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Investigation and comparison of optical properties of CdO and CdGaO transparent conductive metal oxide thin films

Sitki Aktas[1*]

[1*] Department of Mechanical Engineering, Faculty of Engineering, Giresun University, Giresun, Turkey,

Optical analyses of the electrochemically deposited CdO and CdGaO transparent metal oxide thin films were performed at 300 and 800 nm wavelength range using UV-vis spectrometer to aimed to provide an option for optoelectronic application fields. It is found that transmittance, absorption coefficient, extinction coefficient, refractive index, imaginary dielectric constant, real dielectric constant, dielectric loss and optical conductivity values of CdO were 82%, 3.3 x 10^6 m^{-1}, 0.16, 1.26, 0.4, 1.59, 0.27 and 9.5 x 10^{14}, respectively, while these of CdGaO were 45%, 1.18 x 10^6 m^{-1}, 0.04, 1.17, 0.1, 1.17, 0.08 and 3.3 x 10^{14}, respectively. Additionally, the direct energy ban gap of CdO and CdGaO thin films were determined as 2.85 eV and 2.68 eV.

Keywords: *Transparent metal oxide; CdO; CdGaO; optical coefficients*

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**Corresponding author: sitki.aktas@giresun.edu.tr*

1. Introduction

Semiconductor thin films have contributed an impact on development of various technological areas such as health, energy and environmental applications [1-4]. Semiconductor thin films can be synthesized in binary [5-8], triple [9, 10] or even quaternary form [11, 12], or they can be obtained by oxidizing a metal [13-18]. Transparent conductive metal oxide (TCOs) such as SnO2, ZnO, In_2O_3, NiO, CuO, MoO_3, WO_x and CdO which have an importance among the metal oxides, are the basic materials used in flat panel displays, photovoltaic cells, smart windows, light emitting diodes and optical waveguides [19-27]. In addition, in recent years, triple TCOs such as Cd_2SnO_4, $CdIn_2O_4$, $CdSb_2O_6$, $GaZn_2O_3$ and CdO–In_2O_3–SnO_2 have been reported for photovoltaic applications [23, 28, 29]. These materials have great attention due to their high conductivity and high optical transmittance.

CdO thin films among the transparent metal oxides generally display low resistance due to natural defects of oxygen vacancies and cadmium transition sites. The conductivity of pure CdO thin films can be increased by adding suitable dopant with ionic radii equal to and/or smaller than that of the Cd lattice atoms [23]. Hence, this

study was built up as comparison of optical properties of pure CdO and CdGaO (1:1 ratio) thin films. While there are several thin film synthesis methods [30-34], electrochemical deposition technique was preferred since it offers present cheap, environmentally friendly, controllably and quality film production [35-37]. Therefore, CdO and CdGaO thin films were synthesis using low molarity precursor solutions by electrochemical deposition technique and basic optical parameters were detailly examined and compared.

2. Experimental

CdO and CdGaO thin thin films were synthesis in ITO coated glass substrates at -0.7 applied potential at 70 ℃ during 3600 s *via* electrochemical deposition method has three-electrode configuration. In this configuration, ITO coated glass substrate was used a working electrode while reference and counter electrode were preferred as Ag/AgCl and Pt. Electrolyte for CdO was made by mixing 20 ml $Cd(NO_2)_3.4H_2O$ (5 mM) and 20 ml LiCl (250 mM) whilst that for CdGaO 10 ml $Cd(NO_2)_3.4H_2O$ (5 mM) , 10 ml $GaCl_3$ (5 mM) and 20 ml LiCl (250 mM) were used. Metrohm Autolab PGSTAT128N was employed as an electrochemical deposition system. Optical analyses of the CdO and CdGaO thin films were performed with Hach DR600 UV-vis spectrometry at 300 – 850 nm wavelength range.

3. Results

The determination of the optical parameters of thin films provides insight into their suitability for optoelectronic applications. Hereby, measuring the absorbance spectrum of the thin film enable to calculate the absorption coefficient (α) and then energy band gap (E_g) using the following relations [38];

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

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

where, A and t are absorbance and film thickness, respectively and $h\nu$ refers to the photon energy. Also, n is defined as ½ for direct allowed transitions.

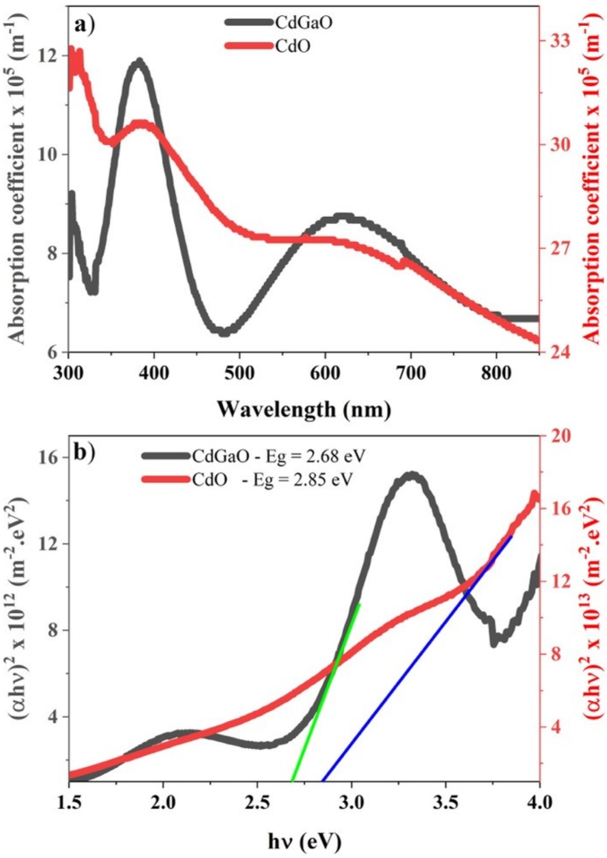

Figure 1: a) Absorption coefficient in respect to wavelength and b) $(\alpha h\nu)^2$ versus $h\nu$ graphs of CdO and CdGaO thin films.

As seen the absorption coefficient versus wavelength graphs of CdO and CdGaO thin film presented in Figure 1a, both films have wide absorption area. (α) value of CdO indicates decreasing trend having three absorption peaks with the increase of the wavelength. One of them is in visible region (at 620 nm) with the value of 2.7 x 10^6 m^{-1} while other two peaks are in near-ultraviolet region with the values of 3.08 x 10^6 m^{-1} (at 389 nm) and 3.06 x 10^6 m^{-1} (at 306 nm). Besides, trend of α value for CdGaO reveals similarity with CdO but the absorption peak in the visible region is more pronounced.

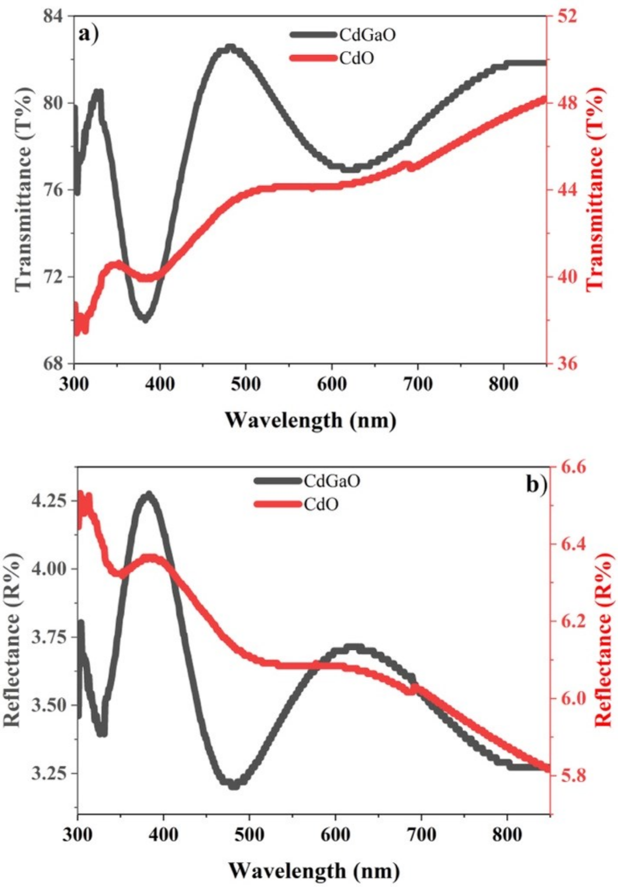

Figure 2: a) Transmittance (T%) and b) reflectance (R%) of CdO and CdGaO thin films.

The peaked α values for CdGaO can be listed as 8.7 x 10^5 m^{-1} at 620 nm, 1.18 x 10^6 m^{-1} at 383 nm and 9.1 x 10^5 m^{-1} at 306 nm. It is obvious that absorption coefficient of CdO thin film is higher than CdGaO and this can be explained by the fact that the atomic diameter of the Ga atom is smaller than Cd atom. It also is possible to find the similar examples in the literature [39, 40]. Energy band gap values of the CdO and CdGaO thin films are 2.85 eV and 2.68 eV, respectively, which were determined from the $(\alpha h\nu)^2$ versus $h\nu$ graph as shown in Figure 1b. The presence of Ga atoms reduced the energy band gap by 0.17 eV and this reduction may be related to the structural change in CdO films after Ga doping. Since, according to Thambidurai *et. al* [31], the structural deformation in CdO films may be caused by the substitution of Ga ions for substituent or interstitial cadmium ions in the CdO lattice. Such Ga ions will introduce some additional energy level in the CdO band gap near the valence band edge, resulting in a reduction in energy associated with the direct transition.

Transmittance (T%) and reflectance (R) of the CdO and CdGaO thin film are determined [38-41] with the relationship of absorbance and shown in Figure 2. T% values of CdO thin film increases with the increase of the wavelength and the highest value is obtained at 850 nm (see Figure 2a). Also, while the T% value is 45% at 700 nm which is the upper limit of the visible region, it is 40% at 400 nm. In the CdGaO thin film, on the other hand, %T values exhibited a fluctuating change and decreased to their minimum values in high absorption regions. The highest T% value is measured as 82% in the visible region and this value is expected for conductive transparent metal oxides. Since the presence of Ga atoms reduces absorption, the %T values are higher in the CdGaO thin film compared to CdO. This behaviour in the especially in absorption region is in agreement with the literature [42]. Besides, R% values of each thin film decrease with the increase of the wavelength as shown in Figure 2b. The highest R% values of CdO and CdGaO thin film can be given as 6.5% at 302 nm and 4.2% at 382 nm, respectively.

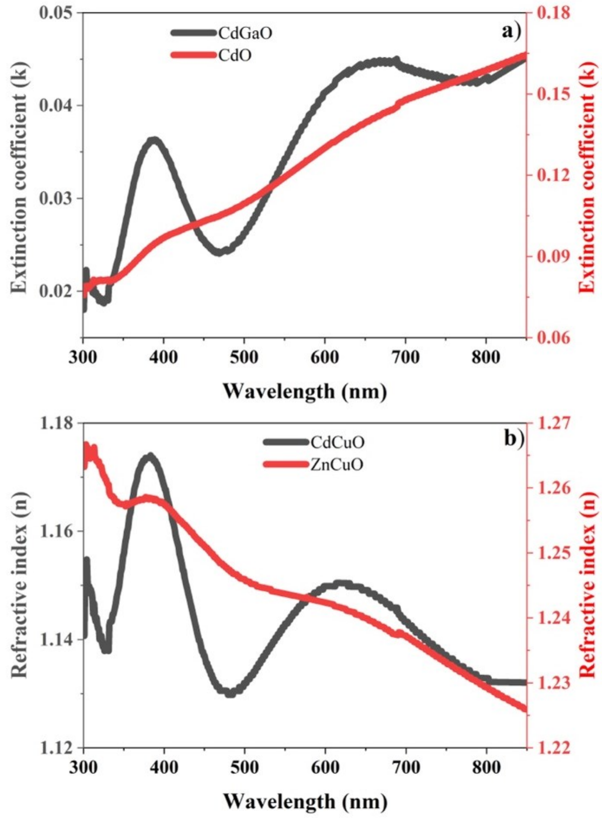

Figure 3: a) Extinction coefficient (k) and b) refractive index (n) of CdO and CdGaO thin films.

Extinction coefficient (*k*) and refractive index(*n*) are calculated using the relation with absorption coefficient [41] and variation of both values in respect to wavelength are presented in Figure 3. The k values of both thin films increased with increasing wavelength as shown in Figure 3a and the highest k value of the CdO thin film is 0.16, while the that of the CdGaO is 0.044. Generally, CdO thin film has 4 times higher k values than CdGaO and this is directly related to the absorption capacities of the films. These obtained k values are higher than CdO and ZnO based thin films [43, 44]. The variation of the n values of the CdO and CdGaO thin films against the wavelength is the opposite of the behaviour of k, and the n values decreases with the increase of the wavelength as given in Figure 3b. The highest n value in CdO thin film is around 1.26, while that of CdGaO is 1.17, and these values are lower compared to metal oxide thin films doped with different metals [30, 45], but higher than some hybrid thin films [46].

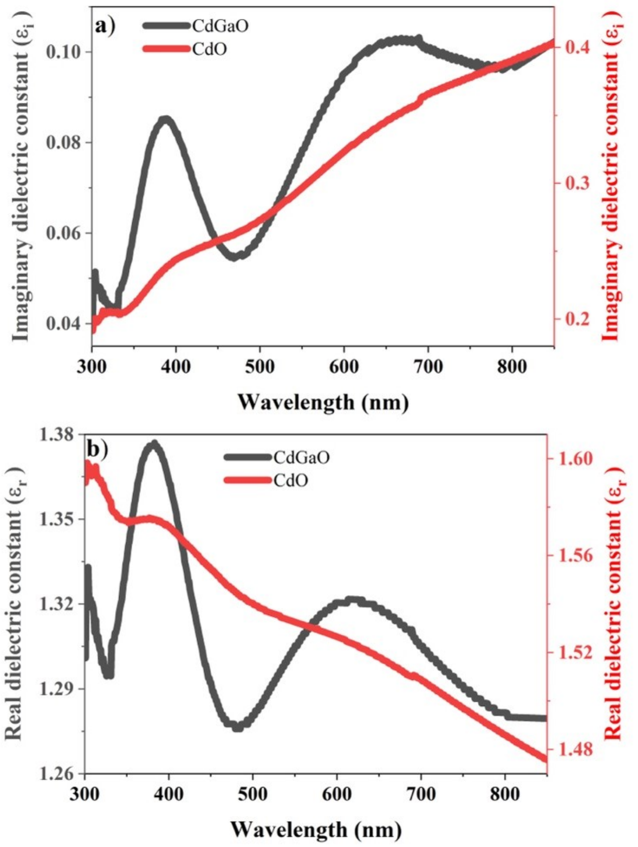

Figure 4: a) Imaginary dielectric constant (ε_i) and b) real dielectric constant (ε_r) of CdO and CdGaO thin films

Imaginary dielectric constant (ε_i) and real dielectric constant (ε_r) which are equal to $2nk$ and $n^2 - k^2$, respectively, are demonstrated in Figure 4. The variation of ε_i values both thin films rise with the increase of wavelength similar to the k values. The highest and lowest k values of CdO are 0.4 and 0.2 while these for CdGaO are 0.04 and 0.1, respectively. ε_r values of both thin films presented in Figure 4b drop similar to n values, with increasing wavelength. Whilst the highest and the lowest ε_r values of CdO thin film are found to be 1.59 and 1.48, these of CdGaO are 1.37 and 1.28, respectively. It is seen that ε_i and ε_r values of the CdO thin film are higher than the values of the CdGaO at all wavelengths. In addition, ε_r values are higher than the ε_i values in both thin films.

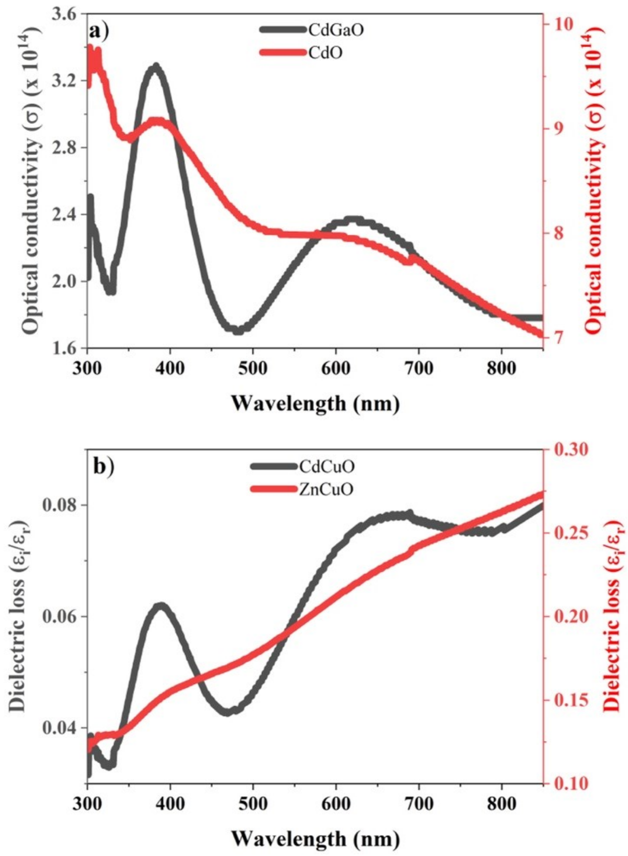

Figure 5: a) Optical conductivity and a) dielectric loss of of CdO and CdGaO thin films.

Optical conductivity (σ) is calculated with the formula of $\sigma = (\alpha n c)/4\pi$, where c is the speed of the light and its variation in respect to wavelength are illustrated in Figure 5a. It is seen that σ values of CdO decreases with the rise of wavelength while the variation of σ values of CdGao are fluctuation. The highest σ value in CdO thin film is 9.5 x10^{14} at 302 nm where the absorption is maximum, while that of CdGaO is 3.3 x 10^{14} at 382 nm and it is also seen that at all wavelengths, the σ values of the CdO thin film are higher than the CdGaO. The dielectric loss ($\varepsilon_i/\varepsilon_r$) values of both thin films increase with the increase of wavelength as illustrated in Figure 5b. Dielectric loss value of the CdO thin film is 0.27 at 850 nm where the loss is the highest while that of CdGaO is 0.08. It is obvious that the in the CdO thin film is greater than the loss in the CdGaO thin film.

4. Conclusion

CdO and CdGaO thin films were deposited on conductive ITO coated glass substrates using low molarity solutions by electrochemical method and some basic optical parameters were investigated and compared. As a result of these analyses, it is observed that the CdGaO thin film has a lower energy band gap than the pure CdO. In addition, it is also obtained that the presence of Ga atoms significantly increases the transmittance values of CdO at all wavelengths. Consequently, it is considered that both thin films have low absorption capacities and are particularly suitable for use in solar cells as a component that transmits light without absorbing it.

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