect on the chemical bath deposition of ZnO were investigated. The effect of pH levels and temperature on the crystalline quality and morphology of the ZnO film are also presented.

Keywords: *zinc oxide; chemical bath deposition; solution growth; nanocrystalline semiconductor*

1. Introduction

Nanocrystalline semiconducting materials have attracted a great deal of attention because of their size dependent properties and wide range of applications. ZnO is one of the most interesting semiconducting materials. It has the band gap energy of 3.37 eV and is considered a potential material for use in solid state emission, solar cells, chemical sensors, piezoelectric transducers, transparent electrodes, photo-catalysts, electroluminescent devices and ultraviolet laser diodes [1–4]. Numerous techniques have already been used to deposit ZnO thin films, including molecular beam epitaxy (MBE) [5], sputtering [6], ion implantation [7], metal-organic chemical vapour deposition (MOCVD) [8], sol-gel deposition [9], spray pyrolysis [10], pulsed laser deposition (PLD) [11], cathodic electrodeposition [12–14] and other solution

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phase methods. The latter are simple to implement in experimental setups and have good potential for scaling-up.

Chemical bath deposition (CBD) [15–19] is one of the solution phase methods useful for the preparation of compound semiconductors from aqueous solutions. It is widely used for the deposition of various metal chalcogenide thin films. It produces good deposits on suitable substrates by the controlled precipitation of the compounds from the solution. The method offers many advantages over other well-known vapour phase synthetic routes. It may allow us to easily control the growth factors such as film thickness, deposition rate and quality of crystallites by varying the solution pH, temperature and bath concentration [20]. It does not require high voltage equipment, works at room temperature, and hence it is inexpensive. The only requirement for this deposition route is an aqueous solution consisting of a few common chemicals and a substrate for the film to be deposited. It often suffers from a lack of reproducibility in comparison with other chemical processes; however, by the proper and careful optimization of the growth parameters, one can achieve reasonable reproducibility.

The major problem of the CBD method is the inefficiency of the process which converts the precursor materials into useful deposits. Two types of nucleation take place in solution: homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation leads to rapid formation of large particles throughout the solution, as precipitate. Conversely, heterogeneous nucleation occurs at the substrate surface and particles grow slowly to form a film. The heterogeneous growth of the film on the substrate is disrupted by the competing homogeneous reaction in solution and the subsequent deposition on the surface of the vessel containing the solution bath. This difficulty is avoided by using a pre-treated substrate for the formation of seed layers or by employing the successive ionic layer adsorption and reaction (SILAR) method. Growing of a ZnO thin film on a glass substrate from an alkaline solution requires a seed layer. However, the deposition of ZnO thin film on a zinc plate does not require a seed layer, unlike other substrates such as glass, ITO or FTO.

To the best of our knowledge, there is no report available on the use of a zinc plate as a substrate for the chemical bath deposition of ZnO thin films. Ku et al. used aqueous solutions of zinc acetate dehydrate (0.05 M) and hexamethylenetetramine for the deposition of ZnO film on ITO [21]. Peng et al. used an equimolar (0.03 M) aqueous solution of zinc nitrate ($Zn(NO_3)_2$) and hexamethyltetramine ($C_6H_{12}N_4$) to deposit ZnO thin films on an ITO substrate [22]. Drici et al. reported CBD growth of ZnO on bare soda glass and ITO coated glass using zinc acetate (0.0188 mol/dm^3) and ethylenediamine (0.03 mol/dm^3). Similarly, Tahir Saeed et al. have also used zinc acetate (0.0188 M) and ethylenediamine (0.03–0.0425 M) for the deposition of ZnO thin films on a glass slide [23].

In our experiment, the deposition bath consisted of equal volumes of zinc acetate ($Zn(O_2CCH_3)_2$), and ethylenediamine ($C_2N_2H_8$) solutions having concentrations varying between 0.25 and 1 M. Zinc plates were used as substrates to grow ZnO thin films from solutions. Subsequent characterization of the plates has been reported. The con-

sequences of using various substrates for the growth of ZnO thin films are also discussed.

2. Experimental

The chemicals such as zinc acetate ($Zn(O_2CCH_3)_2$), and ethylenediamine ($C_2N_2H_8$) were of analytical reagent grade. A hot plate with a magnetic stirrer was used to heat and stir the bath solution. Zinc plates were used as the substrate in this deposition and for further characterization. Bare soda lime glass and SnO_2 coated glass plates were also used as substrates, in order to study how the choice of substrate material affects the deposition of ZnO thin films. All the substrates were cleaned with acetone, and then washed with distilled water. The zinc plate was first scrubbed with emery paper before washing. The film deposition was performed at various temperatures, with and without stirring the bath solution. The bath solutions were prepared with zinc acetate and ethylenediamine, both their concentrations varying between 0.25 M and 1 M. A mixture of solution with the desired density of zinc acetate and ethylenediamine was placed in a 100 cm^3 beaker and the solution was kept in a constant temperature bath. One side of the surface of each substrate, in particular of the zinc plate, was covered with insulating tape before being dipped into the solution. The pH of the bath was varied between 8 and 11 with the use of NaOH solution. The reaction mixture was maintained as constant at a desired temperature for deposition with continuous stirring. The substrates were removed from the deposition solution at various time intervals, washed with distilled water and dried, and then these deposits were subject to various tests. The reflectance of each film was measured with an UV-Vis-NIR spectrophotometer (HR-2000, M/S Ocean Optics). X-ray diffraction patterns were recorded using an X-ray diffractometer (XPERT PRO PANalytical) with CuK_α radiation ($\lambda = 0.1540$ nm) and the analyses of the surface morphologies were performed with a scanning electron microscope (JEOL JSM 840).

3. Results and discussion

3.1. Physical properties of film growth

In the deposition, equal volumes of $Zn(O_2CCH_3)_2$ and $C_2N_2H_8$ solutions with various normality, as given in Table 1, were used for all the substrates. The temperature of the deposition bath was varied from 30 °C to 60 °C. The temperature needed to obtain thin film deposition was at least 50 °C. The deposition conditions, i.e. pH, temperature and the concentration of the bath were varied in order to achieve the deposition of good quality, adherent thin films. The thickness of the film was controlled by dipping the substrate into the solution for a specific time. The growth rate also depended both on temperature of the bath and the stirring conditions: for higher temperatures the

growth rate was also found to be high but the growth rates in depositions with stirring are higher than those in unstirred solutions at the same temperature.

Table 1. Effects of various concentrations of the solutions on film quality

Molarity [M]		pH	Substrate		
Zn	Eth		Glass plate	Zinc plate	SnO_2 plate
			Quality of coating		
1.00	0.25	8–11	–	–	–
0.75	0.50				
0.50	0.75	8–9			thin
		9–10			
		10–11	thin	thin	good
0.25	1.00	8–9	–	–	powdery
		9–10	powdery	powdery	thick precipitate
		10–11	thin	thin	black, thick

In the case of bare glass plates and SnO_2 coated substrates, only a very thin white layer of powdery coating was obtained. The pH of the bath was found to play a major role in this deposition, irrespective of the concentration of the bath. At low pH values (below 8), only poor quality films were produced, irrespective of the substrates used. In zinc plates, for pH < 9, a powder like coating was obtained. For pH ≈10, strongly adherent, smooth, dark gray deposits were obtained. For pH > 10.5, and if the concentration of $Zn(O_2CCH_3)_2$ in the bath is 0.25 M and $C_2N_2H_8$ 1 M, a thick black coating with cracks is produced.

When the concentration of $C_2N_2H_8$ increased, the solution turned milky and precipitate was formed, which may be due to ZnO particles. Initially the deposition solution turned milky due to the formation of ZnO particles by homogeneous nucleation. The particles soon settled on the bottom of the beaker, as a non-adherent powder, and on the top surface of the substrate. The influence of the concentration of solution and pH on the various substrates is summarized in Table 1.

The optimum CBD conditions for achieving smooth, strongly adherent ZnO thin films were found to be: pH around 10, temperature between 50 °C and 60 °C, and concentrations of $Zn(O_2CCH_3)_2$ ca. 0.5 M and of $C_2N_2H_8$ ca. 0.75 M.

3.2. Structural study

The structural properties of the as-deposited and annealed ZnO thin films were analyzed by recording their X-ray diffraction patterns. The XRD patterns were obtained for ZnO thin films deposited using a bath composition of 0.5 M zinc acetate and 0.75 M ethylenediamine, pH = 9.5 at various bath temperatures. Figure 1 shows X-ray diffraction (XRD) patterns of annealed (300 °C for 15 min) ZnO films fabricated at various temperatures. The diffraction peaks of ZnO exhibited a hexagonal plane with

preferred grain orientations along (100), (002), (101), (110) and (201). All of the peaks are well matched with the bulk ZnO, which could be indexed as the hexagonal wurtzite structure of ZnO [24]. All films obtained without annealing exhibited hydroxide peaks (the result not shown).

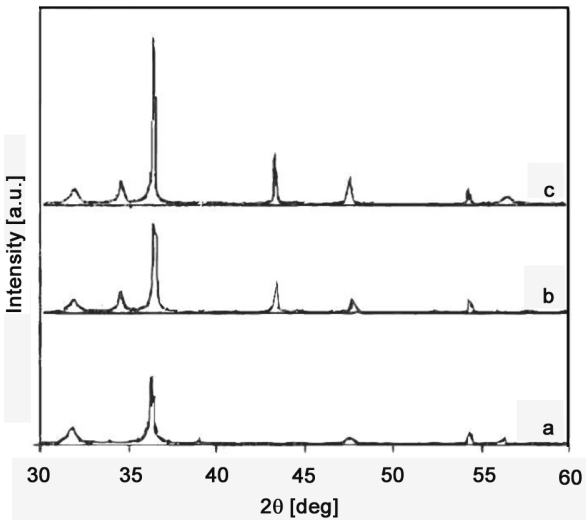

Fig. 1. XRD pattern of the annealed ZnO thin film grown at the bath temperature of: a) 30 °C, b) 40 °C, c) 50 °C

In Figure 1, pattern a corresponds to the film deposited with the bath temperature of 30 °C: it has only one prominent peak, other ones are very small. Patterns b and c show the XRD pattern of the films grown at 40 °C and 50 °C, respectively. They show that peak amplitudes are higher for the films grown with increased bath temperatures.

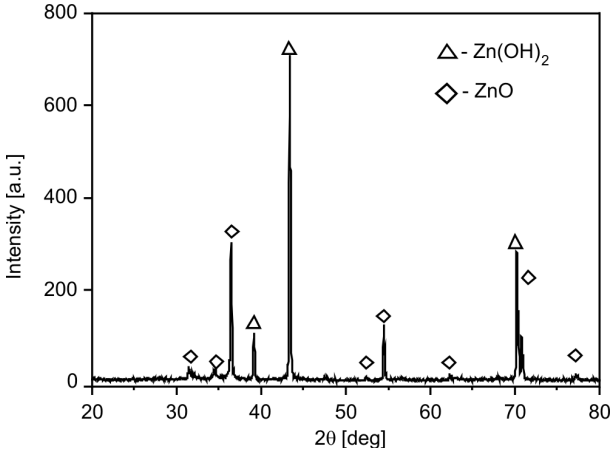

Fig. 2. XRD pattern of the ZnO thin film grown with a bath temperature of 60°

Figure 2 shows the XRD pattern of ZnO film with peaks originating from ZnO and $Zn(OH)_2$ before annealing of the films deposited at 60 °C. ZnO films deposited at considered temperatures also exhibited $Zn(OH)_2$ peaks and ZnO peaks but $Zn(OH)_2$ may be converted into ZnO by annealing in air [25]. Figure 3 shows the X-ray diffraction peaks of the annealed ZnO films deposited at the bath temperature of 60 °C. Annealing of the films at 300 °C for 1 h converted all $Zn(OH)_2$ into ZnO.

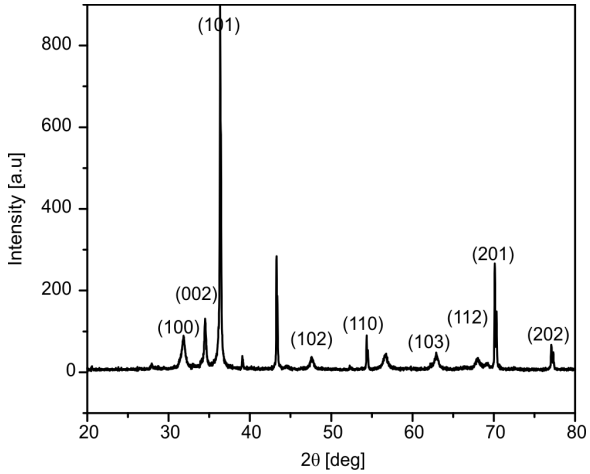

Fig. 3. XRD pattern of the ZnO thin film after annealing at 300 °C, grown at 60 °C

The annealed films crystallized in the hexagonal structure. The lattice parameters were calculated from:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

The mean values of the lattice parameters were found to be a = 3.251 Å, c = 5.213 Å, which are in good agreement with the literature data. A comparison of standard ASTMS data with the deposited ZnO thin films is also shown in Table 2.

Table 2. Comparison of calculated d values with JCPDS data

hkl	Calculated d_{hkl} [Å]	JCPDS d_{hkl} [Å]
100	2.808	2.816
002	2.598	2.602
101	2.471	2.476
102	1.907	1.913
110	1.632	1.626
103	1.469	1.478
112	1.381	1.379
201	1.358	1.360
202	1.232	1.239

In order to evaluate the mean crystallite size of the particles, the Debye–Scherrer formula was used

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Table 3 shows the crystallite sizes and the band gap with the bath temperature. Greater crystallite sizes were obtained for the films grown at higher temperatures, whereas the band gap energy was observed to decrease as the bath temperature increased.

Table 3. Crystallite sizes and band gaps at various temperatures

Bath temperature [°C]	Crystallite size [nm]	Band gap [eV]
30	32	–
40	36	3.33
50	38	3.25
60	41	3.14

3.3. Study of the surface morphologies

The morphologies of the deposited materials were examined using scanning electron microscopy. The films deposited under the optimized conditions were smooth, dark gray in colour and uniformly covered the substrate with good adherence. Scanning electron micrographs of the ZnO films grown under various conditions are shown in Figs. 4–7.

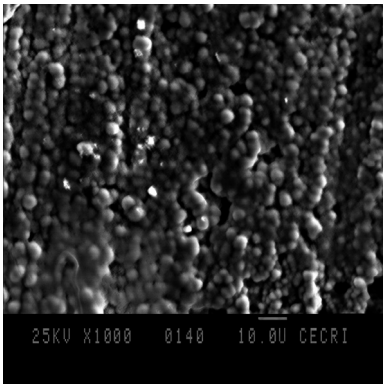

Fig. 4. SEM of the as-grown ZnO thin film deposited at 60 °C

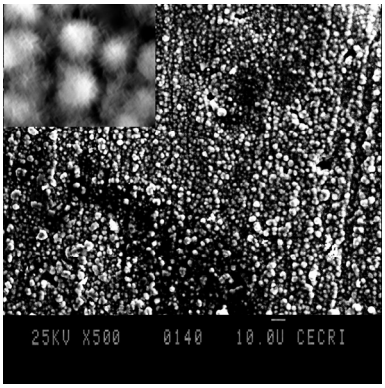

Fig. 5. SEM of the ZnO thin film after annealing at 300 °C for 1 h, a magnified particle in the inset

Figure 4 shows the surface morphology of the as-grown ZnO film deposited at 60 °C. The morphology of the annealed film is shown in Fig. 5. It exhibits well defined grain edges, and the inset shows a magnified view of individual grains. The overall surface structure is seen to have grains of spherical shape, uniformly covering the substrate, without any cracks or pores.

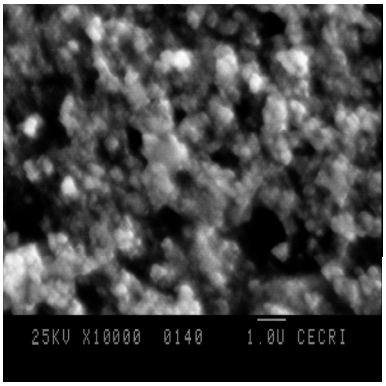

Fig. 6. SEM of the ZnO thin film deposited on a glass plate

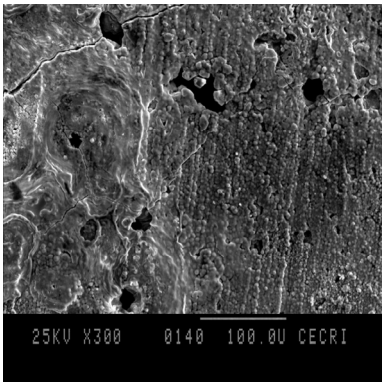

Fig. 7. SEM of the ZnO thin film deposited on a zinc plate for 15 h at 60 °C

Figure 6 presents the morphology of the ZnO film grown on the glass substrate. These films were non-uniform, powdery, and poorly adherent. The precipitated clusters are poorly adsorbed on the surface of the substrate. Figure 7 shows the film grown in a bath with pH = 11 pH for more than 15 h. Its surface is rough and has cracks. Some of these cracks are so severe that they even extend as far as the substrate itself.

3.4. Optical study

In order to study the optical properties of the ZnO thin films deposited by the chemical bath deposition technique, optical reflectance spectra were recorded in the 200–400 nm range, using a Varian Cary 500 instrument. The optical band gap energy of ZnO thin film was determined from the reflectance spectra [26].

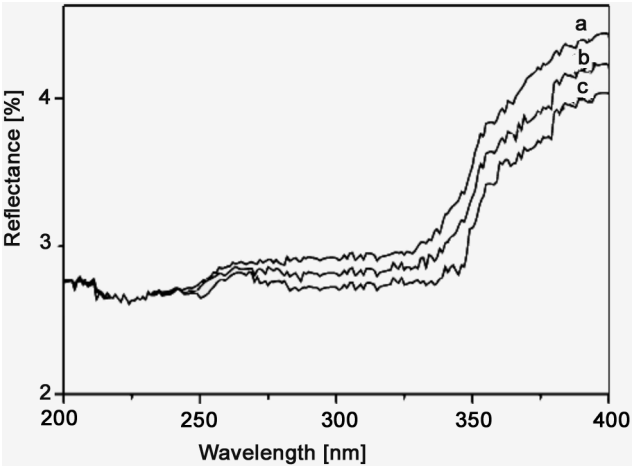

Fig. 8. Optical reflectance spectra of ZnO thin films deposited at: a) 40 °C, b) 50 °C, c) 60 °C

Figure 8 shows the reflectance spectra of the films deposited at 40 °C, 50 °C and 60 °C. The band gap energy (Table 3) of zinc oxide was found to be dependent on the bath temperature. It was found to be close agreement with the reported values [27].

4. Conclusion

The chemical bath deposition technique was successfully used to fabricate ZnO thin films on zinc plates. Structural, optical and morphological studies were carried out. The crystallite size and band gap energy were found to depend on the bath temperature. The band gap decreased as the crystallite size increased. The bath temperature was found to influence the growth of ZnO crystallites: at temperatures above 50 °C, good crystalline film was produced. The pH range 9.5–10.5 was found to be the most suitable for CBD growth of ZnO. The use of zinc as the substrate is conducive to smooth adsorption of zinc ions on the surface and it results in a high-quality coating. A decrease in the band gap was observed upon increasing the bath temperature and size of the crystallites.

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