Annealing Effects on the Optical Properties of Sol-Gel Spin Coated Zinc Oxide (Zno) Thin Films

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Abstract: ZnO thin films of 50 nm thickness have been deposited on uncoated glass substrates by the sol-gel spin coating method at 3000 rpm chuck rotation rate. After the deposition, the samples were annealed in open air at 300^0C, 350^0C and 400^0C respectively. The effect of annealing temperature on the optical and electrical properties of the samples was investigated. It has been observed that the transmittance and the optical band gap vary with the annealing temperature. The resistivity and the sheet resistance were influenced by the annealing. Some of the samples can be used as window layer for solar cells and are also applicable in other opto-electronic applications.
Keywords: Spin Coating, Sol-gel, ZnO, Optical band gap, four-point probe.

INTRODUCTION

Transparent conducting oxide (TCO) thin films have attracted significant research attention in the recent years due to their wide use in electronic and optoelectronic devices. Zinc Oxide (ZnO) is one of the II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure [1, 2]. ZnO is a wide direct band-gap (3.37 eV) Semiconductor with a broad range of applications [3-5]. Due to large exciton binding energy of 60 meV, the II-VI semiconductors have potential applications in Optoelectronic devices such as solar cells [6], Optical wave guide [7]. Light emitting diodes (LED) [8]. Zinc Oxide thin films are applied in thin film transistors (TFT) [9] and have been recognized as spintronic material [10].

Various gas, chemical and biological sensors were based on ZnO thin film [11]. Thin films of ZnO can be prepared by various techniques such as Chemical Vapor Deposition (CVD) [12], Spray pyrolysis [13-15], Sputtering [16, 17], Laser ablation [18-20], spin coating (5, 21-22) and sol-gel [23-25].

The preparation of ZnO thin films has been the subject of continuous research for a long time because the Properties of ZnO thin films show dependence on the technique used. Apart from doping, to increase the functionality of ZnO thin film, the effect of preparation conditions on the properties have to be considered for its effective technological applications. Few works [26] have been done in this direction for ZnO film prepared by sol-gel. In spite of few studies, the sol-gel method has some merits, such as easy control of chemical components and fabrication of thin film at a low cost [2]. As described by [27], films prepared by spin coating tend to be uniform in thickness due to centrifugal force on one hand and the viscous force (friction) on the other hand. The overall processes of spin coating entail depositing and drying.

In this work, the dynamic programming mode was used for the multilayer ZnO thin films spin coating, this allow the substrate to spin during the film deposition. The influence of annealing on optical and electrical properties is reported.

EXPERIMENTAL SECTION

ZnO thin films were deposited by sol-gel spin coating method on uncoated glass substrates. Zinc (ii) acetate dehydrate, 2-methoxyethanol and pyridine were used as the starting materials, solvent and stabilizer. The precursor solution for fabricating ZnO thin films was prepared by dissolving 1g of Zinc (ii) acetate dehydrate in 50ml 2-methoxyethanol under reflux. The precursor was chelated with 0.8 pyridine to make it stable. The glass substrates were pre-cleaned with detergent and then cleaned in methanol and acetone for 10 mins each by using ultrasonic cleaner and then cleaned with deionized water and dried. The coating solution otherwise called the precursor was dropped onto glass substrate which was rotated at 3000 rpm for 3 minutes 5 seconds using the dynamic mode program settings of model number WS-650HZ-23NPP/A3/AR2 spin coater. The steps for the dynamic mode program is shown in Table 1.

Table-1: Steps for the dynamic mode

Steps	Time(s)	Rpm	Acceleration(m/s^2)
Step 1	30	+150	20
Step 2	30	+150	1000
Step 3	120	+3000	3000
Step 4	5	-	6000

From table 1, steps 1 and 2 indicates dispensing, this implies that, as the substrate is spinning, the sol-gel otherwise called the precursor is deposited. The two steps lasted for 30 seconds each. In step 3, we have spreading which lasted for 2 minutes and finally in step 4, the spinning of the substrate comes to rest (that is, stopping) in 5 seconds. After which the deposited film was inserted in a film furnace on a hot plate set at 280°C for 5 minutes and allowed to cool for 4 minutes and taken back for the same process, the processes were carried at eight different times for the three samples in order to obtain a multiple coating layer of ZnO thin films. However, the procedures from coating and drying were repeated eight times. The films were then inserted into a tube furnace and annealed in air at 300^{0} C, 350^{0} C and 400^{0} C respectively for one hour. Figure 1 shows the flowchart which is showing the procedure for preparing ZnO thin films.
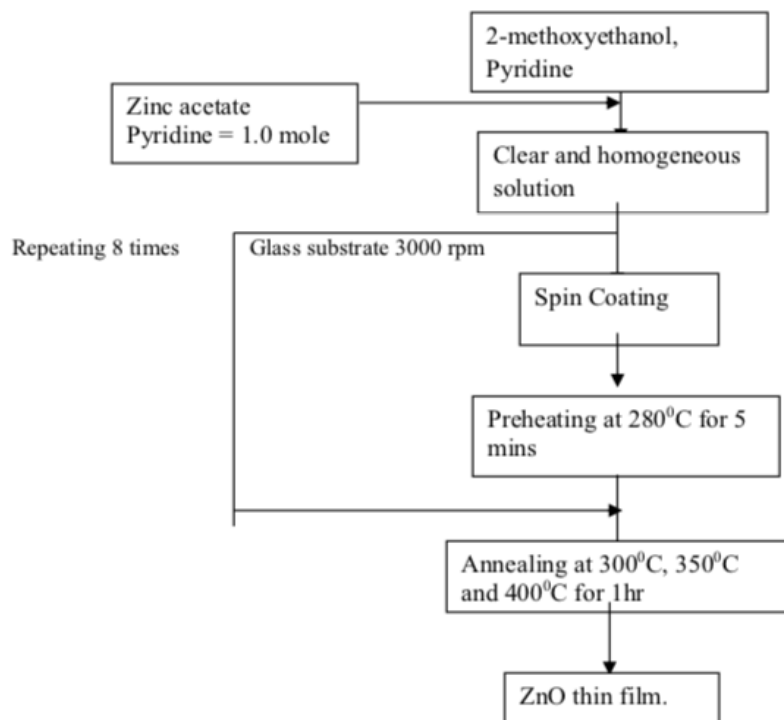
Fig-1: Flowchart of sol-gel method for preparation of ZnO thin films

Characterization

The thickness of the thin film was determined with Veeco Dektak 150 profiler. The transmittance and reflectance measurement of the thin film were carried out at room temperature using UV-VIS Spectrophotometer (AVASPEC 2048) with integrating sphere in the wavelength range of 180-1100 nm from which the optical band gap of the thin films was determined. The conductivity of the film was verified using four-point probe. The samples were referred to as A$_{300}$, A$_{350}$ and A$_{400}$ for the annealing temperatures of 300, 350 and 400^{0}C respectively.

The absorption coefficient (α) is calculated [28] from Equation (1).

$$\alpha = \left(\frac{1}{t}\right)T \tag{1}$$

where t is the thickness and T the transmittance obtained from optical data.

The Kubelka-Munk function is applied to convert the diffused reflectance into equivalent absorption coefficient [4, 18, 29] using (2).

$$\alpha = F(R) = \frac{(1-R)^2}{2R} \qquad (2)$$

where F(R) = Kubelka-Munk function, α = absorption coefficient and R = reflectance as a function of energy. Thus the Tauc relation becomes, $F(R)hv = A(hv - Eg)^n$ where n = 0.5 for direct transitions. Extrapolation of linear regions of these plots to $(F(R)hv)^2 = 0$ yielded the direct band gap of a particular sample.

Equation (2) is usually applicable for those materials which have high light scattering and absorbing particles in their matrix. Therefore, diffused reflectance is effective for determining the band gap of the solar cell absorbers.

The absorption coefficient (α) and the extinction coefficient (k) are related by the formula in Equation (3) [14, 30].

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

The Optical energy band gap (E_g) and absorption coefficient α are related [31] by Equation (4);

$$(\alpha hv)^2 = A(hv - E_g)^r \qquad (4)$$

where α is absorption coefficient, h is Planck's constant, v is the photon energy, A is a constant, E_g is the direct transition band gap and r is the number which characterizes the nature of the electronics transition between valence band and conduction band [32].

For direct allowed transition $r = \frac{1}{2}$ and it is known that ZnO is a direct band gap semiconductor. Thus, by substituting r into Equation (4) and re- arranging, the expression becomes Equation

$$(\alpha hv)^2 = A(hv - E_g)^{\frac{1}{2}} \qquad (5)$$

The sheet resistance, Rs is given by [33] in Equation in Equation (6)

$$Rs = 4.53 \times \frac{V}{I} \qquad (6)$$

where V is the measured voltage between the two inner probes and I is the current passing through the two inner probes. The resistivity, ρ of the thin film is usually determined from Equation (7) given by [14];

$$\rho = 4.532 \left(\frac{V}{I}\right) t = R_s t \qquad (7)$$

where V, I, R_S and t are the voltage, current, sheet resistance and film thickness, respectively.

RESULTS AND DISCUSSION
Optical transmittance
Figures 2, 3 and 4 shows the transmittance spectra of ZnO films annealed at different temperatures. For sample A_{300}, the transmittance is 96%. The spectra for samples A_{350} and A_{400} show transmittances of 99% and 98% respectively. From the figure it can be seen that when the annealing temperature was increased from 350 °C to 400 °C (samples A_{350} and A_{400}), the transmittance decreased from 99% to 98%. This behavior can be related to the increased surface roughness, which dispersed light and causes its diffusion in random directions, resulting in transmittance decrease [31]. [34] reported that thermal annealing in air could improve the optical transmittance of ZnO films, attributing to the oxygen reaction with ZnO. The spectra also show interference fringes which has its origin in the interference of light reflecting between air-film and film-substrate interface. The appearance of interference fringes indicates smooth reflecting surface of the film and low scattering loss at the surface. This phenomenon is usually noticed when the film thickness is larger than $\lambda/2$, where λ is the wavelength of incident light. Increase in transmittance as a result of thermal annealing can be related to among other things structural homogeneity and crystallinity [35-36]. All the samples exhibit

sharp absorption edge at about 350 nm indicating that the incoming photons have enough energy to excite electrons from the valence band to the conduction band [22].
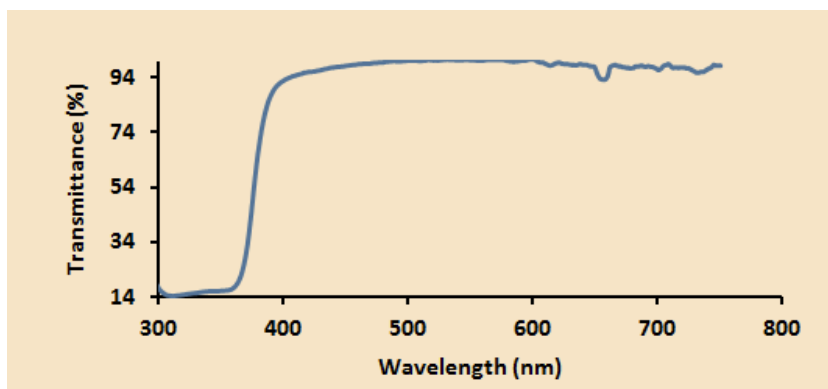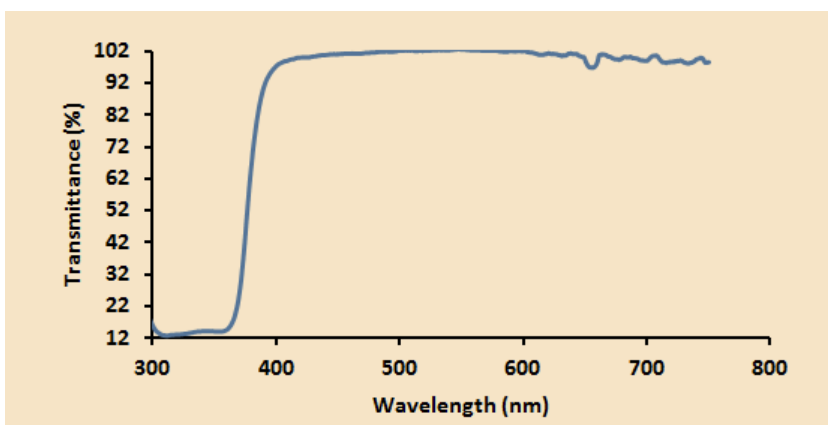

Fig-2: Wavelength versus Transmittance of sample A$_{300}$
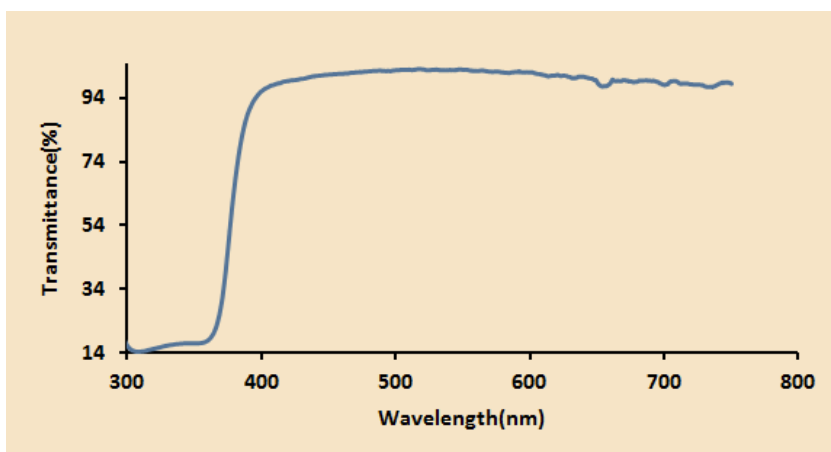

Fig-3: Wavelength versus Transmittance of sample A$_{350}$

Fig-4: Wavelength versus Transmittance of sample A$_{400}$

Optical bandgap
The variation of $(\alpha h v)^2$ and $h v$ as obtained using Equation (4) is shown on Figures 5, 6 and 7 for ZnO thin films annealed at different temperatures. The optical energy band gap is varied and found to decrease with increase annealing due to increase in grain size which may be attributed to the more realignment in orientation and improvement in crystallinity (reported elsewhere).

The Band gap calculated for samples A_{300}, A_{350} and A_{400} are 3.60 eV, 3.41 eV and 3.37 eV respectively. The band gaps of samples A_{300} and A_{350} is higher than that of the bulk ZnO (3.37 eV). This may be caused by the increase in the internal energy of the conduction band, which produces occupied states near to the band edge for which a higher energy photon is required for excitation of a carrier through the band gap [27]. Change in energy band gap can be attributed to the reduction of the structural defects in films network and also to the increase of grain size with annealing [35]. However, from the results, it has been observed that the band gaps of samples A_{350} and A_{400} are closer to that of the bulk ZnO. Low bandgap (bandgap stretching) might be attributed to reduction in oxygen vacancies in the thin films [37]. [38] reported that decrease in band gap can also be attributed to the formation of oxygen vacancy states near the bottom of the bandgap. The obtained energy gap for samples A_{350} and A_{400} make ZnO thin film a promising semiconductor material for fabrication of photovoltaic solar cells [30].
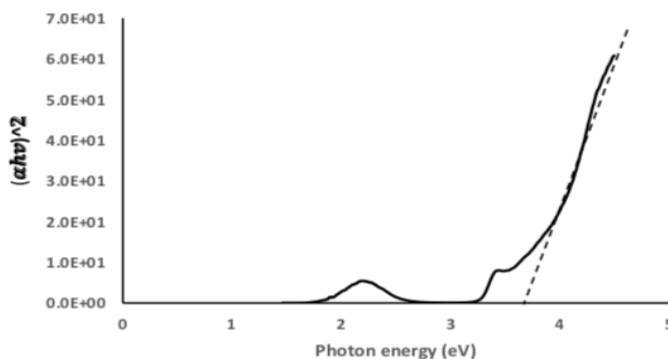

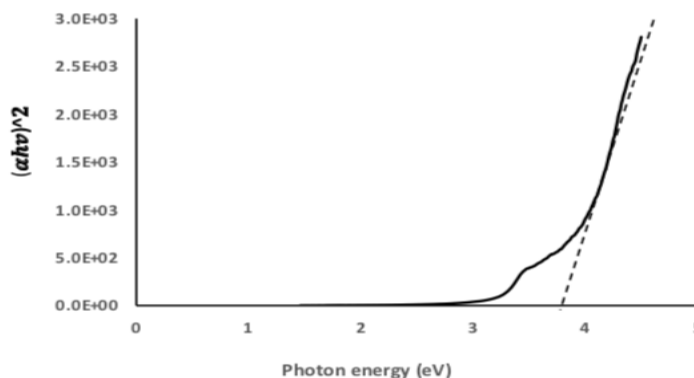**Fig-5: Photon energy versus $(\alpha h v)^2$ of sample A_{300}**

Fig-6: Photon energy versus $(\alpha h v)^2$ of sample A_{350}
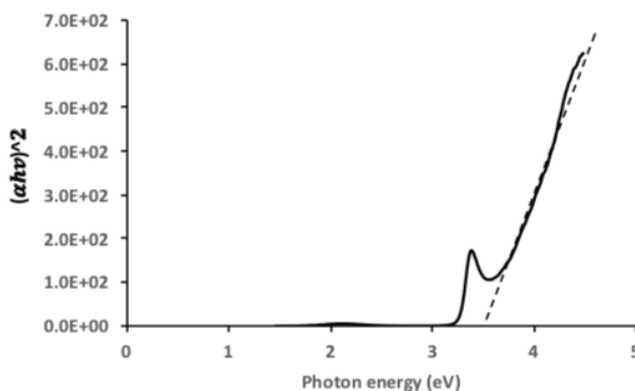

Fig-7: Photon energy versus $(\alpha h v)^2$ of sample A_{400}

Electrical Properties

The resistivity and the sheet resistance were also studied. The resistivity of samples A_{300}, A_{350} and A_{400} were determined at 5.33×10^5, 5.17×10^5 and 4.28×10^5 (Ω.cm) respectively. The resistivity of the films is found to decrease with annealing temperature owing to decrease in grain boundary domains. The electrical resistivity of pure ZnO films depends on the oxygen deficiencies or the presence of interstitial Zn in the ZnO lattice.

The oxygen deficiencies or Zinc interstitials in the ZnO lattice are increased with annealing temperature and may be attributed to the increase in free electrons [36]. The decrease in resistivity as a result of increase in the annealing temperature can also be related to improvement the film crystallinity (reported elsewhere) [15, 39-41]. It has also been suggested by [42] that as the annealing temperature increases, conductivity in semiconductor increases due to hole-electron pair generation. The sheet resistance on the other hand increases with increase in annealing temperature. The sheet resistance for samples A_{300}, A_{350} and A_{400} is 1.07×10^{11}, 1.03×10^9 and 8.57×10^7 respectively.

CONCLUSION

The effect of annealing temperature on the optical and electrical properties of Sol-gel spin coated ZnO thin films have been investigated. The transmittance of the samples varies with the annealing temperature. The Optical band gap for sample A_{400} is 3.37 eV which agrees well with that of bulk ZnO (3.37 eV). The E_g of samples A_{300} and A_{350} stood at 3.60 and 3.41 eV. This property makes the sample novel for use as window layer of solar cells. It is thought that because of these properties, ZnO thin films can be used as a window material in photovoltaic applications.

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