The effect of annealing on Some Optical characteristics of ($CdO:Ag_2O$) films prepared by spray pyrolysis

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تقديـــــم البحث : 2011/11/28
قبول نشر البحث : 2012/1 /23

Abstract:-

Thin films of ($CdO:Ag_2O$) were deposited on glass substrates by spray pyrolysis and annealed in air at 450 ºC. Some optical properties of the thin films were studied after and before annealing. After annealing both transmittance% , Skin depth and optical energy gap increased but localized states and carrier concentrations decreased after heat treatment.

تأثير التلدين على بعض الخصائص البصرية لأغشية ($CdO:Ag_2O$) المحضرة بطريقة التحلل الحراري

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المستخلص:

رسبت أغشية (اوكسيد الكادميوم:اوكسيد الفضة) على قواعد زجاجية بطريقة التحلل الكيميائي ولدنت في الهواء بدرجة 450 ºC. درست بعض الخواص البصرية للأغشية قبل وبعد التلدين .تزايدت كلا من النفاذية المؤيه وعمق الاختراق وفجوة الطاقة بعد التلدين لكن تناقصت الحالات الموضعية وتراكيز الحاملات بعد التلدين .

Introduction:

cadmium oxide (CdO) has revealed itself as a very promising material for use in the photovoltaic industry. It has a high electric conductivity and high optical transparency in the spectral region of sun radiation [1] .

On the other hand, Silver oxide (Ag_2O) is a p-type semiconductor with direct band gap around 1.4eV that is used in photography, optical memory, and as solar energy converters[2]. The physical properties of compound films can be tuned by adjusting the relative proportions of the constituent materials. This strategy has been employed to control numerous thin film properties such as refractive index, dielectric constant, lattice constant ,hardness, charge storage capacity, and surface roughness[3]. Chemical and electrochemical deposition of compound (especially semiconductor) thin films from solutions has regained considerable attention , not only for its economical benefits but also for the formation of thin films in ordered structures owing to its self-assembly character [4] .

It is usual that for solar cell fabrication several deposition and thermal treatment steps

are necessary in order to improve the photovoltaic characteristics. Many of these steps are made in the temperature range of 350 - 500 °C, after the deposition of the window materials [5]. From this point of view, it is very important to know the post-thermal annealing effect on the properties of the window thin films, if we want to use them as heterojunction partners on different solar cells[6].

In this article we present some optical properties of ($CdO:Ag_2O$) thin film before and after annealing.

Experimental part:

The films of this work are prepared by using spray pyrolysis method which is best suited for thin film deposition because of simplicity, convenience, least expenses to produce uniform, adherent and reproducible large area thin films for solar related applications [7], There are varieties of the spray pyrolysis set-up as regards the atomization techniques, such as ultrasonic nebulized, corona, electrostatic spray, etc. The simple form of spray pyrolysis set-up was used, which was designed and fabricated in our laboratory. It uses pressurized oxygen gas to atomize the solution mixture without ultrasonic nebulizaton. Fig. 1 shows the schematic diagram of the spray pyrolysis set-up. It consists of substrate heater. The substrate temperature was controlled using substrate heater with thermocouple feedback.

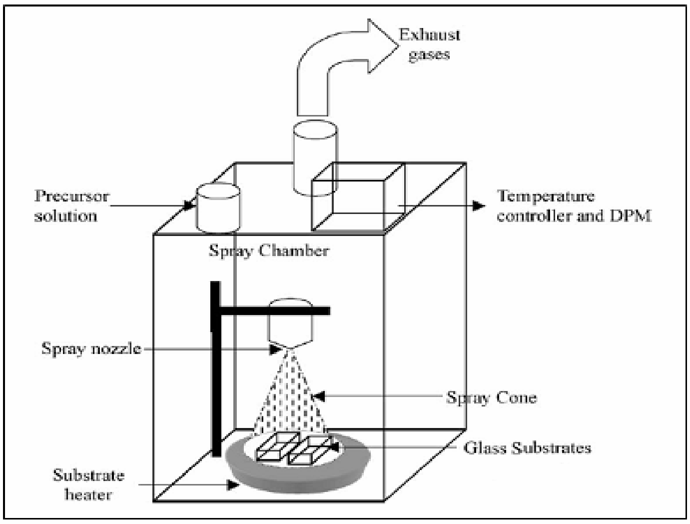

Figure (1) Spray pyrolysis set-up used for thin film preparation.

a mixture of CdO and Ag_2O Thin films were deposited on preheated glass substrates at temperature of (450 °C), The optimized conditions were the following parameters, spray time (10 s) , average deposition (10 cm^3/min) , distance between nozzle and substrate (30 $\pm$1 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 thickness of the sprayed samples was in the range of (250 nm).

This films were annealed at (450 ºC) for two hours .

Absorbance and transmittance spectra were recorded by double beam (UV/VIS) (Shimadzu Corporation Japan) in the wavelength range (300 -900) nm.

Results and discussions:

Figure (2) shows that, the optical transmittance in the range (350-900) nm is about 15% for the film before heat treatment, but it increases to about (20-25 %) after annealing .The increasing of transmission for CdO:Ag_2O might be due to decrease scattering of photons by crystal defects[8], and the free carrier absorption of photons contributed to the reduction in optical transmittance, or might be due to increase of the crystallite size[8]. The increased roughness of the annealed thin films contributed to the drastic decrease of optical transmittance [8]. 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 [9].

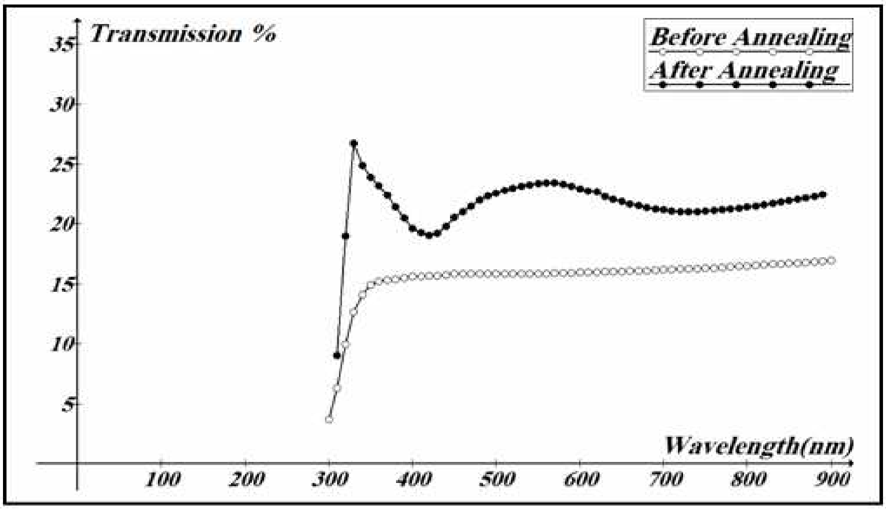

Figure (2) Transmittance % against Wavelength for ($CdO:Ag_2O$) thin films before and after annealing.

The behavior of Absorption Coefficient (α) is illustrated in figure (3), at large photon energy α takes higher values ($\alpha \geq 10^3$) and then decreases with decreasing photon energy, this is attributed to the electronic transitions through the defect centers such as impurities [10] .

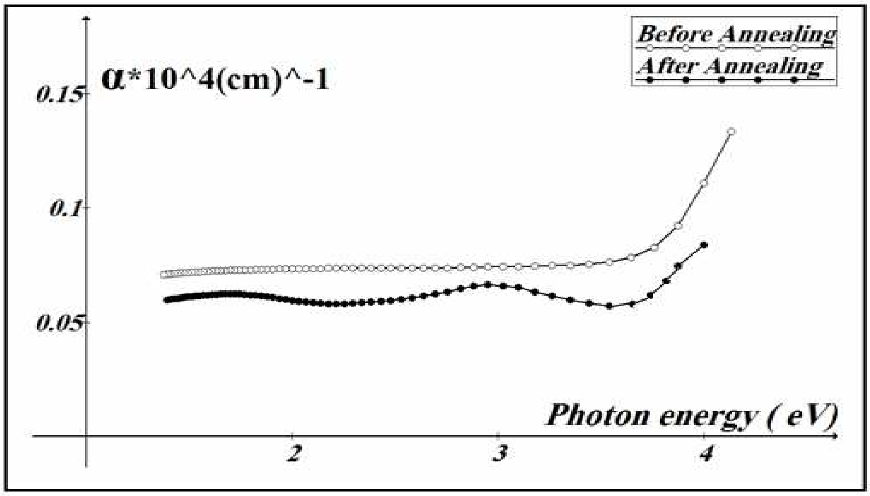

Figure (3) Absorption Coefficient as a function of Photon energy (eV).

The energy gap was calculated from the equation:

$\alpha h\nu = B (h\nu - Eg)^r$ ………………..(1)

Where (α) is the absorption coefficient, ($h\upsilon$) the photon energy , (B) is a constant and (r) is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. r =1/2 for allowed direct transition, r = 3/2 for forbidden direct transition and r =3 for forbidden indirect transition, with r =2 refers to Indirect allowed transitions [11].

The energy gap value was estimated from the extrapolation to zero absorption in the Tauc equation (1). The variation of Eg with Ta is illustrated in figure (4). The allowed direct transition optical energy gaps of (CdO:Ag2O) films were estimated to lie in the range (3.70 to 2.1) eV for the as prepared and annealed films at 450° C, it is slightly decreased with increasing Ta from R.T to 773 K.

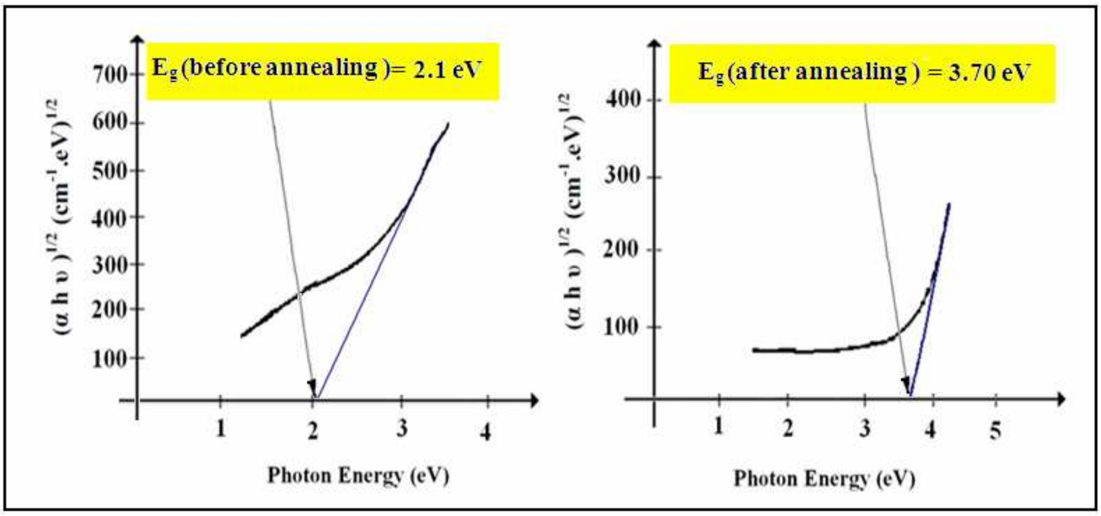

Figure (4) Optical band gap E_g estimation for ($CdO:Ag_2O$) thin film before and after annealing .

The absorption coefficient α(frequency) in the low energy range follows the well knows exponential law, i.e. the Urbach law tail which it is expressed by [12] :

$$\alpha(f) = \alpha_{\eta} \exp(\hbar f/E_e) \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

where E_e is interpreted as the width of the localized states in the band gap. E_e is estimated from the inverse slope of the linear plot between ln(α) vs. photon energy as in figure(5) .In this present study, E_e(Before annealing) = 0.77eV and E_e(After annealing) = 0.52eV. These values of E_e indicate the decreasing of localized states in the band gap after the heat treatment.

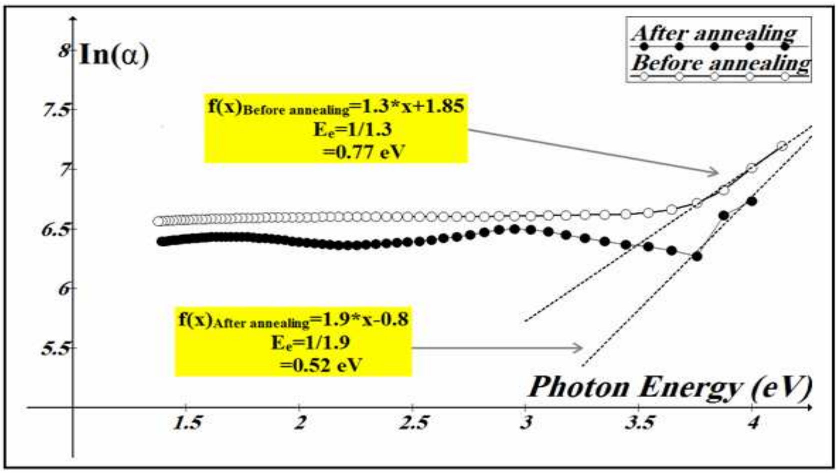

Figure (5) ln α as a function of Photon energy.

The electromagnetic wave will have amplitude reduced by a factor 'e' after traversing a thickness (called the skin depth) [13]. In long wavelength greater than absorption edge, skin depth increases with annealing as shown in figure (6), this might be due to decrease the probability of absorption with heat treatment and the amplitude of the incident photons will be reduced by a factor 'e' through the short distance within the film thickness .

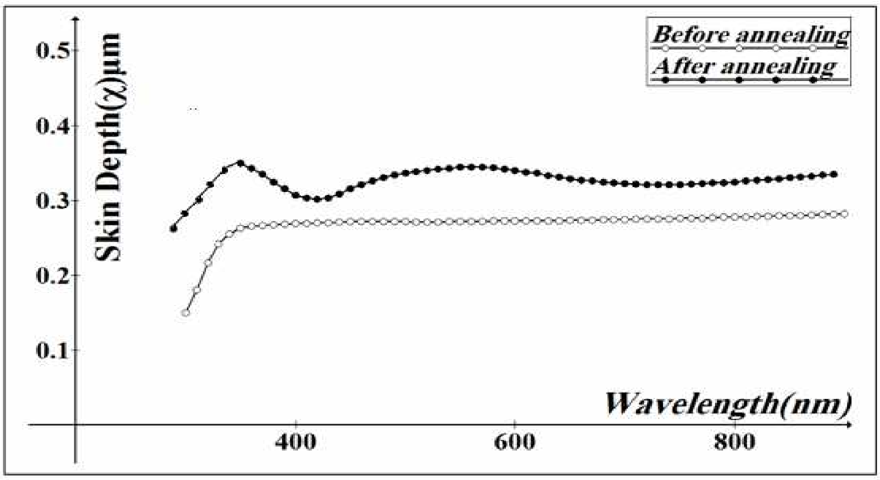

Figure (6) Skin depth (χ) as a function of wavelength.

The real dielectric constant ε_1, which results due to the contribution from the free carrier electric susceptibility, can be written by the following relation [14]:

$$\varepsilon_1 = \varepsilon_i - [(e^2/4\pi^2 c^2 \varepsilon_0)(N/m^*)]\lambda^2 \quad \ldots\ldots\ldots\ldots(3)$$

where ε_1 is real part of dielectric constant, ε_i is the residual dielectric constant due to the ion core, e is the electronic charge, c is the velocity of light, ε_o is the permittivity of free space (ε_0 = 8.85 x 10-12 C/N.m2) and N/m* is the ratio of carrier concentration to the effective mass (m* = 9.10956x 10^{-31} kg). According to the free electron Drude model, ε_1 should be a linear function of λ^2 as it is shown in figure (7).
The carrier concentration decreases from 6.588*$10^{26}$$m^3$ to 2.12*$10^{26}$$m^3$ after annealing , this might be explained as following: When the films are annealed under ambient air at temperature higher than 400^0C, oxygen is chemisorbed on the film surface and in pores, acting as an acceptor by accepting an electron from occupied conduction band states [15], thus reduces the density of donors like defects and carrier concentration.

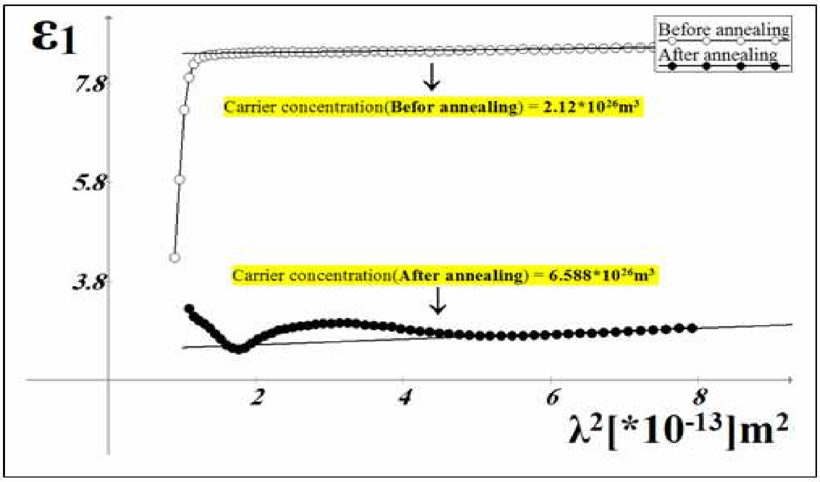

Figure (7) dielectric constant as a function of $(\lambda)^2$ for (CdO:Ag_2O) thin films.

Conclusions:

(CdO:Ag_2O) 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 results show that the E_g is (2.1eV) before annealing and (3.70eV) after annealing , E_e is (0.77 eV) before annealing and (0.52 eV) after annealing.

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