Influence of Annealing Temperature on the Optical Properties of Cu Doped Zinc Oxide Films

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Abstract: ***In this work, Cu-doped zinc oxide films were deposited using the sol-gel method. The impact of annealing temperature on optical properties was examined. The transmission spectra confirm that all the samples had a percent transmission >90 in the visible wavelength range. The refractive index was found to be ~1.8 from the oscillating pattern of the transmittance spectra. It was noted that the annealing temperature has less effect on the bandgap energy, which was determined to be ~3.2 eV. SEM images and recorded EDAX spectra confirm the distribution of grains and the successful incorporation of Cu atoms in ZnO.***

Keywords: CuZnO, transmittance spectra, refractive index, II-VI Semiconductor, P-type

1. Introduction

Zinc oxide (ZnO) is a versatile material that has attracted considerable attention in recent years due to its unique optical, electrical, and structural properties. ZnO has a wide bandgap of 3.37 eV and a large exciton binding energy of 60 mV, making it suitable for various optoelectronic and solar applications [1–3]. The structural, optical, and electrical properties of ZnO films were significantly affected by deposition parameters and dopants. ZnO is a semiconductor material of the intrinsic n-type due to native donor defects such as oxygen vacancies (Vo) or interstitial zinc (Zni) [4]. When ZnO was doped with the IIIrd group, it was observed that the conductivity got enhanced and it remained n-type ZnO [4]. However, it is difficult to fabricate p-type ZnO with sufficient electrical conductivity. When ZnO was doped with Ist and Vth group elements, it formed p-type ZnO. However, the low solubility of dopants, low thermal excitations into the energy level of acceptor impurities, and the introduction of point defects acting as compensators are the main obstacles during the fabrication of P-type ZnO [5]. Recently, several research groups have been trying to improve p-type conduction using dopants from the Ist and Vth groups, like lithium, sodium, nitrogen, phosphorus, silver, and copper [6–9]. As discussed earlier, the addition of different types of impurities can change the properties of ZnO, which are useful in various applications. When copper is doped into ZnO, it enhances its ferromagnetic and photoluminescence properties, as observed by Xu et al. [10]. During this work, it was noted that very little work was carried out using cost-effective methods for depositing p-type ZnO thin films. Therefore, through this work, an attempt has been made to fabricate high-quality cost-effective Cu-doped ZnO films using sol-gel deposition technique. Moreover, since the ferroelectric and photoluminescence properties are examined by others, we aimed to investigate the optical properties of Cu-doped ZnO thin films through this work.

2. Experimental Process

The sol-gel spin coating method, which was earlier used to deposit doped and undoped ZnO, is used in this work for the deposition of Cu-doped ZnO [11–12]. The solution was prepared using zinc acetate dihydrate and copper acetate as sources of zinc and copper, respectively. 2-Methoxyethanol was used as a solvent, while ethanolamine was used as a reagent. A transparent solution was obtained by dissolving zinc acetate dihydrate and copper acetate in 2-methylethanol, and simultaneously, 5 to 7 drops of ethanolamine were added to the solution, which helped to increase the rate of reaction and maintain stability. Then the solution was continuously stirred on the hot plate at 80°C for an hour, and a transparent and clear solution was obtained. The obtained solution was cooled to room temperature, followed by the deposition of films on microscopic glass with a homemade spin coating system. Each time after the deposition process, films were preheated in the open air at 300°C for 10 minutes for the evaporation of organic elements present in the films. After cooling the substrate to room temperature, the next layer was deposited. Finally, samples were post-annealed at 375 °C for an hour in the open air. For the investigation of the optical property, multilayered (10 coatings) films were deposited at various dopant concentrations. Similarly, the film of undoped ZnO was prepared using zinc acetate as a source of zinc, and 2-methyloxyethanol and ethanolamine were used as solvents and reagents, respectively.

Shimadzu UV spectrophotometry was used to record the transmittance spectra of the sample to study its optical properties like refractive index and bandgap energy. In addition to this, the thickness of the films deposited on the glass substrate was determined from transmission spectra using the envelope method, also known as the swapnoel method. The optical band gap was further determined using a tauc plot. The surface morphology and chemical composition were investigated using SEM and EDAX spectra, respectively.

3. Result and Discussion

In the present work, the primary investigation of Cu-doped ZnO films is discussed. To study the effect of post-annealing temperature on optical properties, the post-annealing temperature was varied between 350°C to 425°C for 4 at% Cu doped ZnO film in a controlled environment for an hour.

3.1 UV-Vis Transmission Spectra

The UV-visible transmission spectra of Cu-doped ZnO films deposited on a microscopic glass substrate are shown in Figure 1 as a function of wavelength. The transmission spectra showed that deposited films are highly transparent, and the oscillating nature of the spectra indicates the optimum thickness of the films, which was useful in determining sufficient data for deducing optical properties like refractive index. It is confirmed from the transmittance spectra that the as-deposited films are mostly transparent from the 400 nm wavelength up to most of the visible wavelength range. However, below this range of wavelength, the maximum absorbance occurs and is fully absorbed at approximately a wavelength of ~380 nm. This also indicated that the deposition process does not introduce any significant defects or impurities that could affect the optical properties of the samples.

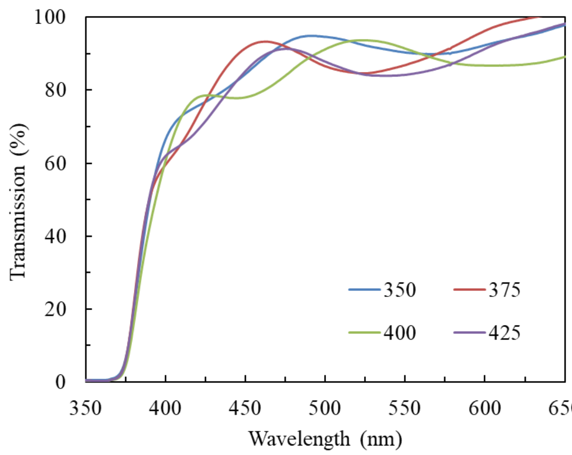

Figure 1: Transmission spectra of Cu doped ZnO, annealed at different temperatures (in ^{0}C)

3.2 Refractive Index and ThicknessCalculation

Since ZnO-based materials are highly under investigation for realizing optoelectronic devices, their refractive index was calculated for the 450nm wavelength using the swanepoel method [13]. This method uses the transmittance percentage of the recorded spectra to calculate the refractive index and thickness of the film. In this work, the refractive index (*n*) was calculated using the following equation:

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \qquad (1)$$

Where,

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2+1}{2} \qquad (2)$$

Here, T_M and T_m are the maximum and minimum transmittance at wavelength. The refractive index of each deposited Cu-doped ZnO films is found to be ~1.88, which is in very good agreement with the refractive index reported by others [14–16]. This work indicates that a dopant concentration of 4 at% has not changed the refractive index of ZnO material. The distribution of the refractive index of Cu-doped ZnO at various annealing temperatures is shown in Figure 2. However, negligible variation is noted in the refractive index of Cu-doped ZnO as compared to ZnO annealed at 400 °C.

Similarly, the thickness of the deposited transparent films were calculated using following equation,

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad (3)$$

The details of the parameters in the above equation and determination of thickness are given in the work by swanpoel et al [13]. The thickness of the as-deposited films is mentioned in Table 1. Since an equal number of ten coatings were applied on the surface of the slides annealed at various post annealing temperatures, the thickness was found to be very much same.

Table 1: Calculated refractive index and thickness of Cu doped ZnO thin films

Post annealing temperature	Refractive Index (at 450nm wavelength)	Thickness (nm)
350	~1.8	447
375	~1.8	432
400	~1.88	447
425	~1.8	441

3.3 Direct Bandgap Energy

Bandgap energy is another important factor that was investigated for the Cu-doped ZnO thin film in this work. We used the Tauc plot method to determine the optical band gap energy of the films from the absorption coefficient, as shown in figure 3. The absorption coefficient was calculated from the following equation:

$$\propto = (h\vartheta - Eg)^{1/2} \qquad (4)$$

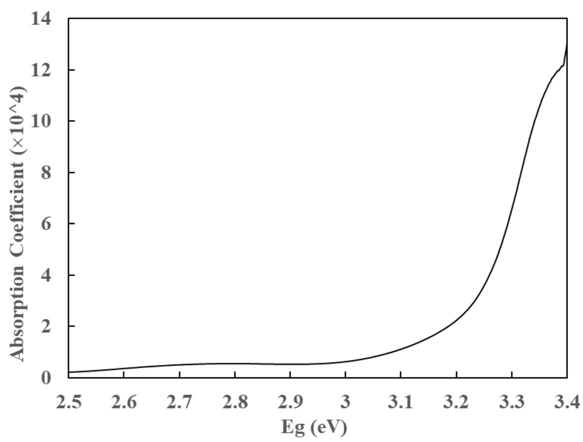

Figure 3: Plot of absorption coefficient versus band gap energy of Cu doped ZnO annealed at 400^{0}C.

From the plot, it was confirmed that the deposited cu-doped ZnO films are direct band gap semiconductor material. Furthermore, with the help of the extrapolation method, the energy band gap is found to be ~3.2 eV, which is in agreement with the CuZnO thin films deposited using several other techniques [17–19].

3.4 Microstructure Analysis using SEM

From the SEM image depicted in Figure 4a, the film morphology of Cu-doped ZnO film annealed at 400^0C was determined. The image of the film was recorded for 1 µm with a resolution of x10,000. It shows the distribution of doped ZnO grains across the surface. The surface appears to be the repeating pattern which is indicative of the crystalline structure of Cu doped ZnO.

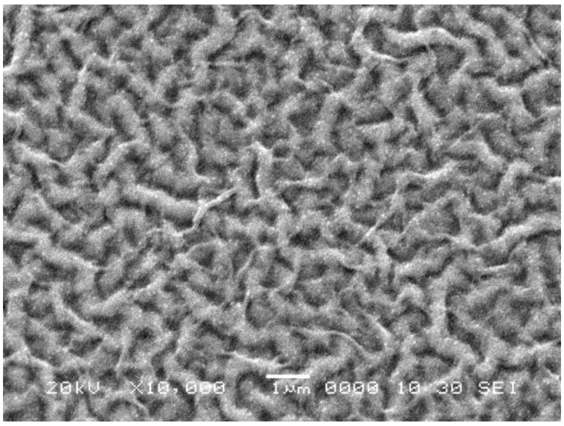

Figure 4 (a): SEM image of Cu doped ZnO film annealed at 400^0C.

Moreover, the SEM images revealed that the films exhibited a uniform and dense grain distribution across the surface, and the grain boundaries are visible, suggesting a good interconnection between the grains.

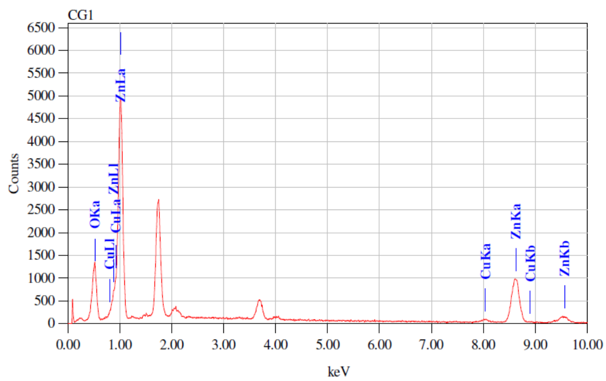

Figure 4 (b): EDAX spectra showing the incorporation of Cu in ZnO film annealed 400^0C.

The presence of Cu in ZnO films was verified by EDAX analysis, as shown in figure 4b. The EDAX spectra showed peaks corresponding to Cu, Zn, and O elements, indicating that Cu was successfully incorporated into the ZnO lattice by the sol-gel method.

4. Conclusion

We used the sol-gel method to produce Cu-doped ZnO films with transparent conducting properties. This work is motivated by the possible applications of P-type ZnO as a transparent conductor in optoelectronics and photonic devices. We report on the optical and structural characteristics of the 4 at% Cu-doped ZnO films prepared at various annealing temperatures. The transparency of the deposited samples was measured using a spectrophotometer. The results showed that the samples had a high degree of transparency, with values above 90% in the visible range. The refractive index of 1.8 was successfully attained during the fabrication of CU-doped ZnO. The band gap value for the doping level (4%) was 3.2 eV. The surface morphology and the Cu incorporation on ZnO were examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDAX). The EDAX spectra confirmed the presence of Cu in the ZnO films. With the results obtained in this work, we intent to investigate further the effect of doping concentration of Cu in ZnO at various annealing temperatures.In conclusion, highly transparent cu-doped ZnO films were successfully prepared and characterized through this work.

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