CdO: Ag Films Deposited by Sol-Gel Process: A Study on their Structure and Optical Properties.

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Abstract: *Undoped Ag–doped CdO films have been prepared by sol–gel spin–coating method. Effects of Ag dopant on the optical properties of CdO film have been investigated. The crystal structure and orientation of the films have been investigated by X–ray diffraction method. CdO and CdO:Ag films have polycrystalline structure with (111) preferential orientation. Ag dopant increases the optical transparency of the films in the visible region. The optical absorption study reveals that the direct optical transitions occur in the optical band gap and the films have a direct optical band gap. The thin films were prepared of undoped, 1% Ag–doped , 2% Ag–doped and 4% Ag-doped CdO films were found to be, 2.39, 2.35 , 2.31 and 2.30 eV, respectively. The optical constants, refractive index, extinction coefficient and optical dielectric constants of these films were determined using transmittance and reflectance spectra. Ag doping concentration affects strongly the optical constants of the thin films. The optical constants and optical absorption edge of the CdO thin film can be controlled by Ag dopant.*

Keywords: CdO ,Sol-gel ,spin coating, x-ray diffraction

1. Introduction

An important Branch, that has been advanced in the last decades is the physics of thin films. Thin films have been extensively Studied for over last two hundred years because of their Potential uses [1].

Thin films is definite as thin layer built up on a solid support by controlled condensation of the individual, ionic species or atomic, molecular, either directly by a physical process, or via a chemical and , or electrochemical reaction[1,2]. The films of Transparent Conductive Oxides (TCO) such as Zinc oxide (ZnO), Indium-tin oxide, tin oxide and cadmium oxide (CdO) have been extensively studied because of their use in semiconductor optoelectronic device technology [3]. Among the TCO, CdO films have been successfully used for many applications, including use in gas-sensing devices, photodiodes, transparent electrodes, phototransistors, and photovoltaic solar cells [4]. CdO is an important material for the fundamental studies. It is now well conceived that the (CdO) shows many excellent properties, which make it suitable as a (TCO). CdO is an (n–type) semiconductor with band gap of approximately (2.5 eV)[5, 6]. CdO high electrical conductivity (even without doping) and high optical transmittance in the visible region of solar spectrum along with a moderate refractive index make it useful for various applications such as solar cells, transparent electrodes, phototransistors, photodiodes, gas sensors ,etc. [7,8]. Many techniques have been used to prepare CdO films such as Spray pyrolysis [9] , Chemical bath deposition ,Chemical vapor deposition [10], Sputtering [11], Dip coating [12], Spin coating [13] and Pulsed laser deposition (PLD) [14].

The optical, the electrical, and the morphological properties of the films could also be different by using various additives in the growth solution. One of the methods is using some organic additives in the growth bath for solution-based synthesis. In general, the optical properties, such as the band gap energy, are quite dependent on the crystal sizes [15, 16]. There are various additives such as saccharin, citric acid, and tartaric acid. The additives are especially used to control the surface morphology and to refine the grain size [17]. Saccharin is famous to be used as a strong leveling agent for the surface and a grain refiner, by decreasing of the internal stresses in the deposits [18, 19].

2. Experimental Part

Undoped CdO films were deposited onto glass substrates by the sol–gel method using a spin–coating method. The CdO precursor solutions were prepared starting from:
1) Cadmium acetate dehydrated (CAD) (2g).
2) Methanol (14 mL).
3) Glycerol (100 μL).
4) Triethylamine (500 μL).

At first, the CdO precursor solution was prepared by the following procedure:

First solution : The cadmium acetate was dissolved in half of the methanol(7 mL) for each g of (CAD) at constant magnetic stirring until a transparent solution was obtained.. The glycerol was added to the solution. Second solution : the trimethylamine previously dissolved in the other half of the methanol (7 mL) was also incorporated. Storing the mixture of the two solution for 24 hours at room temperature . the resulting solution is completely colorless and transparent during preparation and storing . The glass substrates were first cleaned by detergent, and then in methanol and acetone each for 10 min by using ultrasonic cleaner. At last, the substrates were rinsed with deionized water and dried with nitrogen. The dissolving of (0.85 g) silver nitrate in (50 ml) of methanol to prepare a silver and then dopping the original solution with silver in three ratios of 1% , 2% and 4%.The coating solution was dropped into the glass substrate, which

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was rotated at 2000 rpm for (15 s) using LAURELL WS-400B-6NPP/LITE spin coater.

3. Results and Discussion

3.1 Crystal structure of the undoped and Ag–doped CdO films

The X-ray diffraction (XRD) patterns of the (CdO) films prepared at temperatures of (300 °C) are shown in fig.(1). X-ray diffraction XRD spectra of the undoped and Ag–doped CdO films are shown in Fig.(1,2,3,4), these results indicate that all of the films have a polycrystalline structure. The observed diffraction peaks (111), (200), (220), and (311) for CdO thin films are in good agreement with the reported data [20]. It can be seen also that the prepared thin films are highly oriented in the (111) direction [21 ,22]. The average grain size and strain for the films can be determined using the equation [23,24]:

$$D = \frac{0.9 * \lambda}{\beta * \cos \theta} \qquad \ldots \ldots (1)$$
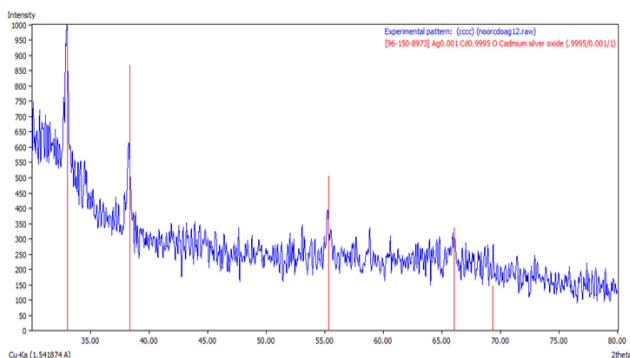
Where : λ= wavelength. β=FWHM . θ= the Bragg angle . D =grain size
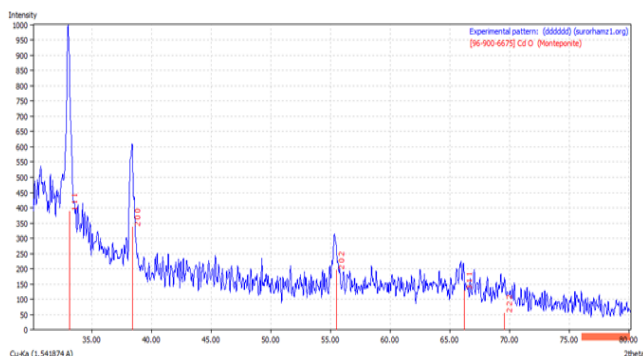
Figure 1: X-ray diffraction pattern for 2 layers CdO thin films annealing at 300 oC

Table 1: XRD results for CdO thin films and Ag-doped CdO for 2 layers
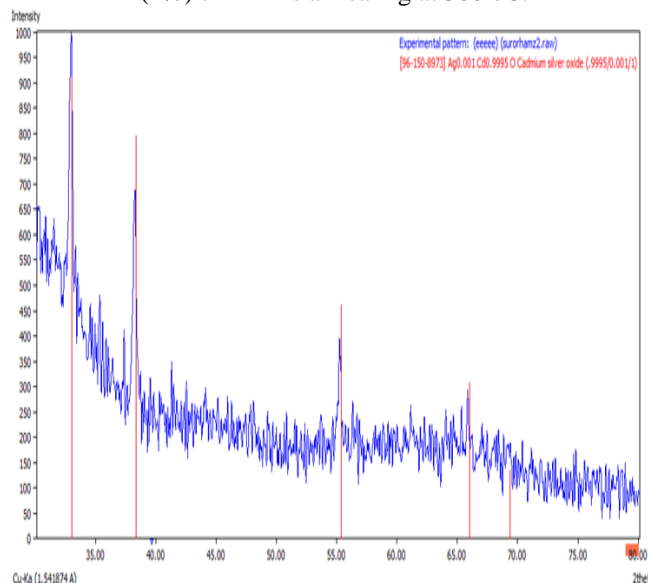
Item	2 theta	FWHM(Deg)	Crystal size (nm)
Pure	55.2077	0.41670	21.530
CdO:Ag 1%	55.2460	0.32000	28.06
CdO :Ag 2%	55.2110	0.27000	33.250
CdO:Ag 4%	55.1586	0.22500	39.843

Figure 2: X-ray diffraction pattern for 2 layers Ag-doped (1%) thin films annealing at 300 oC.
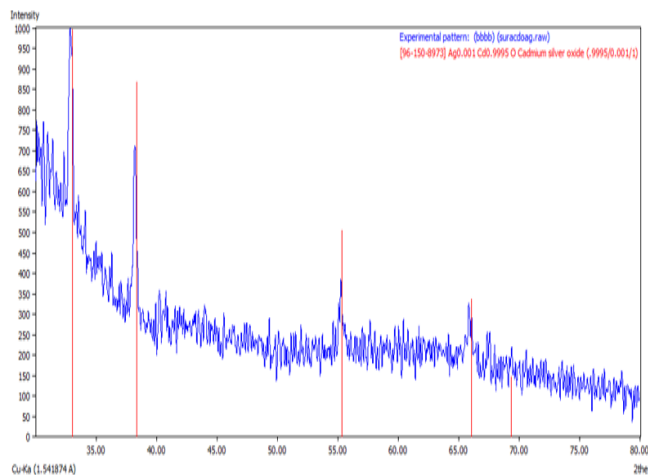
Figure 3: X-ray diffraction pattern for 2 layers Ag-doped (2%) thin films annealing at 300 oC.


Figure 4: X-ray diffraction pattern for 2 layers Ag-doped (4%) thin films annealing at 300 oC.

Table (1) shows that in the case of the first doped ratio, the crystal size of the dopped sample increase in comparable with the pure sample, this means that increasing crystallization is due to the particle size increased. The 4% dopping ratio is the best.

3.2 Optical properties of the undoped and Ag-doped CdO film

The absorbance and reflectance spectra of the films are displayed in fig. (5) Ag incorporate creases the absorbance of the CdO films by doping in the visible region . As shown in fig.(5). The optical absorption edge of the films was determined by the optical absorption, which provides explaining features concerning the band structure of the film .The optical absorption control was evaluated by the following relationship [25]:

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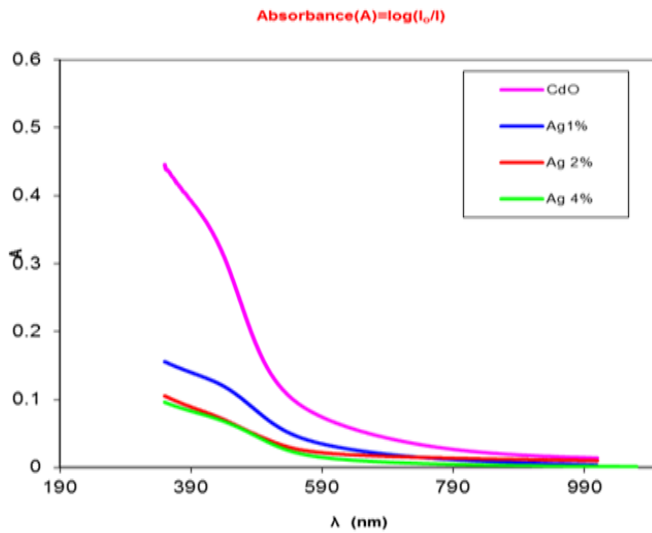
Figure 5: Absorbance of the undoped and Ag-doped CdO Film For 2 layers.
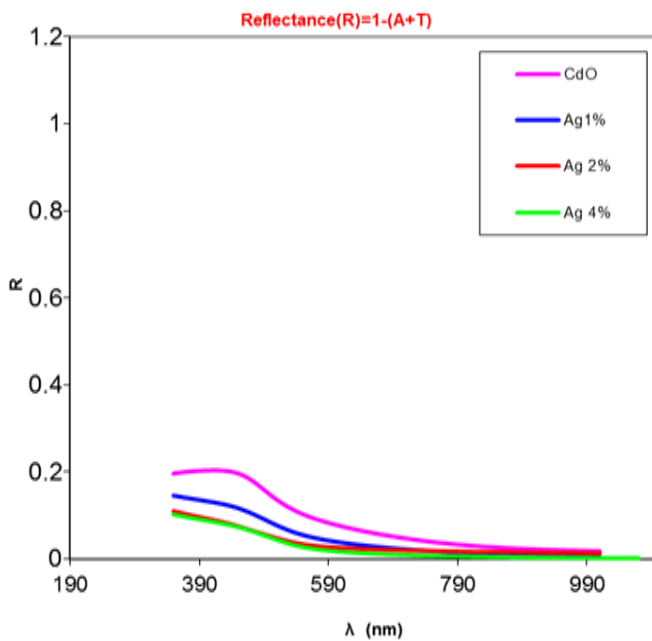
Figure 6: reflectance spectra of the undoped and Ag-doped for 2 layers.

$$\alpha h\upsilon = A(h\upsilon - Eg)^{1/2} \ldots\ldots\ldots 2$$

Where:

A = is a constant.

hυ= is the photon energy .

Eg= is the optical band gap.

The values of the optical band gap (Eg) values of the films were obtained from the intercept of ($\alpha h\upsilon)^2$ vs. hυ curves plotted. Fig. (6) displays the plots of ($\alpha h\upsilon)^2$ vs. hυ. It is seen that Eg values increase with silver (Ag) dopant. The blue shift in the optical band gaps of the films may be attributed to the band Burstein–Moss effect. This effect is frequently observed in n–type semiconductors. The increase of carrier concentration in doped thin film will cause the Fermi level move into the conduction band. The filling of the conduction band by electrons will generally result in blue shift in the near band edge emission.
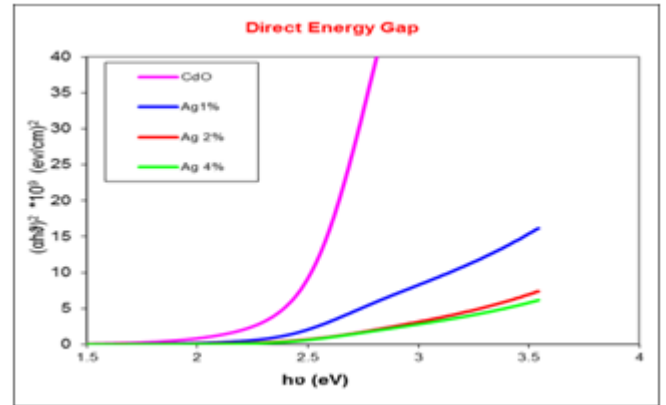
Figure 7: the plots of (αhv)2 vs. photon energy of the undoped and Ag-doped for 2 layers.

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 tail, which is related directly to a like exponential tail for the density of states of either one of the two band edges [26]. The Urbach tail of the films can be determined by the next relation [27]:

$$\alpha = \alpha_o \exp(E/Eu) \ldots\ldots\ldots\ldots 3$$

where:

E= is the photon energy.

αo= is constant .

EU = is the Urbach energy which refers the width of the exponential absorption control . Fig. (8) displays the variation of (lnα) vs. photon energy for the films. This behavior corresponds primarily to optical transitions between occupied states in the valence band tail to unoccupied states at the conduction band edge.
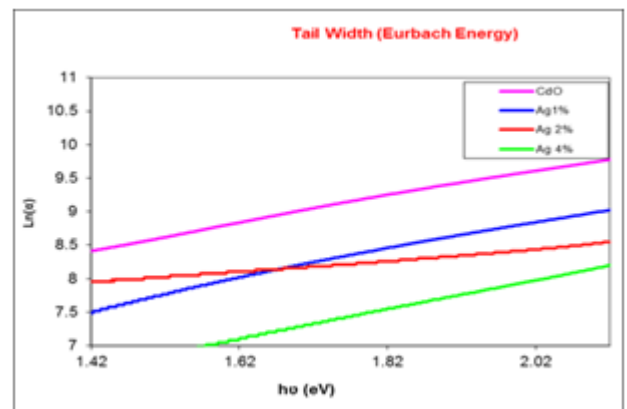
Figure 8: The plots of (lnα) vs. photon energy of the undoped and Ag–doped CdO films for 2 layers .

$$Eu = \left(\frac{d(ln\alpha)}{d(\ln(h\upsilon))}\right)^{-1} \ldots\ldots\ldots\ldots 4$$

Urbach energy values of the films decrease with increasing Silver dopant. The (EU) values change inversely with optical band gaps of the films. The refractive index dispersion plays an important role in the research for optical materials. Because, it is a significant factor in optical communication and in designing devices for spectral dispersion. The refractive index of the films can be determined by the next relation [28].

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$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R^2)} - K^2}$$

…………….. 5

where:

k ($k=\alpha\lambda/4\pi$)= is the extinction coefficient.

The refractive index values of the films were calculated using Eq (5) .
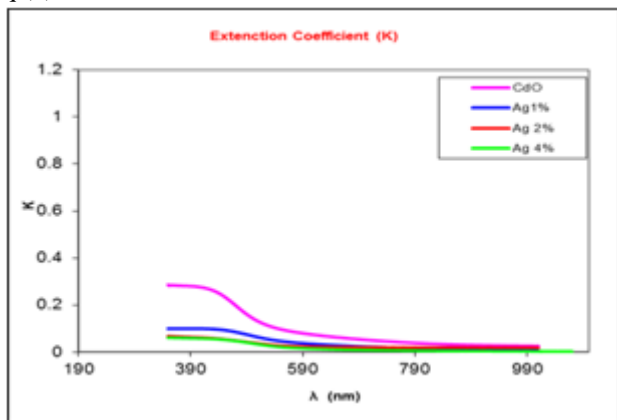
Figure 9: Extinction coefficients of the undoped and Ag–doped CdO films for 2 layers .

Fig.(9) displays the plots of extinction coefficient vs. wavelength for the films. After (400 nm) , the extinction coefficient changes strongly with (Ag dopant) due to the structural changes in the films. As seen in plotted figure of refractive index, the refractive index decreases with (Ag dopant).

4. Conclusions

The undoped and Ag–doped CdO films were deposited by sol–gel spin–coating method. The structural and optical properties of the CdO film were influenced by Ag doping:
1) X-ray diffraction (XRD) effects showed films have (111) preferred orientation.
2) The optical band gap values were initiate to reduction from (2.39, 2.35 , 2.31 and 2.30 eV) with Ag doping. The optical constants, refractive index, extinction coefficient and optical dielectric constants, of these films were determined by transmittance and reflectance spectra. Ag doping concentration affects the optical parameters of the thin films.

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