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Synthesis and Optical Characterization of Zinc Oxide Thin Film

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Abstract

Zinc oxide (ZnO) thin film was prepared by the electroless deposition method using aqueous solution of zinc acetate ($Zn(CH_3(00)_2)$ as a starting material and EDTA disodium salt was employed as a complexing agent. The film was characterized for optical and morphological properties. From the results obtained, the film was found to have transmittance that increased gradually with wavelength in the VIS region of the solar spectrum, with about 0.85 (85%) at wavelength range of 600nm – 900nm. ZnO films were found to have strong absorption of about 0.75 at wavelength of 320nm that depreciates as the wavelength increased. The optical micrograph of the ZnO film illustrates the formation of submicrometer crystallites distributed more or less uniformly over the surface. The band gap of the ZnO film was found to be 3.00 eV.

Keywords: zinc oxide, chemical bath, thin film and optical properties.

Introduction

Zinc oxide (ZnO) is a II-VI semiconductor with a melting point of 1975 ^{o}C [1]. Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende and the rarely observed cubic rocksalt[2]. The wurtzite structure is most stable at ambient condition and thus most common. The zinc blende form can be stabilized by growing ZnO on substrates with cubic lattice structure. The rocksalt structure is only observed at pressures of about 10GPa[3]. Hexagonal and zincblend polymorphs have no inversion symmetry. It is a relatively soft material with approximate hardness of 4.5 on the Mohs scale[4]. It has high heat capacity and heat conductivity and low thermal expansion[5]. It has a relatively large direct band gap of 3.3eV at room temperature and the band gap of ZnO can further be tuned to 3.4eV by alloying with magnesium oxide or cadmium[3]. It has a lattice constant of a = 3.25Å and c = 5.2 Å[6] and a refractive index of 2.008 and 2.029 for the zincblend and wurtzite structure respectively[1]. Owing to its various physical, mechanical and electronic properties, ZnO is a very promising material for semiconductor device application. ZnO/Al coating are being used as heat protective windows[7]. It can also be used on polycarbonate (PC) in outdoor applications, the coating protects PC from solar radiation and decreases the oxidation rate and photo-yellowing of PC[8]. ZnO nanowires can be used in dye-sensitized solar cells and in field emission devices [9,10]. It also has potential applications in lazer diodes and light emitting diodes (LEDS). Some optoelectric applications of ZnO overlap with that of GaN, which has a similar band gap. But compared to GaN, ZnO has a larger exciton binding energy which results in bright room temperature emission from ZnO. It can also be used as a front contact for solar cells[11]. Field effect transistors can use ZnO nanorods as conducting channels[12]. ZnO has also been considered in spintronics applications. If doped with 1-10% magnetic ions, ZnO could become ferromagnetic[13]. This work reports the successful synthesis of zinc oxide (ZnO) thin film using the electroless deposition method. The synthesis of ZnO thin film by electroless deposition method was based on the reaction between zinc acetate ($Zn(CH_3COO)_2$ and sodium hydroxide (NaOH), using Ethylenediaminetetraacetate (EDTA) disodium salt $^{-}(OOCCH_2)_2$ N-CH_2-CH_2-N $(CH_2COO)_2^{-}$ $2Na^{+}$.$2H_2O$ as a complexing agent.

Material and Methods

We synthesized all the films for this work using the electroless deposition method. *ZnO* thin film was deposited on microscope glass slide substrates. The substrate was cleaned prior to deposition process. It was kept overnight in chromic acid. This was followed by rinsing the substrate in distilled water. The substrate was tightly held in a holder so that only a requisite area for film deposition was exposed. The film thickness was measured by optical method.

The deposition of zinc oxide thin film by this method was based on the reaction between zinc acetate, as a source of Zn^{2+}, sodium hydroxide as a source of O^{2-} and EDTA disodium salt as a complexing agent. EDTA disodium salt is used to eliminate spontaneous precipitation of the chemical reagents and ensure ion by ion condensation. Details of bath constituents for the synthesis of ZnO thin films are shown in table–1.

The Optical absorbance spectra of the deposited films were obtained by means of Janway 6405 UV/VIS spectrophotometer. Surface morphology of the thin films deposited on glass substrate was examined by a BHZ - UMA Olumpus optical microscope. From the spectrophotometer, the absorbance in arbitrary units was measured. Parameters such as transmittance, reflectance, refractive index and extinction coefficient were then calculated using the relationship explained below:

For weakly absorbing thin film on a non absorbing substrate, the transmittance (T) can be expressed as [14]:

$T = (1-R^2) \exp(-\alpha t)$, $t = 1/\alpha \{\ln(1-R^2) / T\}$

where R is the reflectance, α is absorption coefficient, t is the thickness of the film.

For semiconductor and insulators, where the extinction coefficient (k) and refractive index (n) are related as $k^2 << n^2$, the relationship between R and n is given by [15] as:

$R = (n-1)^2 / (n+1)^2$, Also k and α are related by: $k = \alpha \lambda / 4\pi$

Where λ is the wavelength of electromagnetic radiation. In high absorption region under photon energy, the relation between absorption coefficient (α) and photon energy (hf) is given by [16]:
$\alpha = (hf-Eg)^n$

Where f is the frequency, h is the Planck's constant, Eg is the energy band gap and n is a number which characterizes the optical processes; n= ½ is for direct allowed transition, n =2 is for indirect allowed transition and n =3/2 is for forbidden direct allowed transition. When the straight portion of the plot of α^2 against hf is extrapolated to $\alpha^2 = 0$, the intercept gives the value of the transition band energy (Eg).

Table-1
Bath constituents for synthesis of ZnO

***Slide* No.**	**1M $Zn(CH_3(00)_2$ Vol. (ml)**	**1M NaOH Vol. (ml)**	**1M ED.T. A Disodium Vol. (ml)**	**Dip time (hrs)**
ZnO_1	10.00	10.00	0.50	24.00
ZnO_2	10.00	10.00	1.50	24.00
ZnO_3	10.00	10.00	2.50	24.00
ZnO_4	10.00	10.00	3.50	24.00
ZnO_5	10.00	10.00	4.50	24.00

Results and Discussion

Figure - 1 shows the plot of thickness versus volume of complexing agent. Figure -1 indicates that thickness increased from about 0.818µm to about 0.877µm with 1.50mls to 4.5mls volume of complexing agent. This indicates that as complexing agent increases, the thickness increases.

Figure - 2 shows the absorption spectrum of *ZnO* thin film in the wavelength range 300 - 1100 nm. The absorbance generally decreased with increase in wavelength and has relatively low values in the infrared region of the spectrum. A strong absorption of about 0.75 was observed at wavelength of 320nm, hence the film has potential application in fabrication of solar cell.

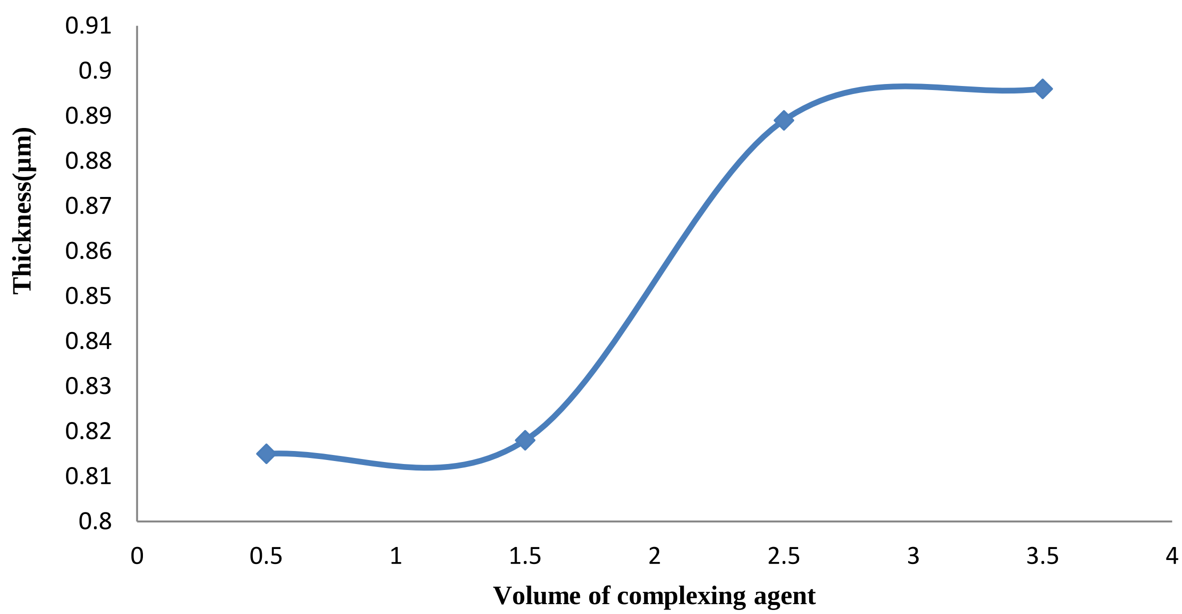

Figure-1
Plot of thickness versus vol. of complexing agent for zinc oxide thin film

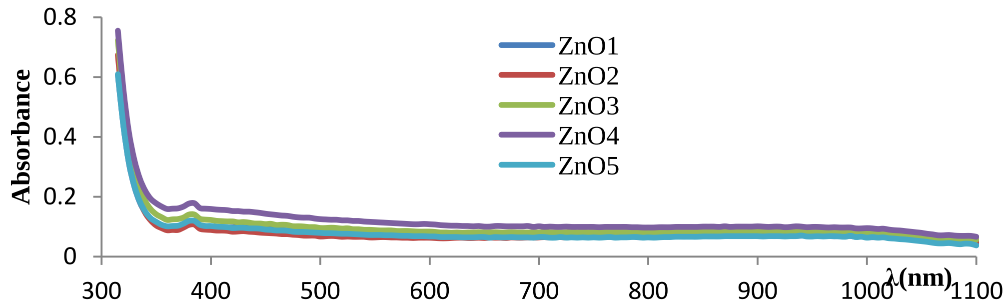

Figure- 2
Plot of absorbance versus wavelength for zinc oxide thin film

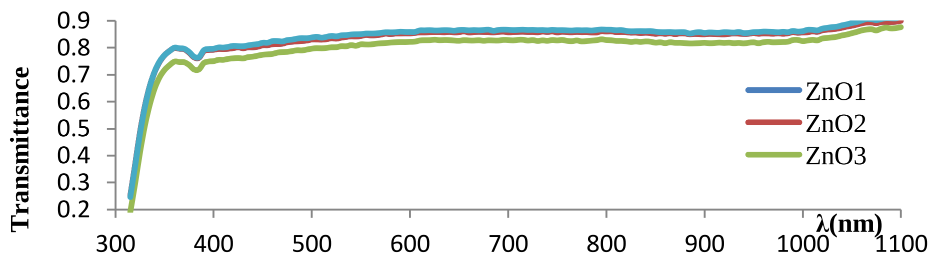

Figure- 3
Plot of transmittance versus wavelength for zinc oxide thin film

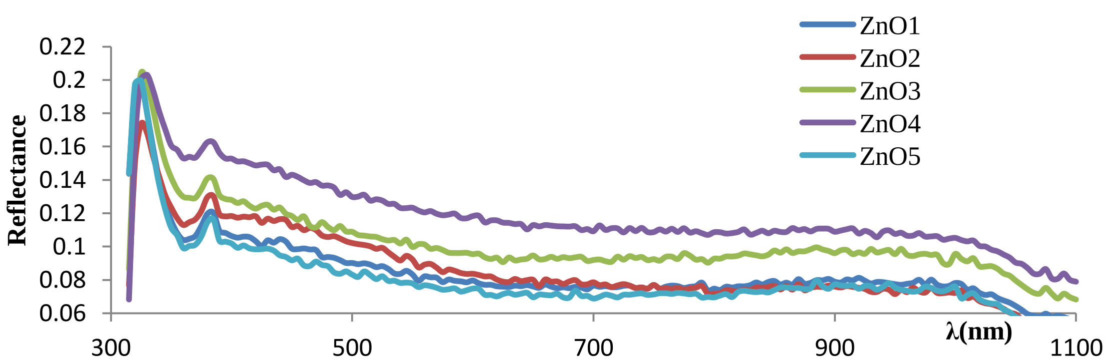

Figure-4
Plot of reflectance versus wavelength for zinc oxide thin films

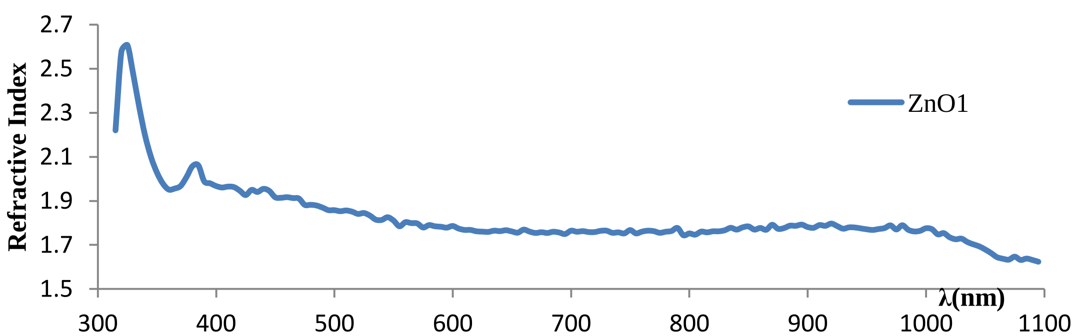

Figure-5
Plot of refractive index versus wavelength for zinc oxide thin film

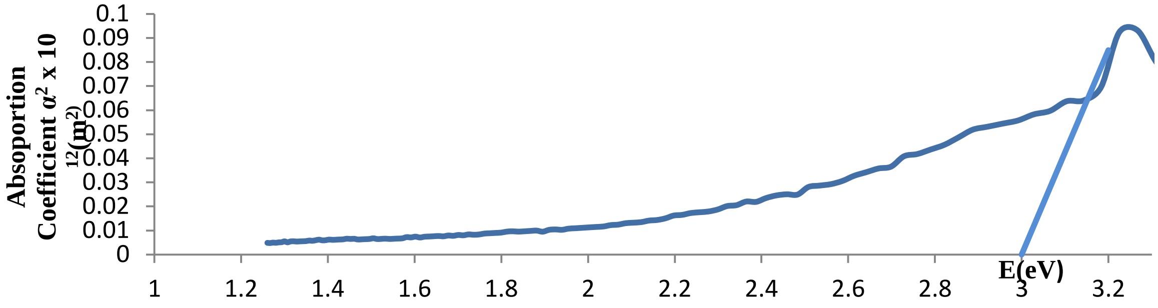

Figure-6
Plot of absorption coefficient squared versus photon energy for zinc oxide thin film

Figure-7
Optical micrograph of zinc oxide thin film

The transmission spectra displayed in figure - 3 shows that the films transmit well in the VIS / NIR region of the solar spectrum. The film's transmittance increases gradually with wavelength in the VIS region of the solar spectrum, with about 0.85 (85%) at wavelength range of 600nm–900nm. This observation is also consistent with the finding of[17] who reported 75% transmittance in the visible region. This high transmittance in the visible region makes *ZnO* films useful aesthetic window glaze material. Also, the high transmittance of the film makes it suitable for solar energy collection because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid.

The typical UV-VIS –NIR optical reflectance spectra of *ZnO* thin films for the different samples are shown in figure - 4. It is evident that the reflectance for all the fabricated film are low. This low reflectance value makes *ZnO* thin film an important material for anti-reflection coating.

Figure - 5 shows a plot of refractive index (n) versus photon energy (hv) of *ZnO thin* film. The refractiveindex (n) of the films increases with the photon energy revealing a refractive index of 2.62 at 340nm. This result revealed that *ZnO* has high refractive index. The high refractive index possessed by *ZnO* films makes it suitable for use as anti-reflection coatings.

Figure - 6 shows the optical micrograph of *ZnO* film. The formation of submicrometer crystallites distributed more or less uniformly over the surface is evident from the figure. The surface morphology of *ZnO* thin film shows high density of grains. The high density of these grains implies that the nucleation has occurred on all sites.

Figure - 7 shows a plot of α^2 versus photon energy (hv) of *ZnO* thin films. The energy gaps for these films are obtained by extrapolating the linear part of the curve to $\alpha^2=0$. This yielded a band gap of 3.00 eV for *ZnO* thin film. This is in close agreement with the finding[3], who reported a band gap of 3.30eV and[18], who reported a band gap 3.44 eV.

Conclusion

Thin film of zinc oxide was prepared by electroless deposition method. It is seen from the present work that increasing the concentration of complexing agent icreases the thickness of the film. The films were found to have strong absorption of about 0.75 at wavelength of 320nm and depreciates as the wavelength increased. The film's transmittance increases gradually with wavelength in the VIS region of the solar spectrum, with about 0.85 (85%) at wavelength range of 600nm – 900nm. The reflectance for all the fabricated films were low. The energy gap for the fabricated *ZnO* thin film was found to be 3.00eV.

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