

EFFECTS OF DEPOSITION MEDIA AND THERMAL ANNEALING ON CHEMICAL BATH DEPOSITED ZINC OXIDE THIN FILMS

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ZnO thin films were successfully deposited on glass substrates by the method of chemical bath. The precursors include zinc sulphate, ammonium solution and deposition medium. The ZnO films were strongly adhered to the substrates. They were subjected to different post deposition annealing temperatures. The optical effects of using PVA, PVP and water media respectively, as the deposition media, were studied. The optical absorbance, transmittance and reflectance of the films were characterized by the Unico UV-2102 PC spectrophotometer in the wavelength range of 200nm – 1000nm, at normal incidence of light. The strong absorbance of the annealed samples of the ZnO thin films grown using the PVP medium suggests that they can possibly be used in the fabrication of solar cells. The films annealed at 400°C have high transmittance in the NIR region.

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1. Introduction

The chemical bath deposition technique has been identified as one of the simplest and low cost methods of thin film deposition [1-2]. The method can be carried out at relatively low temperatures and can allow large area deposition of semiconductor. Deposition of the thin films occurs when the substrate is maintained in contact with the chemical bath and the ionic product exceeds the solubility product [2-3]. The CBD method of thin films has the advantage of allowing one to easily control the growth factors including the film thickness, rate of deposition and crystalline quality. This may be achieved by varying the bath concentration, temperature and the pH of the solution. In spite of these advantages, the CBD technique exhibit low efficiency in terms of profiting the amount of its starting materials [4]. Another major problem associated with the CBD technique is lack of reproducibility as compared with other methods [5], though this may be overcome by careful optimization of the growth parameters [4]. Furthermore, only a small amount of the reagents in the bath is responsible for the film deposition where as large amount of the materials produces colloidal particles in the solution [3, 6].

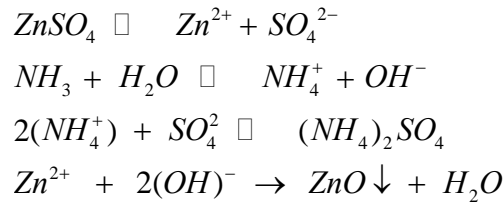
ZnO thin films are among the transparent semiconductors that can be prepared by the CBD technique. Several researches have been done on ZnO thin films using the CBD technique. The transparent ZnO thin films transmit in both the visible and some part of the ultra-violet region of the electromagnetic spectrum. Due to its wide optical band gap of about 3.2eV at room temperatures, ZnO has been used as UV-absorbing additive in many applications ranging from skin creams to advanced plastic and rubber composites [7]. ZnO thin films have been found useful in the fabrication of transparent solar cell contact, gas sensors and varistors [4-5]. ZnO thin films are also noted for their absence of toxicity as well as their abundance in nature [8]. While ZnO was noted as the least toxic among the metal oxides of Zn, Sn, In, Ag and Cd, cadmium compounds are known to be the most toxic and are regulated and even prohibited from some applications [9].

Dimitrov *et al.* [10] studied the effect of processing parameters on ZnO thin films doped with Aluminum. Mauricio *et al.* [4] employed a procedure that improves the efficiency of the CBD method during the growth of ZnO film whereby precipitation occurs only upon the substrate. This involves the exclusive growth of the thin film on the substrate and then annealing at 350°C for 2 hours. Wang Ming-Dong *et al.* [11] demonstrated a new method for the extraction of the optical parameters of ZnO thin films deposited by filtered cathode vacuum arc (FCVA) technique from the transmission spectrum. The growth of ZnO with the CBD processes was demonstrated by Dewei [2] to study their electrical properties.

This paper reports the influence of deposition media on the optical parameters of chemical bath deposited ZnO thin films which were successfully deposited on glass substrates using PVA, PVP and water respectively as the deposition media respectively. The influence of thermal annealing on the films was also examined.

2. Experimental details

The chemical bath solution was prepared using 10ml of 0.1M of zinc sulphate solution, 5ml ammonia solution and 35ml of the solvent to make up 50ml volume of the bath. The three solvents used are polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and distilled water. Commercial quality microscope glass slides with dimensions, 7.5cm X 2.6cm X 1mm, were used as the substrates. As the state of the substrate's surface greatly affects the growth of the deposited film, it is very important to clean the surface of substrate [12]. The substrates were degreased in HCl, washed in detergent and rinsed in distilled water. They were vertically immersed into the bath solution and prevented from touching the walls of the beaker. The chemical bath temperature was maintained at 75°C for 10 hours. The optimum bath deposition conditions were attained by varying the different bath parameters. The possible reaction equation is of the form:



The films were removed and rinsed at the end of the deposition time then left to dry in air. These uniformly deposited ZnO thin films were strongly adhered to the glass substrates. Some of the films were annealed at 200°C and 400°C respectively. The optical absorbance, transmittance and reflectance were measured at normal incidence in the spectral range of 200 – 1000nm with the Unico UV-2102 PC spectrophotometer at scan step of 3nm.

3. Results and discussion

Firmly adhered transparent ZnO films were successfully deposited on the glass substrates using the chemical bath deposition (CBD) method. Based on the theory of optical absorption, the variation in absorption coefficient (α) with photon energy ($h\nu$) for band to band transition is given by the Tauc relationship [13] as:

$$\alpha h\nu = F(h\nu - E_g)^m, \quad (1)$$

where h is the Planck's constant, F is a constant, ν is the frequency of the incident photon and E_g is the optical band gap energy. The value for m is 1/2, 3/2 and 2 for direct allowed transition, forbidden direct allowed transition and indirect allowed transition respectively. For the ZnO thin film, the graph of $(\alpha h\nu)^2$ is plotted against $h\nu$. The intercept on the horizontal axis, when straight

portion of the graph is extrapolated to the point $\alpha = 0$ gives the band gap energy E_g . Figure 1 shows the plot of $(\alpha hv)^2$ against hv .

In solar cells, only photons with energy greater than the band gap can be absorbed to produce photo charges. The part reflected off the surface is due to the difference in the refractive indices n_i and n_o of the material and air respectively. The reflectivity is given by [14]:

$$R = \frac{(n_i - n_o)^2}{(n_i + n_o)^2} \quad (2)$$

The fraction of the absorbed photons in the crystals with thickness t and absorption constant α is given by $(1 - e^{-\alpha t})$ and the fraction transmitted given by

$$T = e^{-\alpha t} \quad (3)$$

Figs. 2, 3 and 4 show the distribution of the optical absorbance, transmittance and reflectance as a function of wavelength respectively at normal incidence in the wavelength range of 200 - 1000nm for both the as-deposited and the annealed samples of the films. The variation of the refractive index with the photon energy for each medium is shown in figure 5. The values of the optical band gaps, the average absorbance, transmittance and reflectance with respect to the wavelength as well as the average refractive indices with respect to photon energies are summarized in Table 1.

3.1 Optical band gap

The as-grown thin film in the PVA medium has wider band gap when compared with those grown in the water and in the PVP media. The band gap of the as-deposited ZnO thin film using the PVA medium was 1.60eV but was increased to 2.95eV as a result of annealing the sample at 400°C. The band gaps values are lower for the samples deposited using PVP and water media. The band gap of the films grown in all the media substantially increased as a result of subjecting them to higher annealing temperatures. The slight difference in the observed optical band gaps of the films with respect to those reported in literature might be as result of the deposition media.

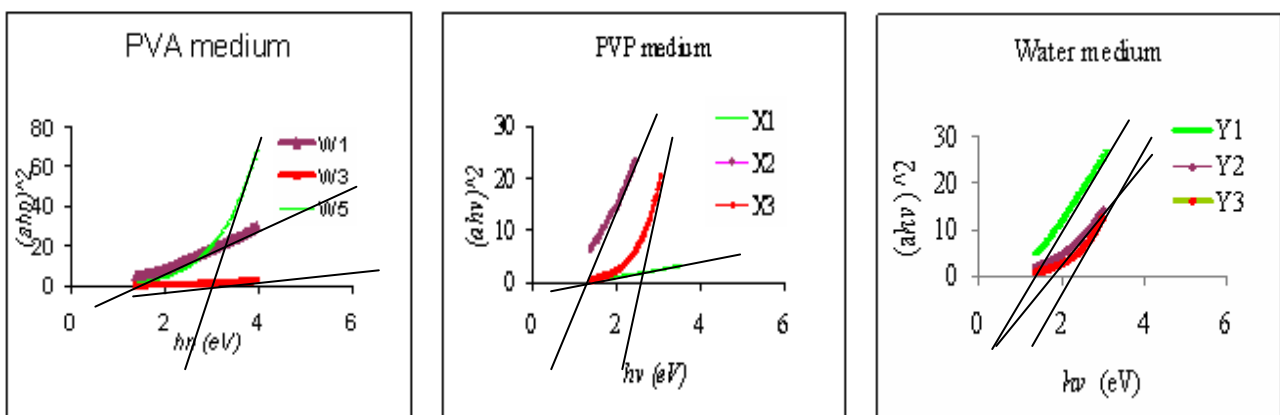


Fig. 1. Plot of $(\alpha hv)^2$ vs. hv for ZnO thin films deposited using (a) PVA (b) PVP and (c) H_2O medium.

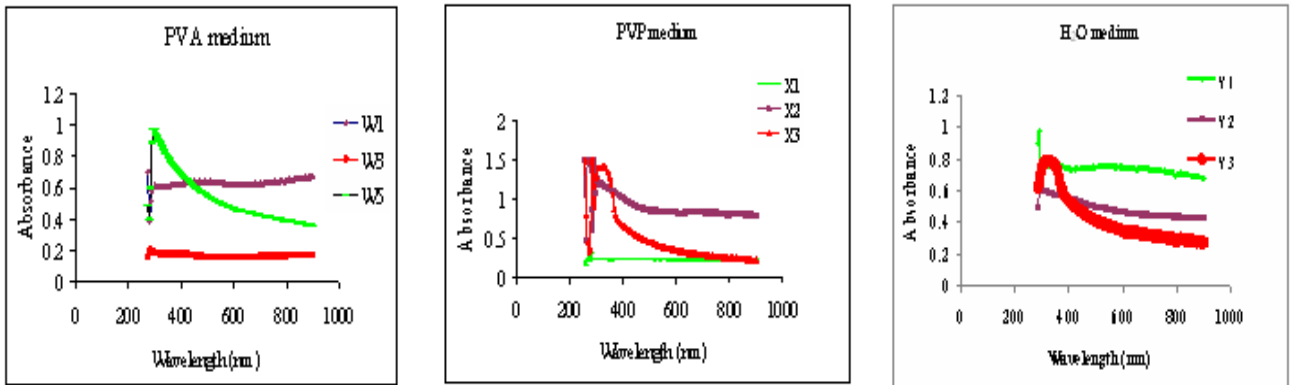


Fig. 2. Absorbance vs. wavelength for ZnO thin films deposited using (a) PVA medium, (b) PVP medium and (c) H₂O medium.

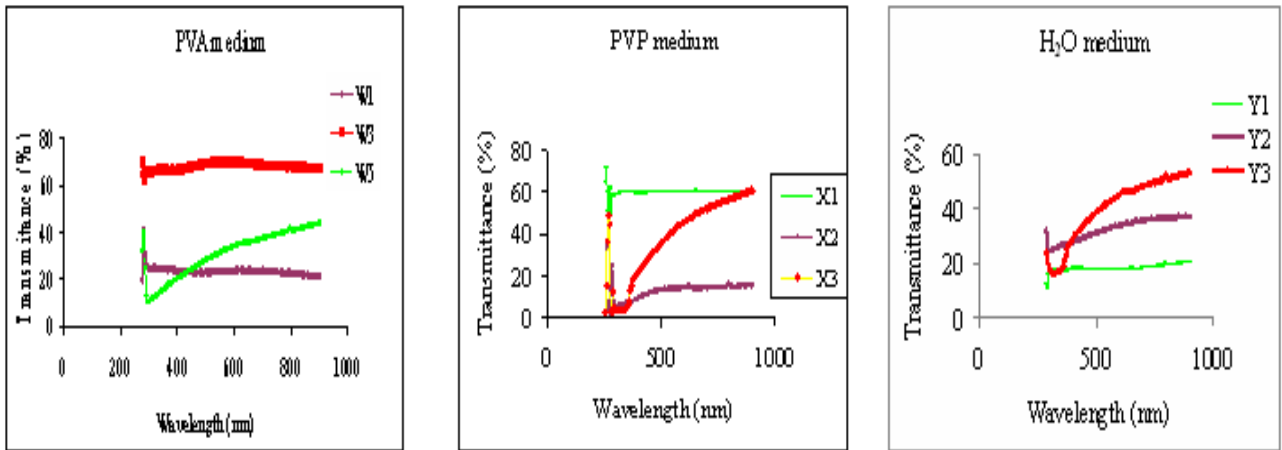


Fig. 3. Transmittance against wavelengths for ZnO thin films in (a) PVA medium (b) PVP medium and (c) H₂O medium

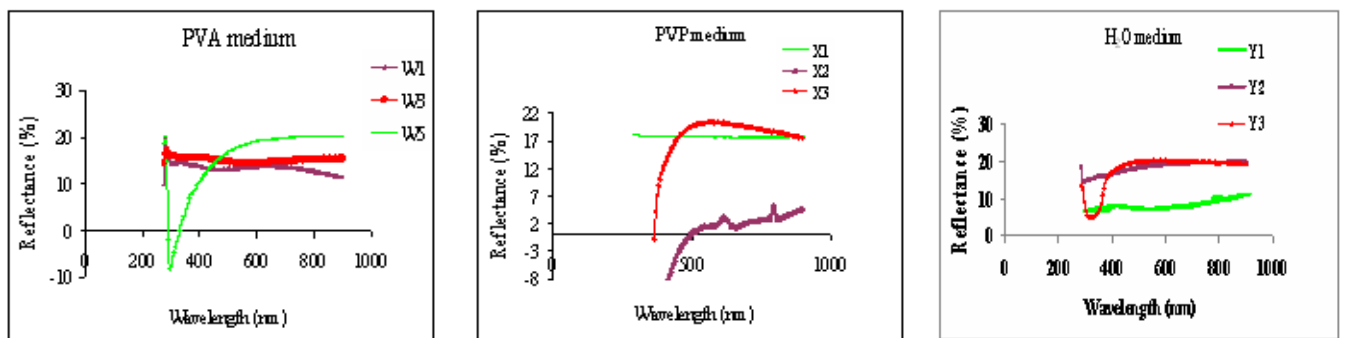


Fig. 4. Plot of reflectance vs wavelength for ZnO thin films in (a) PVA medium (b) PVP medium (c) H₂O medium

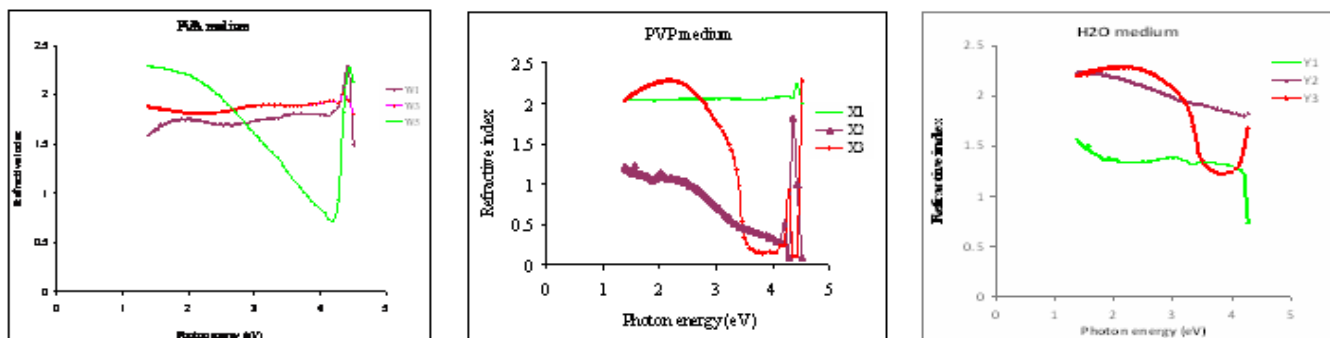


Fig. 5. A plot of refractive index vs. photon energy for ZnO thin films in different media namely (a) PVA (b) PVP and (c) H₂O.

Table 1. The effects of deposition media on the optical properties of the ZnO thin films.

	PVA			PVP			H ₂ O		
Sample code	W1	W3	W5	X1	X2	X3	Y1	Y2	Y3
Annealing temperatures	As-Grown	200°C	400°C	As-Grown	200°C	400°C	As-Grown	200°C	400°C
Band gap	1.60	2.70	2.95	1.50	1.35	2.50	1.25	1.80	2.25
Absorbance (300 - 900nm)	~0.6	~0.2	0.9 - 0.4	~0.2	1.25 - 0.80	1.4 - 0.2	~0.7	0.6 - 0.4	0.8 - 0.3
Transmittance (300 - 900nm)	~23%	~67%	10 - 44%	~61%	6 - 16%	4 - 61%	~18%	25 - 38%	16 - 53%
Reflectance (300 - 900nm)	15 - 11%	~16%	0 - 20%	~18%	0 - 5%	0-20% (350-550nm) & 20-18% (550-900nm)	~19%	25 - 38%	16 - 53%
Refractive index (1.4 - 4.2eV)	1.7	~2.0	1.5	~2.1	0.75	2.2 (1.4 - 2.2eV) & 2.3-0.15 (2.2 - 4.0eV)	1.5	2.0	~2.3 (1.4 - 2.6eV) & 2.3 - 1.2 (2.6 - 3.9eV) 1.2 - 1.7 (3.9 - 4.4eV)

3.2. Absorbance

The absorbance of the as-deposited sample in the PVP medium and the 200°C-annealed sample deposited via PVA medium were very low and constant at about 20% over the UV-VIS-NIR region. Other samples show relatively high absorbance in the VIS region and lower values towards the NIR region. Some of the samples grown using the various media have strong absorbance in the VIS region and as such may gainfully be employed in the fabrication of solar cells

3.3 Transmittance

The transmittance of the as-deposited zinc oxide thin films using the PVP medium is considerably higher than those of the PVA and H₂O deposition media. This is about 61% through out the UV-VIS NIR regions. But the values varied between 4% and 61% for the samples annealed at 400°C, exhibiting greater transmission in the near infra-red region. Both the annealed and the as-deposited samples in water and PVA media show lower range of transmittance, except that the samples of the PVA medium films annealed at 200°C exhibited the highest transmittance of about 67%. The films that were annealed at 400°C 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 [15].

3.4 Reflectance

Most of the films, both as-grown and annealed, show low reflectance in the UV-VIS-NIR region. The sample deposited using the PVP medium and subsequently annealed at higher 200°C exhibited the least reflectance.

3.5 Refractive index

The as-grown sample of the ZnO thin film deposited in the PVP medium has average refractive index of about 2.1 which is almost constant through out the wavelengths under study. Most of the samples both annealed and as-deposited possessed greater values of refractive index at shorter wavelengths.

4. Conclusions

Zinc Oxide thin films were successfully deposited on glass substrates by chemical bath deposition technique. The optical properties of the thin films grown using PVA, PVP and water as deposition media were studied at spectral range of 200 – 1000nm for both the as-grown and the annealed samples. The range of the observed optical band gaps fall between 1.25 and 2.95 eV. Some of the films deposited using the various media show strong absorbance in the VIS region of the electromagnetic spectra while all the films revealed relatively low reflectance in the UV-VIS-NIR regions. All the ZnO thin films annealed at 400°C have relatively high transmittance at the near-infra-red region of the spectrum and are suggested as promising materials for poultry roofs and walls as well as warming materials for homes at temperate regions.

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