Influence of Annealing on Properties of Cadmium Oxide thin Films Prepared by Spray Pyrolysis

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ABSTRACT

CdO thin films have been deposited by Spray Pyrolysis Technique (SPT) on a glass substrate. The structural and optical properties of thin films are studied at different annealing temperatures 100, 200 and 300 C^o. By using X-Ray Diffraction, XRD patterns indicated that films are polycrystalline in nature and cubic phase with preferred orientation along the plane (111). The optical properties using UV-VIS spectroscopy show that the direct band gaps decreased from (3 to 2.75) eV with increasing the annealing temperature from(100-300)C^o, this decreasing could be ascribed to increase of the localized states available in band gap which referred by Urbach's energy value.

Keywords: CdO films, spray pyrolysis, optical properties, structure properties.

تأثير التلدين على خصائص اغشية اوكسيد الكادميوم الرقيقة المحضرة بالرش الكيميائي الحراري

الخلاصة

اغشية اوكسيد الكادميوم الرقيقة تم تحضيرها على قواعد زجاجية بتقنية الرش الكيميائي الحراري. الخصائص التركيبية والبصرية للاغشية الناتجة تم دراستها عند درجات حرارة تلدين مختلفة 100, 200 و300 درجة مئوية. باستخدام حيود الاشعة السينية، حيث ان الاغشية الناتجة ذات تركيب احادي الطور متعدد التبلور عند الاتجاهية البلورية بالمستوي المفضل (111). الخصائص البصرية من خلال استخدام التحليل الطيفي للاشعة المرئية وفوق البنفسجية بينت ان فجوة الطاقة المباشرة تقل من 3 الى 2.75 الكترون- فولت بزيادة درجة حرارة التلدين من 100 الى 300 درجة مئوية وهذا النقصان يمكن ان يعزى الى زيادة المستويات الموضعية الموجودة في فجوة الطاقة والتي استدل عليها بواسطة قيم طاقات اورباخ.

INTRODUCTION

Cadmium oxide (CdO) has attracted a great attention due to its high electrical conductivity and high transmittance with a suitable refractive index in the visible domain of the solar spectrum [1]. This material could be used for different applications such as solar cells [2], temperature controlled in satellites [3], gas sensors [4], photo transistors [5] because of its low electrical resistivity [2], large energy band gap approximately of (2.2 eV) and great luminescence characteristics [5]. Many methods were adopted to grow CdO thin films like vacuum evaporation thermal technique [6], sol-gel spin coating [7,8], spray pyrolysis [9]. Between these fabricated

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methods the spray pyrolysis technique has many circumstances such as low cost of the components and raw materials, simplicity and safety [10]. In this technique, characteristics of films relying upon preparation conditions similar to spray rate, nozzle- substrate and the substrate temperature [1]. CdO is an n-type semiconductor [11], with cubic structure where each ions collared by six ions of different electric charge [12]. It is now well voluntary control that the CdO appears many highest quality properties, which produced it a suitable as a transparent conductive oxide (TCO) [13].
In this work, the variation of the optical and structural properties of CdO thin films obtained by spray pyrolysis method was studied as a function of the annealing temperature in an air ambient. The disarray in the material structure is realized by valuation of the Urbach energy.

Experimental work

In this work, spray pyrolysis method was used to prepare CdO thin film with concentration of (0.1 M) of an aqueous cadmium nitrate solution. The temperature of deposited thin film on the glass substrate was (250 ± 10 C^o), the carrier gas was a compressed air with spray rate of the order ~ 3 ml/min, and spray time 25 min, while the distance between the nozzle and heated substrate was kept at 30 cm.
The film thickness measured by laser interference according to fezue fringes was 0.25μm. The method based on interference of the light beam reflected from thin film surface and substrate bottom. The thickness was determined using the formula [14]

$$t = \frac{\Delta x}{x} \cdot \frac{\lambda}{2} \quad \text{....(1)}$$

Where
(x) is fringe width, Δx is the displacement in fringe position, and λ is wavelength of using light source. After deposition, the prepared thin films were annealed in the air at temperature (100, 200, 300) C^o for 30 min.
The crystal structure of thin film was determined by x- ray diffraction using the (Philips model, PW/ 1710) diffractometer, with monochromatic Cu Kα radiation (λ = 0.15418 nm at 40 KV and 30 mA). Optical analysis was done measured by optical transmission, data were obtained with an UV/ VIS Shimadzu 3101 PC Spectrometer in the (200 to1100) nm range.

Result and discussion

Figure (1) shows the x-ray diffraction pattern of CdO thin films prepared by spray pyrolysis at different annealing temperature 100, 200, and 300 C^o. The main observed peaks can be seen due to diffraction from (111), (200), and (012) planes for CdO and $Cd(OH)_2$ thin films which related to a small amount of the oxidized CdO grains mixed with the Cadmium Hydroxide. The pattern indicate that the presence of polycrystalline thin films with a cubic structure. We can see from this figure that as the annealing temperature increases the relative intensity of the peaks increase too. The small shift in XRD peaks of the films occur due to the mechanical micro stress produced by different sources such as defects, impurities, and vacancies in the films after annealing. These results are in a good agreement with the other reportes [8,13,15].
Figure (2) shows the transmission spectra of CdO thin films grown on a glass substrate and annealed at different temperature 100, 200, and 300 C^o. We can distinguish from this figure that: **a)** all the films are transparent in the visible region,

b) at higher annealing temperature the shift in absorption edge toward higher wavelengths and **c)** decreasing in the optical transmission of the films is anticorealated with the annealing temperature.

The transmission data (*T*) can be used to calculate absorption coefficients α of the films at different wavelengths λ as shown in figure (3) which is given by [13]:

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \qquad \ldots (2)$$

where
d is the film thickness.
The variation of extinction coefficient K as a function of wavelength λ is shown in figure (4), which can be calculated by the following equation[15]:

$$K = \frac{\alpha\lambda}{4\pi} \qquad \ldots (3)$$

So, to study the effects of annealing temperature (the fundamental absorption) which corresponds to electron excitation from the valance band to conduction band, can be used to assess the value of band gap by using Tauc relation [16] :

$$(\alpha h\nu)^{1/n} = A\,(h\nu - E_g) \qquad \ldots (4)$$

where
$h\nu$ is the incident photon energy, A is a constant and exponent n depends on the type of transition assumed the values 0.5, 2, 1.5 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The direct band gap values have been determined by the extrapolation of the linear portion on the photon energy axis by a plot of $(\alpha h\nu)^2$ vs the photon energy $(h\nu)$ as shown in figures (5). The values of E_g decreased for direct transition as the annealing temperature increased from 100 to 300 C^o as shown in table (1). These results are in good agreement with other reported [1,2,9].

Urbach tails of localized states in optical absorption near band edges quantifies the disorder in the films. The band tails width (urbach tails) impresses the structure and optical transition of the band gap, so the existence of urbach tails can be referring by the exponential variation of the optical absorption coefficient below the absorption edge with photon energy and the absorption edge is defined as urbach edge.[8,17,18]
Urbach energy can be evaluated from the slopes of the plots between (ln α) and photon energy(hν) according to the following equation:[17, 19]

$$\alpha(h\nu) = B \exp(h\nu / E_u) \qquad \ldots (5)$$

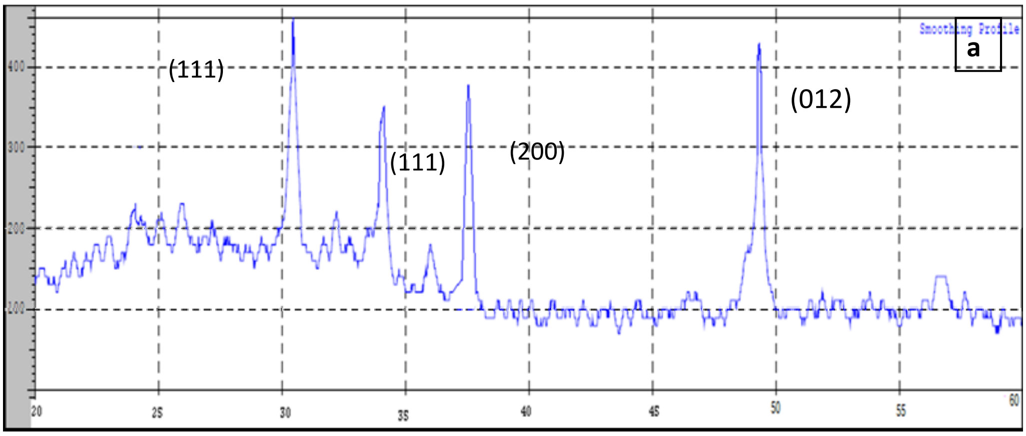
where
(hν) is the photon energy, B is constant and E_U is the Urbach energy which refers the width of band tails of the localized state.
(E_u) values were deduced by relationship:

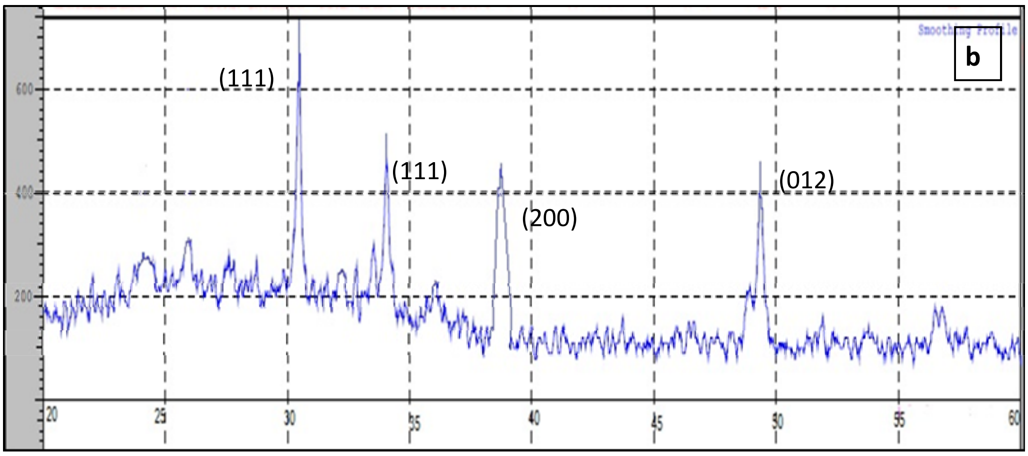
$$E_u = \frac{d(h\nu)}{d(\ln\alpha)} \qquad \ldots (6)$$

Fig (6) shows the variation of ln(α) against (hv) for (CdO) thin films annealing with different temperature. The obtained E_u values are given in table (1), which obvious that the urbach energy increase with increasing of annealing temperature which ascribed the increase of disorder in the bands, and change inversely with values of energy band gap of thin films, this inversely relation was agreement with other workers [17,18].

CONCLUSION

Spray pyrolysis method were used to prepare CdO thin films at 250 C^o. The XRD analysis shows that all annealed films are polycrystalline of cubic phase with preferred orientation along the (111) plane. The optical properties such as transmission, optical band gap, absorption coefficient and excitation coefficient were affected by annealing temperature. The increase in annealing temperature reveals decreasing in energy band gaps while the urbach energy increases. An increase in urbach energy refer that more disorder has taken place.





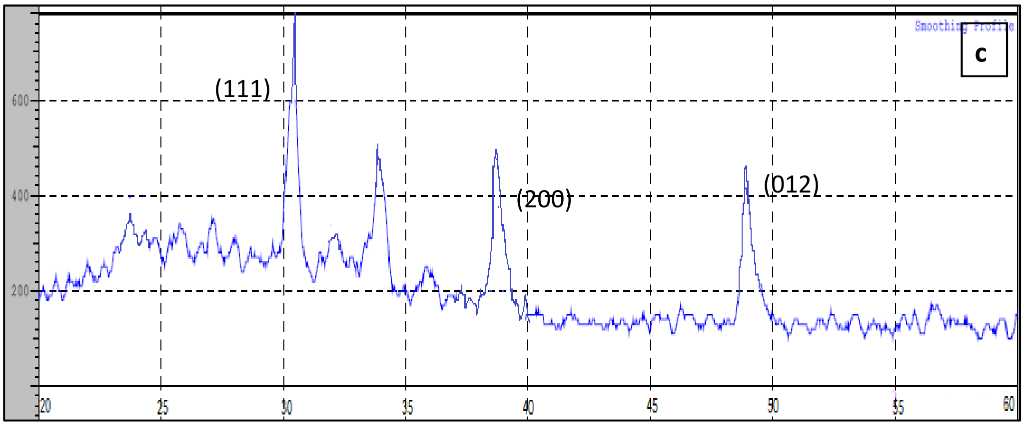


Figure (1): Optical transmission of CdO films annealed at different temperatures as a function of wavelength

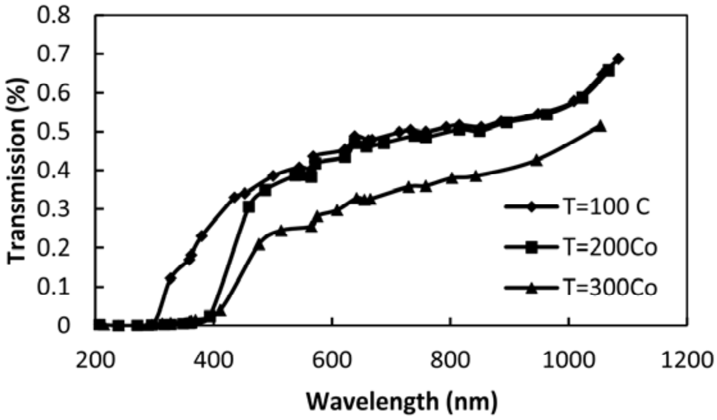


Figure (2): Optical transmission of CdO films annealed at different temperatures as a function of wavelength.

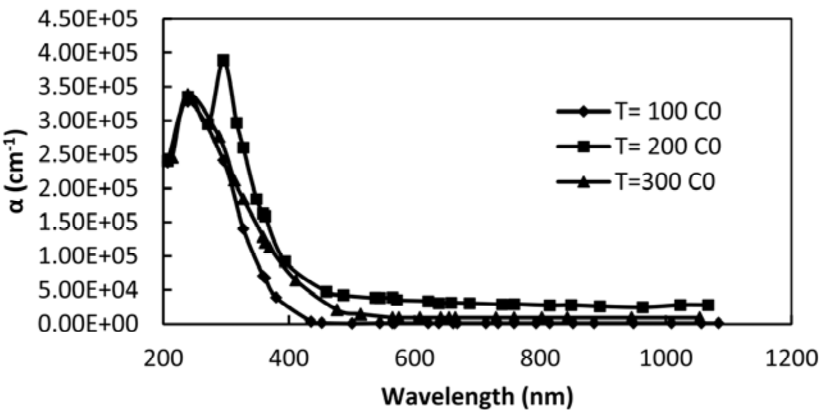


Figure (3): absorption coefficent of CdO films annealed at different temperatures as a function of wavelength

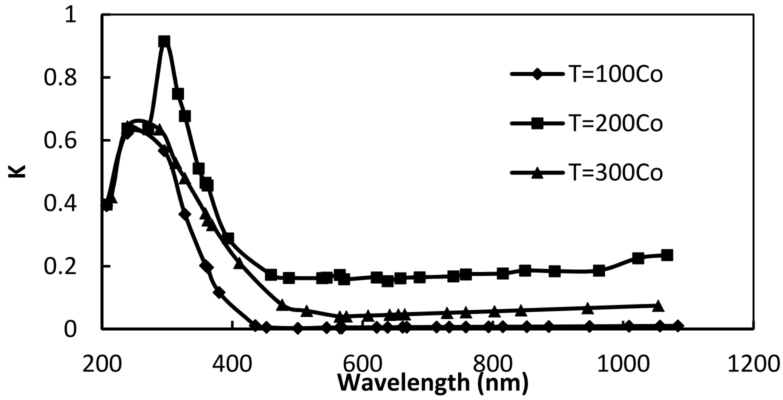
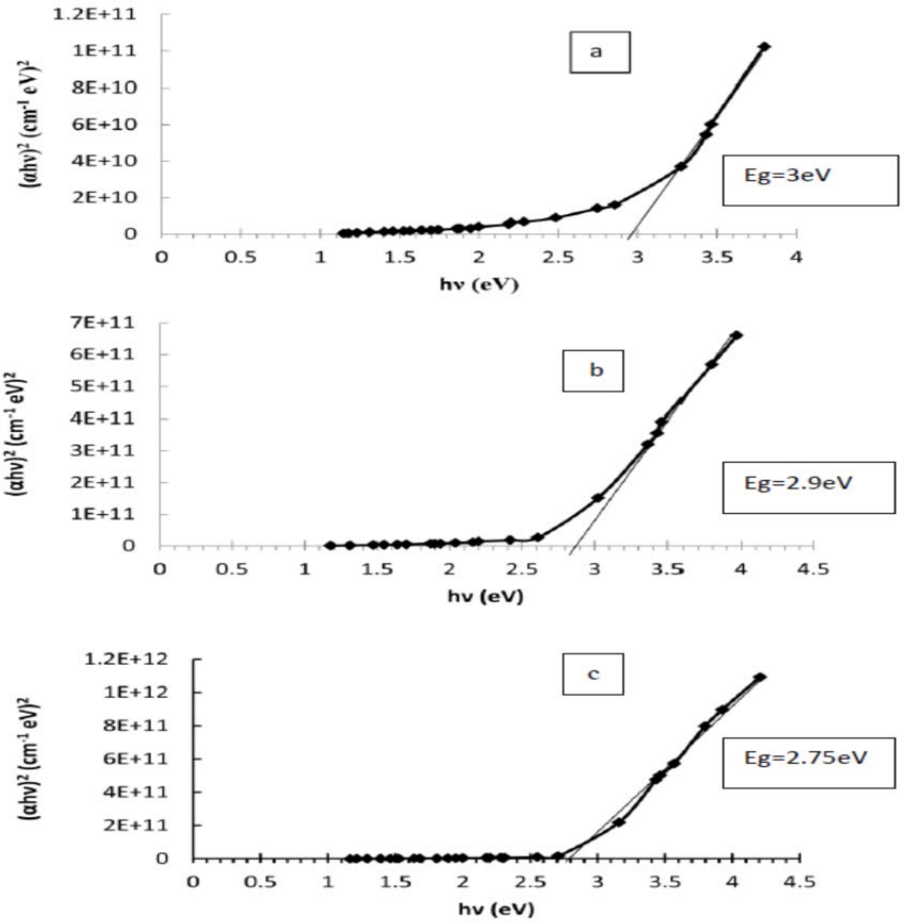
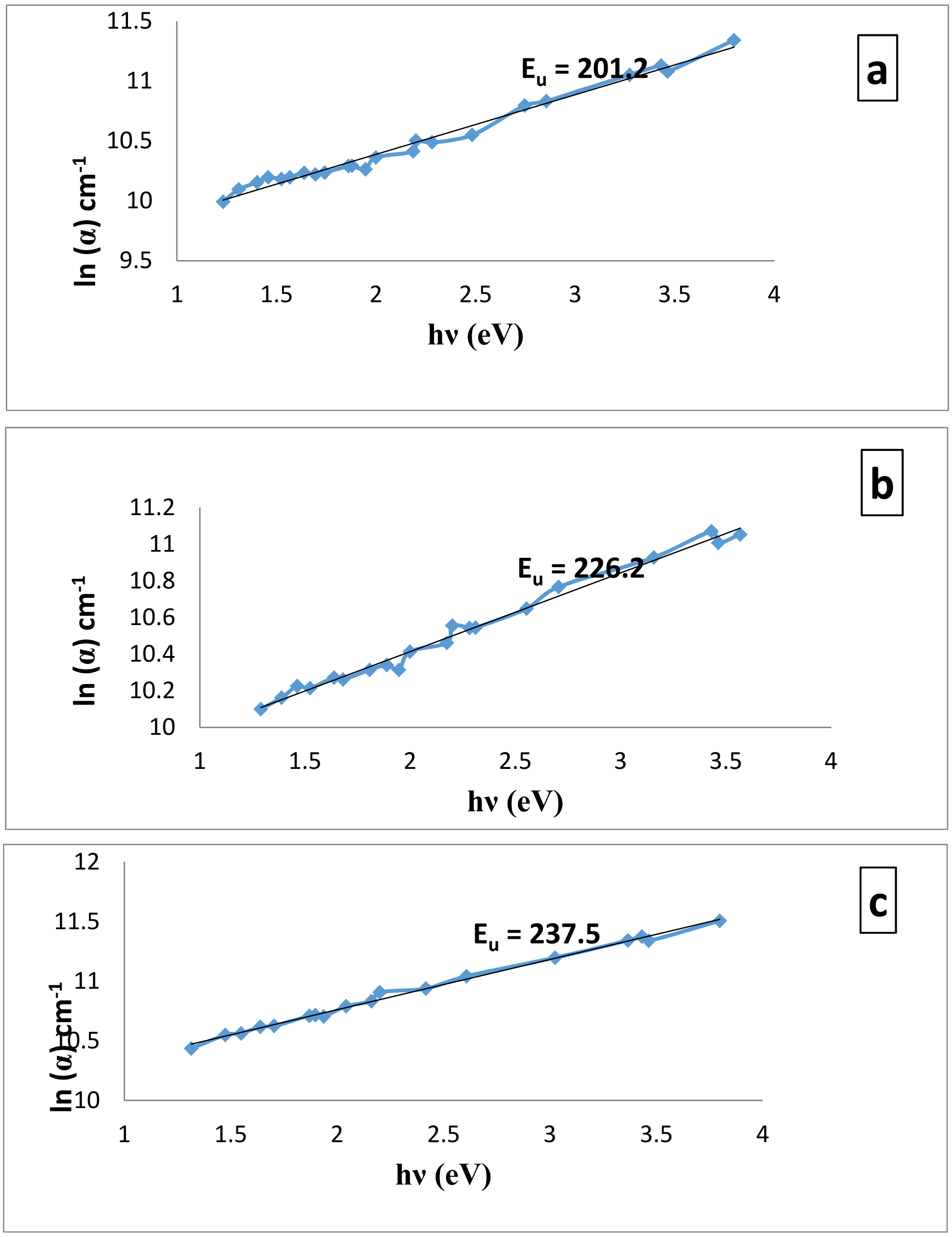


Figure (4): Extinction coefficient of CdO films annealed at different temperatures as a function of wavelength.



Figure(5): Variation of ($\alpha h\nu^2$) Vs (hν) of CdO films annealed at different temperatures a)100 C°, b)200 C°, and c)300C°.



Figure(6): Variation of (ln α) Vs (hν) of CdO films annealed at different temperatures a)100 C°, b)200 C°, and c)300C°.

Table (1): Direct energy band gap and urbach energy (Eg and Eu respectively) values of CdO thin films annealed at different temperatures.

Annealing Temperature(C°)	Eg (eV)	Eu(m.eV)
100	3	201.2
200	2.9	226.2
300	2.75	237.5

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