Optical Band gap of Spin-Coated ZnO: Cu/Co Thin Films Synthesized by Sol-Gel Technique

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Abstract: Co-doped (Cu/Co) percentage of 4% were synthesized using sol-gel spin-coating technique on glass substrate at a temperature of 100ºC. The Optical properties are concluded from absorption and transmission measurements, which are obtained by using double beam UV- Visible1800 spectrophotometer in the wavelength (300-500)nm. It was found that the absorbance increases with increasing the co-doping percentage (1/1, 2/2, 3/3 and 4/4) mol%, while the transmittance is decreased. The optical properties that were measured also included the absorption coefficient, the energy gap and the Urbach energy. It was found that the energy gap values decreased in the range 3.35 – 3.23 and the transmittance rate was 90% within the visible spectrum region.

Keywords: Spin-coated,ZnO films, sol-gel, semiconductor, doping, Optical energy band gap, Optical properties.

1. Introduction

The transparent conductive oxides (TCO) materials have acquired a massive attention in many areas due to their interesting properties. Their characterization are promising to use them such as photovoltaic solar cells and optoelectronics devices [1].
The zinc oxide based semiconductors can present both ferromagnetic and p-type conduction type behaviours at room temperature. This is applicable when it is doped with transition metals such as Cu and Co. Furthermore, controlling the doping level helps to change the electrical properties of a ZnO film from insulator to metal passing through a n-type semiconductor. This is possible while maintaining its optical transparency that makes it useful for transparent electrodes in flat panel displays and solar cells. Moreover, it is classified among the transparent conductive oxides (TCO) due to its high transmittance in the visible and near infrared regions [2, 3].

This work aims to obtain a membrane of ZnO thin film with enhanced structural and optical characteristics with improved physical properties in the visible spectrum region. The sol-gel spin-coating technique was followed to synthesis the ZnO films for two main reasons[1, 4-8]. First, sol-gel technique provides ZnO films that are suitable for scientific studies and technological applications. Moreover, this technique is considered as one of the most economical ways to obtain ZnO films. Copper and cobalt co-doped ZnO (ZnO: Cu/Co) thin films of different co-doping concentrations were deposited on glass substrate by the sol-gel spin-coating technique [9], while the optical properties of the produced thin films were studied to determine the effect of Zno:Cu/Co concentration level on these properties.

2. Materials and methods

The copper nitrate $Cu(NO_3)_2$ and cobalt nitrate $Co(NO_3)_2$ co-doped ZnO thin films were fabricated using the sol-gel spin-coating technique. Aqueous solution of 0.1M of zinc acetate dehydrate ($Zn(CH_3OO)_2.2H_2O$) purity 99.5% and isopropanol ($CH_3CH(OH)CH_3$)of 0.1 M concentration at room temperature was used as a matrix solution to obtain ZnO thin films. The solution was stirred using a hot plate magnetic stirrer for an hour. Some drops of Diethanol amine (DEA C_2H_5-OH) were added drop by drop to obtain a clear transparent solution with continues rotating for two hours [9-13]. The growth of the co-doped (ZnO: Cu/Co) was performed by slowly sprinkling circular well cleaned 10 mm in diameter and 1mm in thickness glass substrate. The gravimetric method was used to measure the thickness of the obtained ZnO:Cu/Co thin films where the measured thickness was about 300±20 nm. The Optical characteristics of the obtained ZnO:Cu/Co films were measured using a double beam UV-spectroscopy Agilent Technologies.

3. Results and Discussion

Optical analysis of ZnO: Cu/Co thin films with different concentrations (1/1, 2/2, 3/3 and 4/4 mol%) were used to study the optical characteristics of ZnO:Cu/Co thin films. The absorbance, transmittance, and reflectance spectra are presented in

Figs.1, 2, and 3 as functions of photons wavelength (λ). In the range of 300-500 nm, Fig. 1 indicates that the absorbance increases upon increasing the doping percentage. These interesting changes can be attributed to the enrolment of Cu/Co atoms within the ZnO structure. Moreover, these changes may cause an increase in the localized impurity levels in the energy band gap of ZnO as the concentration of Cu/Co is raised. Note that the same behaviour of ZnO:Co was observed by Choi and Kim [14] and Bacaksizetal[15, 16].

Furthermore, Fig. 2 indicates an increase in transmittance for each sample until a maximum of each curve is reached at $\lambda \cong 470$ nm. Moreover, a noticeable reduction in the transmittance is detected as the doping concentration is increased. However, comparing figures Fig. 1 and Fig. 2,it is clear that the ZnO:Cu/Co 4% has the lowest transmittance and highest absorbance among the used concentrations

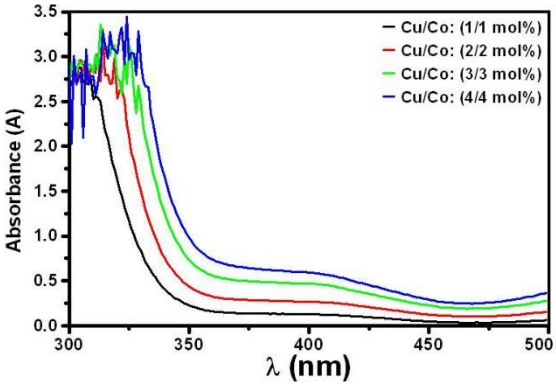

Fig. 1 The absorbance spectrum of the deposited ZnO: Co thin film versus wavelength for different doping concentration levels.

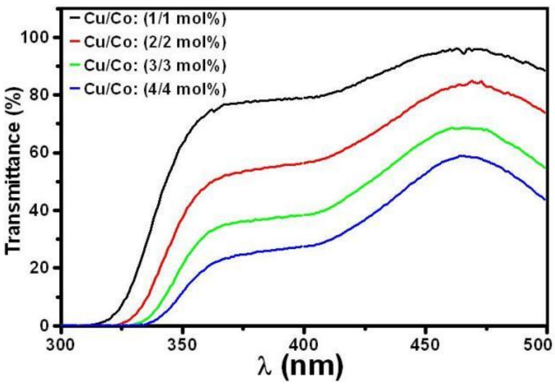

Fig. 2 The transmittance of the deposited ZnO: Co thin film versus wavelength for different doping concentration levels.

The reflectance as a function of the wavelength was measured and presented in Fig. 3. The behaviour of the reflectance spectrum follows the absorbance spectrum since it shows a reduction in the reflectance upon increasing the co-doping level, where the ZnO: Cu/Co4% shows the highest reflectance spectrum. The maximum reflectance can be observed at low wavelengths (300-340 nm) which are equivalent to fundamental absorption edge.

The absorption coefficient (α) spectrum as a function of photon energy (hν) is shown in Fig. 4. The spectra indicate an increase in α values while increasing the photon energy, where the highest values were recorded for the ZnO:Cu/Co4% films. If the film has a thickness t and transmittance ratio T%, then α can be obtained from the Bouger- Lambert law:

$$\alpha = \frac{1}{t} \ln\left(\frac{100}{T\%}\right) \tag{1}$$

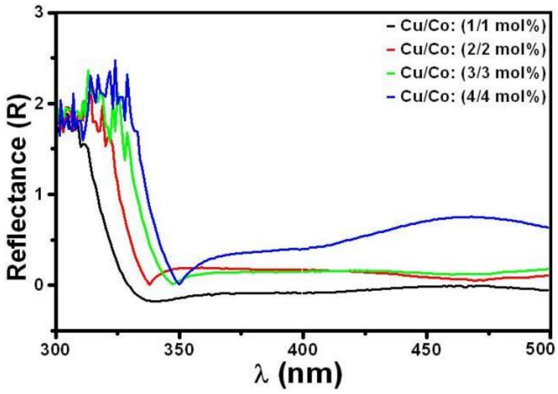

Fig. 3 Reflectance versus wavelength of the incident photon for different co-doping concentration levels of Cu/Co.

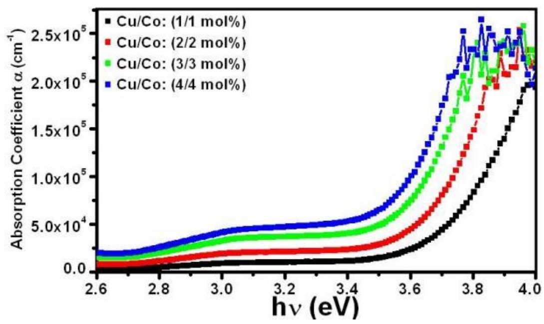

Fig. 4 Absorption coefficient versus photons energy for different doping concentration levels of Cu/Co.

The fundamental absorption edge, which corresponds to the electron excitation of an allowed transition between the top of the valence band to the bottom of the conduction band, is usually used to determine the optical allowed direct band gap using the Tauc equation as follows [17]:

$$(\alpha h\nu)^2 = A[h\nu - E_g] \tag{2}$$

Where, A is a constant, E_g is the energy gap, h is plank constant, and v is the frequency of the photon. Equation 6 is used to obtain Fig. 6 that describes the relation between $(\alpha h v)^2$and $hv$of the films under investigation. The calculated optical allowed direct energy gap E_g values were obtained from the hv-axis intercept of the fitted linear extension to the linear part of the Tauc plot. The results of the extracted values of $E_g$are presented in **Table 1**,where $\mathrm{E_g} = 3.23\mathrm{eV}$ was the lowest recorded value for ZnO:Cu/Co4% films, while
$\mathrm{E_g} = 3.35\mathrm{eV}$was the highest recorded value for the ZnO:Cu/Co1% films.

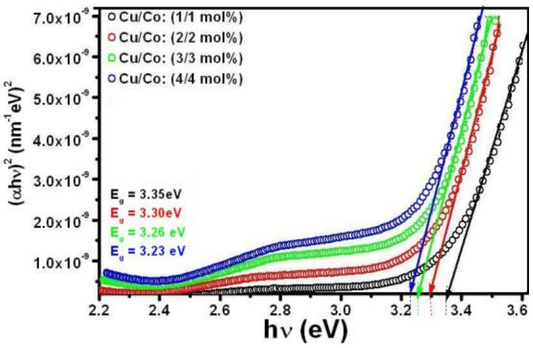

Fig. 5 Dependence of $(\alpha h v)^2$ on the photon energy of co-doped ZnO: Cu/Co thin films.

The curves in Fig. 5 and the E_g values in **Table 1** shows that the increase in co-doping level leads to a reduction in the optical energy band gap, which can be explained by the good conductivity of Cu/Co particles that are located within the ZnO structure.

The spectral dependence of α on the photon energy is illustrated by the Urbach empirical rule, which is given by the following equation:

$$\left[\alpha = \alpha_0 \exp\left(\frac{h\vartheta}{E_u}\right)\right] \quad (3)$$

where α_0 is a constant and E_u denotes the energy of the Urbach band tail. Urbach energy is one of the important parameters in thin film optical studies, which indicates the degree of crystalline in the structure (amorphous or disorder) by providing information about the localized states within the boundaries of the energy band gap. It can be explained due to the existence of the localized energy states at the bottom of the conduction band and the top of the valance band. These localized states can describe transitions of electrons within the energy gap space. According to equation 3, a theoretical linear form can be presented to extract the E_u value as follows [18]:

$$\ln(\alpha) = \ln(\alpha_0) + \left(\frac{hv}{E_u}\right) \quad (4)$$

The slope of the linear part of the $\ln(\alpha)$ vs. hv curve (as presented in Fig. 6) can be used to extract the E_u values, where $E_u = 1/slope$.The extracted values of E_u for the different concentrations are presented in Table 1.

Table1 Evaluated optical energy band gap of ZnO: Cu/Co thin films with different concentration levels.

Co-doping level	1/1mo1%	2/2mo1%	3/3mo1%	4.4mo1%
Optical direct energy gap (eV)	3.35	3.30	3.26	3.23
Urbach tailing energy (eV)	0.38	0.47	0.55	0.60

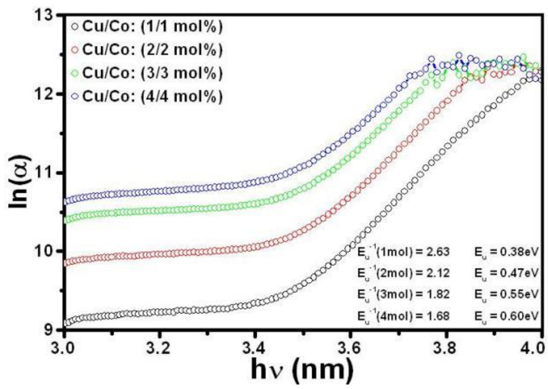

Fig. 6 Urbach curves for different co-doping concentration levels of Cu/Co.

4. Conclusions

Co-doped ZnO: Cu/Co thin films of different concentration levels were prepared by sol-gel spin-coating technique. The analyses of UV-visible spectra show that the transmission of the Co doped films was very high and exceeds 90% in the wavelength range (300-500) nm. Increasing doping levels leads to a reduction in transmittance. On the other hand, it causes a rise in absorbance. In addition, it causes a shift of the fundamental absorption edge to higher wavelength values. As a result, a reduction in optical energy band gaps is observed. The results show that all the deposited thin films have direct optical energy band gaps lying in the range of (3.35- 3.23)eV. In addition, data obtained from absorption and transmittance spectra are used to determine some other optical parameters.

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