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Optical properties of Al-CdO nano-clusters thin films

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ABSTRACT

The aluminum doped cadmium oxide (CdO:Al) thin films were grown onto glass substrates by sol–gel spin-coating method. The structural properties of undoped and Al-doped CdO thin films were studied by atomic force microscopy. AFM results reveal that the studied CdO films were formed from the nano-clusters. The optical transmittance of undoped and Al-doped CdO is decreased with increasing Al contents. The optical band gaps of the CdO films were varied from 2.54 eV to 2.32 eV with increasing Al dopants. The width of localized states in the optical band gap of the films is increased with increasing Al content. The improvement of the optical constant of Al-doped CdO has potential applications as transparent conducting oxide for different optoelectronic device applications.

1. Introduction

Cadmium oxide thin film is an important material for transparent conducting oxides (TCOs) [1] which are critical components as transparent electrodes in flat-panel displays, solar cells, gas sensors, and smart windows [2–5]. Pure and doped indium oxide, zinc oxide, tin oxide and cadmium oxide have been extensively studied because of their utilization in optoelectronic device technology [6–9]. In particular CdO based TCOs has considered a great interest due to their metal like charge

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transport behavior with an exceptionally large carrier mobility and good optical transparency in the visible region [10,11]. CdO is an *n*-type semiconductor with the band gap in the range of 2.2–2.8 eV. But, cadmium oxide is not a popular TCO material due to its low optical band gap. While, CdO is a particularly interesting material because it is one of the semiconducting oxides with high carrier mobility, and has great potential for using in optoelectronic devices [12]. Basically, work on In- [13], Sn- [14] and Fe- [15] Cu- [16] doped CdO have already been reported. Although, Al is a popular dopant in ZnO thin films, a literature survey indicated that there is a little work on the aluminum-doped CdO thin films [17].

Synthesis and characterization of aluminum-doped cadmium oxide (CdO:Al) by sol–gel method have reported [18,15]. Different methods have been adopted to deposit doped and pure CdO films such as metal organic chemical vapor deposition (MOCVD), RF reactive sputtering [19], electron beam evaporation [20], pulsed laser deposition [21], dc magnetron sputtering [22], radio-frequency sputtering [23], spray pyrolysis [24], and chemical bath deposition [25]. On the other hand, this method of preparation pure and doped CdO, the sol–gel route method is one of the most promising available methods for synthesizing nanoparticles of controlled size and morphology.

Sol–gel technique is one of the most promising tools in material science. The versatility of this method allows us to design desired materials at the lower temperatures, alternatively to conventional methods for manufacturing materials. The synthetic route provided by this system is the most feasible one for designing materials possessing unique properties. Generally, it is a process concerning transition of a system from liquid 'sol' (the colloidal suspension of particles) into solid 'gel' [12].

In present study, undoped CdO and Al-doped CdO were prepared by sol–gel calcinations method. Non-vacuum spin coating as a low cost technique was used to deposited thin film of the studied oxides. The optical spectra such as the transmittance and absorbance were measured at different wavelengths to study the optical constant of these films in nano-structure form. The values of the optical band gap and Urbach's energy were calculated compared with the previous work.

2. Experimental details

Undoped and Al-doped CdO were prepared by sol–gel method. Cadmium acetate was dissolved in 2-methoxyethanol (MTE) (0.5 M) as a solvent at a constant magnetic stirring for 10 min and then, mono ethanolamine (MEA) (0.5 M) (C_2H_7NO) as stabilizer was added to the stirring solution. Then, the solution was stirred again constantly for another 2 h at 60 °C. Al doped CdO films were prepared as follow: (0.5 M) cadmium acetate and (0.5 M) with different percents (1%, 5%, 10% and 15%) aluminum nitrate ($Al(NO_3)_2{\cdot}9H_2O$), were dissolved in MTE for 10 min. Afterwards, MEA was added drop by drop with continuous stirring. The final solution was stirred for 2 h at 60 °C to yield a clear and homogeneous solution. The final solution was used as the coating source after cooling down to room temperature.

The glass substrates were cleaned by detergent, methanol and acetone each for 15 min by using ultrasonic cleaner. Finally, the substrates were rinsed with de-ionized water and dried with nitrogen gas. The coating solution was dropped into the glass substrate, fixed at the top base of the spin coater was rotated speed at 1000 rpm for 30 s. After the spin coating, the film was dried at 150 °C for 10 min in a hot plate to evaporate the solvent and to remove the organic residuals. The process of coating/drying procedures was repeated for five times before the film was inserted into a tube furnace and annealed at 430 °C in air for 1 h. The thickness around 200 ± 5 nm as measured by AFM for the studied of Al-doped CdO with different dopants.

The structural properties of the thin films samples were investigated by Park System XE-100E atomic force microscopy (AFM). Also, the thickness of the undoped and Al doped CdO film was determined by using atomic force microscopy. The optical transmittance spectrum in the wavelength of 300–800 nm was recorded using a Shimadzu UV–VIS–NIR 3600 spectrophotometer using an integrating sphere attachment [12].

3. Results and discussion

3.1. Morphology of CdO and Al-doped CdO

The structural properties of the undoped and Al doped cadmium oxide films were investigated by AFM. AFM scans of the surface were carried out to study the change in the surface morphology of the studied films. The 2D AFM images of ($40 \times 40\ \mu m^2$) and ($5 \times 5\ \mu m^2$), Inset:3D images of ($5 \times 5\ \mu m^2$) for undoped and Al-doped CdO samples are shown in Fig. 1. The aluminum doped films show a smooth surface compared to the cadmium oxide films. The average values of the nano-clusters sizes and roughness for the studied oxides thin films are given in Table 1. The size of the clusters is changed with increasing Al dopants except for 15% Al. After doping of 15% Al, the nature of grain size is changed to pyramidal rod. This indicates that the type of grains is changed from cluster to rod with higher dopants content. It is clear also the grain size of the nano-clusters decreases with increasing the Al-contents on the host CdO.

3.2. Optical properties of the undoped CdO and Al-doped CdO thin films

Transmittance and absorbance spectra of CdO and Al-doped CdO films are shown in Figs. 2 and 3, respectively. Fig. 2 shows that the transmittance firstly increases rapidly up to wavelength 550 nm and then remains almost independent of wavelength of the incident beam. It is also observed that transmittance is decreased with increasing Al-doping [17]. It is evaluated that the higher doping concentration decreases the transparency due to increased absorption by free carriers [26].

The variation of the optical absorbance with wavelength is shown in Fig. 3. The calculated values of absorption coefficient are in the order of $10^7\ m^{-1}$. As seen in Fig. 3, the absorbance is increased with increasing Al-doping concentration and a sharp increase is observed near the band edge. Thus, the absorption coefficient can be calculated by the following relation [27–29]:

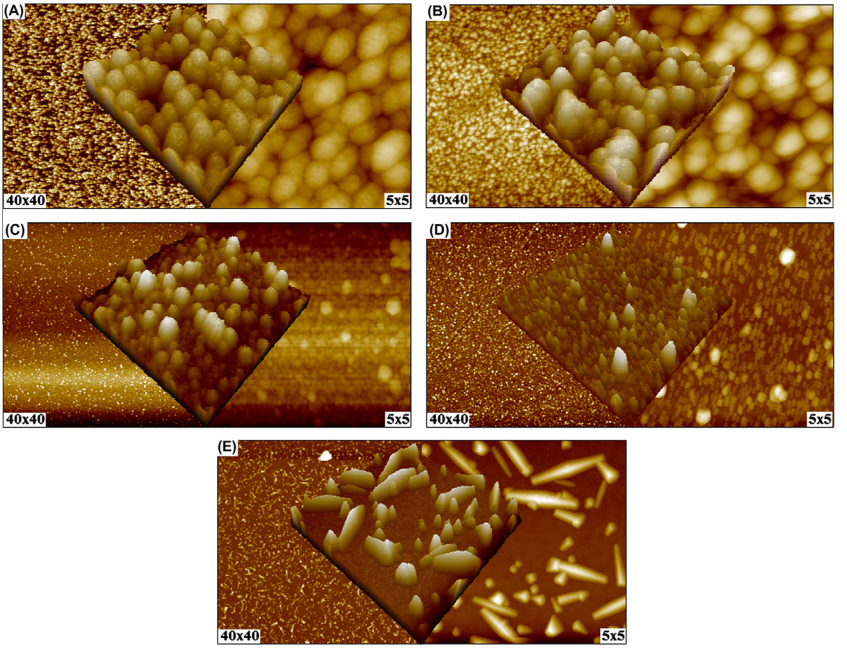

Fig. 1. AFM 2D images of ($40 \times 40\ \mu m^2$) and ($5 \times 5\ \mu m^2$) for (A) undoped CdO, (B) 1%, (C) 5%, (D) 10% and (E) 15% Al-doped CdO thin films, Inset: 3D images of ($5 \times 5\ \mu m^2$).

Table 1
The calculated mean values of the nano-clusters sizes and the roughness of undoped CdO and Al-doped CdO samples.

Samples	Mean nano-clusters sizes $5 \times 5\ (\mu m^2)$ in nm	Roughness (nm)	
		$40 \times 40\ (\mu m^2)$	$5 \times 5\ (\mu m^2)$
Undoped CdO	460.069	105.035	92.966
1% Al-doped CdO	180.518	111.008	78.271
5% Al-doped CdO	148.772	67.937	59.907
10% Al-doped CdO	139.794	25.967	18.713
15% Al-doped CdO	151.134	45.478	37.502

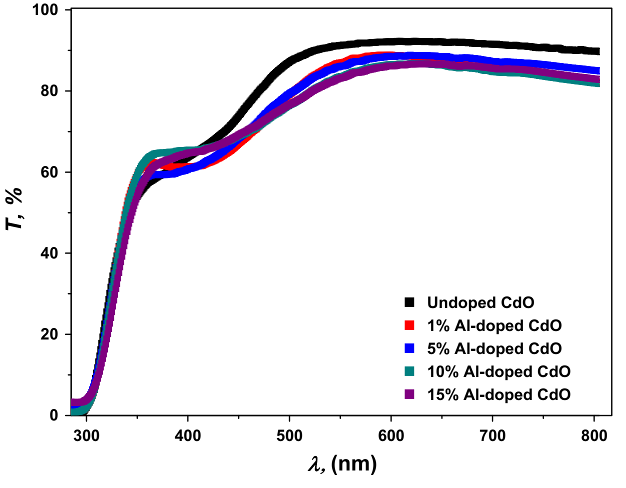

Fig. 2. Transmittance spectra of undoped CdO and 1%, 5%, 10% and 15% Al doped CdO thin films.

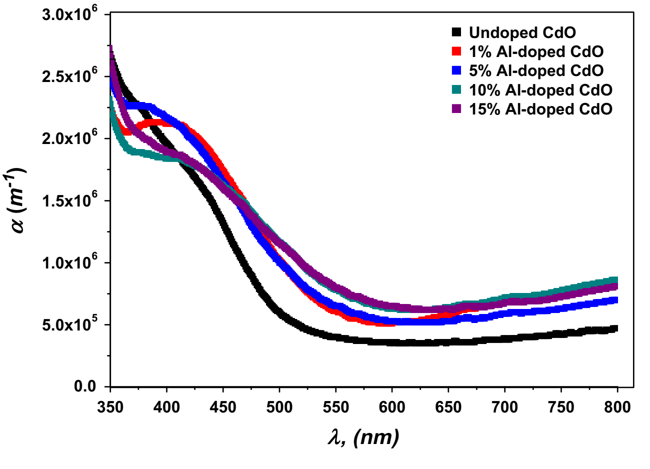

Fig. 3. The plots of α vs. wavelength of undoped CdO and 1%, 5%, 10% and 15% Al-doped CdO thin films.

$$\alpha = \frac{Absorbance}{t} \tag{1}$$

where t is the thickness of pure and Al-doped CdO. The optical transitions in semiconductor materials are taken place by direct and indirect transitions. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the value of the optical band gap E_g and it is related to the optical transition. The relation between the absorption coefficient and the incident photon energy $h\nu$ can be written as [30,31]:

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

where A is a constant depending on the transition probability and n is an index that characterizes the optical absorption process. The parameter n has the value 1/2 for the direct allowed transition and has the value 2 for the indirect allowed transitions. The optical band gap, E_g was calculated by plotting $(\alpha h\nu)^2$ vs. $h\nu$ for direct transitions. Fig. 4 shows the plots belonging to the direct transitions. The optical band gap energy was determined from the intercept on the energy axis after extrapolation of the straight line section of the curves and the obtained values are given in Table 2. Depending on the doping concentration of the films, the direct band energy is varied from 2.54 eV to 2.32 eV [32]. The reported values for direct band gap are (2.10–2.70 eV) of CdO thin films [33–35]. The direct band gap energy obtained in this study is more consistent to the reported direct band gap values. Therefore, we concluded that both the CdO and Al-doped CdO thin films fall under the class of direct band gap materials. The values of the obtained direct band gap E_g for pure and Al-doped CdO are given in Table 2. It is seen that the optical band gap of the CdO film is decreased with the increase of Al content. The change of the optical band gap of Al-doped CdO can be explained by Burstein–Moss shift [36]. In which the optical band gap decreases with increasing Al-contents. The reported band gap by Gupta et al. [21] for Al-doped CdO varying between 2.74 eV and 2.84 eV which is higher than the present study. The higher band gap can be discussed on the basis of different deposition technique from pulsed laser deposition to the sol–gel spin coating techniques.

The width of the localized states available in the optical band gap of the films affects the optical band gap structure and optical transitions and it is called as Urbach's tail [37], which is related directly to a similar exponential tail for the density of states of either one of the two band edges [38]. The Urbach's tail of the films can be determined by the following relation [39]:

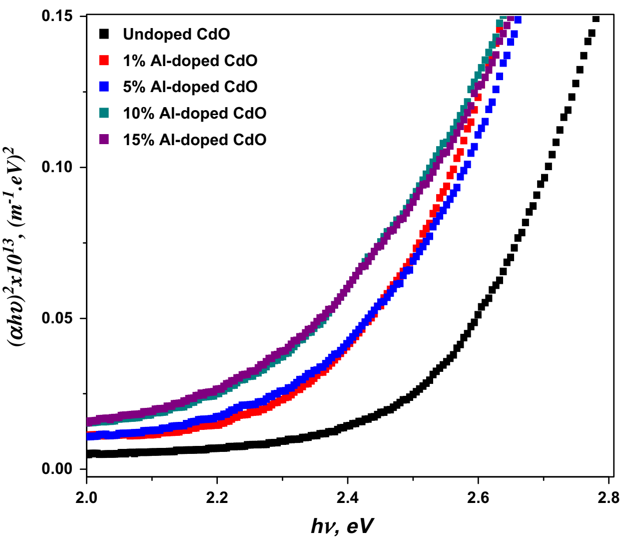

Fig. 4. Plots of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ of undoped CdO and 1%, 5%, 10% and 15% Al-doped CdO thin films.

Table 2
Optical band gap and the Urbach's energy parameters for undoped CdO and 1%, 5%, 10%, 15% Al-doped CdO compared with other work.

Samples	Direct band gap (present study) E_g (eV)	Direct band gap (other work) E_g (eV)	Direct band gap (other work) [32] E_g (eV)	The Urbach's energy (present study) E_U (eV)
Undoped CdO	2.54	2.48 [37], 2.53 [40]	2.49	0.31
0.5% Al-doped CdO	–	–	2.48	–
1% Al-doped CdO	2.42	–	2.46	0.33
1.32% Al-doped CdO	–	2.79 [17]	–	–
2% Al-doped CdO	–	–	2.34	–
5% Al-doped CdO	2.40	–	–	0.46
10% Al-doped CdO	2.36	2.36 [17]	–	0.50
15% Al-doped CdO	2.32	–	–	0.51

$$\alpha = \alpha_0 exp(E/E_U), \quad (3)$$

where E is the photon energy, α_0 is constant and E_U is the Urbach's energy which refers the width of the exponential absorption edge. Fig. 5 shows the variation of $\ln\alpha$ vs. photon energy for the studied films. This behavior corresponds primarily to optical transitions between occupied states in the valence band tail to unoccupied states at the conduction band edge. The Urbach's energy can be written as:

$$E_U = \left[\frac{d(\ln\ \alpha)}{d(h\nu)}\right]^{-1} \quad (4)$$

The obtained E_U values are given in Table 2. Urbach's energy values for the films increase with increasing aluminum dopants. The addition of Al content into CdO creates some defects in the optical band gap of the films and these defects produce the localized states in the optical band gap. The concentration of the defects is related to the density of the localized states. The Al dopants may cause the changes in the localized states to overlap. These overlaps cause a decrease in the optical band gap [40]. The decrease in the optical band gap can be explained by the increase in the degree of disorder

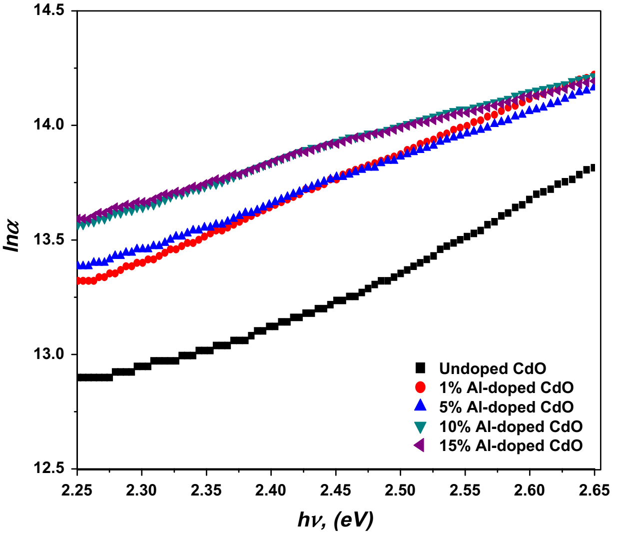

Fig. 5. The plots of $\ln\alpha$ vs. the photon energy of undoped CdO and 1%, 5%, 10% and 15% Al doped CdO thin films.

in the films. The presence of the high content causes expanding of the localized energy levels. Therefore, the decrease in the optical band gap results from the localized states having high content. This indicates that the optical band gap of the CdO films is decreased with the expanding localized states. This confirms that the E_U values change inversely with optical band gaps of the films.

4. Conclusions

Undoped and Al-doped CdO thin films were deposited on glass substrates by sol–gel dip-coating method. The structural and optical properties of these films were investigated as a function of Al doping concentration. The mean values of nano-clusters size and roughness for pure and Al-doped CdO were determined. The direct band gap E_g and the Urbach's energy E_u for undoped and Al-doped CdO samples were calculated. Sol–gel spin coating technique is a good technique for producing nano-structure materials. Al doped CdO is a good candidate in electronic and optoelectronic devices based on the high transmittance and the controlling of the band gap.

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