FABRICATION, OPTICAL PROPERTIES AND APPLICATIONS OF UNDOPED CHEMICAL BATH DEPOSITED ZnO THIN FILMS

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Abstract: Thin films of ZnO were deposited on glass slides from aqueous solutions of zinc sulphate in which ammonium solution and TEA were employed as complexing agents. The film was studied for its optical properties using measurement from a Unico UV-2102 PC spectrophotometer, at normal incidence of light in the wavelength range of 200-1000nm and Olympus PMG for the photomicrograph. The optical characterization shows that the band gap of the deposited film vary with the annealing of the film; the band gap ranged between 1.60eV and 1.80eV. The films were found to have an average transmittance of greater than 55% in the VIS-NIR regions but become more transparent (above 70%) after annealing to 450K in an oven. The films exhibited average reflectance of greater than 11% in the same regions. Other optical parameters such as refractive index, extinction coefficient, real and imaginary dielectric constants and optical conductivities were also estimated. The film could find potential applications in the areas of antireflection thermal coatings for cold climates and for solar cell fabrication.

Keywords: Antireflection thermal coating, chemical bath deposition technique, optical band gap, solar cells, undoped ZnO.

INTRODUCTION

Zinc oxide has been studied in connection with photoelectrochemical cells, electro optical devices [Bahadur et al. 1986] and can be been used as ultrahigh frequency electro acoustic transducers because of their piezoelectric properties [Pushparajah et al. 1994]. It has been proposed to be used as blue-violet optical emission devices, wide band gap high power devices, surface acoustic devices and ferroelectric memories [Cruz-Vazquez et al. 2001]. Thin films of ZnO have been used but its preparation techniques have been restricted to sputtering, vacuum evaporation, chemical vapour deposition, spray pyrolysis, molecular beam epitaxy, sol gel and pulse laser [Pushparajah et al. 1994, Jimenez Gonzalez and Soto Urueta 1998, Sachez-Juarez et al. 1998, Lin and Huang 2004, Lin et al. 2004, Tatsumi et al. 2004]. Many of these techniques are expensive and require high vacuum and controlled formation conditions. Very limited work has been reported on the preparation of ZnO using chemical bath deposition technique [Cruz-Vazquez et al. 2001] though this technique has been extensively used for other materials. Chemical bath deposition technique for preparation of thin films of ZnO from aqueous solution is a promising technique because of its simplicity, by this method a large area of thin film can be deposited without sophisticated instruments. The properties of the deposited
material can be varied and controlled by proper optimization of the chemical baths and deposition conditions.

In this paper, the deposition of ZnO thin films on glass substrates using chemical bath deposition technique from aqueous solution of ZnSO₄ as starting material and the optical properties are reported. Studies on the optical constants and band gap were well discussed in texts [Pankove 1971, Janai 1979, Ezema and Okeke 2003a,b, Ezema and Asogwa 2004].

MATERIALS AND METHODS

A chemical bath deposition method was employed in preparing zinc oxide films on glass substrates at room temperature and annealed under various temperatures. The glass substrates were previously degreased in HNO₃ for 48 hrs, cleaned in cold water with detergent, rinsed with distilled water and drip dried in air. The synthesis of the films was carried out using concentrated ammonia and triethanolamine (TEA). This was done from controlled chemical reaction using TEA and a stable zinc complex, Zn(NH₃)₃SO₄, which slowly releases the zinc ions. The reaction bath for the deposition of ZnO contained 1M1ml ZnSO₄, 1ml 100%NH₃, 1ml 100% TEA and made to 50ml with distilled water and allowed to stay for 24 hours. The reaction baths were tested for pH - value and it was found to be in a purely alkaline medium before the slides were introduced into the chemical baths. It was a hydrolysis reaction of zinc sulphate as reported by Cruz-Vazquez et al. [2001]

$$\text{ZnSO}_4 + \text{NH}_3 \rightleftharpoons [\text{Zn(NH}_3)^{2+} + \text{SO}_4^{2-}]$$

$$\text{Zn}[\text{NH}_3]^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{NH}_3$$

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

But it is occurring at room temperature with TEA and NH₃ acting as complexing agent in alkaline medium.

The reaction baths were observed to be clear solutions for about 4 hrs before they turned cloudy solutions. When the substrates were withdrawn, rinsed with distilled water and drip dried in air, white thin films were deposited on the glass substrates. The films were annealed to 420K in a hot plate for 5 min. and to 450 K in an oven for 2 hrs.

The films were characterized using a Unico UV-2102 PC spectrophotometer and the photomicrograph carried out using Olympus PMG. The optical properties studied included the absorbance (A), transmittance (T) and reflectance (R). These were used to estimate the other properties such as refractive index (n), extinction coefficient (k), dielectric constant (ε), and optical conductivity (σₑ).
RESULTS AND DISCUSSION

The spectral absorbance of the film is shown in Fig. 1 while the spectral transmittance and reflectance of the films are shown in Fig. 2. The film observed absorption peaks at 368nm, 449nm and 566nm. The annealing of film to 420K initially did not show any clear difference as they overlapped with the film deposited at 300K up till 476nm from where the absorbance started showing a marked difference. Although absorbance spectra decreased with increasing wavelength it is observed that the film annealed to 420K and 450K showed lower absorbance than the as-deposited film at 300K.

The reduction in the absorbance of the film due to annealing could be attributed to the changing of Zn(OH)$_2$ to ZnO [Cruz-Vazquez et al. 2001]. Transmittance of the film improved with its annealing. The transmittance (>75%) of the film when annealed to 450K fairly agrees with above 85% transmittance deposited using chemical bath deposition technique [Cruz-Vazquez et al. 2001] and spray pyrolysis [Sachez-Juarez et al. 1998] but low when compared with high transmittance of 90-95% in UV-VIS-NIR regions deposited using spray pyrolysis [Bahadur et al. 1986, Pushparajah...
et al. 1994] and sol gel method [Jimenez Gonzale and Soto Urueta 1998]. It is observed that as the thickness of the film decreases its transmittance increases. For example the as-deposited film with average thickness of about 0.203µm showed average transmittance of about 62% while the film annealed to 450K showed average thickness of 0.069µm with average transmittance of about 75%. This agrees quite well with the report of Bahadur et al. [1986] that film with greater thickness shows more absorption in the visible range. The reflectance of film decreased from the UV region towards the NIR region on average of 12 to 17% which is moderately high. The moderately high transmittance and reflectance of the film throughout the UV-VIS-NIR regions makes it a good material for applications as antireflection thermal control coating material.

Fig. 3: Refractive index (n) as function of photon energy (hν) for ZnO thin films under various treatments.

Fig. 4: Extinction coefficient (k) as function of photon energy (hν) for ZnO thin films under various treatments.

Plots of n and k against hν are displayed in Figs. 3 and 4 respectively. The refractive index lies between 1.68 and 2.09 at 500nm which fairly agrees with the refractive index between 1.60 and 2.20 at wavelength of 500nm for Li doped ZnO films prepared by spray pyrolysis [Pushparajah et al. 1994]. The average refractive index for the film ranges between 1.64 and 1.98 and on the average observed three peak points, which
ranged between 2.28 at 368nm and 1.72 at 569nm. From minimum values that ranged between $1.34 \times 10^{-3}$ and $2.47 \times 10^{-3}$ at a high-energy region, $k$ rises to maximum values that range between $1.76 \times 10^{-2}$ and $2.97 \times 10^{-2}$ the low-energy region of 1.24eV. The average values of $k$ ranged between $1.50 \times 10^{-2}$ and $2.21 \times 10^{-2}$.

The plots of $\varepsilon_r$ and $\varepsilon_i$ against $h\nu$ are shown in Figs. 5 and 6 respectively.

Fig. 5: Real dielectric constant ($\varepsilon_r$) as a function of photon energy ($h\nu$) for ZnO thin films under various treatments.

Fig. 6: Imaginary dielectric constant ($\varepsilon_i$) as a function of photon energy ($h\nu$) for ZnO thin films under various treatments.

From minimum values that ranged between 1.23 and 1.77 at the low-energy region, $\varepsilon_r$ rises to maximum values that ranged between 3.88 and 5.19 at 3.370eV and on the average started decreasing to minimum values that ranged between 2.28 and 3.34 at 1.24eV in the low-energy region. On the other hand, from minimum values that ranged between $3.01 \times 10^{-3}$ and $6.55 \times 10^{-3}$ in the high-energy region, $\varepsilon_i$ rises to four peak values that ranged between $4.91 \times 10^{-2}$ and 1.08 and lie in the range between 2.19eV and 3.67eV.

The plots of optical conductivity, $\sigma_o$, against $h\nu$ are shown in Fig. 7. The spectral curves resemble that of Figs. 4 and 6 and four distinct peaks exist that ranged between $0.13 \times 10^{14}$ S$^{-1}$ and $0.42 \times 10^{14}$ S$^{-1}$ and lie between 2.19eV and 3.67eV.

Fig. 8 shows the direct transition band gap plots for ZnO films. The direct transition band gaps lie between 1.60eV and 1.80eV.
This is low when compared with the resulting band gap of 3.29eV obtained for Al-doped ZnO prepared by r.f. magnetron sputtering [Lin et al. 2004] and intrinsic band gap of 3.20eV prepared by spray pyrolysis [Bahadur et al. 1986]. The reason for our low value of the band gap could be attributed to lack of doping (since doping of a material increases the energy band gap) and the preparation conditions of the film. However, the obtained band gap is within the solar spectral region for which the film could find potential applications in solar cell fabrication. The variation observed in the band gap could be attributed to changes observed in the grain size of the films when annealed as seen in the photomicrographs. The photomicrographs of the as-deposited film and the films annealed at various temperatures are shown in Fig. 9.

Variation in the morphology shows that annealing of the films not only affects their crystal structure but their absorption coefficient as well. The film deposited at 300K shows a little or no crystal structure but when annealed shows evidence of crystal structure. It can be understood that the film deposited at 300K is Zn (OH)_2, which looks more like amorphous film and on annealing becomes ZnO.
Zinc oxide films with thickness that ranges between 0.069 and 0.203µm have been successfully deposited on glass substrates at room temperature using chemical bath deposition technique and annealed at various temperatures. The characterized films reveal that n ranges between 1.64 and 1.98, ε between 2.71 and 3.94 and σ between 0.11 x 10^14 S^-1 and 0.226 x 10^14 S^-1. The moderately high transmittance of the film over the solar spectrum and a low band gap range (between 1.60eV and 1.80eV) make ZnO thin films good material for solar device applications such as solar cell fabrication, thermal control and antireflection coatings.

References


