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Annealing Effect on the Structural and Optical Properties of Sol-Gel Deposited Nanocrystalline CdO Thin Films

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Abstract

In this paper CdO thin films have been prepared by using SOL-GEL method with spin coating technique, by depoited four layers of mixtuer solution contians Cadmium acetate dehydrate, Triethylamine, glycerol and ethanol.The spin coated solution were dried at 100°C and annealied at (300,350 and 400 °C temperatures). The x-ray diffraction techniques and UV-VIS spectrophotometer have confirmed the structural and the optical properties the prepared thin films. CdO thin films were found to have polycrystalline nature with cubic rock salt phase. The crystallinity being improved, the FWHM decreases and the grain size of the CdO thin films increased with increasing the annealing temperatures. The average grain size is observed in the range (23.97 - 30.47) nm which indicate that the prepared film have a nanocrystalline structure. From optical analysis, it can be seen that there are an increases in the absorbance and decreases in the trancemittance of the prepared films with the increasing of the annealing temperatures.The optical band gap decreases from 2.556, to 2.081 eV with increasing of annealing temperature fromm 300 to 400° C, this suggested that the optical band gap for CdO nanocrystalline thin films is strongly dependent on the annealing temperature.
Keywords: CdO thin films, Sol–gel spin–coating, Structural and Optical properties, annealing temperature.

1. Introduction

Transparent conducting oxides (TCOs) have long been a subject of various investigations due to its unique physical properties and applications in commercial devices [1, 2, 3]. (TCOs) are electrical conductive materials with a comparably low absorption of light and high optical transmittance in the visible region of the solar spectrum along with a moderate refractive index[2,3]. Among these TCOs, CdO is an important material for the fundamental studies. It is now well conceived that the CdO shows any excellent properties, which make it suitable as a TCO[4]. CdO is an n–type semiconductor with band gap of approximately 2.5 eV, CdO is cubic structure with each ion surrounded by six ions of opposite electric charge, octahedrally arranged [4,5].CdO films have been successfully used for many applications, including phototransistors [5], gas sensor [6], transparent electrodes, photovoltaic solar cells [7], liquid crystal displays, photodiodes, IR detectors and anti reflection coatings and optoelectronic devicess [7,8].CdO thin films have been prepared by different techniques such ultrasonic spray pyrolysis[9] , electrodeposition [10], chemical bath deposition [11], vacuum evaporation [12] , Pulse Laser Deposition [13] and Sol.Gel. deposition method[14] In this work, CdO film has been deposited by sol–gel method spin coating procress, which is a very simple and economical method.

2. Experimental work

CdO films were deposited onto glass substrates by the sol–gel method using a spin coating method. In order to obtain acceptable results and measurable samples, Cadmium acetate dehydrate is used, which is white solid Sault $Cd(CH_3COC)_{2\cdot2}H_2O$ supplied from FLUKA-GARANTIE co-England. With a molecular weight of 266.52 g/mol and a purity of 98% as a source for cadmium, Cubis® Analytical Balance MSU224S-0CE-DU, satoriues Gmbh-Germany with 0.1 mg readability is used, Cadmium acetate dehydrate was dissolved in methanol. Digital Hotplate stirrer, UK, Jenway co, model SD162 is used to insure complete dissolving. Glycerol is used to obtain gel from this solution. Triethylamine supplied from SIGMA-ALDRICH co-USA with Molecular Weight 101.19 was added to methanol, and then added to mixture. Then applying following procedure to obtain solution: 7 ml of methanol is added to 2 g (7.5 mmol) of cadmium acetate dehydrate. In order to obtain a transparent solution, continuous slow stirring is required. Adding 0.11 ml (1.5 mmol) of glycerol with continuous stirring, a solution of 0.52 triethylamine in 7 ml of methanol is prepared separately, and subsequently added with 1 hour stirring to cadmium acetate solution. Then storing the mixture of the two solutions for 24 hours at room temperature, the resulting solution is completely colorless and transparent during preparation and storing. The glass Substrates have been *cleaned by distilled water in order to remove impurities and residuals from the surfaces, then they cleaned* by dipping in methanol for 5 minutes, then dipping in acetone for 5 minutes, dipping in de-ionized water for 10 minutes, cleaning by Hcl for 10 minutes and finally dipping in de-ionized water for 10 minutes, For reaching best results. Samples exposed to ultrasonic cleaner inside de-ionized water for 15 minutes and dried

carefully by nitrogen gas. The coating solution was dropped onto substrates and then the substrates were rotated at 2000 rpm for 20 second. After the spin coating, the films were dried at 100◦C for 5 min. This coating/drying procedure was repeated for four times and then annealed at (300,350 and 400)◦C temperatures in air for 1 h. Structural studies have been investigated by using X-ray diffractometer (ADX-2700-CuK_ 1.5406 A˚) radiation in 2θ range 20–70◦. Scanning electron microscopy images and EDSX analysis were obtained using SEM (INSPECT-550). The transmission and absorbance spectra of the prepared films were measured using UV–vis spectrophotometer from PG instruments model (T-90) in the wavelength range (300-800)nm .

3. Results and discussion

3.1. Structural properties

X-ray diffraction patterns (XRD) of prepared four layers CdO thin films at different annealing temperatures (300, 350 and 400) ˚C shown in fig. (1). CdO thin films are found to have polycrystalline nature and grown in the cubic rock salt crystal structure . The planes (111), (200), (220) and (311) indicate the CdO Cubic rock salt phase with strongly preferred orientation at (2θ = 33.109 ^{o}) along the (111) planes. The observed diffraction patterns are in good agreement with the standard crystallographic data for the CdO metals of JCPDS card 05-0640. From the fig. it can be clearly seen that the preferential orientation peak with increase the annealing temperature became sharper and more intense, especially for (111) planes. This may be attributed to the crystallinity of the CdO films being improved with increasing the annealing temperatures . The d-values(interplaner distance) were calculated by using Bragg's law and compared with the standard values of JCPDS card as in table (1). The lattice constant (a) evaluated for CdO thin films using the equation[15]:

$$d_{hkl} = a/\sqrt{h^2 + k^2 + l^2} \qquad (1)$$

and it was about 4.68 Å, which is almost identical with the standard value . The average grain size (crystal size) is calculated from XRD data using Scherer's formula [16]:

$$g.s = K\lambda/\beta \cos\theta \qquad (2)$$

where K is the Scherer constant, β is the full width at the half maximum (FWHM) and λ is the wavelength of the radiation. The results shows that the grain size of the CdO thin films increased from (23.97 to 30.47) nm with increasing of annealing temperature from 300 400 ^{o}C. The average crystal size values gives an indicate that the CdO prepared films are nanocrystalline in nature. These results was found in a good agreement with the literatures J. Santos-Cruz and et al. [17], T. Singh and et al. [18] and A. Abdolahzadeh Ziabari and et al.[19]. The XRD results of CdO thin film shown in table (1).

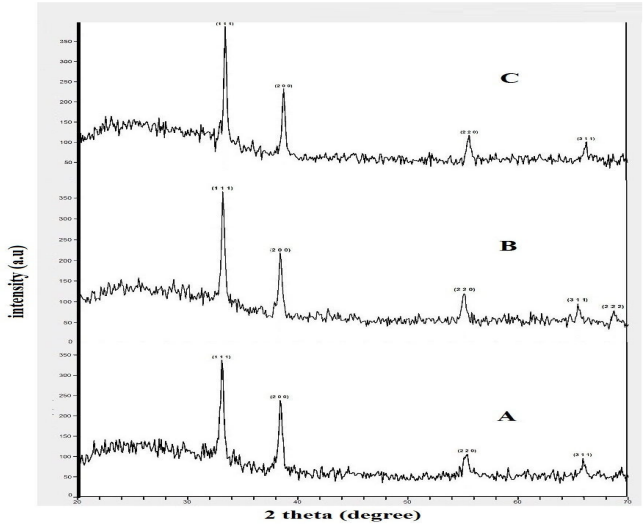

Figure 1. XRD pattern of four layers CdO thin film annealed at (A: 300, B: 350 and C: 400)° C.

Table 1. XRD results for CdO thin films prepared at different annealing temperatures.

No.	Annealing temperature °C	2θ°	d(Å) (Observed)	d(Å) (standard)	Miler indices	Lattice constant (a) Å	g.s (average grain size) nm
1	300	33.109	2.7034	2.712	111	4.681	23.97
2		38.42	2.3411	2.349	200	4.681	
3		55.365	1.658	1.661	220	4.689	
4		65.922	1.4158	1.416	311	4.695	
5	350	33.309	2.6876	2.712	111	4.655	24.65
6		38.504	2.3361	2.349	200	4.672	
7		55.039	1.6671	1.661	220	4.715	
8		65.441	1.425	1.416	311	4.726	
9	400	33.407	2.68	2.712	111	4.641	30.47
10		38.703	2.3246	2.349	200	4.649	
11		55.575	1.6523	1.661	220	4.673	
12		66.229	1.41	1.416	311	4.676	

3.2. Optical properties

Fig.(2) shows the absorption spectra of the deposited CdO thin films at different annealing temperatures. We can observe from the Figure that the highest absorbance of CdO thin films were in the UV region about 360 nm wavelength The fundamental absorption edge shifted towards the longer wavelengths and lower energies, this shift may be attribute to the improvement of the crystallinity of the films and to the changes of the quality of the CdO film with increasing the annealing temperature. These results are consistent with other published results such as J. Santos-Cruz et al. [17] and A. Abdolahzadeh Ziabari et al. [19].

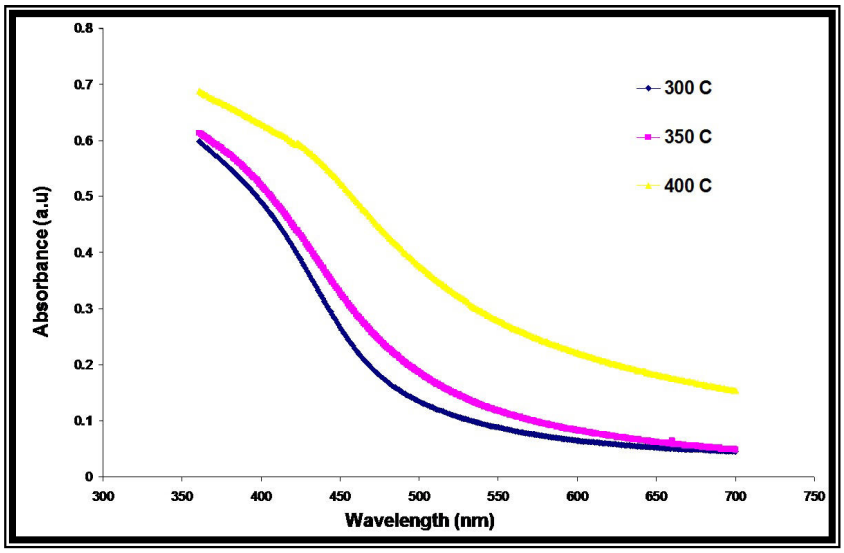

Figure 2. Absorbance spectra of deposited four layers CdO thin film at different annealing temperature.

The optical transmittance of the prepared films was tpically higher than 70% at wavelengths beyond the absorption edge. The variation of the transmittance versus wavelength at different annealing temperature shown in the fig. (3). IT is absorbed that the transmittance decreases with increasing of annealing temperature it is clear that the decreases or the shift towards longer wavelengths is not sharp. The parallel transmission shift however indicates that it is related to changes in film structure. It can be seen also that the increase in transmittance in UV region is not sharp. This indicates that the absorption band gap transitions in the studied films are due to direct and indirect transitions.

These results are consistent with other published results such as A. Abdolahzadeh Ziabari et al. [19] and (A.A. Dakhel and F. Z. Henari) [12].
The optical energy gap values (Eg) for CdO thin films have been determined by using Tauc relation[20]:

$$\alpha(h\nu) = A\left(h\nu - E_g^{opt}\right)^r \qquad (3)$$

where α are the absorption coefficients of CdO thin films , hυ is the energy of the incident photon, r = 0.5 for a direct transition semiconductor. The direct forbidden energy band gaps were calculated from

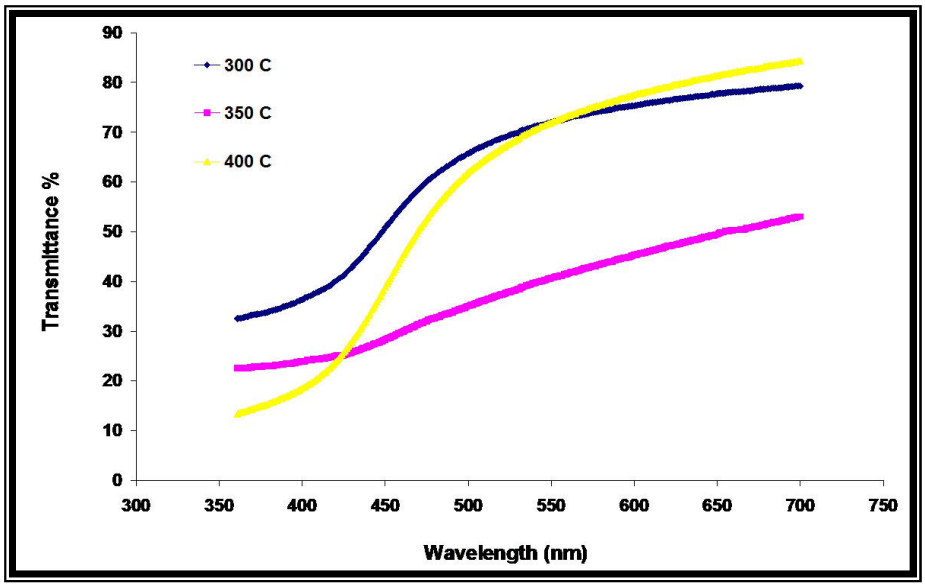

Figure 3. Transmittance spectra of deposited four layers CdO thin film at different annealing temperature.

the plots $(\alpha h\upsilon)^2$ versus hυ. This was made by extrapolating the linear portion of the curves until they intercept the photon energy axis, i.e., at $(\alpha h\upsilon)^2 = 0$ (see inset of Fig. 4). The optical energy values decreases from 2.556 to 2.081 eV sequentially with increasing of annealing temperaturesfrom 300 to 400 ^{i}C , this shift may be attributed to the changes of the quality of the CdO film with increasing the annealing temperature. After annealing temperature increases, thermal induced defects increase dramatically. This could result in an evident red - shift of the optical absorption edge with increasing the annealing temperature. These results are consistent with other published results such as the literatures in references [10, 17, 19].
The extinction coefficient is calculated using the relation[20,21]:

$$k = \alpha\lambda/4\pi \qquad (4)$$

Fig. (5) show the variation of extinction coefficient as function of photon energy of CdO prepared thin films.The extincstion coefficient (k) behaves just like the absorption coefficient (α) because they are joined by previous relation. However, the shape of the curve of extinction coefficient is almost constant in the low energy (is less than the absorption edge) and possibly due to scattering resulting from surface roughness. As well as, the potential high observe an increase in the extinction coefficient and a sharp increase at the absorption edge, this is due to increase in absorption coefficient in the occurring of direct electronic transitions. The extinction coefficient values increased with annealing temperature increasing, this is due to the decreasing of the optical band gap. The extinction coefficient of the films has an inverse relation with the transmittance spectra The results were in agood agreement with the literature references [19, 22,]

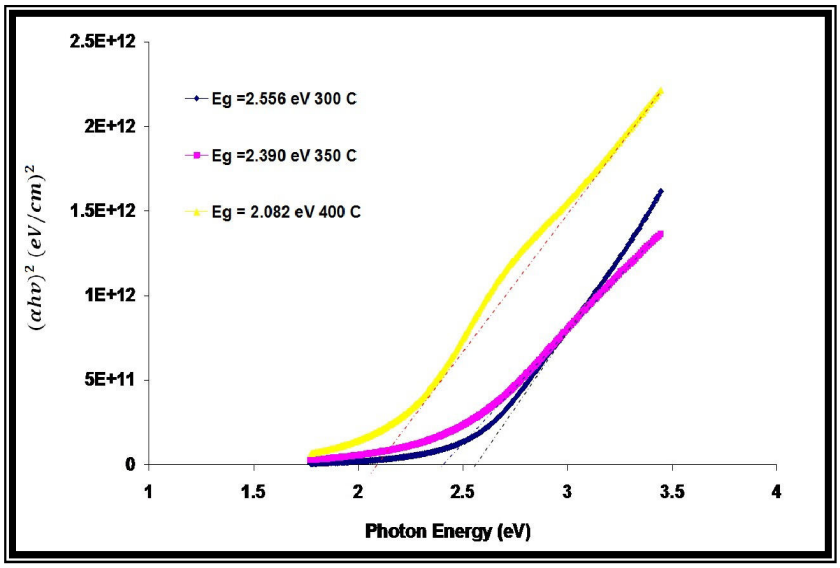

Figure 4. Direct energy gap of four layers CdO thin films at different annealing temperatures.

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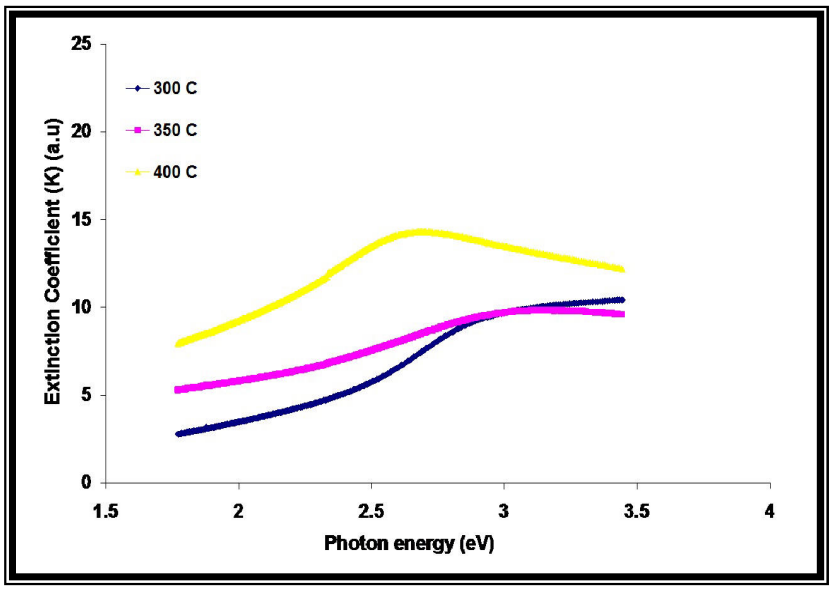

Figure 5. Extinction Coefficient of four layers CdO thin film at different annealing temperatures.

3.3. Surface morphology

The surface morphology of the CdO thin film deposited on the Si substrate at different annealing temperature is observed in the SEM images shown in the Fig**.6.** The results showed that the thin films exhibit a uniform surface morphology over the entire substrate and that the films are of good quality. The EDX spectrum and atomic composition of the CdO/Si is shown at the right side of SEM images. The morphology of the prepared films indicates that the size of the particles (grains) increased with the increasing of annealing temperatures. All prepared CdO thin films is otherwise uniformly, coated with the exception of few defects and those prepared from same procedure reviewed in the experimental part on Si substrate as shown in the figure. The results was agree with the literature references [23, 24].

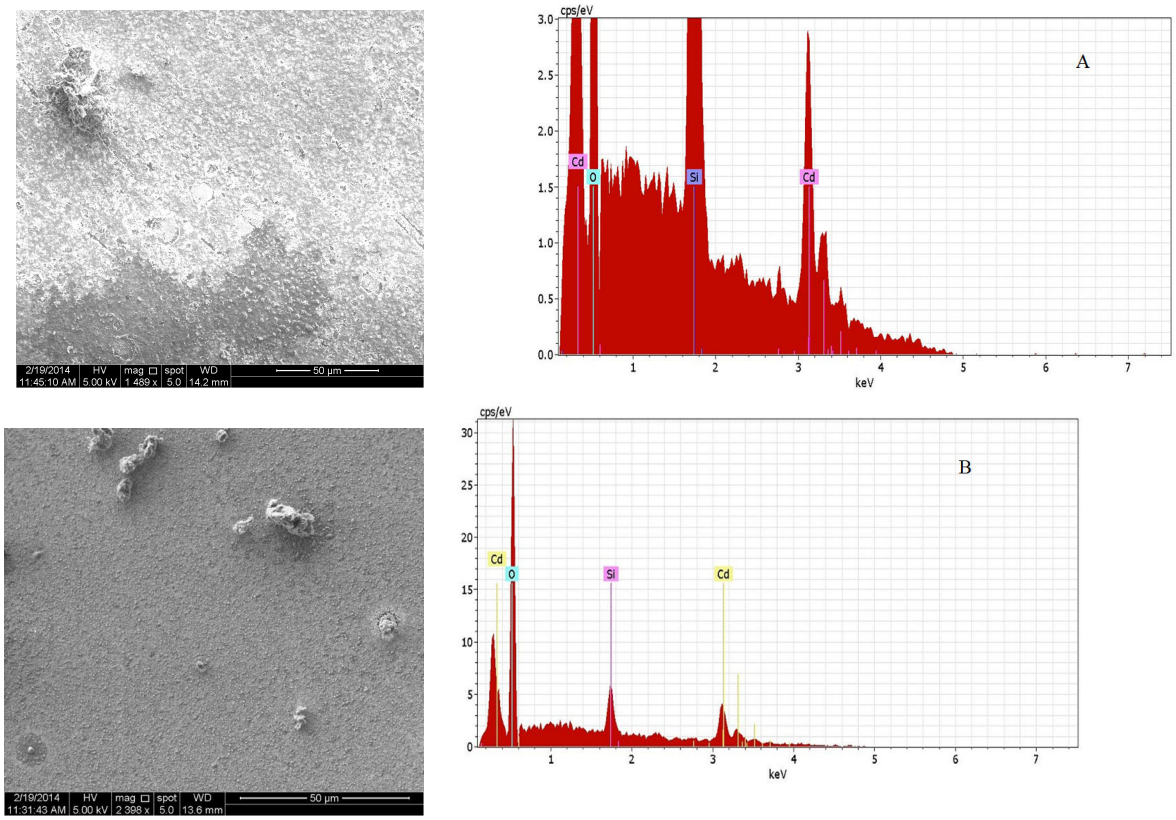

Figure 6. SEM and EDX Images of four layers CdO/Si thin film at different annealing temperature (A) 350°C , (B) 400°C.

4.Conclusions

CdO thin films had been deposited on glass and p-Si sbtrates by Sol.-Gel. Spin coating technique at 300,350and 400 ^{o}C annealing temperatures. The XRD results showed that the crystal structure of CdO thin films were polycrystalline in nature with Cubic (rock salt) phase and the increase of annealing temperature enhanced the crystallinity of the film and increased the crystallite size,moreover the prepared CdO thin films have a nanocrystalline structure . The optical studies showed that the CdO films were highly transparent in the visible region of the spectrum and transmittance decreased with increasing of annealing temperature. The absorption edges of the CdO thin films had been shifted towards longer wavelengths (lower energies) as respect to the increases of annealing temperature. The band gap of CdO thin films had been decreased when the annealing temperature increasing. This suggested that the optical bandgap for CdO nanocrystalline thin films was strongly dependent on the nnealing temperature and annealing ambient.

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