Study the Effect of Annealing Temperature on Some Physical properties of CdO Thin Film Using a Gas Sensor for CO and H$_2$

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ABSTRACT

We have investing the effect of annealing treatment of CdO films, deposited by chemical deposition using successive ionic layer adsorption and reaction (SILAR) technique , on the film properties . The CdO thin film were Prepared by using cadmium acetate at concentration (0.03M) and base solution from ammonium hydroxide solution on glass substrate. .It's found that the optical, electrical and gas sensing (H$_2$, CO) properties of the films are effected by the annealing temperature.

Keywords*: Thin film; Cadmium oxide; Sensor and SILAR; Temperature of annealing

دراسة تأثير حرارة التلدين على الخواص الفيزياوية والتحسسية لغازيH$_2$,CO لأغشية CdO

الخلاصة

تم في هذا البحث ترسيب أغشية رقيقة من اوكسيد الكادميوم CdO باستخدام طريقة الطبقة الأيونية المتعاقبة التكثيفية (SILAR) على قواعد زجاجية باستخدام خلات الكادميوم وبمولارية 0.03 مولاري مع محلول من هيدروكسيد الامونيوم .الخصائص التركيبية والتحسسية للأغشية المرسبة والملدنة تم دراستها . وجد من خلال النتائج بأن الخواص الكهربائية والبصرية والتحسسية لغازي CO, H$_2$ تتأثر بدرجة حرارة التلدين حيث لوحظ بأن معدل الحجم الحبيبي والتحسسية تزداد بعد التلدين .

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INTRODUCTION

T hin film technologies play the pivotal role specifically in the field of microelectronics, optical coating, integrated optics and superconductors etc. The changes in chemical and electrical properties by the irradiation of the thin films are utilized for optical and micro machines. By deposition of the oxide films like Sn, Cd, Zn, and alloys [1-2] recently, semi-conducting, thin films of various oxide materials like ZnO, SnO$_2$ and CdO etc. have shown significant results as regard to gas sensing properties [3- 4] which is tremendously being used in the field of gas sensors. Numerous techniques are being used to prepare good oxide films. CdO thin film has its own interest particularly in applications like transparent electrodes TCO (transparent conducting oxide), optical switching and optical limiting etc. [5 -6]. Hall effect measurement have been obtained by using HMS 3000 system(Ecopi A ,B = 0.55T) .The results of relationships of (V$_H$) and(I) Show the n-type behavior of charge carries of the prepared CdO thin films deposited by successive ionic layer adsorption and reaction on glass substrates. These thin films have been used in gaseous sensors because they have got a large energy gap and a capacity of a great adsorption of CO and H$_2$.

EXPERIMENTAL

CdO thin films have been deposited on glass substrates using (SILAR) technique. Aqueous solution of cadmium acetate [Cd(CH3COO)$_2$.2H$_2$O]has been taken as the source cadmium(cation)in 0.03M. solution was prepared by mixture of cadmium acetate and ammonium hydroxide. The complexing agent ammonium hydroxide was used to stabilize the crystallite size. The pH of the prepared solution was measured and found 8.3 to be and at 0.03M. The glass substrate was cleaned by chromic acid followed by distilled water rinse. The cleaned substrate was immersed first in cadmium acetate (0.03M) and ammonium hydroxide solution for 30s. and then immersed in quantitative amount of double distilled water in 15s at 95°C. The glass substrate was immersed in 0.005M of Hydrogen peroxide (anion) solution for 40s, and then immersed in double distilled water in 30smaintained at the same temperature as shown in Figure (1). This cycle was repeated several times in order to increase the overall film thickness of CdO. In this way, the substrate was covered with a thin layer of the complex solution. The overall reaction process can be expressed as decomposition of cadmium acetate to form cadmium oxide when placed in Hydrogen peroxide as part of the CdO was deposited onto the substrate as a strongly adherent film and they appeared in dark yellow is colour. Finally, we annealing the film in air at different temperatures (400, 500) °C for 35 minutes. As film thickness was determined by weighing method using the formula:

$t = w.t / A \rho$

$A = L \times W \qquad W = 0.003g , A = 2.5 \times 2.5 = 6.25cm^2 \qquad \rho = 7.14 g / cm^3$

$t = .0003 / 6.25 \times 7.14 = 672 nm .$

Where 't' is the thickness of the film, w is the weight gain, A is the area of the coated film and ρ is the density of CdO.

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The possible chemical reaction that takes place on the substrate to produce CdO may be as follows :

$$Cd(CH_3COO)_2 + NH_3 \longrightarrow [Cd(NH_3)_3]^{+2}$$

$$[Cd(NH_3)_3]^{+2} + H_2O_2 \longrightarrow Cd(OH)_2$$

$$Cd(OH)_2 \xrightarrow[90°C]{\Delta} CdO + H_2O$$
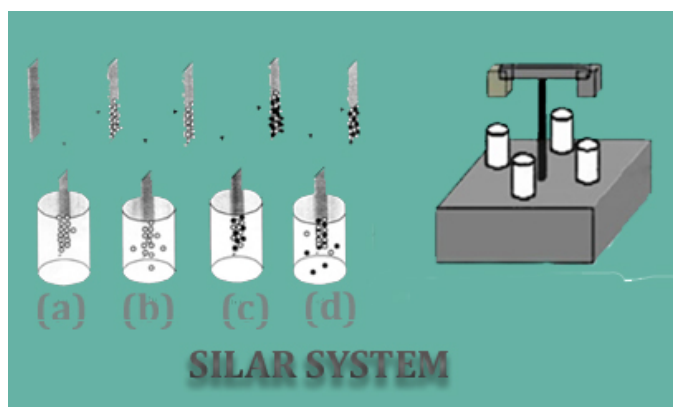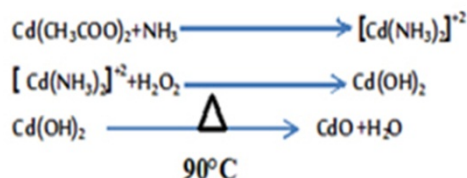
Figure (1) SILAR setup and procedure for CdO thin film preparation.

RESULTS AND EXAMINATION
X-ray diffraction (XRD) Aberrations.

CdO thin film prepared by SILAR system examined by X-ray diffraction do meter of (Shemadzu CuKα = 1.5A°) and Obtained patterns shows the Polycrystalline structure. The peaks are appear due to diffraction from (111), (200) and (220) planes cubic phase formation as compared with standard[X-ray diffraction data file [N 1997 JCPDS prevalent].We observed that the increasing of annealing temperature of CdO thin films are leads to increase the intensity as shown in Figure (2: a, b ,c). Grain size was calculated by compensation values that were obtained from the X-ray diffraction patterns of the previous figures in the Sherrer equation [7].

$$D = K \lambda / \beta \cos\theta \qquad \text{...............} \quad (1)$$

D: is the grain (G.S).
K: is a constant (0.94).
λ: is the wavelength of Cu Kα.
θ: is the Bragg's angle .
β : Full Width at Half Maximum (FWHM).

The values of grain Size calculated from equation (1) and intensity after annealing more than they are before annealing and the reason is the higher annealing temperature of the CdO thin film improved structural properties of the thin films prepared due to the increase of Crystallization to decrease structural defects of CdO thin films.
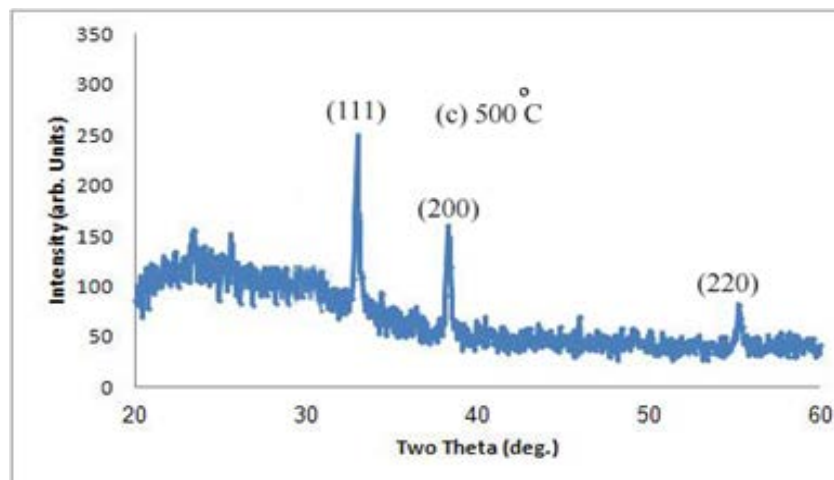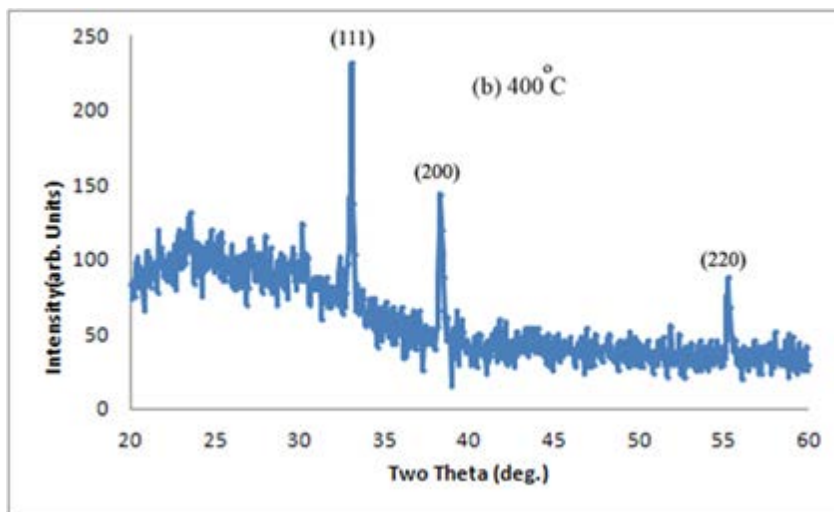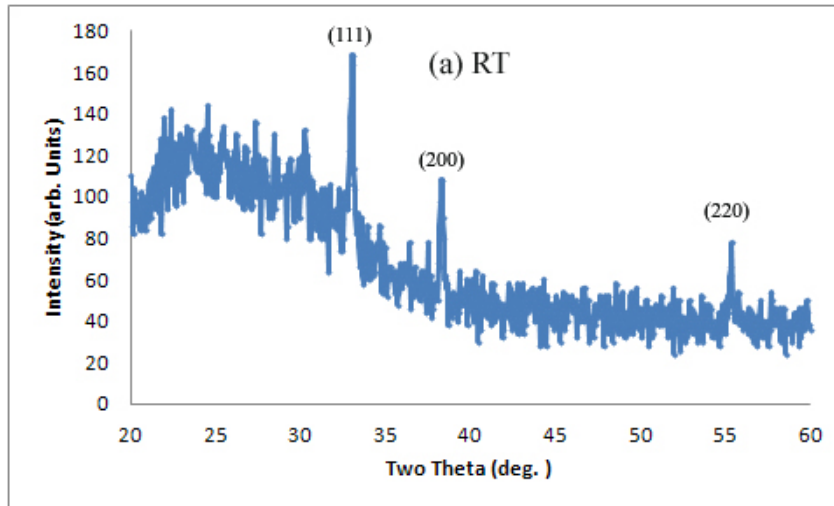
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Figure (2: a, b, c) XRD Patterns of CdO Thin films before and after annealing.

Gases Sensitivity Measurements

The shown system in Figure (3) has been used to measure prepared CdO thin films sensitivity for the (CO, H$_2$).After connecting the deposited aluminum electrodes on the CdO thin films with wires and the sample was fixed on a base inside a chamber. The working gases were pumped in to the chamber and recording the change in thin films resistance with time (per 10 seconds) and measure the current corresponding to the voltage in absence and presence of the gases to determine the impact of them on CdO thin films:
We calculate the sensitivity(S) from as the following equation[2]:

$$S = (R_g – R_a) / R_a \times 100\%\ldots\ldots\ldots\ldots(2) \text{ ,where,}$$

R_g:Electric resistance of the thin film in presence of gas
R_a :Electric resistance of the thin film in absence of ga**s**

CdO thin films suffer from the height of potential barrier in the reducer by using H$_2$ gas closed to 6 ppm; where ions (charge carriers) required a substantial amount of energy to cross that barrier ,that means decrease conductivity, as well as a decrease in potential barrier in the oxidizing gas such as CO and CO$_2$because of the adsorption of oxygen and the formation of pair (hole - electron) that increase the conductivity .
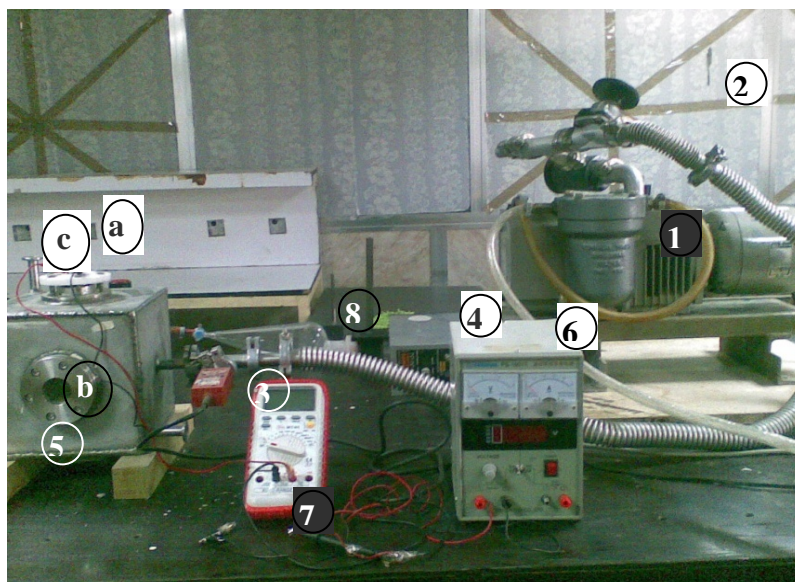

Figure (3) Gas Sensing measurement setup (1- Rotary pump vacuum bellows 2-conductivity tubes 3- vacuum head 4-reader of pressure 5- system Chamber   a- electrical feed through and pump gas b- Glass window c-Lead throw 6- DC . Power supply 7- multi meter 8- metal base.

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PROPERTIES OF THE I - V

The voltage- current properties of the CdO thin films in absence and presence of CO gas , are show in Figure (4: a and b) where the curve is linear at room temperature. This manner depends on each of the gas and the used semiconductor type. If the gas was an oxidizing factor such as CO ,the current value through the gas occurrence is greater than it in gas absence because the ions move from the material having a lower tendency to grab electrons, this material is called a reductive factor to the material having a higher tendency to CO and it's also called the oxidizing factor. The first gas effect is oxidized and the second is reduced, as shown in Figure (5: a and b).
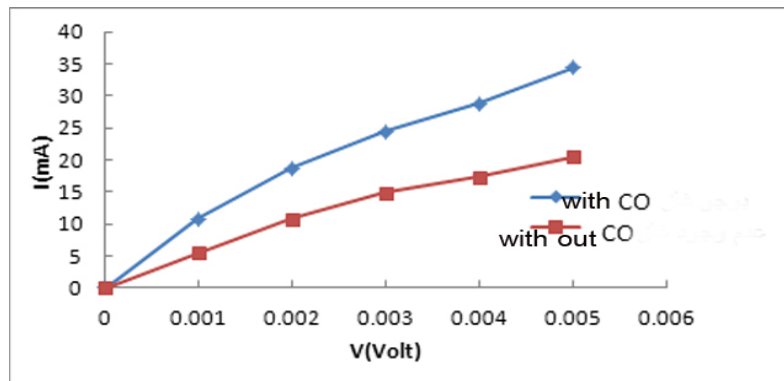

Figure (4:a) The voltage – current characterties in the absence and presence of CO after and before annealing.
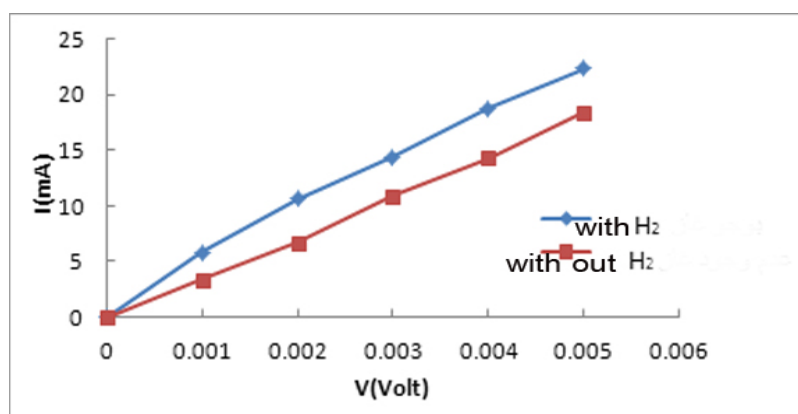

Figure (4:b) The voltage – current characterties in the absence and presence of H₂ after and before annealing.
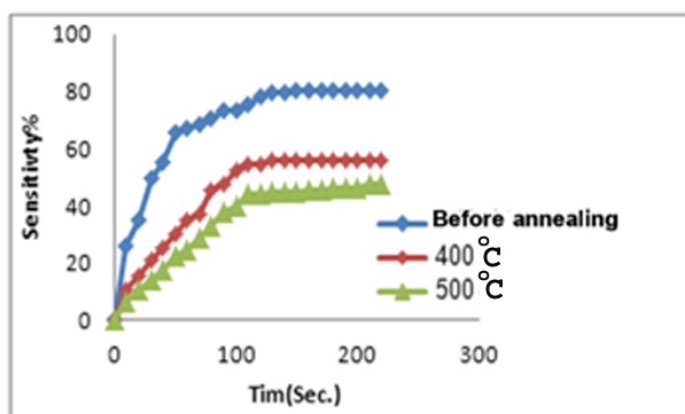
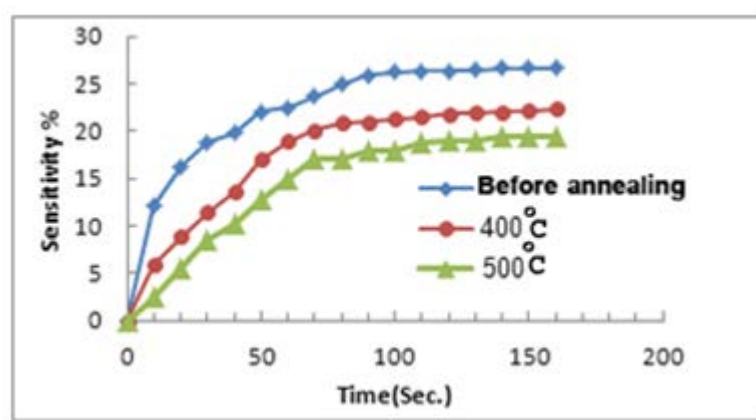**Figure (5:a) CdO thin film sensitivity CO after and before an annealing.**

Figure (5:b) CdO thin film sensitivity for H$_2$ gas after and before annealing.

Table (1) the resistance changes (increase or decrease) to Change in gas atmosphere [6].

Classification	Oxidising Gases	Reducing Gases
p-type	Resistance decrease	Resistance increase

n-type	Resistance increase	Resistance decrease

OPTICAL PROPERTIES

The absorption coefficient was calculated as a function of photon energy (h ν) of deposited CdO thin films and with annealing treatment as shown in Figure (6:a, b, c). We are found that the absorption coefficients increased at the annealing temperature increased, this behavior is attributed to local levels forming near the edge of conduction .

The optical energy gap for the prepared thin film is estimated to be in (2.8 -2.3) eV. The energy gap is found to decrease with increasing annealing temperature as show in Table (2). The decrease in energy gap is related to the increase in localized levels due to native defects such as inters title Cd atoms and oxygen vacancies.

The optical energy gap value is calculated for an allowed direct transition of CdO thin films before and after annealing by applying equation (3):

$$\alpha h\nu = A\,(h\nu - Eg)^r \ldots\ldots\ldots\ldots(3)$$

Where A: Constant depends on the nature of the material, Eg : energy gap

In allowed direct transition r = 2 .A plot drawn between $(\alpha h\nu)^2$ versus hν is shown in Figure (7). The direct band gap energy of CdO has been obtained from the intercept of the straight line drawn on the energy axis. Figure (8) shows the $(\alpha h\nu)^{1/2}$ versus hν of the indirect band gap has been determined by the similar way. The values of optical band gap obtained for direct and indirect transitions are shown in Table (2 and 3), which indicates that both direct and indirect band gap decreases with increase of annealing
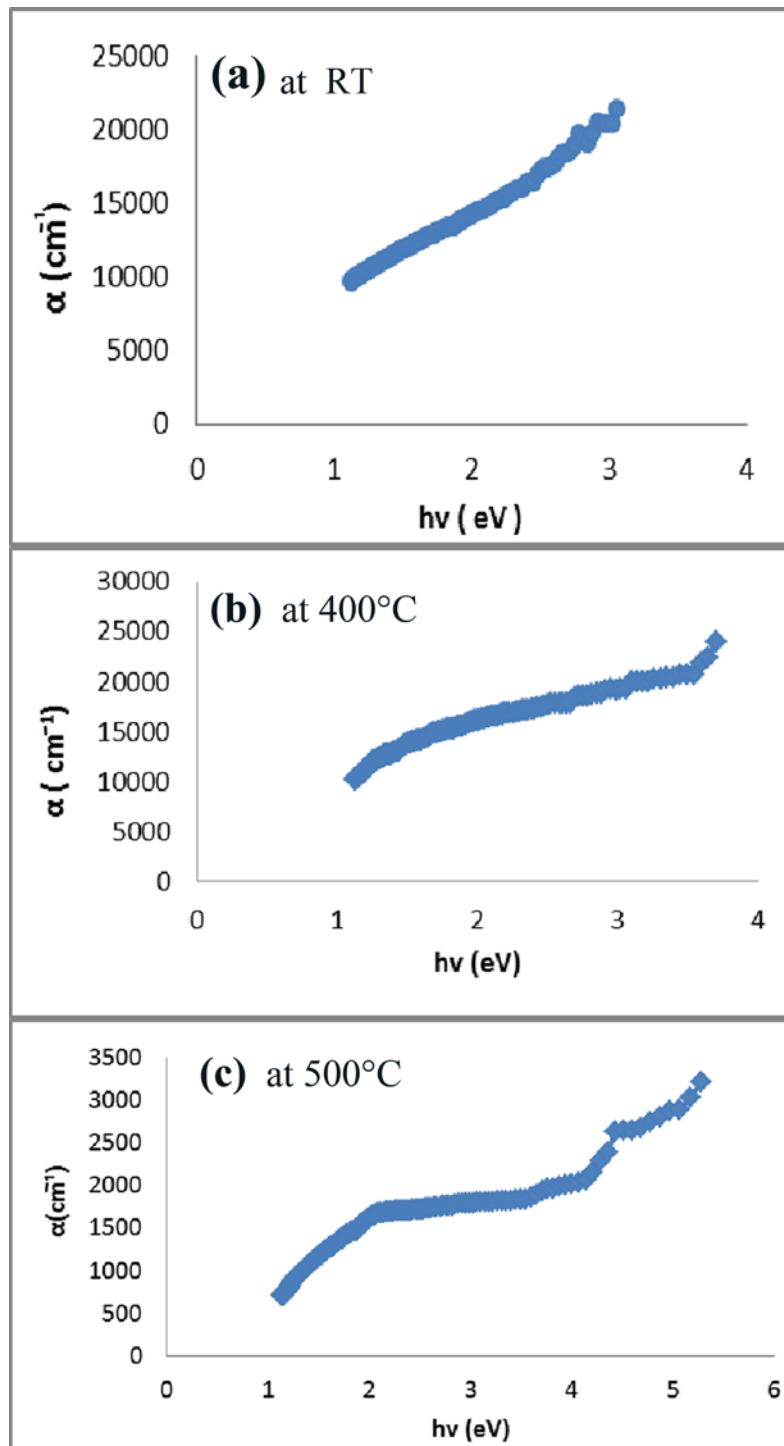
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**Figure (6):a. absorption coefficient (α)as a function of photon energy (h v)before annealing
b. absorption coefficient (α)as a function of photon energy (h v)at 400°C annealing and c.
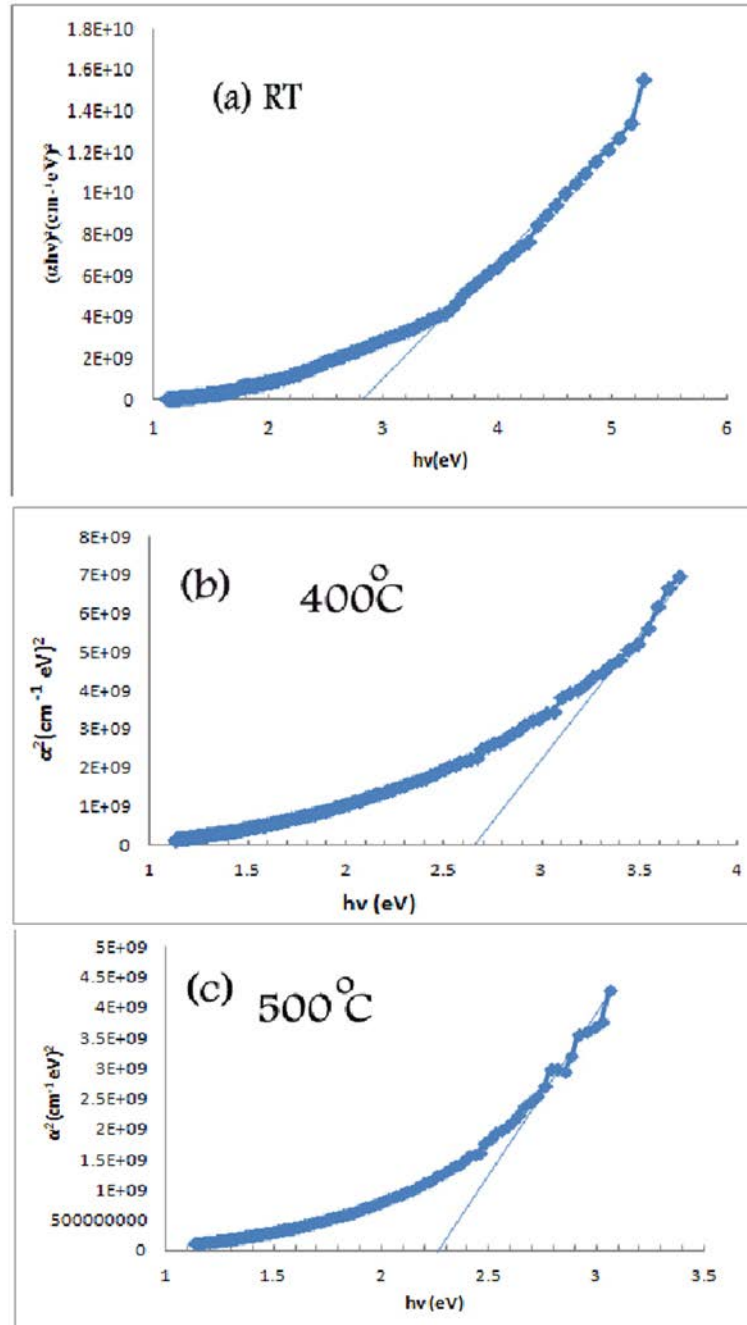absorption coefficient (α)as a function of photon energy (h v)at 500°C annealing.**

Figure (7):a. The energy gap as a function of photon energy (h v)before annealing   b. The energy gap as a function of photon energy (h v)at 400°C annealing   c. The energy gap as a function of photon energy (h v)at 500°C annealing.

Table (2) the values of the energy gap before and after annealing.

Sample	Ta(°C)	Eg(eV)
CdO	R.T	**2.8**
	400	**2.6**
	500	**2.3**

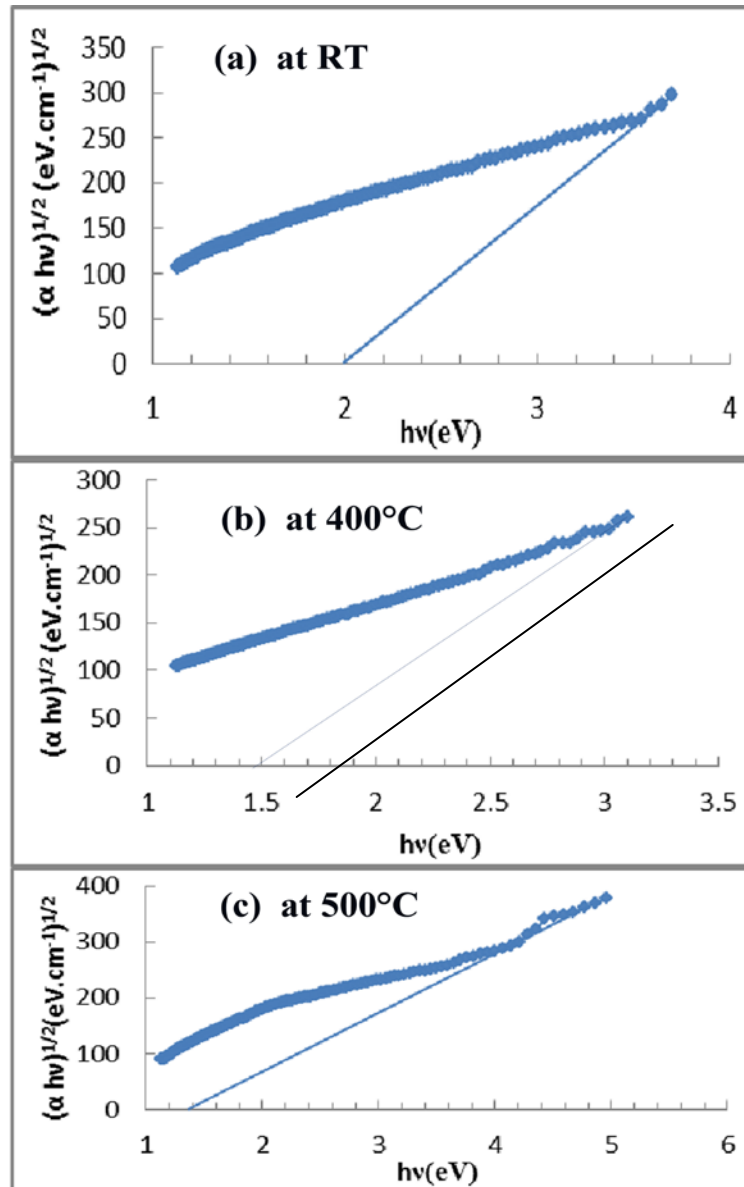**Figure (8):a. Indirect band gap energy (αhv)$^{1/2}$ as a function of photon energy (h v) before annealing b. at 400°C annealing c. at 500°C annealing.**

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Table (3) the values of the indirect energy gap before and after annealing.

Sample	Ta($^\circ$C)	Eg(eV) indirect
CdO	**R.T**	**2**
	400	**1.5**
	500	**1.2**

CONCLUSIONS

1-The results of the X-ray examinations that XRD of the prepared CdO thin films which have a poly crystallization structure and have a cubic type before and after annealing. The annealing led to an increase of the grain size .

2-The prepared CdO thin films had used to detect low ppm of the gases in the atmosphere, which depend on the detection mechanism concept of the process of gases adsorption on the semiconductor oxide surface based on the defects size presence and a crystalline structure of a thin film, where oxygen atoms appear in the ions O2form on the thin film surface , that work to form the depletion layer and the barrier potential growth at the granular borders and it also represents a source of gas molecule shunting which are adsorbed on the surface

3- The band gap 2.8 eV which was decreased to 2.3 eV after annealing. This has been attributed to the decrease in defect levels.

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