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Effect of annealing temperature on the structural and optical properties of CdO thin films grown by pulsed laser ablation

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ABSTRACT

In this work CdO films were prepared by using pulsed laser deposition (PLD). The search had included studying some of the structure and optical properties of CdO thin film before and after annealing with different temperature. The effect of the annealing treatment on the structural and optical properties on the film quality investigated. The results of X-ray examination showed that that the diffraction is from cubic phase of polycrystalline structure. Heat treatment helps to have good crestenelity.

The energy gap at room temperature (2.23 eV) and it increase with annealing to (2.7eV). The heat treatment helps to have good crestenelity. The grain size decreases with increasing annealing temperature.

KEYWORDS CdO, Thin film, pulsed laser ablation, effect of annealing temperature.

1- Introduction

There is no doubt that semiconductor changed the world beyond anything that could have been imagined before them [1]. One of the basic building blocks of all modern electronic devices is the semiconductor. Semiconductors can conduct or block electrical current. Because of this ability, semiconductors serve an important function in everything from relays to the integrated circuits of computers [2].

Semiconductor thin films have found extensive applications in electronic and optical devices. The wide band gap properties of semiconductors, like CdO, are of interest particularly for applications such as solar cells and transparent electrodes TCO [3-4]. Measurements of nonlinear optical properties are very interesting from the point of the view of optoelectronic and all optical devices such as lasers modulators and optical switches [5,6]. Cadmium oxide CdO is conducting, transparent in the visible region with a direct band gap of 2.5 eV and indirect band gap of 1.98 eV [7,8].

The wide band gap properties of semiconductors, like CdO, are of interest particularly for applications such as solar cells and transparent electrodes TCO [9]. Measurements of nonlinear optical properties are very interesting from the point of the view of optoelectronic and all optical devices such as lasers modulators and optical switches [10,11]. Cadmium oxide CdO is conducting, transparent in the visible region with a direct band gap of 2.5eV. CdO is an n-type Semiconductor [12, 13]. Various techniques have been employed to prepare CdO thin films such as spray pyrolysis [14], sputtering [15,16], solution growth [17], activated reactive evaporation [18], pulsed laser deposition [19] and sol-gel method [12]. In this paper CdO thin film was prepared by pulsed laser deposition (PLD).

CdO films have a cubic structure such as NaCl, lattice constant equal 4.69 Å. At growth temperature below 250°C, the films are weakly crystallized, with grains randomly oriented on the glass substrate. At temperatures above 300°C, the CdO films are strongly crystallized, with a preferred (200) orientation.[19] CdO films have a dark brown color , mass density 8.15 g/mol , molten temperature at 1773K [10] .

Cadmium oxide is a reddish powder and Its color varies from greenish-yellow brown to nearly black depending on its thermal history and partical size. It has face center cubic crystalline structure in which each atom is surrounded by six other atoms of opposite electrical charge.

CdO have been widely used as a transparent conducting oxide thin films due to its unique properties such as, high transmission coefficient in the visible range of the electromagnetic spectrum, high electrical conductivity.

2- Theory:

2-1 Structural Properties

X-ray diffraction and determine the crystalline structure of the prepared thin film using X-ray diffraction instrument with the specifications of source Cu-Kα and wavelength of 1.54050 A°. The spacing of the planes, d_{hkl}, is the interplanar spacing (in Angstrom) calculated using Bragg's law equation (1) [20].

$$Sin\theta = \lambda / 2d_{hkl} \qquad (1)$$

The distance between two lattices (d) can be determined from the angle that the reflection occurs is the Bragg's law equation.

The particle diameter was calculated by using Scherrer's equation (2) [21].

$$D = K\lambda / \beta\cos\theta \qquad (2)$$

Where D is the grain (G.S),K constant equal to (0.94), λ is the wavelength of CuK_{α} (the source of radiation was CuK_{α}) equal to (1.5406A°), Θ is the Bragg›s angle, B full width at half maximum (in radian) of the peak.

2-2 Optical properties

Investigation of the optical properties for semiconductor are the most important source of information on the electronic band structure , type of the transition , permittivity , and other properties of semiconductor [22].

The optical properties of a semiconductor are related to intrinsic effect. Based on the intrinsic location of the top of the valence band (V.B) and the bottom of the conduction band (C.B) in the band structure, the electron–hole pair generation occurs directly or indirectly [23].

Optical Absorption and Absorption Edge

The absorption depends on the photon energy (hν); where h is Plank΄s constant, ν is the incident photon frequency, The maximum wavelength (λ) of the incident photon which creates the electron–hole pair defined as equation (3) [24].

$$\lambda c(\mu m) = \frac{hc}{E_g} = \frac{1.24}{E_g(eV)} \quad (3)$$

The intensity of the photon flux decreases exponentially with distance through the semiconductor according to the following equation (4) [24].

$$I = I_o \exp(-\alpha t) \quad (4)$$

Where *Io* is the incident light intensity, *I* is the transmitted photon intensity, *t* is the thickness of the film, α is the absorption coefficient, which is defined as the relative number of the photons absorbed per unit distance of semiconductor.

Direct Transitions

The direct transition in general occurs between top of valence band and bottom of conduction band (vertical transition) at the same wave vector $\Delta k = 0$ for conservation of momentum. The allowed direct transition refers to that transition which occurs between top of the valence band and bottom of the conduction band when the wave vector equal to zero ($k = 0$)

This transition is described by the following relation (5) [23]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \quad (5)$$

where *B* is inversely proportional to amorphousity.

Optical Constants

The optical constants are very important parameters because they describe the optical behavior of the materials. The absorption coefficient of the material is a very strong function of the photon energy and band gap energy. Optical constants included refractive index (*n*), extinction coefficient (*k*), and real (ε_r), and imaginary(ε_i)parts of dielectric constant.

The refractive index value can be calculated from the formula (6)[25]:

$$n = \left(\frac{4R}{(R-1)^2} - k^2\right)^{1/2} - \frac{(R+1)}{(R-1)} \quad (6)$$

R is the reflectance, and can be expressed by the relation (7) [26]:

$$R = \frac{(n-1)^2 + k^2}{(n-1)^2 + k^2} \quad (7)$$

The extinction coefficient, which is related to the exponential decay of the wave as it passes through the medium, is defined as relation (8) [27]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (8)$$

λ is the wavelength of the incident radiation and α is given by equation (9)[25]:

$$\alpha = 2.303\frac{A}{t} \quad (9)$$

A is the absorbance.

The real and imaginary part of dielectric constant can be calculated by using the following equations (10),(11),(12)[28]:

$$(n - ik)^2 = \varepsilon_r - i\varepsilon_i \quad (10)$$

where

$$\varepsilon_r = n^2 - k^2 \quad (11)$$

and

$$\varepsilon_i = 2nk \quad (12)$$

3- Experimental work

High purity (99.99%) cadmium oxide powder was used as a source for deposition of CdO films on soda lime glass substrates (2.5x6) cm^2 using pulsed laser ablation. The glass substrate were first treated with detergent and washed in running water and alcohol its concentration is 96% respectively. The substrates then dried with a fine tissue paper and cleaned with isopropyl alcohol (IPA) in an ultrasonic cleaner. All the films were deposited by Nd:YAG pulsed laser of 600 mJ and a pulse duration of 10ns by a coating unit. The source to substrate distance is 2cm. Thickness of the films was 400nm. weighting method was used to measure the thickness of the films using the following equation:

$$m = 2\pi\rho_m r^2 t$$

Where m is the mass of the evaporated material, r is the distance between the boat and the substrate, ρ_m is material density, t is the film thickness. The time of deposition is 1.95sec by 800 shout. The pellet of CdO was used as source for CdO. A vacuum of 10^{-1} mbar was maintained in the chamber during deposition. The substrate temperature during deposition was at room temperature. The annealing process done for sample two at 373K for sample three 473K for sample four 573K for sample five 673K, the time for annealing for all samples 1 hr. The structures of the prepared thin films were obtained using the X-ray diffraction (XRD) techniques. The X-ray diffract meter type (Philips) was used with the following features, Source $Cu_{K\alpha}$, current 20mA, voltage 40kV and wavelength 1.5405 Å.

The optical transmission spectra of the deposited thin films were measured by UV-VIS spectrophotometer, the optical properties was calculated as a function of the photon energy at the wave length in the range 340-1100 nm.

Surface topography was studied by using atomic force microscopy (AFM) using (Scanning probe Microscope type AA3000), supplied by Angstrom Advanced Inc. to determine the nano spikes dimensions range of the prepared thin CdS films deposited on glass substrate and their statistical distribution.

4- Results and discussion:

X-ray diffraction

To study the annealing effect for film, which has been deposited under optimum conditions on glass substrate with a different annealing temperature of (373, 473, 573 and 673) K. The X-ray pattern of as deposited and annealed films onto glass substrate are shown in Figure (1) and Table (1).

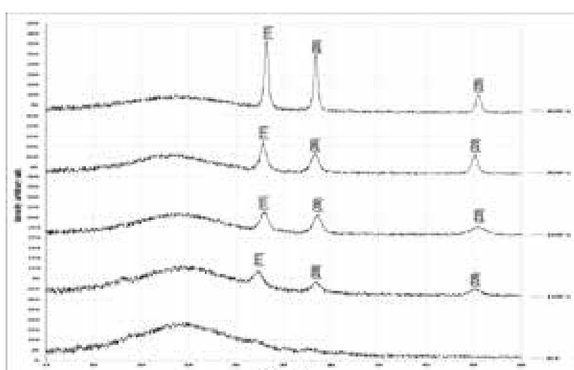


Fig. (1) X-ray diffraction patterns 0f the five CdS thin films deposited on glass substrate

at room temperature (b) annealed at 373K (c) annealed at 473K (d) annealed at 573K

(e) annealed at 673K

Table (1) Structural parameters (2Θ, FWHM, d_{hkl}, G.S, hkl) for CdO thin films at different annealing temperature. [29]

T_a (°c)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl
RT	-	-	-	-	-	-
	32.338	1.2153	2.7662	6.8	2.7108	(111)
100	38.414	1.0717	2.3414	7.8	2.3477	(200)
	55.081	1.4468	1.6660	6.2	1.6600	(220)
	32.917	0.868	2.7189	9.5	2.7108	(111)
200	38.530	1.060	2.3347	7.9	2.3477	(200)
	55.370	1.389	1.6579	6.5	1.6600	(220)
	32.859	0.810	2.724	10.2	2.7108	(111)
300	38.299	0.926	2.348	9.1	2.3477	(200)
	55.139	0.752	1.664	11.9	1.6600	(220)
	33.206	0.579	2.696	14.3	2.7108	(111)
300	38.356	0.521	2.345	16.1	2.3477	(200)
	55.486	0.579	1.655	15.5	1.6600	(220)

From this figure the film at room temperature is amorphous with very small picks appear in the same position of the large pick of the annealed films, which shows the change of film after annealing with different temperature, it can be observed that peaks at 2θ = (32.338, 38.414 and 55.081) degree appeared which correspond to diffraction from C(111), C(200), C(220), crystalline planes respectively. These values are comparable with standard card (96-900-8610) cubic a=4.6953A°[29], and confirm that the diffraction is from cubic phase of polycrystalline structure. There is a small shifting with increasing of annealing temperature. This is agree with other literature [30]. Heat treatment helps the atoms to rearrange theme selves and eliminate defect density in the film resulting in a good crestenelity. Also the diffraction pick of annealing films becomes sharper duo to the coarsening of the grin. Also the intensity of the picks increases with increasing annealing temperature, from as deposited film to the 673K for all directions.

From the X-ray diffraction pattern the average grain size of all samples can be determine by using the well-known Deby-scherrer formula [31]

$G.S._{hkl} = k\,\lambda / \text{FWHM} \cos\theta$

Where K (0.94), λ the wavelength of X-ray, FWHM the full width at half maximum of the pick in radians, θ Bragg›s angle.

It can observe that the grain size decreases with increasing annealing temperature from (2.7108 to 1.6600) for all plans, this is agree with [32].

Optical Studies

The optical properties for thin CdO films with 400 nm thicknesses on glass substrate for different annealing temperature (T_a = 373 473,573,673)K have been determined using UV-visible recording spectrometer in the region of (400–1100) nm before and after annealing. Also the energy gap and optical constants have been determined.

Figure (2) shows the transmittance spectra of wavelengths from 400 nm to 1100 nm for CdO films for different annealing temperature (Ta = 373,473,573, 673)K on glass substrate. Transmittance increase with increasing annealing temperature and this is agree with [33]. This high transmittance means that the absorptance and reflectance are too low. it is clear from the figures that in the range of the visible light the transmittance is almost 70%.

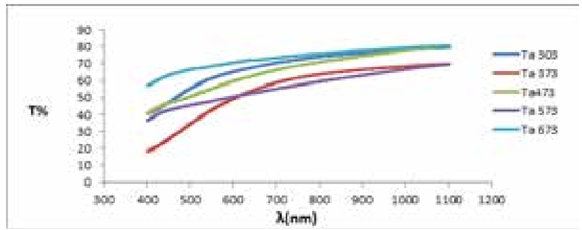


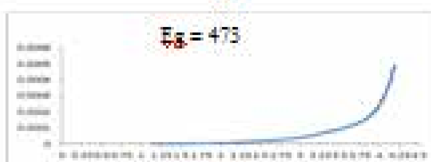
Fig (2) the transmittance spectra of CdO thin films at different Ta.

The optical energy gap values (E_g) for thin CdO films have been determined by using Tauc equation which is used to find the type of the optical transition by plotting the relations $(\alpha h\nu)^2$, $(\alpha h\nu)^{2/3}$, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ versus photon energy ($h\nu$) and select the optimum linear part. It is found that the first relation yields linear dependence, which describes the allowed direct transition. Then E_g^{opt} is determined by the extrapolation of the portion at α=0 as shown in Figs. from (3- a) to (3- e)

Fig.(3a-e) reveals that the values of direct optical energy gap, in general, increase with the increase of annealing temperatures from 373K to673K from 2.5eV to 2.7eV. and at room temperature the molecules rearrange them selves.

(a)

(b)



(c)

(d)

(e)

Fig. (3a-e) $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for thin CdO films before and after the annealing a- (Ta = 373K) b-(Ta = 473K) c-(Ta = 573K) d-(Ta = 673K)

Table (2) The values of E_g and optical constants for thin CdO films at different T_a .

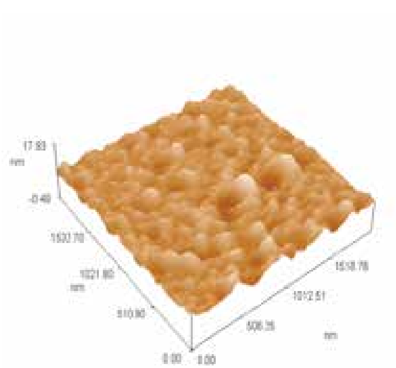
TK	α	E_g	T%
273	0.001191	2.23	0.62101
373	0.00270	2.5	0.34029
573	0.00204	2.6	0.44229
673	0.001116	2.7	0.63988

TK	n	k	ε_r	ε_o
273	1.916455	0.052708	3.670021	0.202024
373	2.05443	0.10639	4.209381	0.437141
573	2.148797	0.077129	4.611378	0.33147
673	1.876082	0.040779	3.51802	0.153009

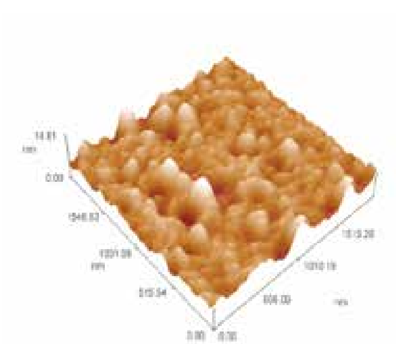
From Table (2) in general values of n increase with increasing T_a, The same behavior are observed for extinction coefficient k. Another noticeable remark is that the k decreases with increasing wavelength. The behavior of ε_r is similar to that for the refractive index. All values of optical constants are tabulated in Table (2)[33].

Atomic Force Microscopy Analysis (AFM)

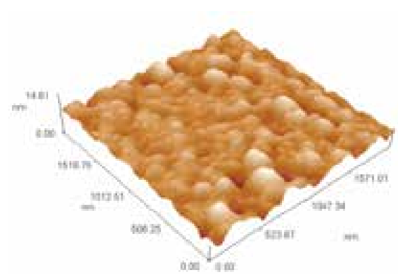
The grain size (grain diameter) and average roughness of CdO thin films prepared by laser deposition have been measured using AFM for as deposited (273K) and annealed at T_a= (373,473, 573, 673) K of 400 nm thicknesses, Figure (3a - e) show the effect of annealing temperature on the prepared films.



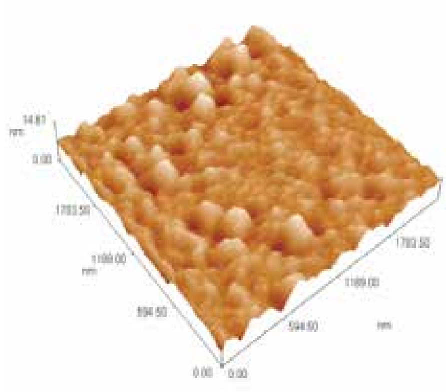
a



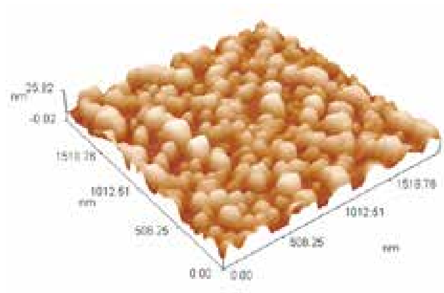
b



c



d



e

Fig.(4) AFM image before and after annealing for different (Ta = 373,473,573,673)K for CdO thin films

Table (3)The effect of annealing temperatures for CdO thin film on average crystallite and roughness.

TK	Roughness average nm	Pick to pick	Grain size nm
298	0.854	9.32	94.51
373	1.11	12.8	96.66
473	1	10.8	102.00
573	0.96	11.4	89.27
673	3.59	17.7	88.78

It is obvious from Table (3) in general the average grain size increase from (94.51) to (102.00) with increasing annealing temperature from room temperature to 473K, and this attributed to the improvement of crystalline structure and then decreases from (89.27) at (Ta = 573K) to (88.78) at (Ta = 673K) and this is may be duo to create defect at high temperature and this because rearrangement of atom in film and reduce the vacancy defect. the films before annealing show uniformly spherical grains and the shape of grains changes into ellipsoidal. These results is agreed with[35]. There is no cracks or holes and well covered to the glass substrate. Figure (4) shows amorphous surface with out well defined grain boundaries before the annealing and after the annealing it show uniform shape and almost spherical grain shape and this agreed with the results obtained from the X-ray diffraction tests.

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