Journal of Materials and Electronic Devices 1 (2023) 67-72

JOURNAL OF MATERIALS AND ELECTRONIC DEVICES
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Comparison of optical properties of Cu- and In-doped CdO thin films having low dielectric loss

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Cu- (1%) and In- (1%) doped CdO thin films were produced using one-step electrochemical deposition method and their optical analyses were investigated with UV-vis spectrophotometer. The determined optical parameters were examined in depth and compared. It is obtained that the maximum absorption region of Cu- and In-doped CdO thin films were in ultraviolet region. The maximum absorption coefficient, energy band gap, average transmission, maximum extinction coefficient and refractive index values of Cu-doped thin film were found to be 1.8 x 10^6 m^{-1}, 2.66 eV, 73.01%, 0.054 and 1.21, respectively, while these for In-doped CdO thin film were, 1.1 x 10^6 m^{-1}, 2.48 eV, 72.45%, 0.078 and 1.17, respectively. Additionally, optical dielectric loss values of the Cu- and In-doped thin films were determined, and it was found that real dielectric constant values were considerably higher than imaginary dielectric constant values and dielectric loss values were quite low in both films. Optical conductivity of the Cu- and In-doped CdO thin films were also determined as 5.14 x 10^{14} and 5.14 x 10^{14}, respectively.

Keywords: *Metal oxide; Cu-doped CdO; In-doped Cd;, optical propertie;, high transmittance.*

Submission Date: 12 January 2023
Acceptance Date: 06 March 2023

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1. Introduction

Metal oxide thin films are widely employed in optical, thermal, electrical, and solar energy applications. Cadmium oxide (CdO), tin oxide (SnO), zinc oxide (ZnO), indium tin oxide (ITO), tungsten trioxide (WO_3), copper oxide (CuO) and titanium dioxide (TiO_2) have a prominent place among the transparent metal oxides [1-5]. CdO was historically the first example of a transmittance metal oxide described by Badeker in 1907 [6]. Cadmium oxide thin films have received a lot of interest in recent years because of their potential uses in optoelectronic devices [7]. As CdO can be used as pure form, it can either be used as heterojunction or doped form and there are many studies related to them [8-11]. Metal doped CdO studies are generally on the doping of the same metal at different rates. Hence, studies of different metals doped into CdO under the same conditions are very few in the literature. CdO and doped CdO thin films were synthesized using several methods such as spin coating [12], sputtering [13], thermal evaporation [14], hydrothermal [15] and electrodeposition [16]. Compared to the mentioned methods, electrochemical deposition is a useful and important method owing to not need to expensive equipment and vacuum components and makes possible to produce quality films. In this study, due to the advantages of the electrochemical deposition method and the lack of literature; 1% Cu and 1% In-doped CdO thin films were synthesized using low concentration solutions by electrochemical method and their basic optical parameters were analyzed and compared in detail.

2. Experimental

Electrochemical method was used to synthesis 1% Cu- and 1% In-doped CdO on ITO/glass substrates having resistance smaller than 20 Ω. ITO/glass substrate was used as a working electrode after cleaning with acetone and propenal. In addition, as a reference electrode Ag/AgCl reference electrode and counter electrode Pl plate were used. 5 mM $CuCl_2$, 5 mM $InCl_3$ and 5 mM $Cd(NO_2)_3.4H2O$ were preferred as Cu, In and Cd sources. Also, 250 mM LiCl was used as a buffer layer. Deposition of thin films were carried out by appling -0.7 V applied voltage during 3600 s at 70 ℃ using Metrohm Autolab PGSTAT128N. In order to analyse optical properties Hach DR600 UV-vis spectrometry was employed.

3. Results

Optical properties of the semiconductor thin films have a vital place in opto-electronic applications. The appropriateness of the application area is determined by the behavior of the thin film in relation to the energy of the incident light on it. For instance, in thin films to be used as absorbent material it is desirable to have high absorption and extinction coefficients and low transmittance values. Besides, the situation is reverse for thin films to be preferred as a window layer or an interface layer. In this study, optical characterization of 1% Cu- and 1% In-doped CdO thin films were performed between 300 – 850 nm wavelength range.
Absorbance (A) spectrum and thickness of the film (D) are used to calculate the absorption coefficient (α) as given in follow equation [11];

$$\alpha = \frac{2.303\ .\ A}{D} \quad (1)$$

Absorbance coefficient (α) of the Cu- and In-doped CdO thin films versus wavelength graph is shown in Figure 1a. Absorption coefficient of the Cu-doped CdO thin film increased with decreasing the wavelength, approximately 600 nm gave a broad peak then reached its maximum value of 1.8 x 10^6 m^{-1} at 370 nm and carried to decreasing trend. On the contrary, absorption coefficient of the In-doped CdO thin film after a small increase gave a broad peak at around 600 nm (similar to Cu-doped CdO) and its maximum value was measured as 1.1 x 10^6 m^{-1} at 384 nm. Interband π–π* electronic transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) are detected at the wavelength with the highest absorption [17]. It is stated that Cu-doped CdO thin film had higher absorption coefficient than In-doped CdO thin film. This difference can be related to the atomic radius of the dopant atoms, as well as to the chemical bonds formed by the dopant atoms and the CdO compound. Since, it was observed the absorption coefficients of the several ratio Al doped CdO thin film were changed by dopant ratio [18].
The spectrum dependence of absorption around the basic absorption edges can reveal information about direct or indirect interband transitions [19].
Energy band gap (E_g) is determined using the photon energy ($h\nu$) as given in equation below [20];

$$(\alpha h\nu) \approx (h\nu - E_g)^n \quad (2)$$

n is taken as ½ for direct allowed transitions. E_g is obtained from the graph of $(\alpha h\nu)^2$ versus $h\nu$ graph by extrapolating of the straight-line portion of the plot to the $x-$ axis.
Figure 1b shows the $(\alpha h\nu)^2$ versus $h\nu$ graph of the Cu- and In-doped CdO thin films. Energy band gap value of the Cu-doped CdO thin film was 2.66 eV, while that of the In-doped CdO was 2.48 eV. It is clear that dopant atoms played a vital role in variation of the energy band gap. Additionally, obtained E_g values were lower than the value of Al-doped CdO [11] thin film, while they were higher than the Mg-doped CdO thin film [21]. It is seen that different doping atoms alter the E_g values of CdO thin films.

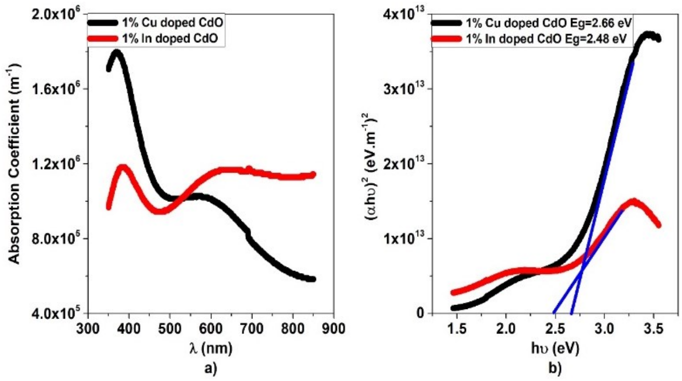

Figure 1: a) Absorption coefficient versus wavelength and b) $(\alpha h\nu)^2$ versus $h\nu$ graphs of Cu- and In-doped CdO thin films.

Transmittance (T) is calculated with the relation of absorbance as given by;

$$A = -logT \quad (3)$$

and by neglecting multiple reflections, transmittance is described with the following equation;

$$T = (1-R)^2 \exp(-A) \quad (4)$$

where, R is the reflection and rearranging the equation 4 enable to determine the reflection as given by;

$$R = 1 - (\frac{T}{\exp(-A)})^{1/2} \quad (5)$$

Figure 2a shows the variation of the transmittance (T%) and reflectance (R%) values of Cu-doped CdO thin film in respect to wavelength. The transmittance (T%) and reflectance (R%) values of In-doped CdO thin film are also presented in Figure 2b. As clearly seen in Figure 2a and 2b, T% and R% values showed opposite trends against to wavelength. It is seen that the %T values increase and the %R values decrease as the wavelength for the Cu-doped CdO thin film increases and its maximum and minimum T% values were obtained at 850 nm and 370 nm with the values of 85% and 58%, respectively while the maximum and minimum R% values of this thin film were found to be 5.2% at 370 nm and 3% at 850 nm, respectively. Besides, T% and R% values of In-doped CdO thin films fluctuated with the increase of the wavelength and T% values small alteration with the 74% maximum (at 474 nm) and 70% minimum (385 nm) values. Even in the region of the maximum absorption approximately 4% decreased occurred. Furthermore, R% values of In-doped CdO were taken the values between 4.25% to 3.85%. It is obvious that Cu-doped CdO have smaller T% values that In-doped CdO thin film in the maximum absorption region and This can be explained by the fact that Cu atoms doped in CdO cause more photon absorption [22]. In the visible region, the average T% value of Cu-doped CdO was 73.01% while that of In-doped CdO was 72.45% and these values are in correlation with the literature [23, 24]. Average R% values of Cu- and In-doped CdO were determined as 4.03% and 4.07%, respectively.

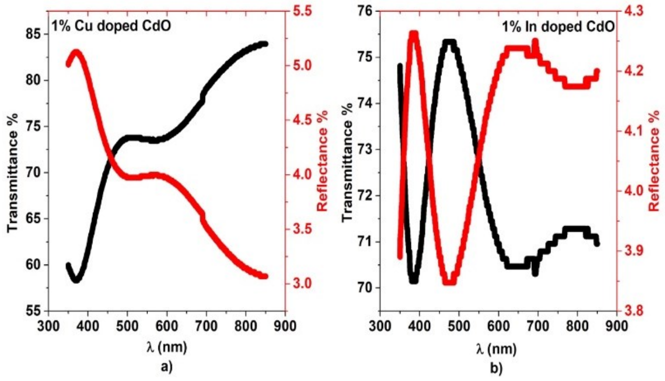

Figure 2: Transmission and reflectance (R%) versus wavelength graphs of a) Cu- doped CdO thin film and b) In-doped CdO thin film.

The following equations use the relationship between the absorption coefficient and reflectance to compute the extinction coefficient (k) and refractive index (n) [25, 26];

$$k = \frac{\lambda \cdot \alpha}{4\pi} \tag{6}$$

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{1-R^2} - k^2} \tag{7}$$

where, λ refers to the wavelength.

Figure 3a shows the k and n values versus wavelength graph of Cu-doped CdO thin film. Additionally, k and n values of In-doped CdO thin film are demonstrated in Figure 3b. It is seen that k and n values of Cu-doped CdO thin film exhibited similar behaviors by increasing with the decrease of the wavelength. Both values peaked at approximately 650 nm and 0.054 maximum k values and 1.21 n values were obtained in near-ultraviolet region at around 380 nm. On the other hand, k values of In-doped CdO thin film decreased with decreasing the wavelength, n values exhibited a fluctuation change and the maximum k and n values were calculated as 0.078 at 850 nm and 1.174 at 384 nm, respectively. It is seen that the k values of In-doped CdO thin film in the infrared and visible regions were higher than Cu-doped CdO and in near ultraviolet region was vice versa. Furthermore, it is observed that Cu-doped CdO had higher n value than In-doped CdO in the maximum absorption region. It is seen that difference of the dopant atoms significantly affects the variation of k and n values with wavelength.

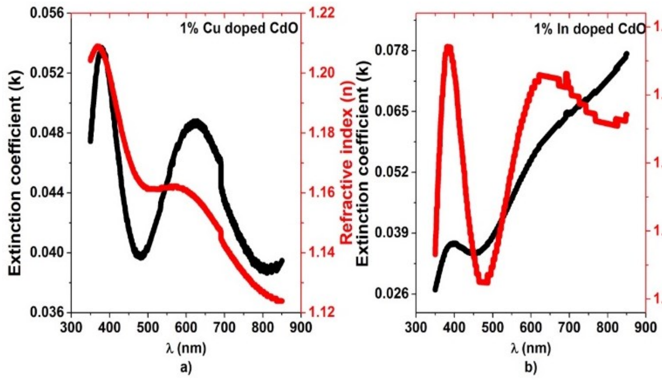

Figure 3: Extinction coefficient (k) and refractive index (n) versus wavelength graphs of a) Cu- doped CdO thin film and b) In-doped CdO thin film.

Imaginary dielectric constant (ε_i), real dielectric constant (ε_r) and optical conductivity (σ) are calculated using determined k and n values as given by equation 8, 9 and 10 [27, 28]. Calculating the ε_i and ε_r values makes possible to define dielectric loss with the formula of

$$\varepsilon_i = 2nk \tag{8}$$

$$\varepsilon_r = n^2 - k^2 \tag{9}$$

$$\sigma = (\alpha n c)/4\pi \tag{10}$$

where, c is the speed of the light.

Imaginary and real dielectric constant with respect to wavelength for Cu- and In-doped CdO thin films are shown in Figure 4a and 4b, respectively. It is seen that ε_r values were higher than ε_i values for both thin films as shown in Figure 4. The maximum ε_i and ε_r values of Cu- and In-doped CdO thin films were calculated as 1.45 and 1.375, respectively, while the minimum of these were 0.13 and 0.18, respectively.

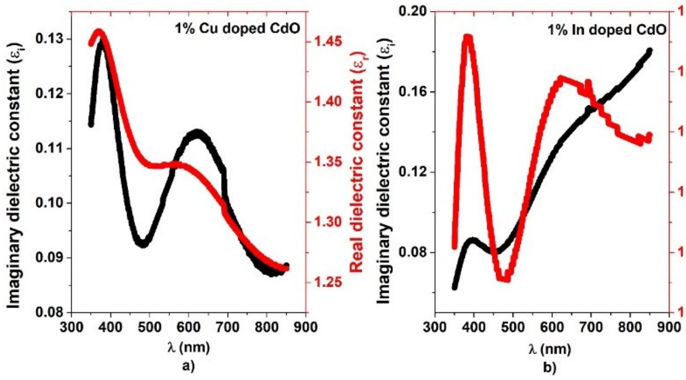

Figure 4: Imaginary dielectric constant (ε_i) and real dielectric constant (ε_r) versus wavelength graphs of a) Cu-doped CdO thin film and b) In-doped CdO thin film.

Dielectric loss can be defined as the combination of a film's flaws and the ratio of power lost in the film to the total amount of power passed through the film. The dielectric loss could be small enough for a material to be used as a dielectric material in any practical application [29]. For any dielectric material, dielectric loss is thought to be due to frequency dependent rotation of the electric dipole, and the leakage current [30, 31]. Figure 5a shows the dielectric loss values of the Cu- and In-doped CdO thin films against to wavelength. Dielectric loss values of the Cu-doped CdO had two peaks points with the values of 0.085 at 629 nm and 0.089 at 380 nm while that of In-doped CdO dropped with decreasing the wavelength. The increase of incident photon power leads to the increase of loss. The maximum dielectric loss of In-doped CdO was obtained at 850 nm with the values of 0.13 and in the near ultraviolet region, where the absorption is maximum, this value is 0.06. The loss was higher in the In-doped CdO thin film in the wavelength range of 530-850 nm, on the other hand, that was higher in the Cu-doped CdO in the 350-530 nm wavelength range. While Cu-doped CdO thin film in the long wavelength region of the visible region and near infrared region are suitable for using dielectric materials, it is more suitable to use In-doped CdO thin films in the low wavelength region of the visible region or in the near-ultraviolet region.

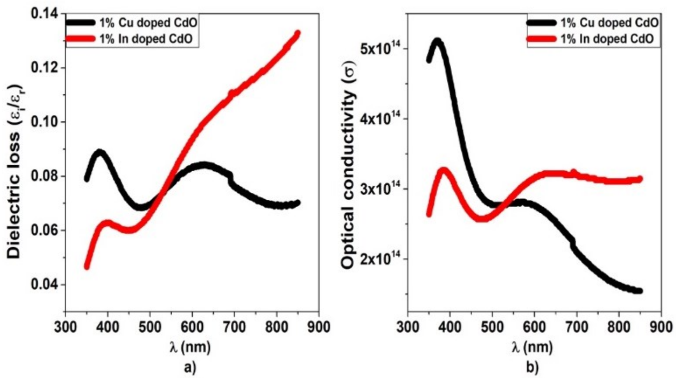

Figure 5: a) Dielectric loss versus wavelength and b) optical conductivity versus wavelength graphs of Cu- and In-doped CdO thin films.

Optical conductivity is a powerful material to determine electrical properties of the materials. In most cases, when a system is subjected to an external electric field, charges are redistributed, and current is induced. The rise in optical conductivity suggests that incident photon energy greatly influences how quickly electrons absorb photons of a given energy [32]. In Figure 5b, graph of variation of σ values of Cu- and In-doped CdO thin films versus wavelength is given. σ values increased with the increase of power of the incident light and approximately reached its maximum value of 5.14 x 10^{14} at approximately 370 nm in Cu-doped CdO thin film. On the other hand, σ values in In-doped CdO gave a shoulder peak at 624 nm with the value of 3.24 x 10^{14} and the decrease in σ values continued till 475 nm. Afterwards σ values increased again in near-ultraviolet region and reached its maximum value of 3.3 x 10^{14} at 383 nm.

4. Conclusion

Cu- and In-doped CdO thin films were successfully produced using low concentration solutions in one-step. Basic optical parameters of the fabricated thin films were detailly examined and compared with each other and CdO thin films produced by similar and different methods. Cu-doped CdO thin film could be a strong alternative to transparent metal oxide application thanks to transmittance values of 85% in high wavelengths and 75% in the visible region. Additionally, the low absorption capacity of the films and the low dielectric losses might exhibit as another important findings of this research.

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