Annealing Effect on the Optical Properties of $(ZnO)_x(CdO)_{1-x}$ Films Obtained by Spray Pyrolysis

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Abstract
The effect of the annealing on the optical transmission , absorption coefficient, dielectric constants (ε_r),(ε_i) ,Skin depth and the optical energy gap of $(ZnO)_x(CdO)_{1-x}$ thin films with (x=0.05) deposited on preheated glass substrates at a temperature of (450 C°) by chemical pyrolysis technique were performed . These films show direct allowed inter band transition that influenced by annealing at (450 C°) for two hours . And it also found that the optical energy gap has been increased from about (2.50 eV) before annealing to about (2.65 eV) after annealing , from the analysis of the absorption and transmission spectra in the wavelength range (380-900nm) . The results show that all these parameters were affected by annealing.

Key words: $(ZnO)_x(CdO)_{1-x}$ thin film, optical properties, Chemical Spray pyrolysis, annealing effect

Introduction
Transparent conducting oxide (TCO) thin films have been widely used in solar cells applications. CdO and ZnO have high transparency in the visible region of the electromagnetic spectrum and show n-type conductivity, mainly due to oxygen vacancies[1].

Cadmium oxide is an oxygen deficient n- type conducting due to oxygen vacancies [1], and has NaCl structure [2]. Cadmium oxide has been considered as a promising material for solar cells [3] , due to high electrical conductivity and its high transparency in the visible region, also for these properties , CdO could be used as a gas sensor , low-emissivity windows, wear resistant applications, flat panel displays , Thin film resistor, light emitting diode,heat reflectors [4-7].

ZnO materials have received broad attention due to their well-known performance in electronics, optics and photonics. The interest in doping ZnO is to explore the possibility of tailoring its electrical, magnetic and optical properties. Zinc oxide can be doped with a wide variety of ions to meet the demands of several application fields [8]. ZnO can be found easily as n-type because of Zn interstitials and oxygen vacancies. Recently, the doping of different elements has been attempted to induce new interesting properties, such as for transparent electrodes [9]. For the development of optoelectronic devices with ZnO, it is necessary to have high quality materials of both n-type and p-type.

we report the effect of annealing at (450 ºC) on the optical properties of $(ZnO)_x(CdO)_{1-x}$ grown by spray pyrolysis.

Experimental Details
Thin films of $(ZnO)_x(CdO)_{1-x}$ have been prepared by chemical pyrolysis technique

The spray pyrolysis was done with a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at temperature of 450°C, the chemical solution was achieved by adding 2.974 gm of (Zn (NO3)2 6H2O) on 100 ml of distilled water , and adding of 3.0847gm of (Cd(NO3)24H2O) on 100 ml of distilled water by using magniting stirrer achieved by taking 0.1 M of dissolve in distilled water as equations[9]:

$$M = \frac{Wt}{Mwt} \times \frac{1000}{V} \quad .... \quad .... \quad .(1)$$

Where:

M: Concentration mol.

Mwt: Molecular weight from (Zn (NO3)2 6H2O) and (Cd(NO3)24H2O).

Wt: wanted weight dissolved in distilled water.

V: Volume of distilled water.

The optimized conditions were the following parameters, spray time (15 sec) and the spray interval (2min), average deposition (10 cm^3/min) , distance between nozzle and substrate (30 cm) and the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2} . Thicknesses of the samples were measured using the weighting method. The accuracy of thickness measurements was (750 nm) These films were annealed at (450 ºC) for two hours , Optical transmittance and absorbance were recorded in the wavelength range (380-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan).

Results and Discussions

Fig. (1) shows the spectral distribution of transmittance for the as deposited and annealed $(ZnO)_x(CdO)_{1-x}$ films at (450 °C) in the wavelength range (300-900) nm.

In this spectral region, transmittance of annealed $(ZnO)_x(CdO)_{1-x}$ film is higher than that for as deposited on. The increasing of transmission for $(ZnO)_x(CdO)_{1-x}$ might be due to decrease scattering of photons by crystal defects, and the free carrier absorption of photons contributed to the reduction in optical transmittance, or might be due to increase of the crystallite size. The increased roughness of the annealed thin films contributed to the drastic decrease of optical transmittance [10], From this figure it is observed that the transmittance decreases at the low wavelength region, which is the spectral region of fundamental absorption, in this region the incoming photons have sufficient energy to excite electrons from the valence band to the conduction band and thus these photons are absorbed within the material to decrease the transmittance. For this reason, this region carries the information of the band gap of the material [11].

Figure (2) shows the absorption coefficient (α) of annealed and as deposited $(ZnO)_x(CdO)_{1-x}$ films versus photon energy, from this figure α (annealed $(ZnO)_x(CdO)_{1-x}$) > α (as deposited $(ZnO)_x(CdO)_{1-x}$), this might be attributed to the increase of defect states which leads to increase absorption coefficient. Absorption of photons creates electron-hole pairs. In turn, the field of such pairs may modify the electronic structure and hence of optical properties of $(ZnO)_x(CdO)_{1-x}$ film [12]. According to the solid band theory , the relation between the absorption coefficient and the energy of incident light is given by $(\alpha hf)^n=B(hf-Eg)$ [13] , in which B is a constant ,Eg is the optical band gap energy and n is the ½ and 2 for the allouued transition being indirect and direct ,respectively .

Figure (3) shows a plot of $(\alpha hf)^2$ as a function of photon energy .The direct (n=2) band gap value of annealed and as deposited$(ZnO)_x(CdO)_{1-x}$ films are determined from the curve extrapolation. These values are 2.65 eV and 2. 50 eV respectively . This may be the cause for the decrease in band tail width, and then increase energy gap.

Refractive index is one of the fundamental properties for an optical material , because it is closely related to the electronic polarizability of ions and the local field inside materials.

The refractive index (n_o) is related to the optical reflectance (R) by the following relation [14]:

$$n_o = \left(\left[\frac{4R}{(R-1)^2} - K \right]^{1/2} - \frac{R+1}{R-1} \right) \text{------------- (1)}$$

Where (K) is the extinction coefficient.

The behavior of refractive index is nearly similar to the reflectance , the refractive index increases with annealing ,We can observe from Fig.(4) ,The decrease in refractive index could be attributed to the decrease of optical absorption in this range.

The extinction coefficient ($k_\circ$) can be determined by using the relation [15]:

$$k_o = \frac{\alpha\ \lambda}{4\ \pi} \quad \text{------------- (2)}$$

Where ( ) is the absorption coefficient and (λ) is the wavelength of the incident photon. Figure (4) Shows the variation in ($k_\circ$) as a function of the Photon energy, It can be noticed that the extinction coefficient increases with annealing.

The variation of the real (ε_r) and imaginary (ε_i) parts of the dielectric constant values versus Photon energy for $(ZnO)_x(CdO)_{1-x}$ films before and after annealing are shown in Figure (5). The behavior of ε_r is similar to that of refractive index because the smaller value of($k_\circ^2$) compared with ($n_\circ^2$) [16]:

$$\varepsilon_r = n_\circ^2 - k_\circ^2 \text{------------(3)}$$

while (ε_i) is mainly depends on the ($k_\circ$) values, which are related to the variation of absorption coefficient [16]:

$$\varepsilon_i = 2n_\circ\, k_\circ \text{-------------(4)}$$

The variations of these two parameters with incident photon energy were shown in Figure (5). From these curves It is found that ε_r and ε_i increases after annealing.

The real and imaginary parts of the dielectric constant indicate the same pattern and the values of real part are higher than imaginary part [16].

It is useful to define a characteristic ‘‘skin’’ thickness that is subject to an appreciable density of optical energy .A convenient form used widely is simply the inverse of α, i.e. χ

= 1 / α . In other words, the electromagnetic wave will have amplitude reduced by a factor 'e' after traversing a thickness (called the skin depth) [17]. The behaviors of the curves in Figure (6) can be divided in to two parts . In the first region below λ=440 nm, skin depth decreases with annealing . While for the second region higher than λ=440 nm ,the skin depth increases with annealing as compared with the deposited on. due to increase the probability of absorption with annealing.

Conclusions

$(ZnO)_x(CdO)_{1-x}$ thin films were deposited onto glass substrates heated at $450C^0$, by chemical pyrolysis technique . The heat treatment changes the optical characteristics under investigation in this study. The result show that the E_g is (2.50 eV) before annealing and (2.65 eV) after annealing.

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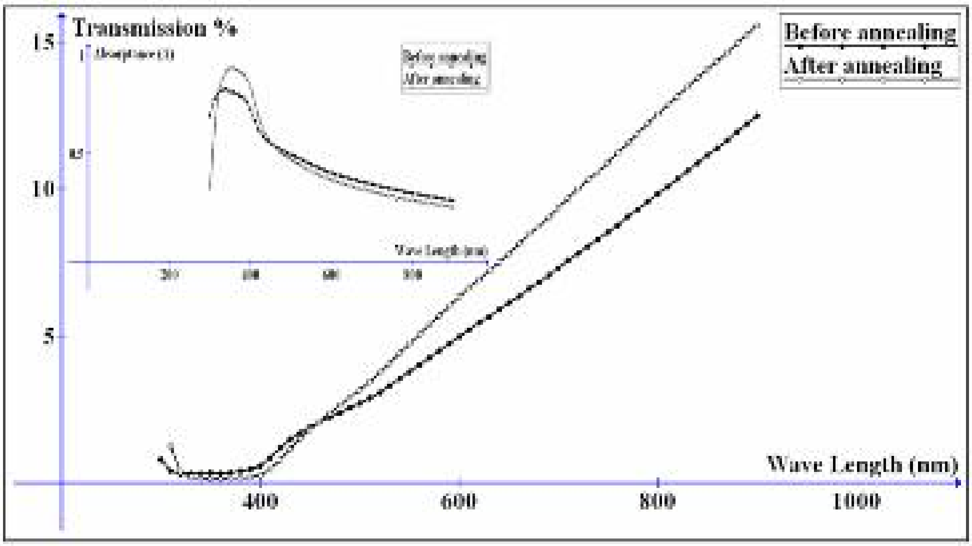

Fig. (1): Optical transmittance of $(ZnO)_x(CdO)_{1-x}$ films. The inset shows Absorptance versus Wavelength

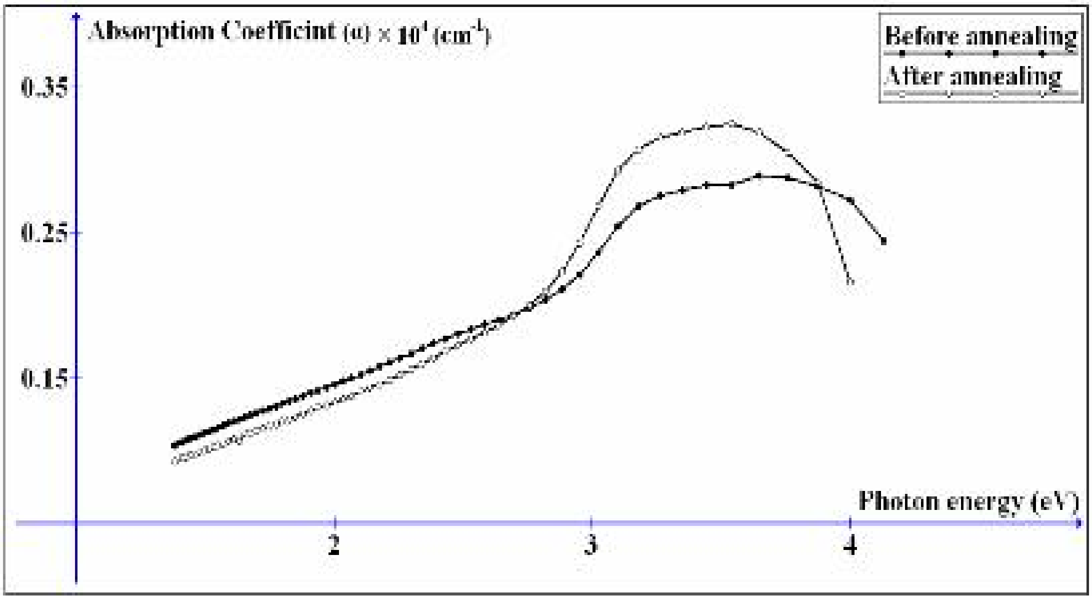

Fig. (2): Absorption coefficient versus Photon energy for $(ZnO)_x(CdO)_{1-x}$ thin film before and after annealing

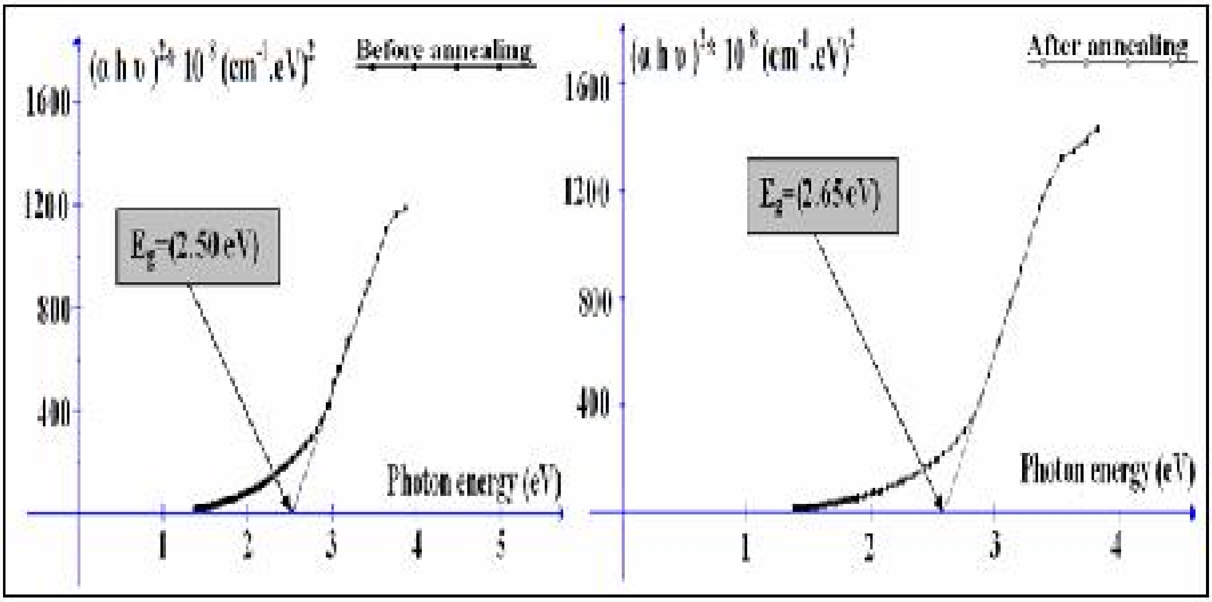

Fig. (3): Optical band gap Eg estimation for $(ZnO)_x(CdO)_{1-x}$ thin film before and after annealing

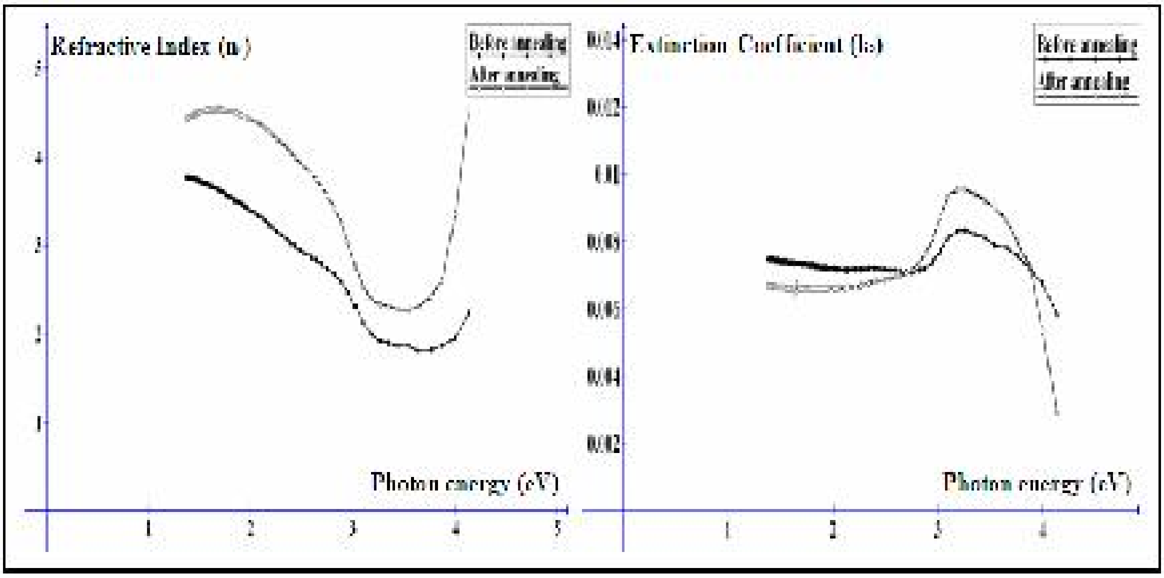

Fig.(4): (n∘)&(k∘) versus Photon energy for $(ZnO)_x(CdO)_{1-x}$ thin film before and after annealing

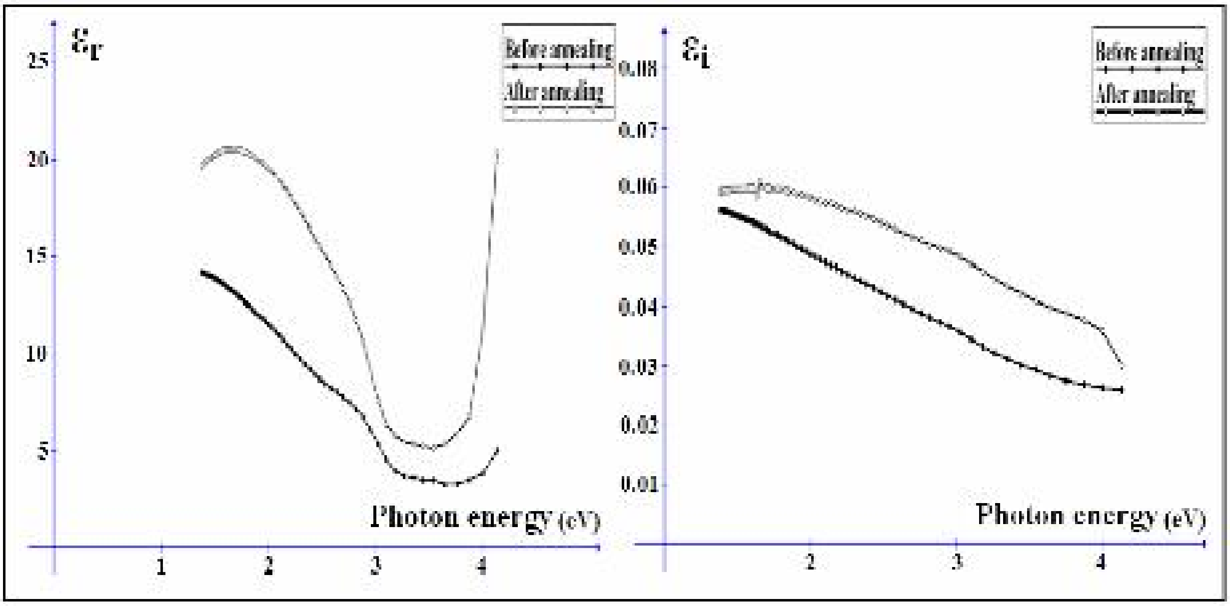

Fig.(5): ε_r & ε_i versus Photon energy for $(ZnO)_x(CdO)_{1-x}$ thin film before and after annealing.

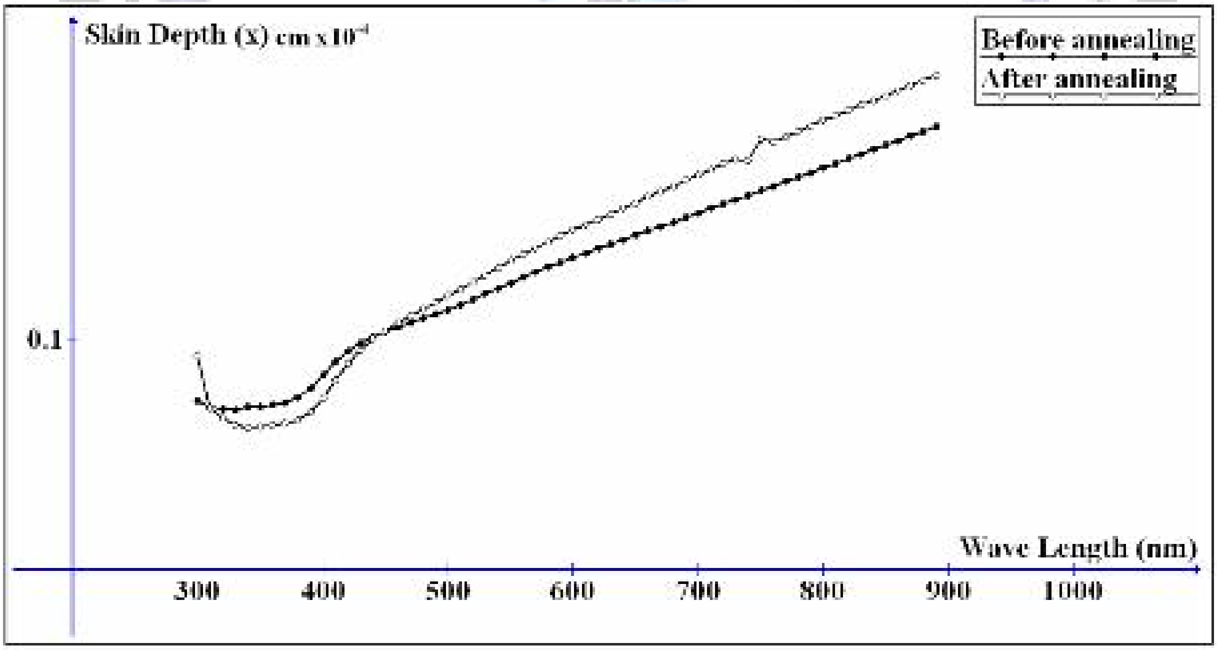

Fig. (6): Skin Depth versus Wavelength for $(ZnO)_x(CdO)_{1-x}$ thin film before and after annealing

تأثيرات المعاملة الحرارية في الخصائص البصرية لأغشية $(ZnO)_x(CdO)_{1-x}$ المحضرة بطريقة التحلل الكيميائي الحراري

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الخلاصة

درس تأثير التلدين في النفاذية البصرية ، ومعامل الامتصاص، وثابت العزل الحقيقي والخيالي، وعمق الاختراق ، وفجوة الطاقة البصرية لأغشية $(ZnO)_x(CdO)_{1-x}$ الرقيقة وبنسبة (x=0.05) المرسبة على قواعد زجاجية مسخنة لدرجة (450 C°) والمحضرة بسمك (750 nm) بطريقة التحلل الكيميائي الحراري . أظهرت هذه الأغشية فجوة طاقة مباشرة مسموحة متأثرة بالتلدين بدرجة حرارة (450 C°) ولمدة ساعتين . وكذلك وجد أن قيمة فجوة الطاقة البصرية ازدادت من (2.50 eV) قبل التلدين إلى (2.65 eV) بعد التلدين ، ومن تحليل طيف الامتصاصية والنفاذية في مدى الأطوال الموجية (380–900nm) ، أظهرت النتائج هذه المعلمات ان كافة قد تغيرت بسبب التلدين.

الكلمات المفتاحية :أغشية $(ZnO)_x(CdO)_{1-x}$ ، الخواص البصرية، التحلل الكيميائي الحراري، تأثير المعاملة الحرارية