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Effect of CO_2 Laser Irradiation on the Optical Properties of Cadmium Oxide Thin Films Grown by Chemical Spray Pyrolysis (CSP) Method

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Abstract: *This paper deals with the effect of CO_2 laser* irradiation *on the optical properties of cadmium oxide (CdO) films prepared by chemical spray pyrolysis (CPS) technique. The films deposited on glass substrate using such as an ideal value concentration of (0.1) M Cd(NO3)2.4H2O at temperature (350°C) ,using 6 spray rate during (10) second for each spray .Transmittance ,absorption, absorption coefficient, optical constants, optical energy gap were recorded in order to estimate these films. The obtained films were exposed to CO_2 continuous laser with energy (2) Watt at interval time (15) sec at (1) meter far from the source, extend of wavelength (300-1100) nm .Results of the (CdO) films reported after irradiation showed on improvement of optical energy gap which is shifted from (2.25) eV to (2.09) eV.*

Keywords: *Thin Films (CdO), CO_2 Laser Irradiation, Optical Properties of (CdO), Chemical Spray Pyrolysis.*

I. Introduction

Transparent conducting oxides (TCOs) thin films hated more attention in recent years because of their applications in semiconductor optoelectronic device technology such as solar cells, photo transistors, diodes, transparent electrodes and gas sensors [1].

In recent years, researchers have focused on Cadmium oxide (CdO) which is one promising (TCOs) from II to VI group of n- type semiconductors. CdO is a transparent in visible and NIR spectra region , its characteristics of a direct band gap of 2.3 eV and indirect band gap of 1.36 eV and a high electrical conductivity (10.2 -10.4 Ω-cm) [2,3].

A variety of techniques have been reported to prepare CdO using different techniques such as sol- gel, Dc magnetron sputtering, radio - frequency sputtering , spray pyrolysis ,chemical vapor deposition, chemical bath deposition, and pulsed laser deposition [4-9].

Some recent studies [10-18] showed the effects of irradiation on the optical and structural CdO thin films properties.

In the present work, we report results of investigations carried out in order to study the effect of optical properties (reflectance, refractive index, dielectric constant, optical bandgap) of CdO thin films before and after of CO_2 laser irradiation at time (15) sec.

II. Experimental

2.1 SAMPLE PREPARATION

In order to prepare CdO thin films, CdO solution with an ideal concentration of an a aqueous solution (0.1)M of Cd(NO3)2.4H2O was prepared by dissolving it in water and resulting mixture was stirred at room temperature for 15 minutes to prepare CdO films separately as following:-

$$Cd(NO_2)2.H_2O \rightarrow CdO + 2NO_2 + O_2 \quad \ldots\ldots(1)$$

Obtained CdO solution was deposited on glass substrates (26*76*1) mm using chemical spray pyrolysis technique. The glass substrates were cleaned with acetone and then in ethanol for 20 minutes. The slides were removed from the ethanol and dried with special paper at room temperature. The spray pyrolysis was achieved and designed glass atomizer, which has an output nozzle about 1 mm.

The CdO films were deposited on preheated glass substrate using (0.1)M concentrations of Cd(NO3)2.4H2O with a total volume of 100 ml was used for each deposition, under the optimization parameters : spraying rate 6 spraying within 10 sec, the carrier compressed air was maintained at a pressure of (1.2 bar) , distance between nozzle and substrate about 30 cm.

2.2: CHARACTERIZATION

Optical transmittance and absorbance were recorded in wavelength range (300-1100) nm using UV-Visible spectrophotometer (UV/VIS 1800 Shimadzu). In order to study the influence of the radiation on the optical properties of obtained samples of CdO films , a 2 Watt CO_2 laser was used at irradiation time (15) sec and at (1) meter far from the source.

2.3: OPTICAL ABSORPTION

The main optical absorption process responsible for electron transitions in semiconductors; are inter–band transitions, and transitions via impurities or lattice defects, when the light incident on a semiconductor sample, if the energy of the individual photons is greater than the semiconductor band gap, then the photons can be absorbed, transferring their energy to an electron. This process as illustrated in "Fig.1" elevates the electron from the valence band into conduction band. The absorption process therefore creates an electron-hole pair (EHP), because it results an electron in the conduction band, and a hole in the valence band [19].

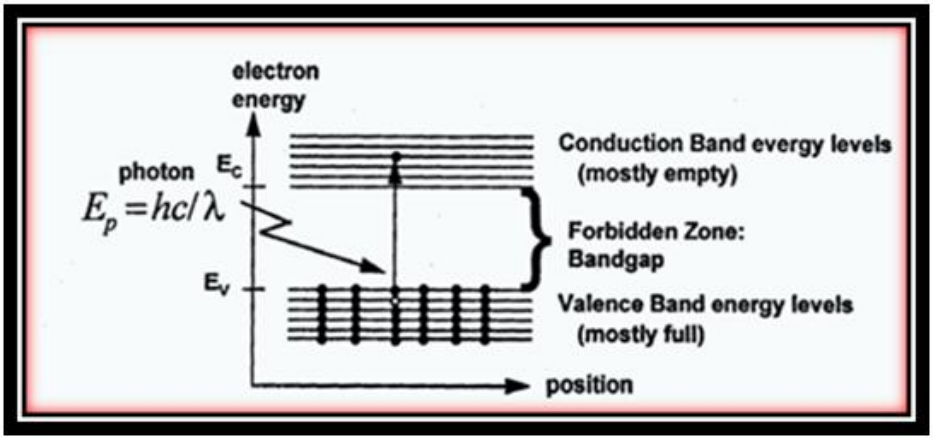

Fig.1: Optical absorption in a semiconductor [19].

The fundamental absorption refers to the band transition i.e. the excitation of an electron from the valence band to the conduction band .Electromagnetic waves interact with electrons in the valence band and they excite them into the conduction band [20].

The percentage of incident light absorbed by a particular semi-conductor depends on the transition probability of electron between the valence band and the conduction band. The fundamental absorption edge is divided into three distinct areas, as shown in "Fig.2"**.**

- High absorption region: the absorption coefficient value in this area is about ($\alpha \geq 10^4$ cm^{-1}) and obeys tauc equation.
- Exponential region: the absorption coefficient value in this area is about ($1 < \alpha < 10^4$ cm^{-1}) and obeys urbach equation.
- Low absorption region: the absorption coefficient value in this area is about
- ($\alpha < 1$ cm^{-1})[21].

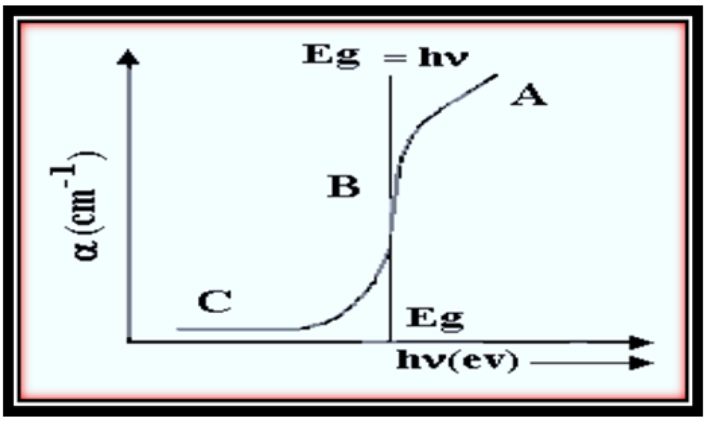

Fig. 2: Areas of absorption edge.

A- High absorption region. B- Exponential region. C- Low absorption region [21].

2.3: OPTICAL BANDGAP

Near the absorption edge the absorption coefficient can be expressed as:

$\alpha h\nu = A^* (h\nu - E_g)^{1/2}$ ……..(2)

For direct transition. Taking the square for both sides of the equation:

$(\alpha h\nu)^2 = A^*(h\nu - E_g)$ ……. (3).

At the point $\{(\alpha h\nu)^2 = 0\}$, $E_g = h\nu$ which achieve energy conservation law as in the following equation

$h\nu = E_i - E_f$ …… (4).

Where E_i = Primary energy level and E_f = Final energy level [22].

2.4: OPTICAL CONSTANTS

The optical behavior of material is generally utilized to determine its optical constants, the quantity (n, k) are collectively called optical constants of the solid, where n is the refractive index and k is the extinction coefficient [23].

In this study, the reflection, transmission and absorption of CdO thin films have made it possible to determine the optical constants conveniently. The optical absorption is described by an absorption coefficient (α), which can be derived from transmission measurement .If I_o is an incident light intensity, which is coupled into the sample, the transmitted light intensity that leaves the sample of thickness t is given by [24].

$$I = I_o \frac{(1-R^2)exp(-\alpha t)}{1-R^2\, exp(-2\alpha t)} \quad \text{..... (5).}$$

Where R is the reflectivity and α is the absorption coefficient. For large (αt), near the absorption edge $1\text{-}R^2\, exp(-2\alpha t) \approx 1$.That is, $R^2 \exp(-2\alpha t)$ is much less than unity. Then "equation 5" can be reduced to:

$I = I_o (1-R^2) \exp(-\alpha t)$ ……. (6).

The following relation which expresses the idea that all the incident power is either, reflected, absorbed or transmitted and can be utilized [25].

$R+A+T=1$ …… (7).

For unpolarized light at normal incidence (perpendicular) to a surface the fraction of light reflected is given by [19].

$$R = \frac{(n-1)^2}{(n+1)^2} \quad \text{…… (8).}$$

Eq. (8) can be rewritten for n, one gets:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad \text{…… (9).}$$

In the absence of reflection "equation 6" expressed by Lambert law [26] as:

$I = I_o e^{(-\alpha t)}$ …… (10).

The ratio of I/I_o is called the transmittance T, then $T=e^{(-\alpha t)}$,

$$ln = \frac{1}{T} = \alpha t \quad \text{…… (11).}$$

Converting equation this one gets:

$$2.303 \log\left(\frac{1}{T}\right) = \alpha t \quad \text{……(12)}$$

The absorbance (A), then is defined as logarithm (base 10) of the reciprocal of transmittance T;

$A = -\log(T) = \log(1/T)$, Then

$$\alpha = 2.303 \left(\frac{A}{t}\right) \quad \text{…… (13).}$$

2.5: EXTINCTION FACTOR DETERMINATION

A wave propagating in z direction with a frequency (υ), can be described by [27]:

$$E = E_o e^{[i2\pi\nu\left(t-\frac{z}{v}\right)]} \quad \text{…… (14)}$$

The velocity of propagation through a semiconductor having a complex index of refraction $n_c = n\text{-}ik$ is related to the velocity of propagation in vacuum (c), by $v = c/n_c$, therefore:

$$\frac{1}{v} = \frac{n}{c} - \frac{ik}{c} \quad \text{…… (15).}$$

Substituting "equation 15" into "equation 14" one gets

$$E = E_o e^{(2i\pi\nu t)} e^{(-2i\pi nz/c)} e^{(-2\pi\nu kz/c)} \quad \text{..... (16).}$$

Note that the last term is damping factor. The fraction of incident power is available after propagation a distance z through a material

$\frac{p(z)}{p(0)} = e^{(-4\pi vkz/c)}$ ..... (17).

The reduction of power on passing through a thickness z is often described by the absorption coefficient

$\frac{p(z)}{p(0)} = e^{(-\alpha z)}$ ..... (18).

By comparison "equation 18" and "equation 17" it's seen that α and k are related by

$\alpha = \frac{4\pi vk}{c} = \frac{4\pi k}{\lambda}$ ..... (19).

Or $k = \frac{\alpha\lambda}{4\pi}$ ..... (20).

Where k is imaginary part of n, it is called the extinction coefficient.

2.6: DIELECTRIC CONSTANTS

Dielectric constants represent material susceptibility to polarization, as well as represent a material response to different frequencies with complex behavior, when the optical frequency represented by optical wave electronic polarization will be the dominate, the interaction between light and medium charges, and the resulting polarization of medium charges usually described by the complex dielectric constant of the medium, which is expressed in the following equation

$\varepsilon = \varepsilon_1 + i\varepsilon_2$ ..... (21).

Where (ε) Dielectric constant, (ε_1) and (ε_2)Real and imaginary part of dielectric constant respectively. The dielectric constant could be calculated by the calculation of refractive index, the relation between complex dielectric (ε)constant and complex refractive index (N) is shown below:-

$\varepsilon = N^2$ ..... (22).

Note that N=n-ik ..... (23)

From "equations 21, 22 and 23" we get

$\varepsilon_1 - i\varepsilon_2 = (n-ik)^2$ ..... (24)

Finally real and imaginary parts of dielectric constant could be written from "equation 27" as:

$\varepsilon_1 = n^2 - k^2$ ..... (25).

$\varepsilon_2 = 2nk$ ..... (26).

Where ε_1 and ε_2 are real and imaginary part of dielectric constants respectively, where dielectric loss tangent could be calculated from equation below [28]:

$\delta = \varepsilon_2/\varepsilon_1$ ..... (27).

III. Result And Discussion

3.1: THE OPTICAL SPECTRUM OF CdO FILMS

"Fig.3" shows the optical absorbance A of CdO films variation before and after irradiation of laser CO_2. Further observation shows that the absorbance of the CdO films increases after irradiation of laser CO_2. This is probably ascribed to the increase of particle sizes and surface roughness. Furthermore, the absorption edges of the CdO films have a small shift with increasing of laser irradiation. There are two possible factors resulting in the red shift of absorption edge. One is that the increase of crystalline size can cause red shift of absorption edge.

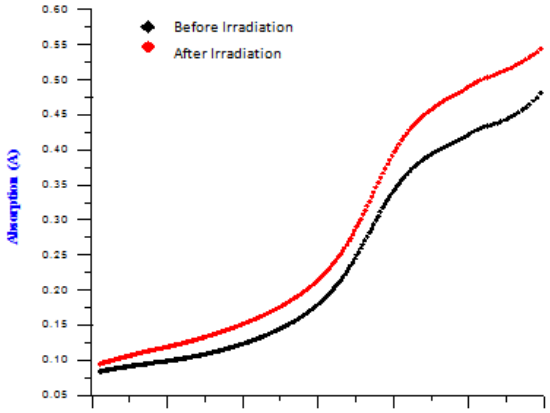

Fig.3: The Optical Absorption Spectra A of (CdO) Thin Films with photon energy before and after irradiation CO_2.

"Fig.4" shows the variation of absorbance coefficient α with photon energy (eV) for CO_2 laser irradiated CdO samples. The calculated values of absorption coefficient are in order of 10^4 cm^{-1}. It is seen that the absorbance coefficient increases with the photon energy. In the range of more than 2.8 eV the absorbance coefficient increases rapidly after exposure sample at 15 sec with CO_2 laser.

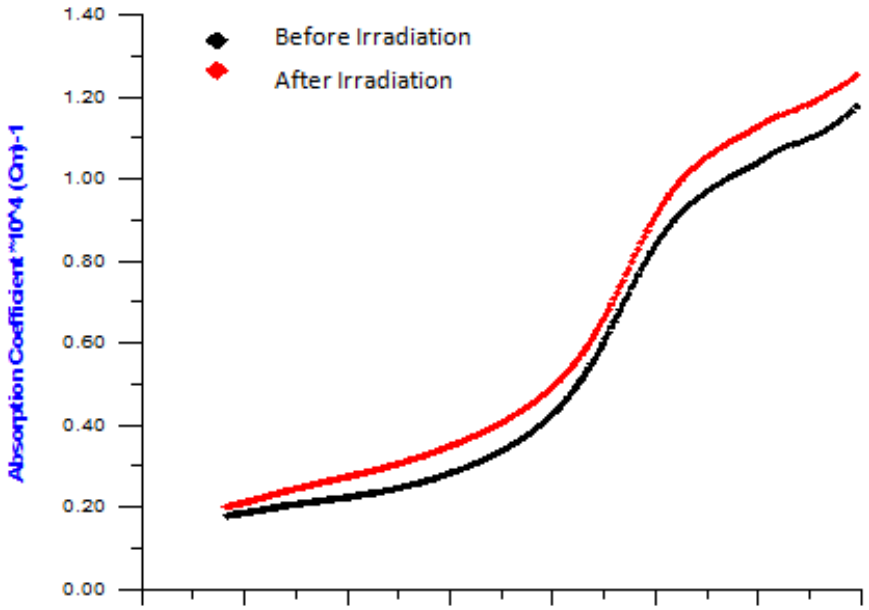

Fig.4: Variation of absorption coefficient with photon energy of (CdO) Thin Films before and after irradiation

"Fig.5" shows the typical transmission spectra in wave length range 400- 1800 nm for the CdO films in the study before and after irradiated CO_2 laser.

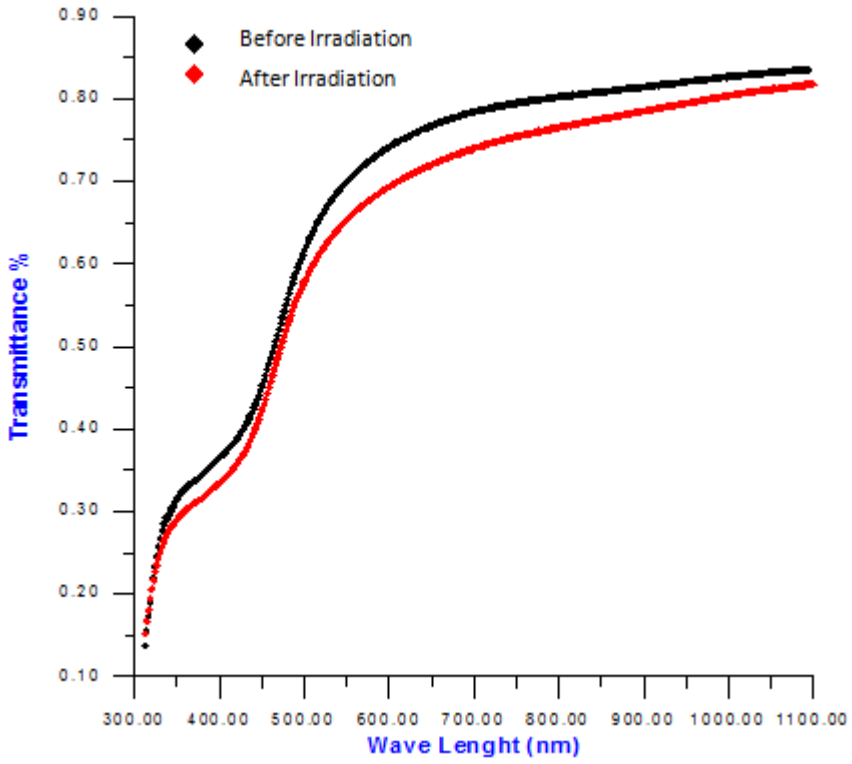

Fig.5: Effect of the CO_2 laser treatment on the optical transmittance for CdO thin Films before and after irradiated samples.

"Fig.6" shows the dependence of refractive index of CO_2 laser irradiated CdO films on photon energy. The refractive index of all samples lies between 1.6 and 2.78. It is seen that the refractive index is rises rapidly up to 2.75 eV of photon energy. Refractive index increases with CO_2 laser irradiation on the CdO films; this is due to the major contribution of electronic transition for interval (15 sec) of CO_2 laser irradiation and this may leads to a significant change in the optical parameter [18].

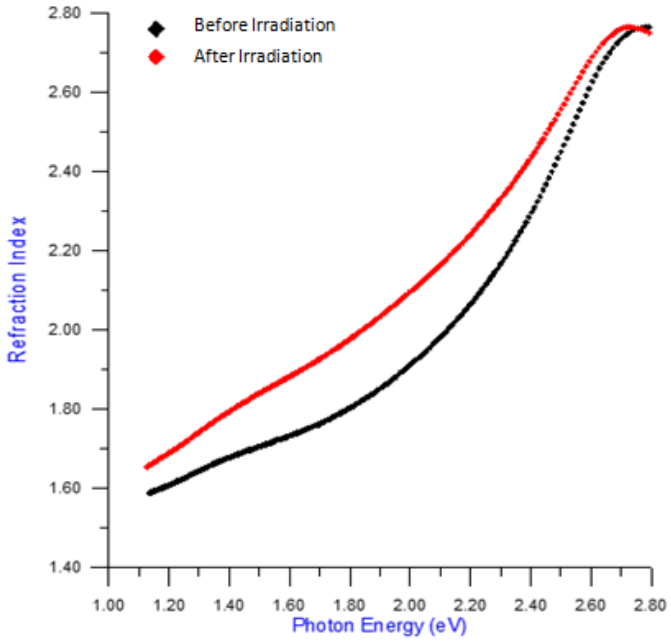

Fig.6: Variation of refractive index n as a function of photon energy of (CdO) Thin Films before and after irradiation CO_2.

"Fig.7" shows the variation of extinction coefficient k with the photon energy incidence on the CdO films before and after irradiation on CO_2 laser. It is clear that the values of k changed in the range 0.0138-0.0169 and the values of k increases with increasing in photon energy. The lower value of extinction coefficient represents samples possessing high transmittance.

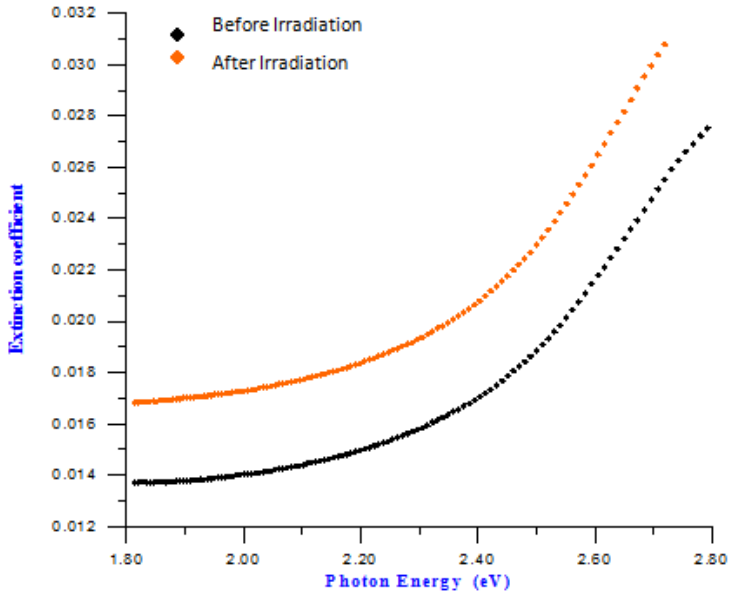

Fig.7: Extinction coefficient k variation with the photon energy of (CdO) thin films before and after irradiation CO_2 laser.

The variation of ε_1 and ε_2 values of CO_2 laser irradiated CdO samples with incident photon energy is shown in "Fig.8 A, B". It can be seen the real part dielectric constant ε_1 is less < 2.2 eV, then it start increasing with increasing photon energy as shown in "Fig.8 A" , and this spectral variation of $\varepsilon_1$is quite similar to those of refractive index. This characteristics of low dielectric constant that the sample possesses optically quality with lesser defects and this parameter is highly important to making optoelectronic materials. This is an expected situation due to small value of extinction coefficient which is contribute the value of ε_1."Fig.8B" shows an imaginary part of the dialectic constant ε_2. The real and imaginary part values increases obviously after irradiation of CO_2 laser which is good contribution to dielectric constants.

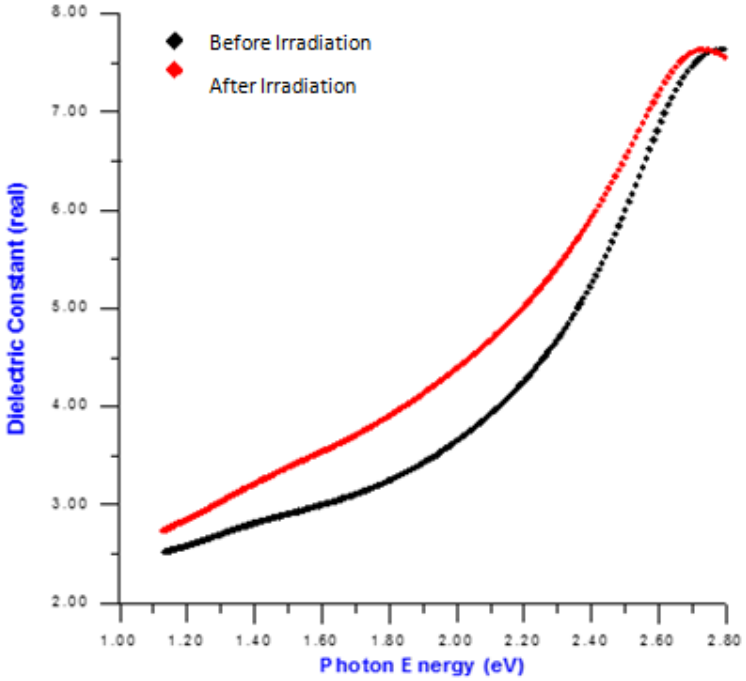

Fig.8 A: The variation of real part of dielectric constant $\varepsilon_1$with photon energy of samples of (CdO) Thin Films before and after irradiation CO_2.

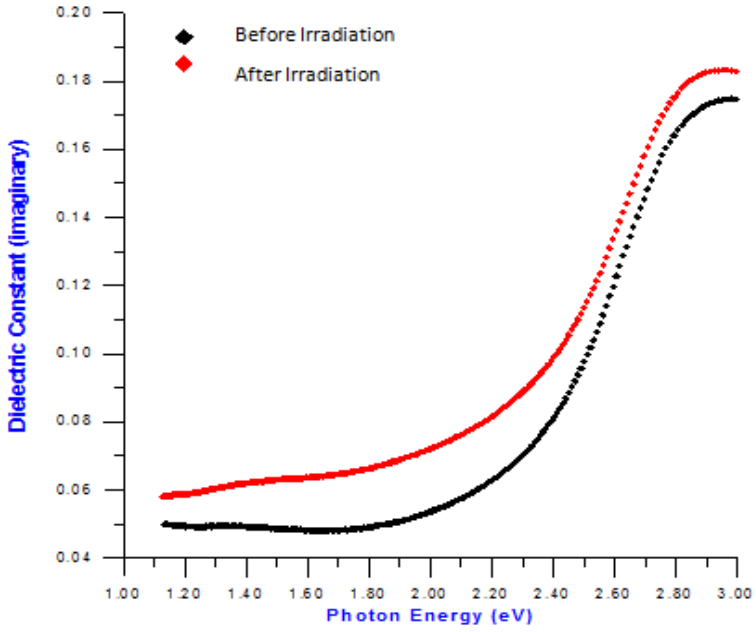

Fig.8 B: The variation of imaginary part of dielectric constant $\varepsilon_2$with photon energy of samples of (CdO) Thin Films before and after irradiation CO_2.

3.2: OPTICAL ENERGY GAP

The optical energy gap values (E_g^{opt})for (CdO) films before and after irradiation of CO_2 laser have been determined by plotting the relation of [$(\alpha h\nu)^2$] versus $h\upsilon$ (eV)] for direct energy gap as shown in "Fig.9" .The direct bandgap values were determined by extrapolating the linear portions of these graphs to the energy axis at $(\alpha h\nu)^2$. The films exhibited a reduction in the energy optical gap, it is decreased from 2.25 eV to 2.09 eV after CO_2 laser irradiation of at 15 sec of CdO films. The shift of optical energy can be explained in terms of quantum-size effect in which the film with large crystallites [29], thus resulting in an improvement in crystalline of CdO films and so the density of localized states decreases.

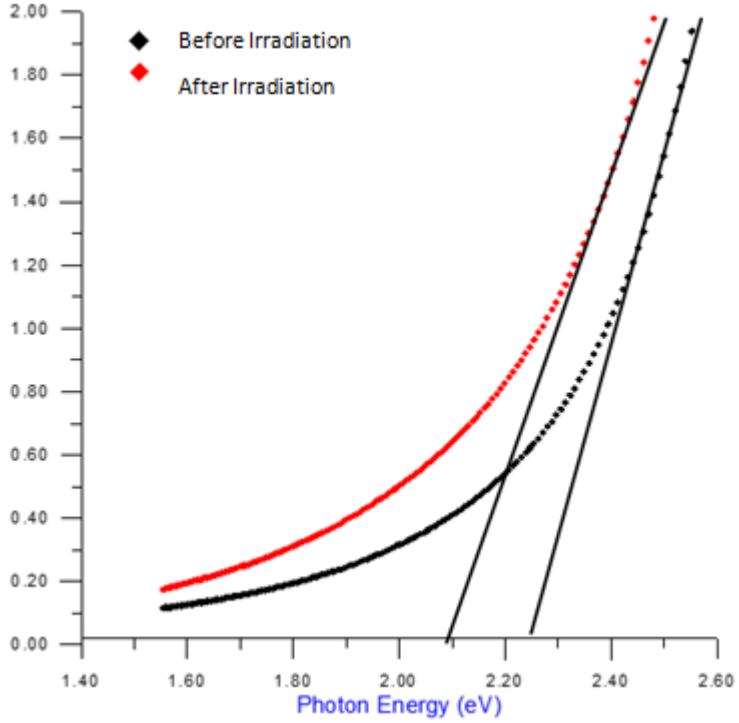

Fig.9: plotting of $(\alpha h\upsilon)^2$ as a function of the photon energy for CdO films before and after (15 sec) irradiation of CO_2 laser.

IV. Conclusions

Optical analysis of CdO films show that the chemical pyrolysis technique is a useful method for the deposition of CdO films. The effect of CO_2 laser irradiation on the optical properties has been investigated. The optical transmittance of CdO films have small decrease after CO_2 laser irradiation. The measured absorbance and reflectance of the CdO films were post irradiated at laser CO_2 within time 15 sec were plotted, it was found that the properties deteriorates, both the absorbance and reflectance increases while the transmittance decreases due to irradiation increase the regularity of the internal arrangement of the atoms and reduce structural defects, or could be explained by the increased surface roughness of the deposited CdO films. Good variation of bandgap values has been observed.

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