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Influence of Thickness on Optical Properties of ZnO Thin Films prepared by Radio Frequency Sputtering Technique

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Abstract- *Zinc oxide (ZnO) thin films of 75.5nm and 130.5nm were deposited at room temperature onto chemically and ultrasonically cleaned corning glass substrate by radio frequency technique and annealed at 150°C under nitrogen atmosphere for 60 minutes. The Zinc target of purity 99.99%, diameter 40mm and thickness 6.35mm was used. The optical properties of the films were ascertained by employing UV-VIS-NIR spectrophotometer (model AVASPEC 2048 MODEL). Influence of the thickness of the films on the optical properties was studied by keeping other deposition parameters constant. The optical transmittance spectra revealed an average transmittance of 81.49% and 84.26% for the 75.5nm and 130nm respectively. The band gap of the films was found to decreases with increase in thickness of the films. The band gap energy (E_g) is in the range of 3.28eV to 3.31eV respectively. Other optical parameters such as Absorbance, Reflectance and Urbach energy were also found to be thickness dependent. These effects of thickness on optical properties of ZnO thin films are suitable for solar cell applications.*

Key words: ZnO, Sputtering, Film Thickness, Band Gap Energy, Urbach Energy

1.0 INTRODUCTION

ZINC OXIDE (ZnO) is an attractive material for a large variety of applications such as microelectronics, piezoelectric, optoelectronic and photovoltaic devices. It is a wide-band gap oxide semiconductor with a direct energy gap of about 3.37 eV. Zinc oxide has emerged as one of the most promising materials, due to its optical and electrical properties associated with high chemical and mechanical stability. This makes it a lower cost material when compared to the most currently used transparent conductive oxide materials such as ITO (indium tin oxide) and SnO2 (Bensmaine et al., 2007). The synthesis and characterization of polycrystalline materials have attracted much attention not only because of their exceptional properties but also due to their structure, temperature dependent properties and great potential for many technological applications. Recently there has been an increase in research and development of II-VI materials that are widely used for glazing windows, solar energy collectors, and low cost flat panel solar cells. These films offer a large number of applications in solid-state device technologies such as the target material for television cameras, microwave devices, switching devices, infrared detectors, diodes and Hall effect devices (Ziul et al., 2010). Thin films have also exhibited a wide variety of applications in environmental engineering, catalysis and gas sensor systems because they can be fabricated in small and large-scale dimensions. During the last years, several deposition techniques for thins film have been developed and studied, such as, ion-beam-assisted deposition, chemical vapor deposition CVD (Buba and Adelabu., 2010), pulsed-enhanced chemical vapor deposition (PECVD) (Tabenskaya et al., 1995), spray pyrolysis (Godbole et al., 2011), molecular beam epitaxy (MBE), sol-gel processing (Singh et al., 2009), reactive DC sputtering and magnetron sputtering technique which is one of the most widely used due to its reproducibility and efficiency (Bingyao and Weidon, 2008; Chaoyang et al., 2007; Chongmu et al., 2008; Jae et al., 2003). The objective of this paper is to study the thickness effect on ZnO thin films grown by radio frequency (Rf) magnetron sputtering at 150°C considering the fact that a lot of researchers studied such effect on films but at high annealing temperatures. Radio frequency magnetron sputtering exhibits interesting advantages such as the low substrate temperature, good adhesion of the films on the substrates, and a high deposition rate.

2.0 EXPERIMENTAL

Zinc oxide films deposited by RF magnetron sputtering are very sensitive to the deposition parameters; these should therefore be optimized in order to obtain highly orientated ZnO films. Fig. 1 shows the apparatus of RF magnetron sputtering. It consists of a cylindrical plasma chamber, sputtering gas inlet, vacuum pump etc.

The distance between the cathode and the substrate holder was 100 mm. The deposition chamber was pumped down to a base pressure of 5×10-7mbar by a turbo molecular pump prior to the introduction of the argon/oxygen gas mixture for ZnO thin film production. The pressure was fixed at 4.6×10-3mbar and the time of

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deposition was 60 minutes. The RF power was set at 60 watts.

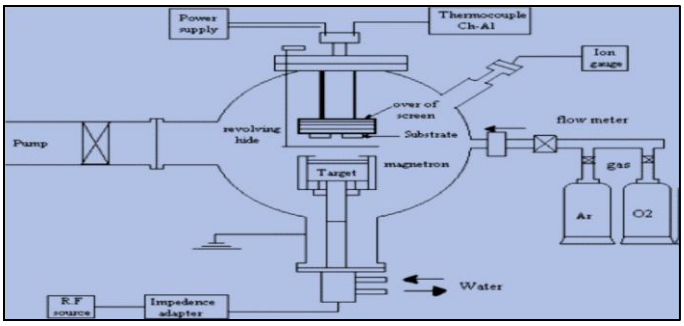

Fig. 1: Radio frequency magnetron sputtering system

The substrate holder temperature was kept at room temperature and the oxygen percentage in Ar/O2 gas mixture was kept at a ratio ZnO films were deposited by RF magnetron system on corning glass substrates. The Zinc target (purity 99.99%) diameter was 40 mm and 6.35 mm thick. of 1 to 1.The details of the deposition conditions were summarized in the table 1. After the deposition, the two samples were annealed under nitrogen atmosphere at 150°C for 60 minutes by the use of carbolite horizontal furnace. To determine the optical characteristics the films, UV-VIS-NIR (AVASPEC 2048 MODEL) spectrophotometer with a wavelength range of 180-1200nm was used. The transmittance of the samples was calculated using equation (1)

$$T = \frac{1}{10^{A}} \qquad (1)$$

Where A is absorbance.

In order to determine the optical band gap of the films, equation (2) was employed

$$\alpha h\upsilon = B(h\upsilon - E_g)^m \qquad (2)$$

Where B is a constant, m value is respectively 1/2 and 2 for direct and indirect transitions. The variation of $(\alpha h\upsilon)^2$ with photon energy hυ of ZnO thin films. The intercepts (extrapolations) of these plots (straight lines) on the energy axis give the energy band gaps.

To calculate Urbach energy, it is assumed that the absorption coefficient near the band edge shows an exponential dependence on photon energy and this dependence is given as;

$$a = a_0 \exp(\frac{hu}{E_u}) \qquad (3)$$

where α_o a_0 is a constant and E_u is Urbach energy interpreted as the width of the tails of localized states, associated with the amorphous state, in the forbidden gap. The Urbach energy was obtained from the plot of photon energy vs. ln (α).

TABLE 1: DETAILS OF DEPOSITION PARAMETERS USED IN THIS STUDY

S/N	Parameter	Deposition Details
1	Substrate	Corning Glass 7059
2	Target/Target diameter	ZnO Ceramic target 4N/4cm
3.	Substrate/Target Distance	7 cm
4.	Annealing Environment	Nitrogen/Air
5.	Annealing set points	150°C
6.	Annealing Ramp rate	10°C/min.
7.	Annealing period	60 minutes
8.	Film Thickness	75.5nm and 130.5nm
9.	Deposition pressure	4.6×10^{-3} mbar
10.	Argon/Oxygen flow rate	1 standard cubic centimeter (sccm) at 1:1 ratio
11.	Substrate temp	Room Temp.
12.	Rf power	60 W.
13.	Deposition time/period	1 Hour

3.0 RESULTS AND DISCUSSION

3.1 Transmittance

Fig. 2 shows the wavelength dependence of optical transmittance spectra of ZnO thin films deposited on corning glass by reactive RF magnetron sputtering at different thicknesses (75.5nm and 130.5nm). Both films sputtered at ambient temperature shows an average transmittance of 81.49% and 84.26% respectively in the wavelength range from 350 to 750 nm. It is clear from Figure (2), that the optical transmittance increases slightly with increasing of film thickness. Similar trend was reported by Chitra et al., (2013) and Asel and Ali (2015). The sharp absorption edge was observed at the wavelength of about 400nm and shifted towards higher wavelengths. Displacement of the absorption edge is due to Fermi level moving into the conduction band with the increase in carrier concentration according to the theory of Burstein-Moss effect (Guilleen and Herrero, 2010).

3.2 Reflectance

Figure 3 depicts the plot of reflectance versus wavelength for ZnO thin films of thicknesses 75.5nm and 130.5nm. The film having a thickness of 75.5nm shows an average reflectance of 38.78%, while 130.5nm thickness exhibits an average reflectance of 30.76%. These indicate that as thickness increase thin film become less reflective.

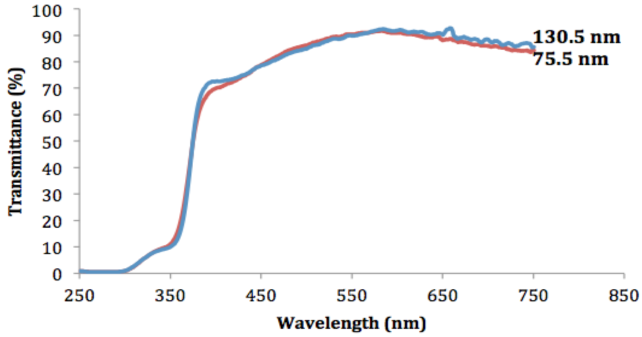

Fig. 2: Transmittance vs. wavelength for 75.5nm and 130.5nm thick thin film

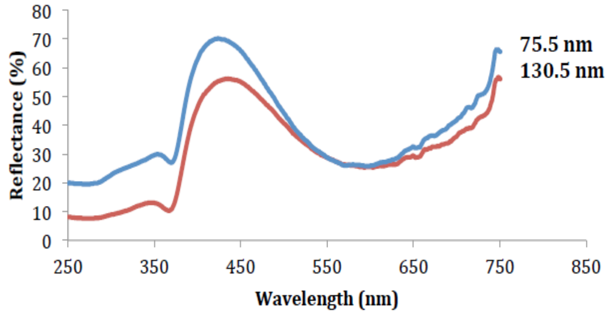

Fig. 3: Reflectance vs. wavelenght for 75.5nm and 130.5nm thick thin film

3.3 Absorbance

Fig. 4 shows the plots of absorbance against wavelength for the 75.5nm sample and 130nm thick sample respectively. The films started absorbing the incident radiation from 380nm in the visible spectrum. It can also be seen that all the samples have shown very high absorbance in the UV region and low absorbance in the visible and infrared regions of the solar spectrum.

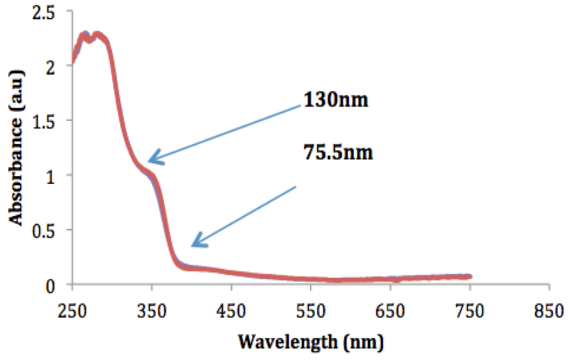

Fig. 4: Absorbance vs. wavelenght for 75.5nm and 130.5nm thick thin films

3.4 Energy band gap

The variation of (αhυ)2 with photon energy hυ of ZnO thin films of 75.5nm and 130.5nm is shown in Fig. 5. It has been observed that the plots of (αhυ)2 versus hυ are linear over a wide range of photon energies indicating the direct type of transitions. The direct band gaps (Eg) of 75.5nm and 130.5nm thin films were determined at 3.31eV and 3.28eV, respectively. This implies that band gap energy decreases with increase in ZnO film thickness.

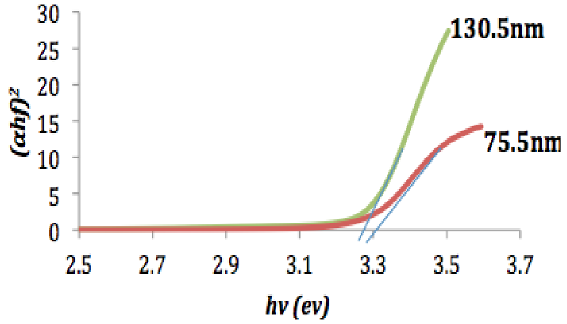

Fig. 5: (αhf)2 vs. hf for 75.5nm and 130.5nm thick thin film

The band gap obtained for both samples is less than that of the bulk (3.37eV). This difference may be due to the fact that the values of band gap (E_g) depends on many factors two of which include structural defects and the crystal structure of the films. Moreover, departures from stoichiometry form lattice defects and impurity states. (Boa et al., 1998) reported that the band gap difference between the thin film and crystal is due to the grain boundaries and imperfections of the polycrystalline thin films. The difference seen in the band gap between the film and bulk is due to the grain boundary, the stress and the interaction potentials between defects and host materials in the films.

3.5 Urbach energy (E_u)

The photon energy vs. ln (α) plots for ZnO thin films of 75.5nm and 130.5nm are shown in Figure 6. The values of Eu obtained from this figure are given in Table II. It is believed that the exponential dependence of α on photon energy may arise from random fluctuations of the internal fields associated with the structural disorder in many materials. The Urbach energy (Eu) value of 130.5nm thick sample is (2.4eV) higher than that of 75.5nm thick sample which has 2.3eV. This suggests that the film thickness increases the Urbach energy referred the width of the band tail. This is probably due to the structural disorders in the samples and increase in the degree of amorphous character (Tariq and Almushtak, 2010). The change in the value of E_u is also associated with the breakdown of crystal structure of

ZnO at high annealing temperature (Ezema and Nwankwo, 2010).

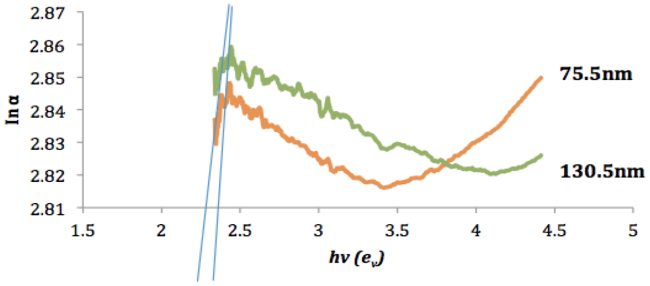

Fig. 6: ln α vs. hv for 75.5nm and 130.5nm thick thin

TABLE II: VALUES OF URBACH ENERGY (E_U)

Sample thickness (nm)	Urbach energy (E_u)
75.5nm	2.3eV
130.5nm	2.4eV

4.0 CONCLUSION

ZnO thin films of different thicknesses were prepared on glass substrate by RF sputtering technique. Changes in the optical properties of these films were studied with respect to their thickness. The band gap energy (E_g) was found to increase with thickness. Other optical parameters such as Absorbance, Reflectance and Urbach energy were also found to be thickness dependent. These effects of thickness on optical properties of Rf sputtered ZnO thin films are suitable for solar cell applications.

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