Annealing effects on the Interband Transition and Optical constants of cobalt doped Cadmium oxide Thin Films

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Abstract

The CdO: Co films have been deposited on substrate temperature at 400 °C by spray pyrolysis method using cadmium chloride and cobalt chloride as a precursors for Cd and Co ions, respectively. The effect of annealing temperature on optical constants of Co: CdO thin films are investigated using UV-Visible spectrophotometer in the range of (300-900) nm at room temperature. The absorbance and optical parameters such as α, n, ε_1, ε_2, and χ are increased when the annealing temperature increases, while the energy gap decreased from 2.5 eV before annealing to 2.48 eV after 500 °C annealing temperature. Urbach energy is increased with the increasing of annealing temperature from 353 meV for sample before annealing to 715 meV for the same samples annealed at 500 °C.

Key words: Co doped CdO, Optical properties, annealing temperature.

Introduction

CdO thin films present low resistivity. Studies have been made however with the objective of decreasing the resistivity even further and getting more stable films. CdO films have been doped with different impurities such as indium, copper, tin and fluorine (F) [1–3], and annealed in different controlled atmospheres. Resistivity values around 10^{-4} Ωcm can be obtained [4-6].

Enhancing the electrical properties of transparent conducting oxides(TCOs), specially conductivity, can be done either by increasing the charge carrier concentration or by improving the mobility of those carriers.Increasing carrier concentration can be achieved by heavy doping of the TCO materials. This will,however, degrade the transparency due to increased free carrier absorption [7],
Among these transparent conducting oxides, cadmium oxide (CdO) has received a considerable attention for solar cell application due to its low electrical resistivity and high transparency in the visible range of solar spectrum [8].

Cadmium oxide thin films prepared by various techniques, spray pyrolysis [9–11], ion beam sputtering [11], chemical bath deposition [12], activated reactive evaporation [13], thermal oxidation [14], reactive sputtering [15-16] and sol–gel [17].
The aim of this study is to study the effect of annealing temperature on the interband transition and optical constants of CdO thin film that doped by 1% Co, utilizing chemical spray pyrolysis technique.

Experimental Details

Co doped CdO thin films were prepared by chemical pyrolysis method. The Cadmium chloride supplied from (BDH Chemicals Laboratory, England) with 0.1 M dissolved in redistilled water, and doped by 1% Cobalt . The optimization conditions were arrived at the following : spray time was 8 s followed by 2 min to avoid the excessive cooling , the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Pascal, distance between nozzle and substrate was about 29 cm, and the solution flow rate was 5 ml/ min. These prepared films are deposited on glass substrates at a temperature of 400 °C.

Gravimetric method was used to determine the film thickness, which to be 350± 30 nm, and the UV-VIS spectrophotometer with a double beam (Shimadzu UV-VIS Japan) was used for recording the optical transmittance with a wavelength range of (300-900) nm. The as deposited samples were exposed to 2 hours annealing temperature of 450 and 500 °C respectively.

Results and Discussions

The optical properties of Co doped CdO thin film are determined by recording absorption spectra by UV-Visible spectrophotometer in the range of (300-900) nm at room temperature. Fig.1 represent the relationship between the absorbance versus wavelength. From this figure, it can show that the absorbance increased with increasing annealing temperature, the absorption edge was shifted to lower wavelength (blue shift) as the annealing temperature increases
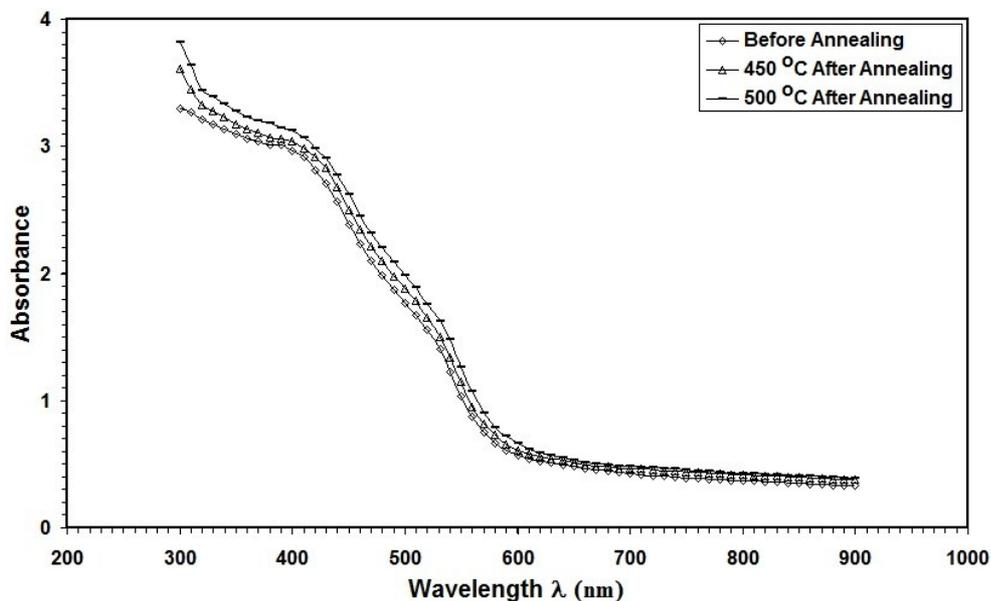

Fig. 1 Variations of absorbance as a function of wavelength.

The absorption coefficient(α)was calculated from the transmittance spectra using the relation [18].

$$\alpha = \frac{\ln(1/T)}{d}$$

(1)

Where (T) is the transmittance and (d) is the film thickness. The variation of absorption coefficient versus wavelength is shown in Fig. 2. From this figure, it can notice that the absorption coefficient increased with increasing annealing temperature. This results an be explained according to an increase in order of crystallinity as the annealing temperatures increased
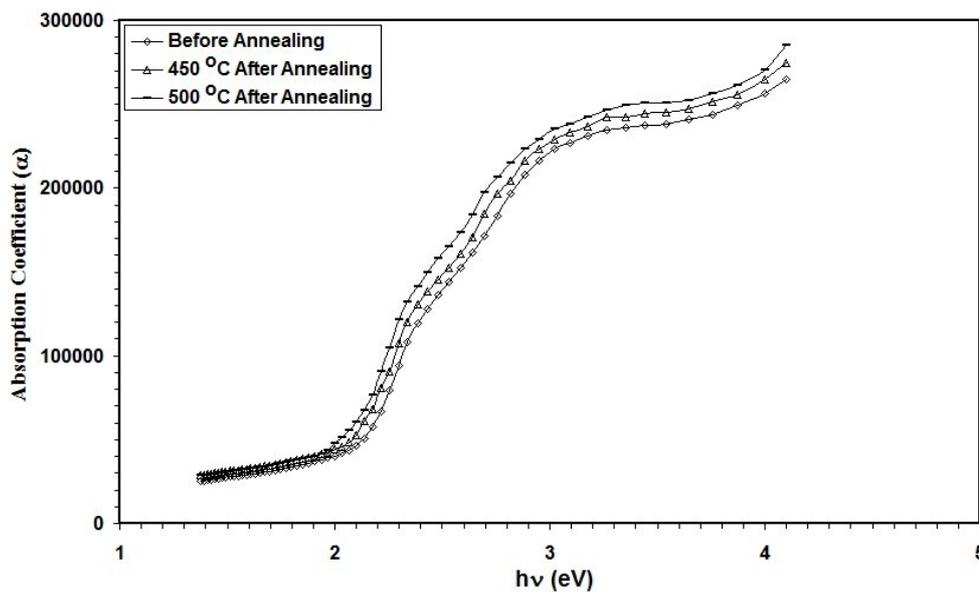
Fig. 2. Variation of absorption coefficient as a function of wavelength.

The relationship between absorption coefficient and the optical band gap is expressed to calculate the band gap by the following relationship [19]:

$$\alpha h\upsilon = A(h\upsilon - Eg)^m$$

(2)

Where A is an energy-independent constant and Eg is the optical band gap and m is a constant which determined type of optical transition. The direct forbidden energy band gap was calculated from the plot $(\alpha h\upsilon)^2$ versus hυ, and by extrapolation the linear portion of the curves until they intercept the photon energy axis as shown in Figs. (4-6). From these figures, it can be noticed that there is a increasing in energy gap with the increasing of annealing temperature. This might be interpreted as the relation between crystallite size and the optical energy gap [20].
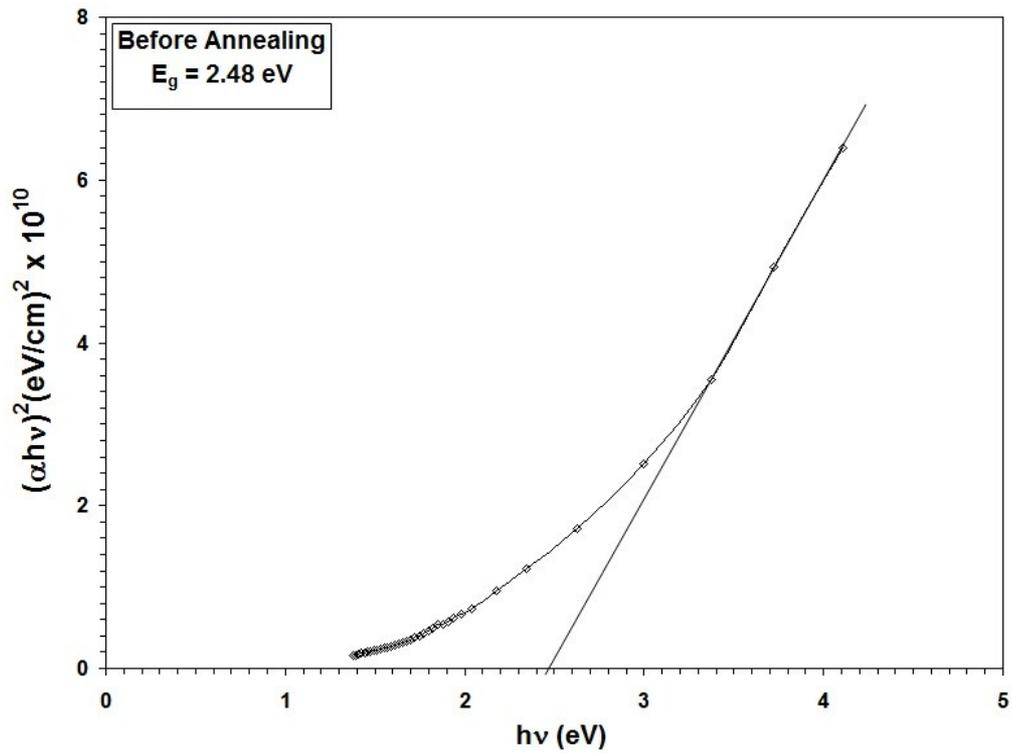
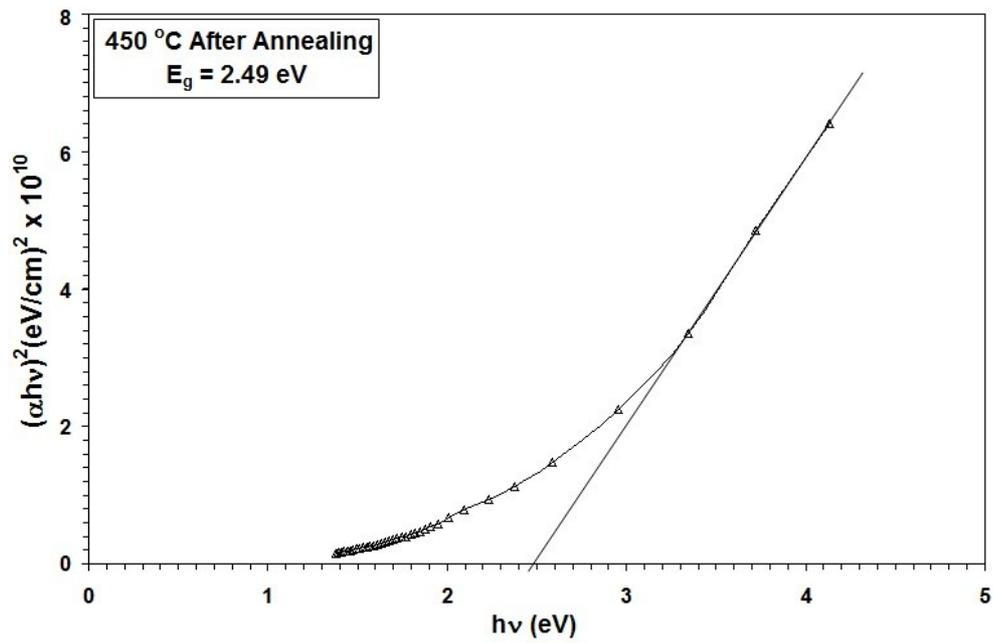**Fig. 4** $(\alpha h\nu)^2$ vs. $h\nu$ plot of Co:CdO thin film before annealing.

Fig. 5 $(\alpha h\nu)^2$ vs. $h\nu$ plot of Co:CdO thin film at annealing temperature of 450 ^{o}C.
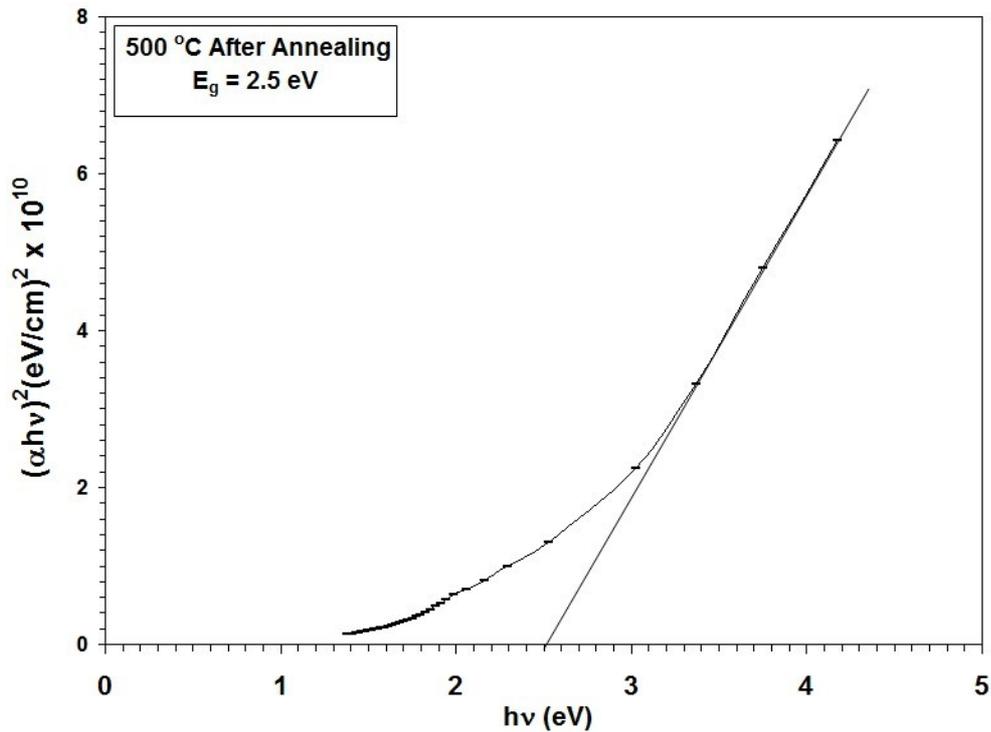
Fig. 6 $(\alpha h\nu)^2$ vs. hν plot of Co:CdO thin film at annealing temperature of 500 $^{\circ}$C.

The width of the localized states available in the optical bandgap affects the optical bandgap structure and optical transitions and it is called as Urbach tail, which could be determined by the following relation [21]:

$$\alpha = \alpha_0 \exp\left[\frac{E}{E_U}\right]$$

(3)

Where E is the photon energy, (α_o) is constant, and E_U is the Urbach energy which refers the width of the exponential absorption edge. Fig.7 represent ln α as a function of photon energy (hν). Urbach energy, decreased with increasing annealing temperature from 715 eV before annealing to 335 eV after annealing by 500°C.
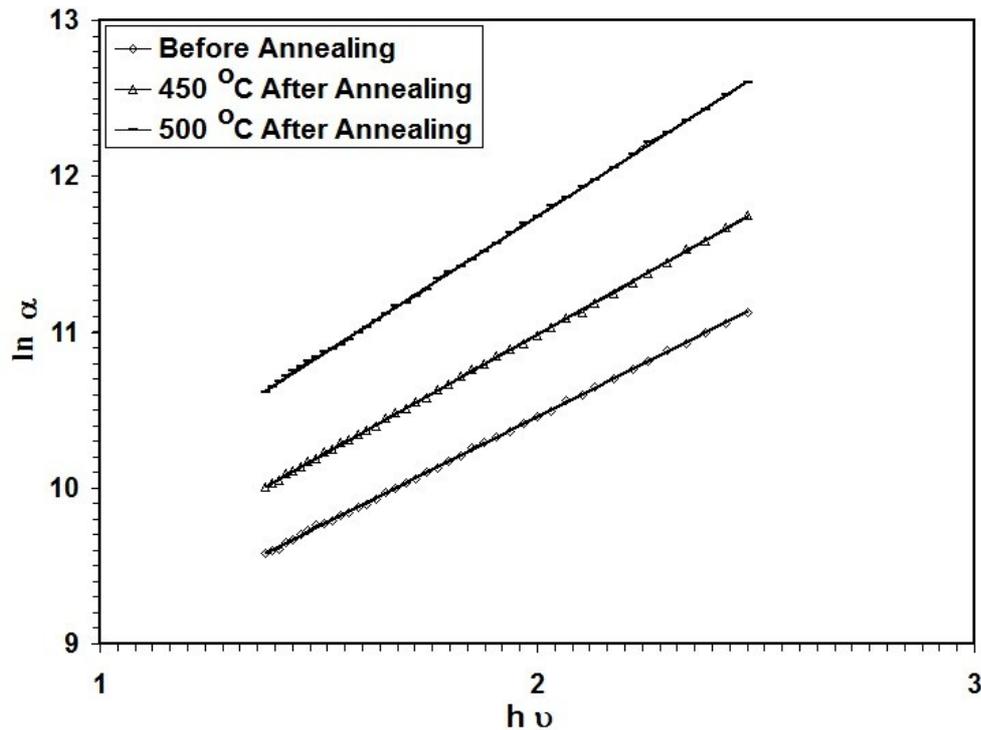
Figure 7: ln α as a function of hυ.

The refractive index of the samples can be obtained from the following equation [22].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (3)$$

Where k is the extinction coefficient. The refractive index values as a function of wavelength, before and after the annealing treatment, are shown in Fig. 8, and it can notice the increasing of refractive index when the annealing temperature increases for prepared thin film.

The real and imaginary parts of complex dielectric constant are expressed as [23]:

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

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

Where ε_1 is the real part and ε_2 is the imaginary part of the dielectric constant. The dependence of the real (ε_1) and imaginary (ε_2) parts of the dielectric constant on photon energy are shown in Figs. (9,10). From these figures it can notice that the real and imaginary parts of dielectric constants increase with increasing annealing temperature, and it can show the peaks in the wavelength at 550 nm for all prepared thin films.
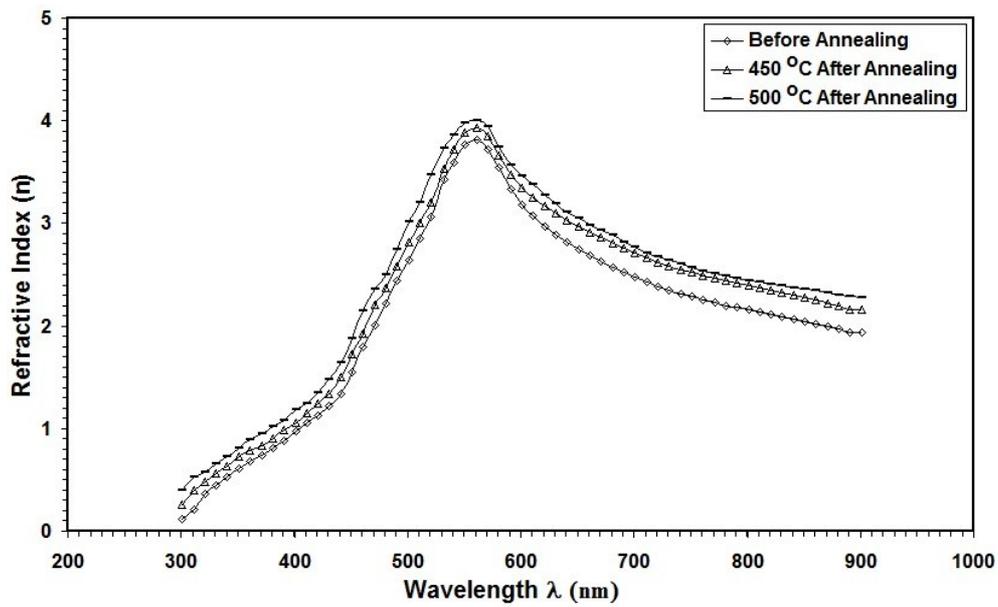
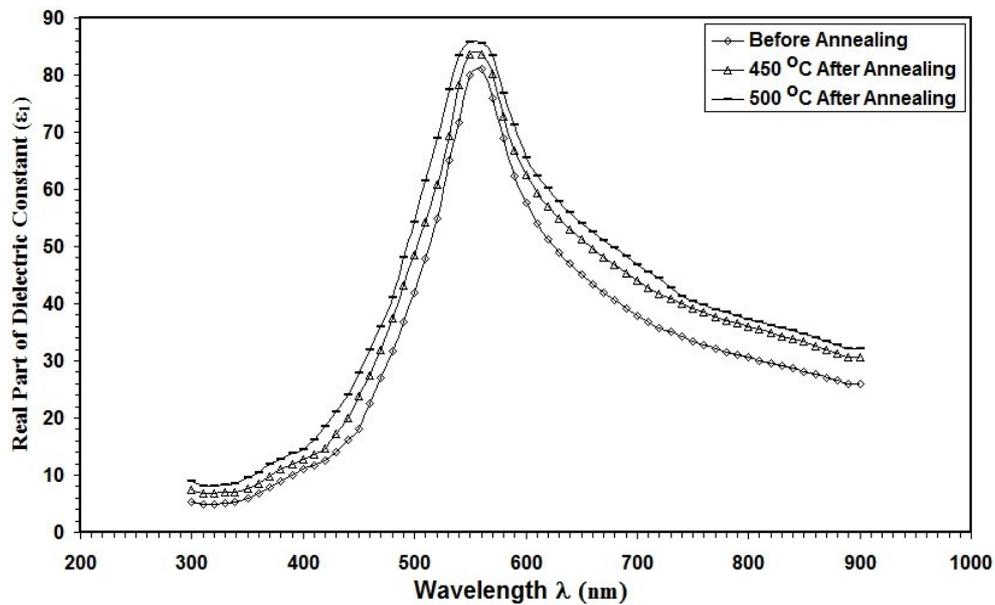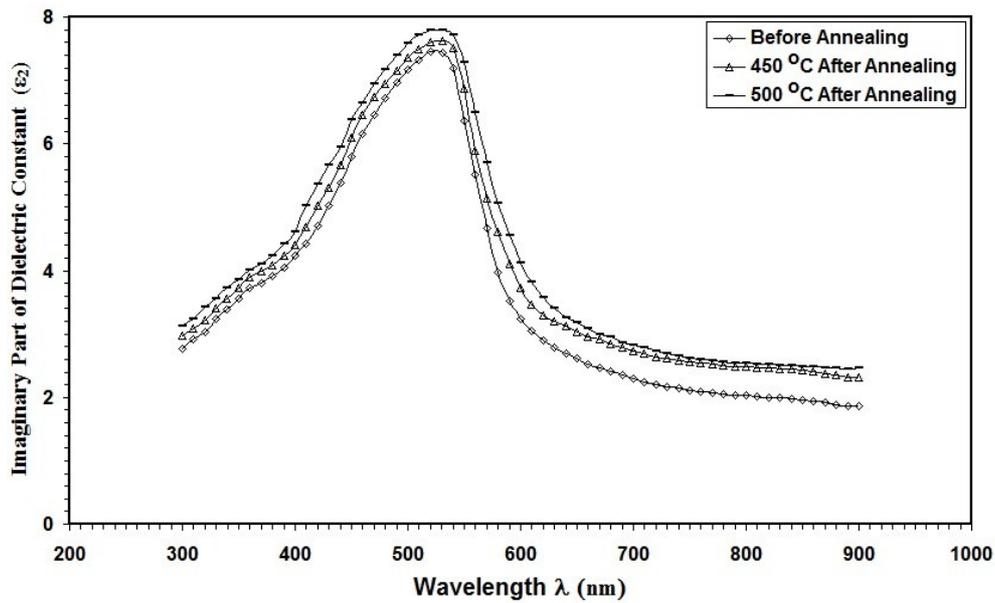**Fig. 8** Variation of refractive index as a function of wavelength.

**Fig. 9** Variation of real part of dielectric constant as a function of wavelength.

Fig. 10 Variation of imaginary part of dielectric constant as a function of wavelength.

The skin depth (χ) could be calculated using the following relation [24]:

$$\chi = \frac{\lambda}{2\pi K} \tag{6}$$

Where λ is the wavelength of the incident photon and K is the extinction coefficient.

Fig. 11 represent the relationship between skin depth versus wavelength. From this figure, it can be noticed that the skin depth increased with increasing annealing temperature, so the skin depth is transmittance related.
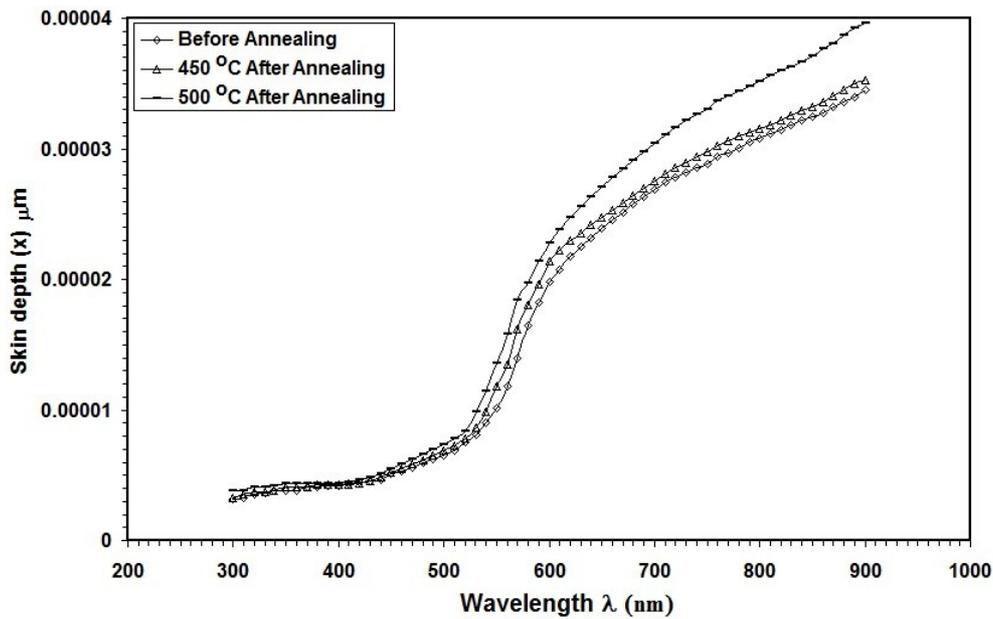
Fig. 11. Variation of skin depth as a function of wavelength.

Conclusions

The optical properties of Co:CdO thin film is studied for various annealing temperature that deposited on a glass substrate (400 ^{o}C) by chemical pyrolysis method. The energy gap is shifted towards the higher energies when the annealing temperature increases to 500 ^{o}C.The absorbance and optical parameters such as α, n, ε_1, ε_2, and χ are increased as the annealing temperature increases.

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