Optical characterization of Iron doped cadmium oxide thin films prepared by the Spray-pyrolysis method

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Abstract:

Undoped and Fe doped CdO samples with 5 wt% of Fe were synthesized by spray pyrolysis method. Optical properties of the samples in spectral range (300 – 900)nm are studed. The doping increases the optical transmittance of CdO and reduces optical band gap (E_g) from 2.49 eV to 2.46 eV . Extinction Coefficient (K_0), Absorption Coefficient(α), skin depth(χ), Refractive index(n), optical conductivity and dielectric constants have been calculated and correlated with doping.

Introduction

Cadmium oxide (CdO) is an important semiconducting material with varying band gap from 2.2 to 2.9 eV, it is one of the promising transparent conducting oxides (TCO) from II to VI group of semiconductors which has great potential for optoelectronic devices [1]. It is known to be an n-type semiconductor with non-stoichiometric composition due two the presence of either interstitial cadmium or oxygen vacancies, which act as doubly charged donors. It is used in various applications including gas sensor [2,3,4], Phototransistor [5] , inter-layers for diodes [6], which are based on its specific optical and electrical properties.

In particular, cadmium oxide is a promising material for solar cell applications due to its high electrical conductivity and optical transmittance in the visible region of the solar spectrum, In addition, cadmium oxide is uniquely positioned amongst other transparent conducting oxides for application in photometry due to its absorption of light in the blue region of the electromagnetic spectrum [7].

In this work, we present the action of doping CdO with Fe on it's optical properties. These thin films deposited by Spray-pyrolysis, which is a very simple and economical technique.

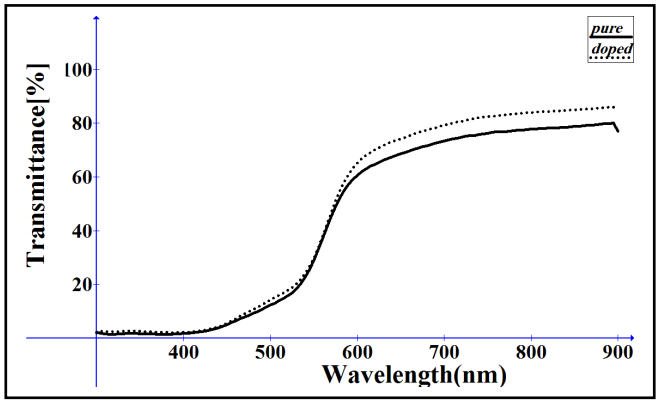
Experimental details:

Thin films of CdO 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 taking 0.1 M of (Cd(NO3)24H2O) dissolve in distilled water ,homogeneous mixture was achieved by using magnetic stirrer. The optimized conditions were the following parameters, spray time (15 sec) , 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. Optical transmittance and absorbance were recorded in the wavelength range (300-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan).

Results and discussion:

The action of doping with Iron on transmission % of cadmium oxide thin films in the wavelength range (300-900) nm is illustrated in figure (1). Doping process increases film's transmission from about 65% for pure film to greater than 75% for that one doped with 5% Iron .



Figure(1) Transmittance% as a function to Wavelength.

Near absorption edge there is no sharp fall in the T% of the films "as expected due to the strong absorbance of the films in this region", this is may attributed to the presence of sub-band gap levels associated with defects.

Generally the equation (written here in a simplified form) used to determine the band gap nature and the value of Eg (the gap energy) is [8]:

$$\alpha = \frac{c}{hf}(hf - E_g)^n \qquad \text{- - - - - - - - - - - - - - (1)}$$

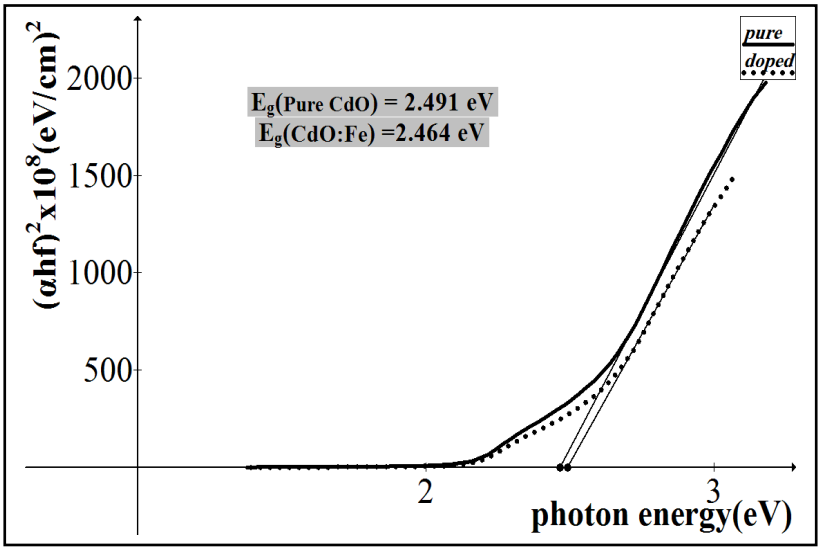
Where c is a constant nearly independent on photon energy and known as the disorder parameter. The value of the optical energy gap Eg is obtained by plotting $(\alpha hf)^{1/n}$ in the high absorption range followed by extrapolating the linear region of the plot $(\alpha hf)^{1/n}$ =0. This extrapolated value is used to define the so called optical gap. The plots of $(\alpha hf)^{1/n}$ against hf (n =1/2, 3/2, 2 and 3) give linear relation. For CdO films the most

fit for equation (1) gave the value of n =1/2. This indicates that allowed direct transitions are responsible for absorption in CdO films.

For direct transition, the absorption coefficient α is given by the following relation obtained by Mott and Davis [9].

$$(\alpha hf)^2 = B(hf - E_g^{opt}) \qquad \text{- - - - - - - - - - - - (2)}$$

Where B is a constant independent of the photon energy, hf is the photon energy, E_g^{opt} is the direct allowed energy gap. Figure (2) shows the variation of $(\alpha\ hf)^2$ with hf for pure and Fe doped CdO samples. The optical energy gap, for direct allowed transitions, can be obtained by extrapolating the linear portions of the curves to α hf = 0

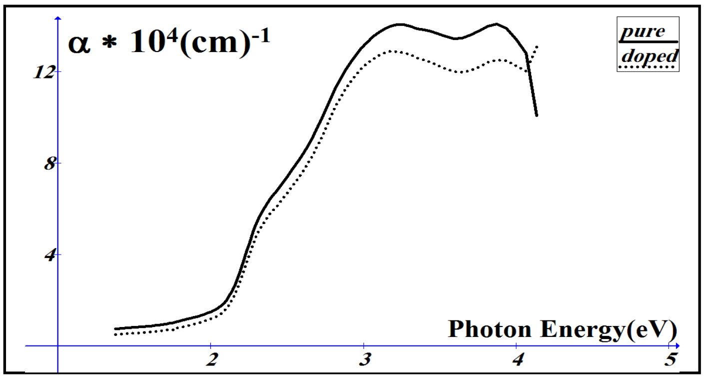


Figure(2) Band gap E_g estimation for Pure & doped CdO films.

This figure shows the decrease in band gap upon Fe doping, from 2.49 eV to 2.46 eV.

From the literature data, the direct band gap values for CdO films prepared by different techniques ranged between 2.2 eV and 2.8 eV [10, 11]. The relative lower values, obtained for our samples for direct band gap can be attributed to the greater density of donor states near the conduction band because the presence in the films of the Cd interstitials and oxygen vacancies will determine a higher concentration of the donor states below the conduction band [12] . Due to these donor states, the band structure may be changed, given rise to the density of states tails extended into the forbidden band [13]. Consequently, a reduction of the effective band gap will take place.

The dependence of the absorption coefficient α, on photon energy is important in studying energy band structure and the type of transition; it was estimated by the transmittance data. From figure (3) absorption coefficient decreases with doping, this



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

behavior could be explained by the variation of the carrier concentration with doping as we will notice later. At short wavelength (α) takes higher value ($\alpha \geq 10^4$) cm^{-1} and then decreases with increasing λ (decreasing photon energy), this might be attributed to the lattice absorption bonds correspond to the electronic transitions between highest filled energy bands to lowest empty band as well as transition through the defect centers such as impurities.

The carrier concentration N_{opt} can be obtained using Drude's theory of dielectrics. The real dielectric constant ε_r , which results due to the contribution from the free carrier electric susceptibility, can be written by the following relation[14]

$$\varepsilon_r = \varepsilon_i - [\frac{e^2}{4\pi^2 c^2 \varepsilon_o}\left(\frac{N}{m^*}\right)]\lambda^2 \quad \text{- - - - - - - - - - - - - - -(3)}$$

where 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_o = 8.85 x 10^{-12} C/N.m^2) and N/m* is the ratio of carrier concentration to the effective mass (m* = 9.10956 x 10^{-31} kg). According to the free electron Drude model, ε_r should be a linear function of λ^2 as it shown in figure (4). The values of carrier concentration N_{opt} for our films are N_{opt}(pure)=1.32*10^{26} m^{-3} , N_{opt}(doped)=1.43*10^{27} m^{-3}.

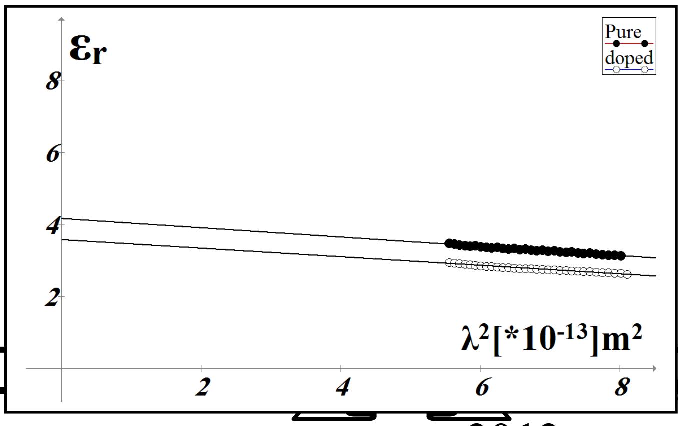
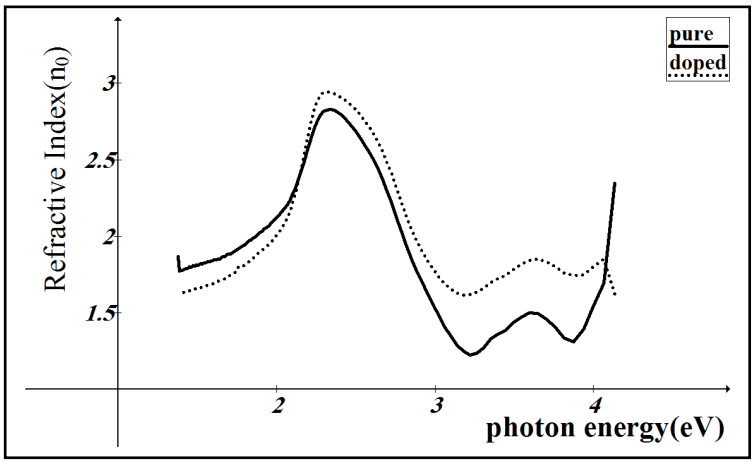


Figure (4) Real dielectric constant vs. $(\lambda)^2$ for CdO thin films.

Figure (5) shows the variation of refractive index with photon energy, in general it increases as a result of doping.



Figure(5) Refractive Index vs. Photon energy.

Figure (6) shows the extinction coefficient (k_0) as a function of photon energy, the behavior of (k_0) is corresponding to that for (α). In general (k_0) decreases with increasing wavelength , and its have high values in spectral region with high absorption coefficients , but its values are small in "transparent" region where absorption coefficients are low ; this behavior refers to direct electronic transitions.[15.]

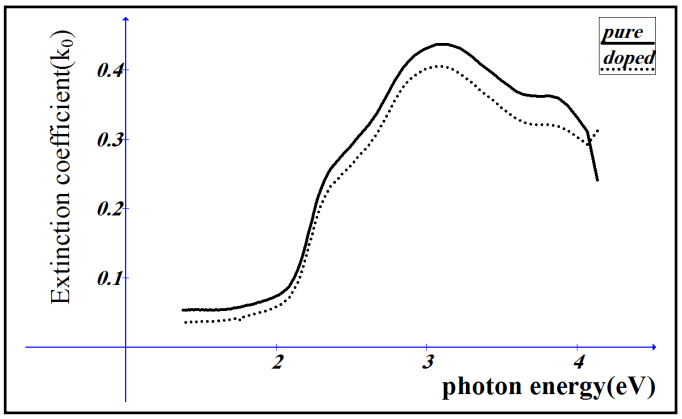
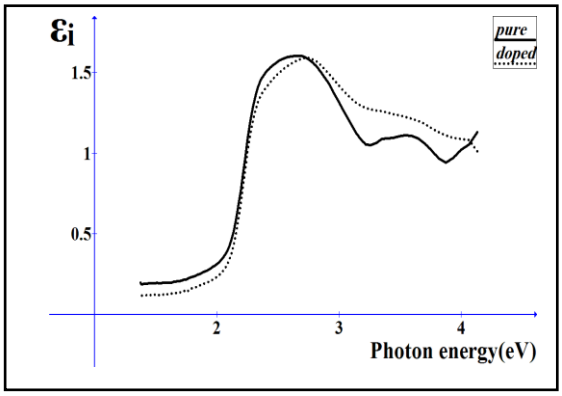


Figure (6) Extinction Coefficient as a function of photon energy

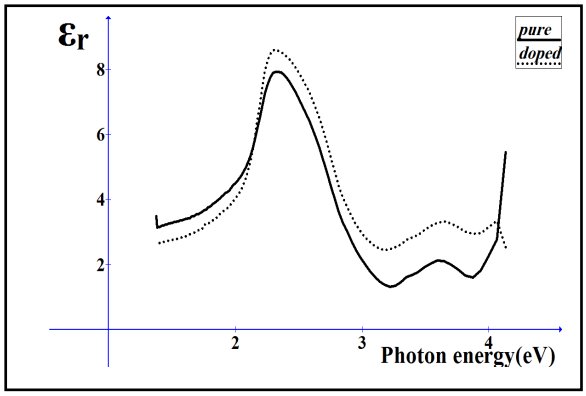
The dielectric function $\boldsymbol{\varepsilon}(\omega)$ describes the response of a material to an electrical field E, this response depends on the angular frequency ω of the field so that its value for high-frequency optical fields ($\boldsymbol{\varepsilon}_{opt}$) is different from the value at low frequency or static fields ($\boldsymbol{\varepsilon}_{st}$). In order to include absorption, the dielectric function is written in complex notation:

$$\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) \quad \text{- - - - - - - - - (4)}$$

with the real part ε_r describing polarization and the imaginary part ε_i describing gain ($\varepsilon_i > 0$) or absorption ($\varepsilon_i < 0$). The variations of dielectric constants with photon energy were determined and shown in figure (7) and (8). The real dielectric constant has a higher value than the imaginary dielectric part, with the imaginary part having a peak at 704nm. The real dielectric peaks at 596nm and appears to have varied slowly till at 632nm.



Figure(7) ε_i versus Photon energy.



Figure(8) ε_r versus Photon energy.

The electromagnetic wave will have amplitude reduced by a factor 'e' after traversing a thickness (called the skin depth χ) [16] , a convenient form used widely is simply the inverse of α: [$\chi = 1 / \alpha$]. Figure(9) shows χ as a function to wavelength,

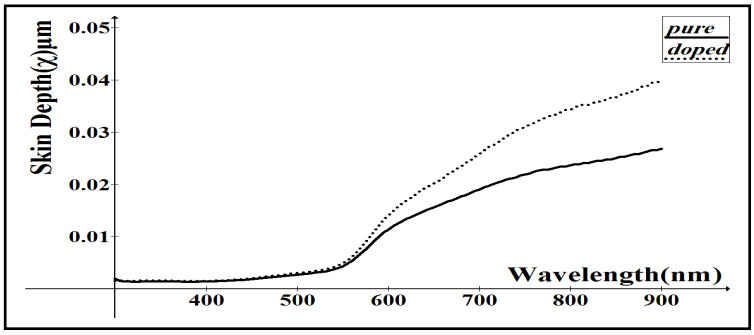


Figure (9) variation of skin depth as a function of wavelength.

In long wavelength greater than absorption edge, skin depth increases with doping, this might be due to decrease the probability of absorption with doping .

The optical conductivity (σ) of the films depends directly on the wavelength (λ) and absorption coefficient (α^2). With the aid of the Drude formula [17] : $\sigma = [\alpha^2 c \varepsilon_o \lambda / 4\pi]$ - - - - - - - - - - - (5)

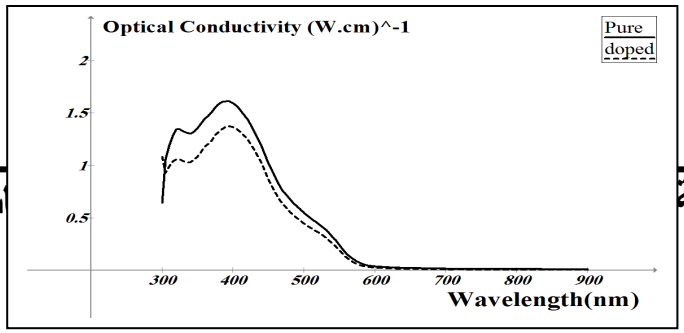


Figure (10) Optical conductivity as a function of wavelength .

From the curves, the effect of doping is decreasing of optical conductivity. All curves show saturation in optical conductivity at visible spectrum.

Conclusions

The actions of doping with doping Fe on CdO thin film are:

- Decreasing the energy gap from 2.491 eV to 2.464 eV ,
- Decreasing the absorption coefficient and extinction coefficient,
- The carrier concentration increases from $1.32*10^{26}$ m^{-3} to $1.43*10^{27}$ m^{-3} for pure and doped films respectively.
- ε_1 has similar trend to the variation of refractive index and
- ε_2 values are related to the variation of α .
- decreasing optical conductivity.

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المستخلص:

رسبت أغشية اوكسيد الكادميوم النقية والمشوبة بالحديد بتركيز 5% على قواعد زجاجية باستخدام تقنية الرش . درست الخصائص البصرية للنماذج بالمدى الطيفي (300 – 900)nm . زاد التشويب من النفاذية البصرية وقلل من الفجوة البصرية من 2.49 الى 2.46 الكترون فولت . معامل الخمود ، معامل الامتصاص ،عمق الاختراق ، معامل الانكسار،التوصيلية البصرية و الجزء الحقيقي والخيالي من ثابت العزل الكهربائي درست وربطت مع التشويب.