Annealing Effect on the Optical Properties of $(CdO)_{1-x}$ $(Mg)_x$ Thin Films

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Abstract

$(CdO)_{1-x}$ $(Mg)_x$ thin films with (x = 0.06) deposited on perheated glass substrates at temperature 350°C by chemical spray pyrolysis technique. We have studied the effect of annealing temperature at (400, 450) °C. Optical absorption studies in the wavelength range 300–900 nm in order to calculate the optical constants such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant. Results illustrate that the refractive index decreased at 600 nm while the extinction coefficient slightly increases after annealing, on the other hand, the values of real and imaginary parts of the dielectric are found to be decreases with increasing annealing. The skin depth is found to be decreases as the annealing temperature increased to 450 °C, so the skin depth is a transmittance related.

Keywords: TCOs, Optical Constants, Spray Pyrolysis technique, CdO.

Introduction

Transparent conductive oxides (TCOs) films are used in variety of applications because of their special optical and electrical properties such as wide band gaps, high electrical conductivity and high optical transparency in the visible spectral region [1]. Among them, cadmium oxide CdO seems to be the most appropriate material for different applications due to its unique optical and electrical properties. Cadmium oxide is an n-type semiconductor, have a face center cubic (FCC) structure with direct band gap 2.2-2.7 eV and an indirect band gap of 1.98 eV[2, 3], Which has extensive applications in solar cells, low emissive window optical communications, photovoltaic device, flat panel display, IR heat mirror, transparent electrodes, thin film resistors and gas sensors[4, 5].

Different techniques are used to prepare CdO films such as spray pyrolysis [6], chemical bath deposition (CBD) [7], chemical vapour deposition [8], reactive evaporation [9], DC magnetron sputtering [10], metal organic chemical vapor deposition (MOCVD) [11], and sol-gel method [12]. Among these methods, the spraying technique is a simple, economic and commonly used method and it is well suited for the preparation of cadmium dioxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, high growth rate and mass production capability for uniform large area coatings [13]. In addition, the CdO film prepared by the spraying technique is also physically and chemically resistant against environmental effects and adheres strongly to different substrates.

It is intended the determination of optimum conditions that leads to the manufacturing of well crystallize, conductive and transparent cadmium oxide thin films in this paper. The optical constants of the films were examined in association to the annealing temperature.

Experimental procedure

The preparation of films under investigation have been done by spray of an aqueous solution of 0.1M $CdCl_2$ and $MgCl_2$ both from Sigma-Aldrich, these materials were dissolved in double distilled water and ethanol, a few drops of HCl were added to make the solution clear, a total volume of 50 ml was used in each deposition. The spraying process was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 350°C, with the optimized conditions that concern the following parameters, spray time was 8 sec and the spray interval 3 min was kept constant to avoid excessive cooling, the carrier gas (filtered compressed air) was maintained at a pressure of $10^5 Nm^{-2}$, distance between nozzle and substrate was about 29 cm, solution flow rate 5 ml/min. The samples were weighed before and after spraying to determine the mass of the films [14]. Knowing the dimensions of the substrates used, the thicknesses can be determined using the following equation [15]:

$$d = \frac{\Delta m}{\rho_m \, lL} \qquad ....(1)$$

Where Δm is the difference between the mass after and before spraying, ρ is the density of the bulk material, l the width and L the length of the sample. Thickness of the films was found to be around 400 nm. Optical transmittance and absorbance were recorded in the wavelength range (300-900) nm using UV-VIS spectrophotometer (Shimadzu Company Japan). In order to explore the influence of annealing temperature on the parameters under investigation, the as deposited films annealed to 400°C and 450°C.

Results and discussions

The optical properties of $(CdO)_{1-x}$ $(Mg)_x$ thin films by means of optical absorbion in the UV-Vis region of (300–900) nm have been investigated.

Fig. 1 shows the optical absorbance spectra for all films. The position of the absorbance spectra is observed to shift towards the higher wavelength side after annealed to 400°C and 450°C. This indicates that the band gap of the material decreases with increasing of annealing temperature, which is due to the removal of H_2O vapor from film and/or removal of defect levels after the heat treatment which is a common phenomenon in chemically deposited thin films [16]. Similar results of enhancement of the CdO films by annealing were also pointed out by Biju et al. [17] and Rusu et al.[18].

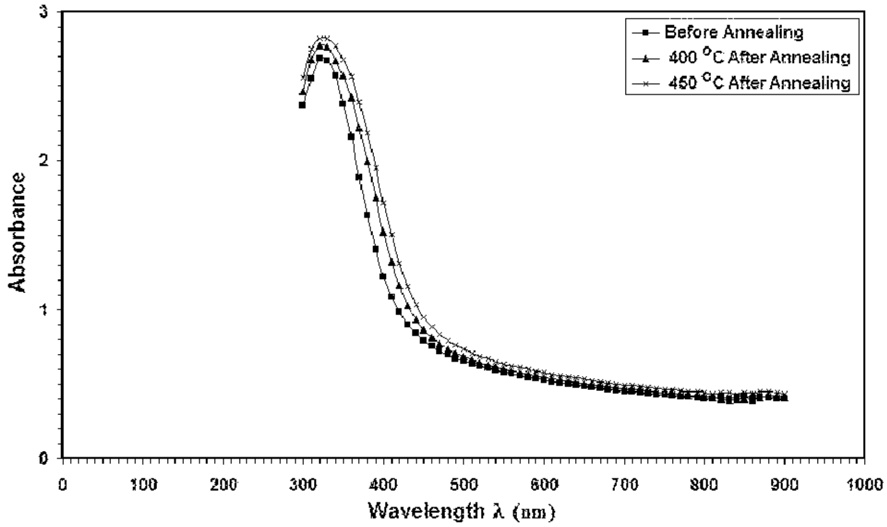


Fig. (1) Absorbance of different thicknesses $(CdO)_{1-x}$ $(Mg)_x$ thin films versus wavelength.

Refractive index of the films is an important parameter for optoelectronic devices design such as optical filters, solar cells, high stability resistors, displays devices. In order to calculate the optical constant refractive index (n) and the extinction coefficient (k) of the films at different wavelengths, we can use the following relations [19]:

$$n = [1 + R/1 - R] + [4R / (1-R)^2 - k^2]^{1/2} \quad \text{----------- (2)}$$

$$k = \alpha\lambda/4\pi \quad \text{------------------------ (3)}$$

Where (α) is the absorption coefficient and λ is the wavelength. The refractive index of the prepared films was calculated by using Eq. (2) and the variation of refractive index with wavelength is shown in Fig. 2. All films showed similar behavior in refractive index spectra. There is a little decrease in refractive index values for the films after annealing. Refractive index values of the samples are varied between (2.4–2.8) at long wavelengths. The variation of refractive index can be attributed to the density and the surface roughness [20]. Fig. 3 shows the variation of extinction coefficient with the wavelength for all films. It can be notice that all films have a similar k variation belonging to wavelength of polarized light, and there is slightly decrease in the extinction coefficient after annealing. The extinction coefficient of a material is directly related to its absorption characteristic. The average refractive index and extinction coefficient values of the films at 600 nm are given in Table 1.

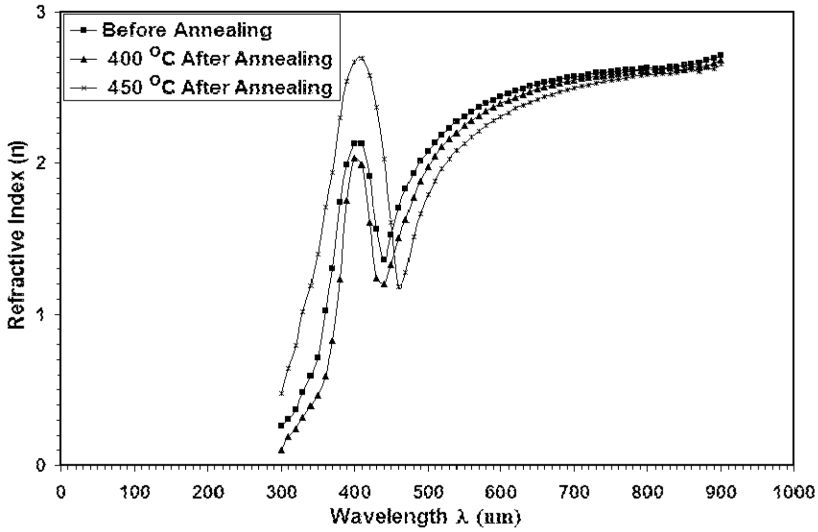


Fig. (2) Refractive index versus wavelength for $(CdO)_{1-x}$ $(Mg)_x$ thin films.

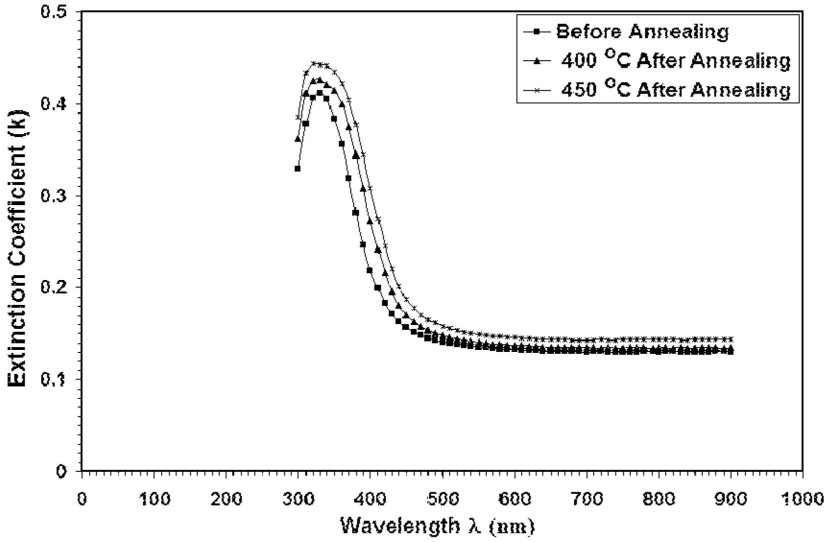


Fig. (3) Extension coefficient versus wavelength for $(CdO)_{1-x}$ $(Mg)_x$ thin films.

Table (1)

Average refractive index and extinction coefficient values for all films at 600 nm.

	n at λ= 600 nm	k at λ= 600 nm
As deposited	2.41	0.154
Annealed at 400°C	2.32	0.145
Annealed at 450°C	2.18	0.140

The real ε_1 and imaginary ε_2 parts of the dielectric constant were obtained using the formulas as [21]:

$\varepsilon_1 = n^2 - k^2$ .... (4)

$\varepsilon_2 = 2nk$ .... (5)

The variation in the real (ε_1) and imaginary (ε_2) parts of the dielectric constant for all films are shown in Figures (4) and (5). The values of the real part are higher than those of the imaginary part. The values of real and imaginary parts of the dielectric are found to be decreases with increasing annealing temperature.

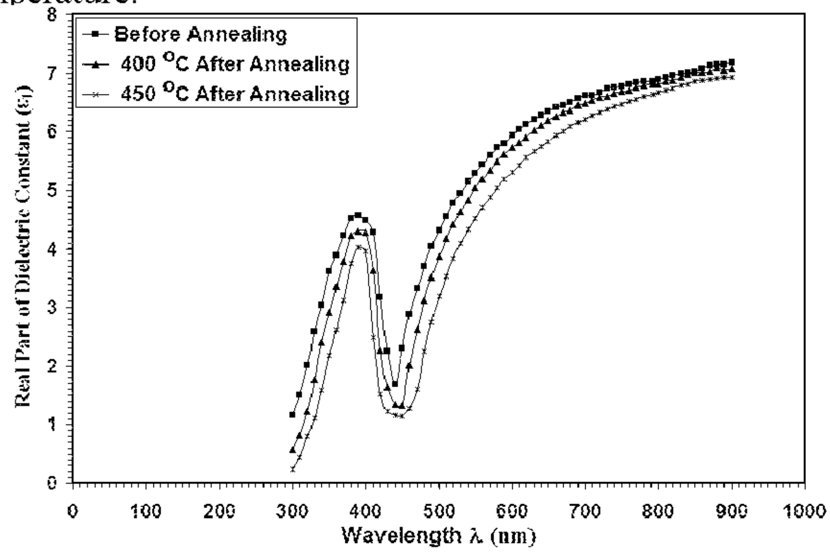


Fig. (4) Real part of the dielectric constant versus wavelength for $(CdO)_{1-x}$ $(Mg)_x$ films.

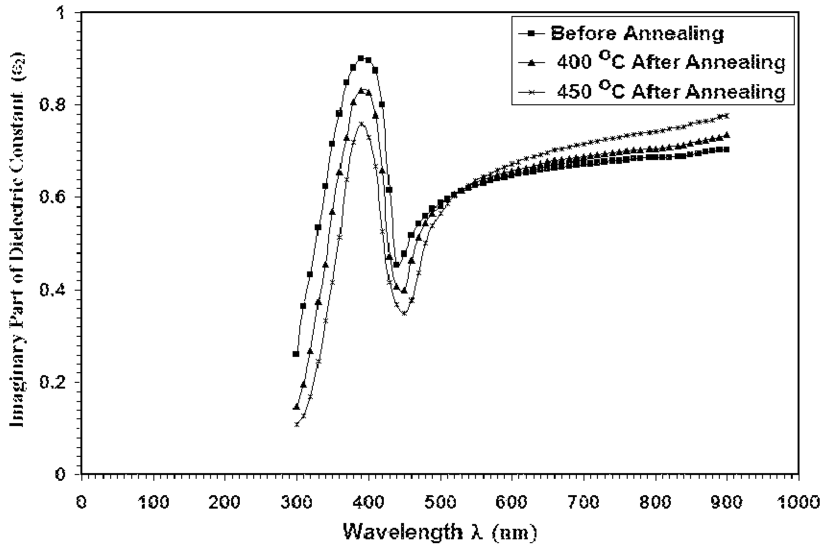
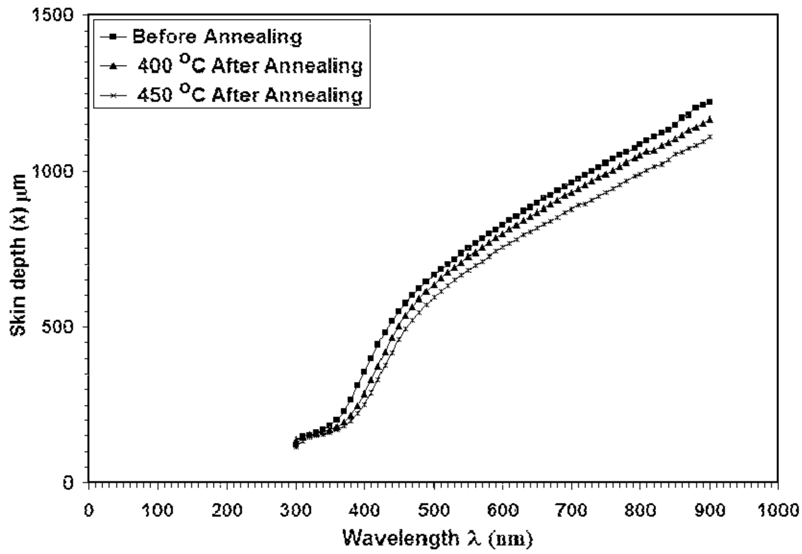


Fig. (5) Imaginary part of the dielectric constant versus wavelength for $(CdO)_{1-x}$ $(Mg)_x$ films.

The skin depth could be calculated using the following relation [22]:

$\chi = \lambda / 2\pi k$ ……………..(6)

Where λ is the wavelength of the incident photon, k is the extinction coefficient. Fig. (6) shows the variation of skin depth as a function of wavelength for all films. It is clear from the figure that the skin depth increase as the wavelength increase, this behavior could be seen for all samples, but the skin depth decreases as the annealing temperature increases to 450°C, which means that the skin depth is a transmittance related.



Conclusion

The optical properties of $(CdO)_{1-x}$ $(Mg)_x$ films grown on glass substrates have been investigated. Results indicate that the optical parameters are strongly affected by annealing temperature. As the annealing temperature increases to 450 °C, the refractive index decreased at 600 nm while the extinction coefficient slightly increases. The real and imaginary parts of dielectric constant were calculated and they are tending to decrease after annealing. Furthermore, the skin depth decreases as the annealing temperature increases.

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تأثير المعاملة الحرارية على الخصائص البصرية لأغشية $(CdO)_{1-x}$ $(Mg)_x$ الرقيقة

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الخلاصة

حضرت أغشية (CdO)1-x (Mg)x الرقيقة وبنسبة (x = 0.06) المرسبة على قواعد زجاجية مسخنة لدرجة حرارة 350 مئوية بطريقة التحلل الكيمياوي الحراري. درس تأثير التلدين وبدرجة حرارة 400 و450 درجه مئوية. تم دراسة طيف الامتصاصية في مدى الأطوال الموجية (300–900) نانومتر وذلك لغرض حساب الثوابت البصرية مثل معامل الانكسار، معامل الخمود، ثابت العزل بجزئية الحقيقي والخيالي. أوضحت النتائج بأن معامل الانكسار يقل عند الاطوال الموجية 600 نانومتر ومعامل الخمود يزداد بعد التلدين, بينما ثابت العزل بجزئية الحقيقي والخيالي وكذلك عمق القشرة جميعها تقل بزيادة درجة حرارة التلدين الى 400 درجه مئوية.