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Effect of CO_2 Laser Irradiation on the Topographic and Optical Properties of CdO Thin Films

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Abstract:

In this study, cadmium oxide (CdO) was deposited on glass bases by thermal chemical spraying technique at three concentrations (0.05, 0.1, 0.15) M and then was irradiated by CO_2 laser with 10.6 µm wave length and 1W power. The results of the atomic force microscope AFM test showed that the surfaces of these CdO thin films were homogenous and that the laser irradiated effect resulted in decreasing the roughness of the surface as well as the heights of the granular peaks, indicating a greater uniformity and homogeneity of the surfaces. The optical properties were studied to determine laser effect. The results of optical tests of these thin films showed that the photoluminescence spectra and absorption shifted towards longer wavelengths with increased concentration, and the transmittance was high at high wave lengths. There was a decrease of energy gap values at (0.05, 0.15)M concentrations which were (2.1, 2.25)eV receptively, and an increase in the energy gap value at 0.1 M concentration which was 2.55 eV, and other optical properties have been studied in this paper .In general, we observe that the values of the optical constants of the concentrations (0.05, 0.15)M increase after laser irradiation and are lesser after irradiation at concentration 0.1 M.

Key words: CdO thin film, CO_2 laser, Laser irradiation, Optical properties, Topographic.

Introduction:

Laser materials treatment, such as laser irradiation process (1,2), is considered as important industrial applications which have been studied in several researches and still in continuous work out (3). Laser absorption of material affects the temperature distribution which influences the thermal stress development and the final quality of parts (4). Different lasers have been used for this purpose, including carbon dioxide (CO_2) laser (5).

A major development occurred in the production and investigation of the physical properties of transparent conducting oxide (TCO) materials due to their electrical and optical properties such as low resistivity and high optical transmittance, and have great importance in the semiconductor, electronic and optoelectronic devices (6,7). One of (TCO) materials is cadmium oxide (CdO) (8,9) which has received considerable attention mainly due to its important potential applications (7,10,11), which include photovoltaic solar cells, gas sensors, transparent electrodes, and other optoelectronic devices, which have low resistivity and high optical transmittance (11). CdO is defined as an inorganic compound, and found in nature in two formulations crystalline and random, its crystalline formula is of a brown or red color, while its synthetic formula is colorless (12). A variety of techniques have been reported to prepare CdO using different techniques such as sol- gel, pulsed laser deposition (8), Dc magnetron sputtering, radio - frequency sputtering, spray pyrolysis, chemical vapor deposition and chemical bath deposition (9,13,14,15). In this research, chemical spray pyrolysis method was used to prepare CdO thin films, whose system consists of (spray nozzle, electrical heater, potential divider, thermocouple, air pump and the system heating air), and there are several factors that have an effect on the homogeneity of thin films ,they can be summarized as follows: the vertical distance between the end of the capillary tube in the spray device and the glass base placed on the electric heater, substrate temperature, pyro lysis rate, pyrolysis time, air pressure and substrate position.

The surface topography of thin films differs from one sample to another due to the effect of the preparation conditions and the chemical spray pyrolysis (CSP) method. Many factors directly affect the surface nature of thin films including

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spraying period, spray rate, base temperature, the vertical distance between the nozzle of the device and the base and air pressure.This is because the surface nature of thin films directly affects the optical and structural properties of thin films prepared (16).

It is possible to use the material whatever form and whatever the quality of chemical composition is, fluoridation does not cause any damage or change in the composition of the subject matter of the study, this makes the measurement method be used in the analysis of precious metals and jewelry. The importance of fluoridation methods is apparent when analyzing a heterogeneous body because it is possible to analyze simple parts of the material (17).

The objective of this research is to use laser beams to improve some of the topographic and optical properties of cadmium oxide thin films prepared by one of the common methods: chemical thermal spraying method, topographic and optical tests using atomic force microscope and uv - visible spectroscopy, as well as the use of fluorine technology.

Materials and Methods:

Cadmium oxide thin films were prepared in a thermal chemical spraying method using ($Cd(NO_3)_2.4H_2O$), a solid white powder substance with a molecular weight of 308.47 g/mole and 99.9% purity, and the solution was prepared with three concentrations: (0.05, 0.1, 0.15)M. The required weight of the material was dissolved in distilled water using the stirrer magnetic to ensure that the material was completely dissolved in the distilled water. A homogeneous solution of cadmium oxide was obtained at laboratory temperature and then it was kept in a volume vial for 24 hours to ensure there was no sediment, in order to ensure full compliance. When the solution was sprayed on the glass bases and with the heat, the cadmium oxide was deposited on the surface of the base according to the reaction:

$$Cd(NO_3)_2.4H_2O \longrightarrow CdO + 2NO_2 + O_2 \; \ldots\ldots 1$$

Thin films are prepared on thin glass bases, which have been cleaned using water, ethanol and then acetone. CdO thin films have been deposited on these glass substrate by the chemical spray pyrolysis method under the optimization parameters: spraying rate 6 within 10 sec, carrier compressed air was maintained at a pressure of 1.2 bar, distance between nozzle and substrate about 30 cm, and Fig1, show the chemical spraying system.

The prepared CdO thin films were cut into three pieces and exposed to the CO_2 laser beam whose spot diameter is 0.5 cm with 10.6 µm wave length and 1W power. The samples were placed within 1 m of the laser output, and then the examined sample was taken for the area exposed to radiation, to determine the laser effect on its topographic and optical properties.

Atomic force microscope AFM type AA 3000 SPM was used to study the topography of the surfaces of the prepared thin films, and the spectral properties of these thin films are measured by spectral florescence and absorption, where the fluorine spectra were obtained by using Pl spectroscopy, and UV–Visible Spectrophotometer was used to perform optical measurements before and after laser irradiation, where the device of the two-beam type, one passes through the thin film to be measured visually, and the other passes through the glass slide in the window reference.

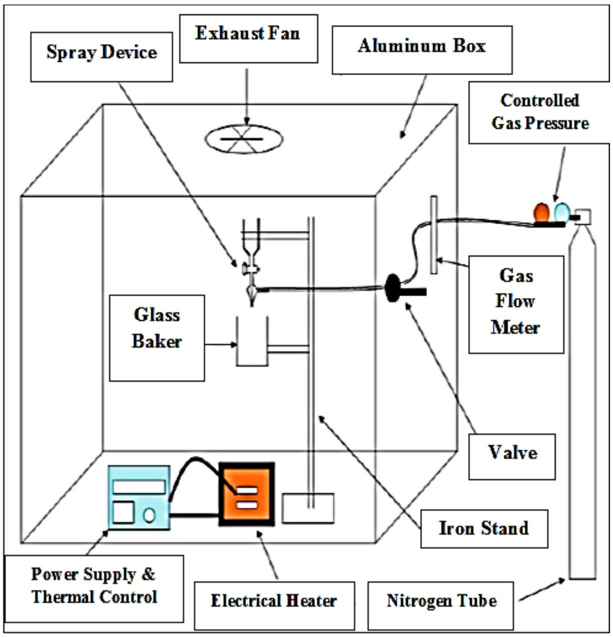
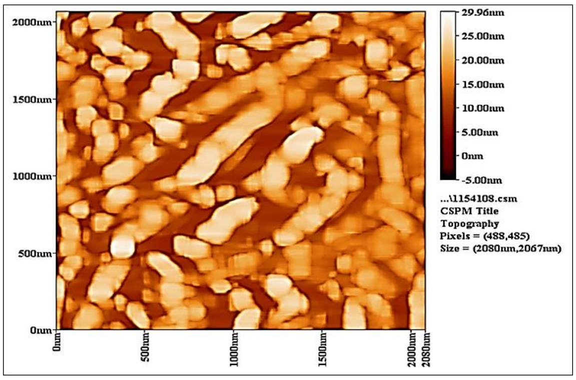


Figure 1. Chemical Spraying System (12)

Results and Discussion:

Thin Films Surface Topographic

The surface roughness rate of CdO thin films and the square root mean average were obtained from the topography of the roughness of the two-dimensional 2D surfaces. The three-dimensional 3D surface thickness of the thin films (the highest crystalline granular peaks on the surface) was obtained from 3D images. The rate of particle size of the thin films was obtained from the graphs of the distribution of granular aggregates formed on the surfaces of the thin films. The planned graphs show how the size of granular aggregates is distributed on the surfaces of the thin films by certain percentages.



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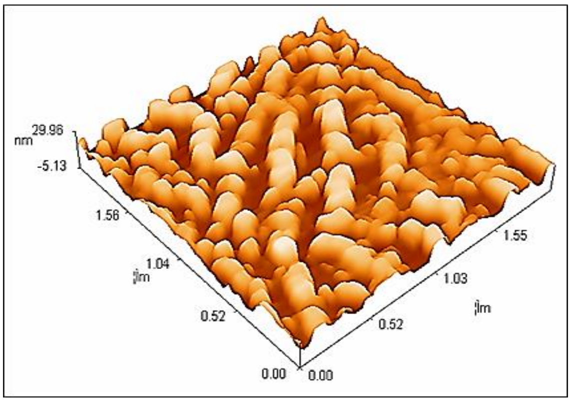

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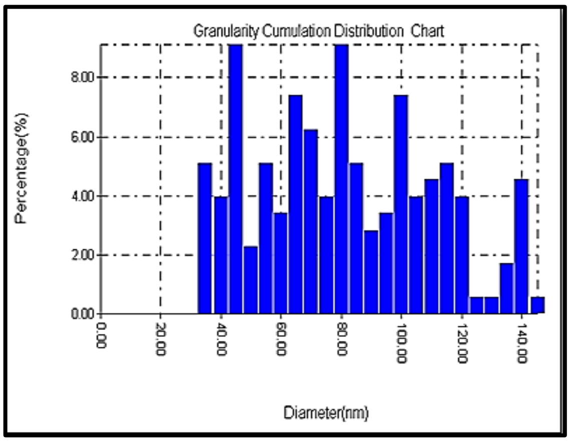

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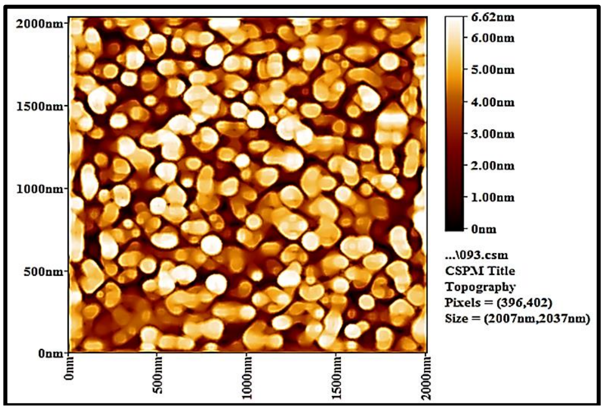
Figure 2. Topographic surface of CdO thin films at (0.05 M) concentrations before laser irradiation:(a)2D, (b)3D, (c)distribution of particle size



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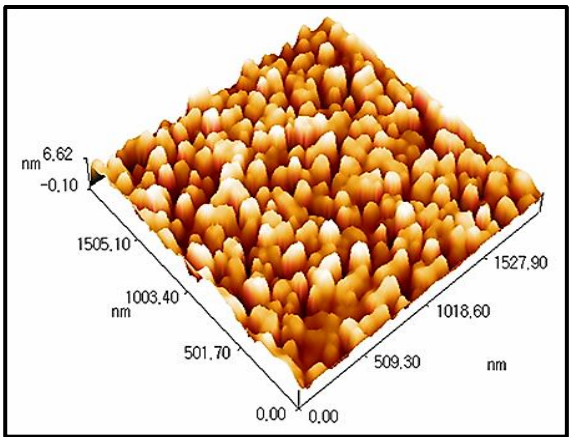

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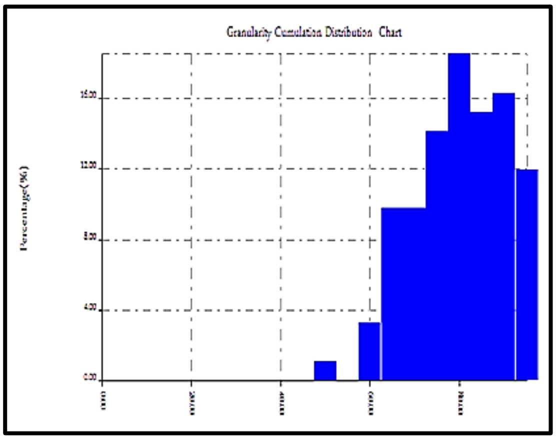

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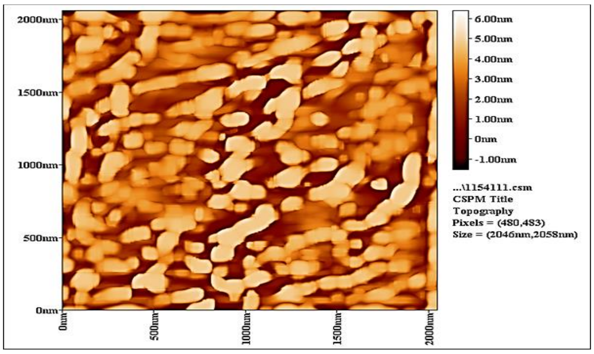
Figure 3. Topographic surface of CdO thin films at (0.05 M) concentrations after laser irradiation:(a)2D, (b)3D, (c)distribution of particle size



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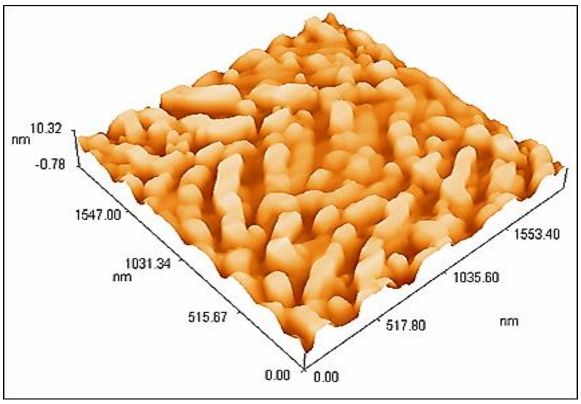

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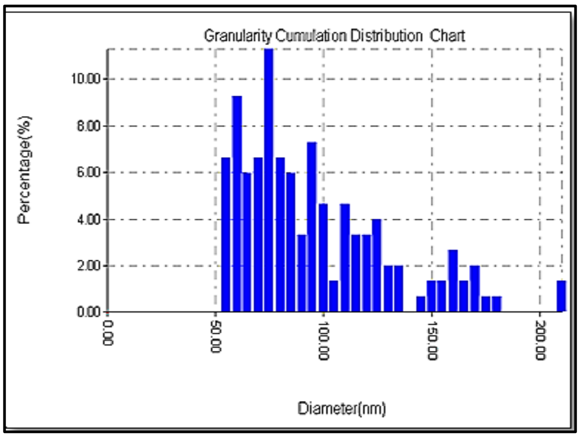

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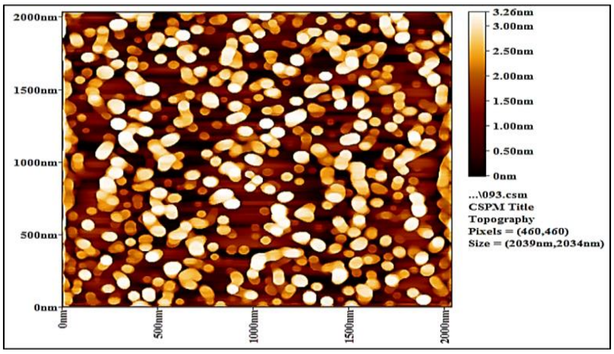
Figure 4. Topographic surface of CdO thin films at (0.1 M) concentrations before laser irradiation:(a) 2D, (b) 3D, (c) distribution of particle size

Figures 2, 4 and 6, show that all thin films (before irradiation) are homogeneous and that the material is spread almost evenly on the floors, and increased surface roughness is also observed. The effect of the laser irradiation on these surfaces is shown in Figs 3, 5 and 7, which resulted in a decrease in the roughness and average square root of the surfaces granular. This indicates the homogenization of the crystalline growth of the thin films surfaces after laser irradiation in general



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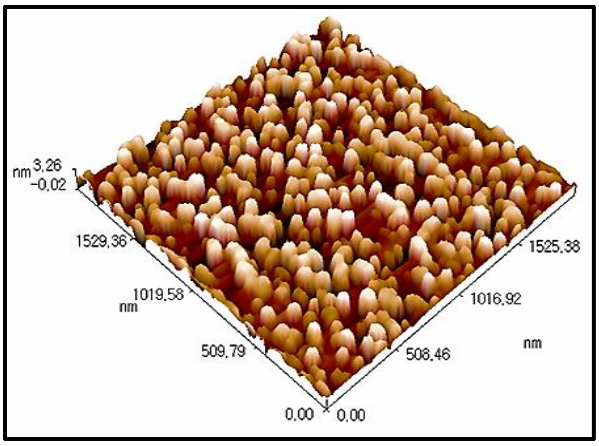

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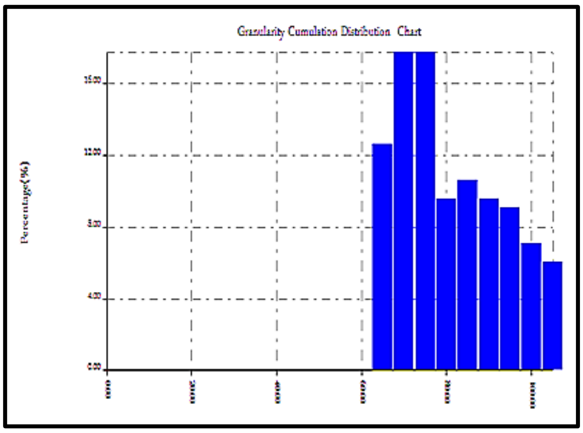

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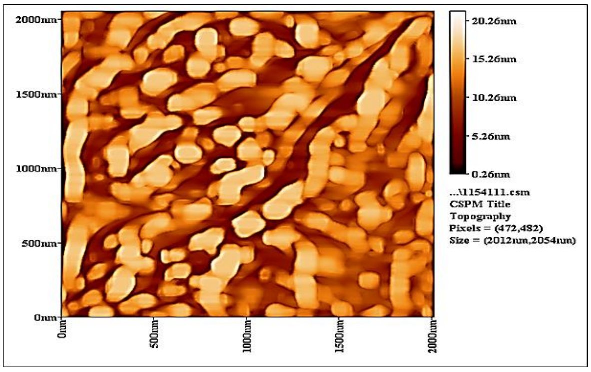
Figure 5. Topographic surface of CdO thin films at (0.1 M) concentrations after laser irradiation:(a) 2D, (b) 3D, (c) distribution of particle size



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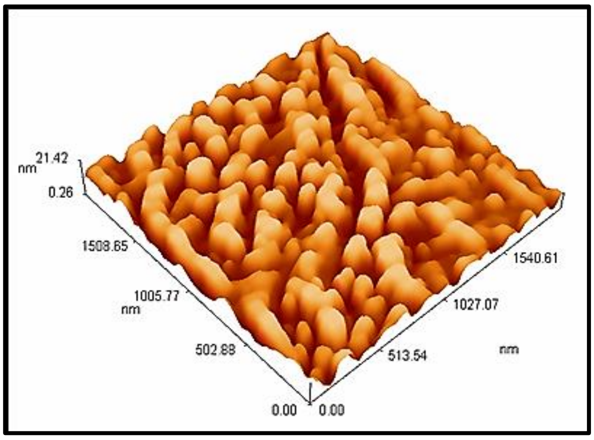

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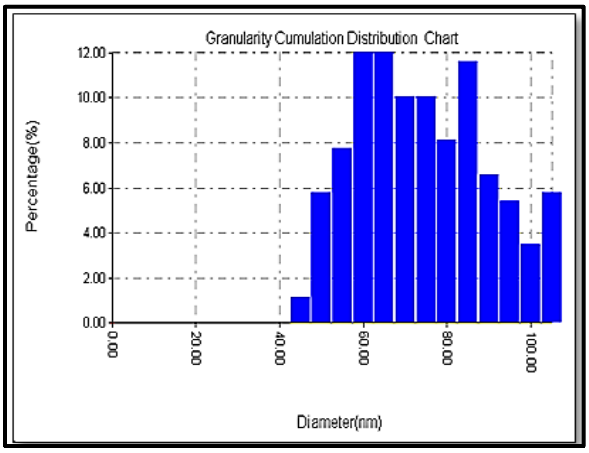

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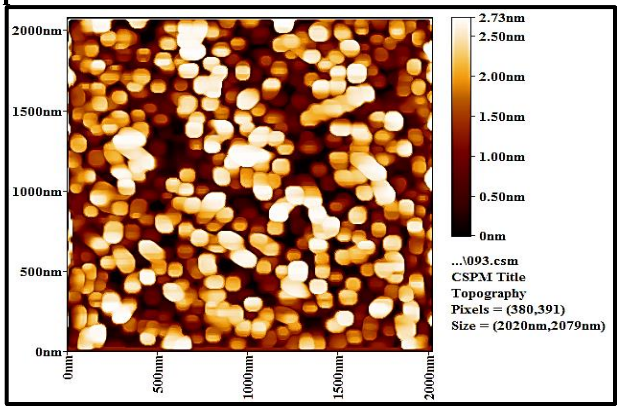
Figure 6. Topographic surface of CdO thin films at (0.15M) concentrations before laser irradiation:(a)2D, (b)3D, (c)distribution of particle size



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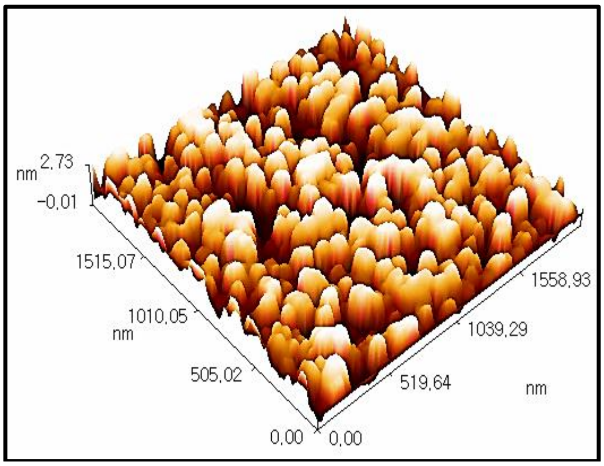

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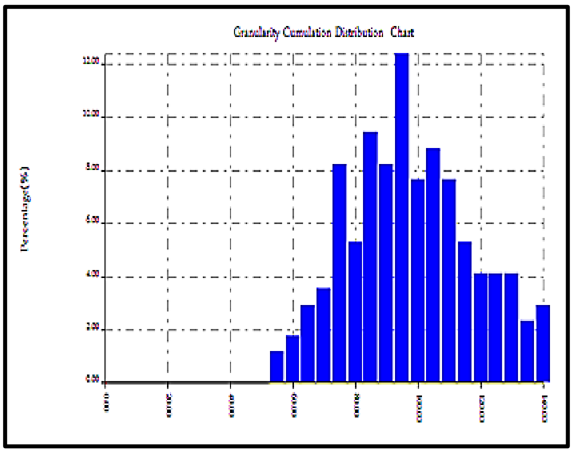

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Figure 7. Topographic surface of CdO thin films at (0.15 M) concentrations after laser irradiation: (a) 2D, (b) 3D, (c) distribution of particle size

Thin Films Optical Properties

Absorbance, Transmittance & Reflectivity:

Irradiation by CO_2 laser led to an increase in the absorbance values (A) of CdO thin films in both (0.05, 0.15)M concentrations compared to their pre-irradiation values consistent with the reference (11), this is probably ascribed to the increase of particle sizes and surface roughness. While at 0.1 M concentration it starts high and then decreases especially at high wave lengths as we see in Fig 8, it was found that the absorption edge shifts towards higher energies (shorter wavelengths), the figure demonstrates that the absorbance decreases due to the increasing optical absorption and the increasing attenuation of incident beam. In contrast, the transmittance values (T) were shown to decrease in both (0.05, 0.15)M concentrations, and in 0.1 M it starts low and then increase especially at high wave lengths on the contrary of absorbance behavior, that is clear in Fig 9. While Fig 10, show us the reflectivity (R) spectrum of both (0.05, 0.15)M concentrations that we find that the values start less than their values before irradiation and then rise at high wavelengths, and at 0.1 M the reflectivity values start higher than their values before irradiation and then begin to decrease at high wavelengths. In general, the reflectivity is low at the energies regions which are lower than the energy gap (E_g) and the peak reflected in the reflectivity curve corresponds to the value of the energy gap.

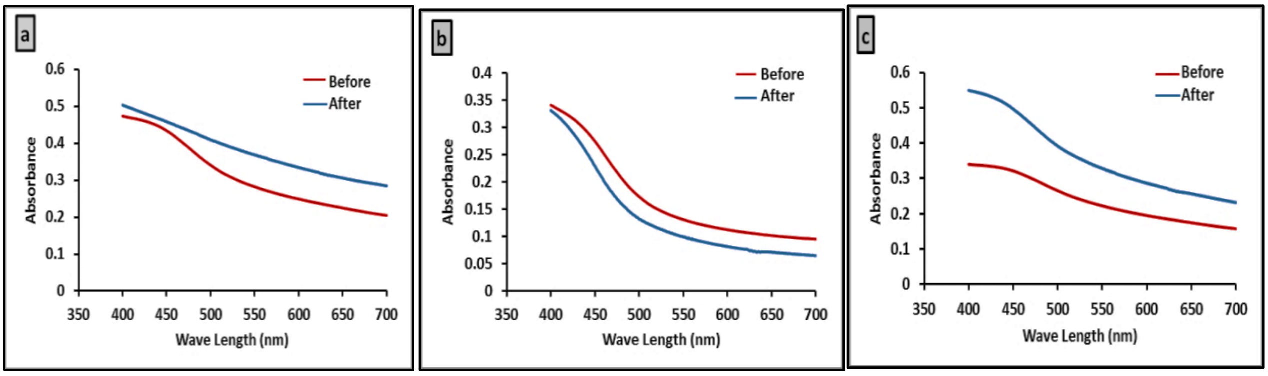

Figure 8. Absorbance spectrum of CdO thin films at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

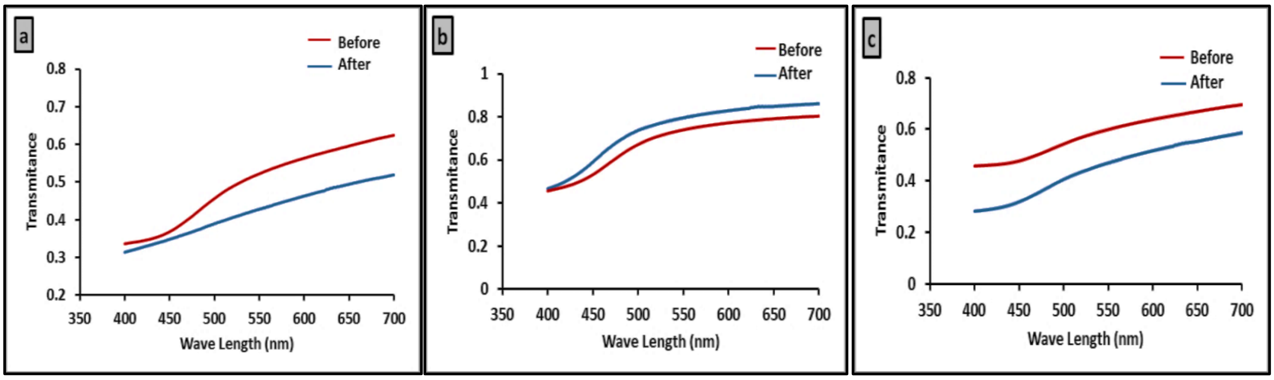

Figure 9. Transmittance spectrum of CdO thin films at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

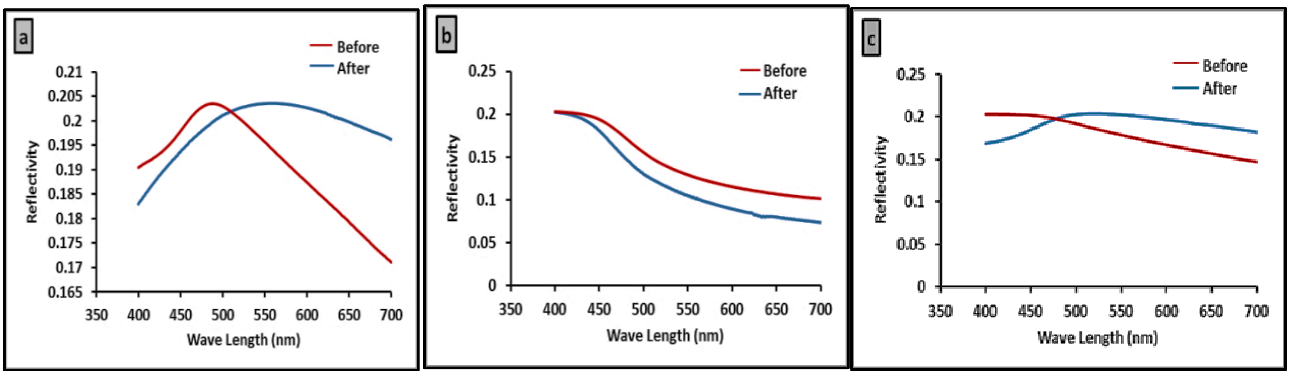

Figure 10. Reflectivity spectrum of CdO thin films at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

The Optical Constants:

Fig 11 clarifies the changes in the values of the absorption coefficients (α) of CdO thin films with change of wavelength, it shows a behavior that is similar to the absorption spectra, and this coefficient was obtained by (18):

$$\alpha = 2.303\,\frac{A}{t} \qquad \ldots\ldots 2$$

where (t) represents thickness of thin films. We can find that (α) decreases rapidly when there is increasing in the wavelength and then shows a tardy decrease at high wavelength. The highest value of (α) is at the beginning of the curve at the low wavelengths (high photons energies) when it is ($\alpha > 10^4$ cm^{-1}), indicating direct electronic transitions.

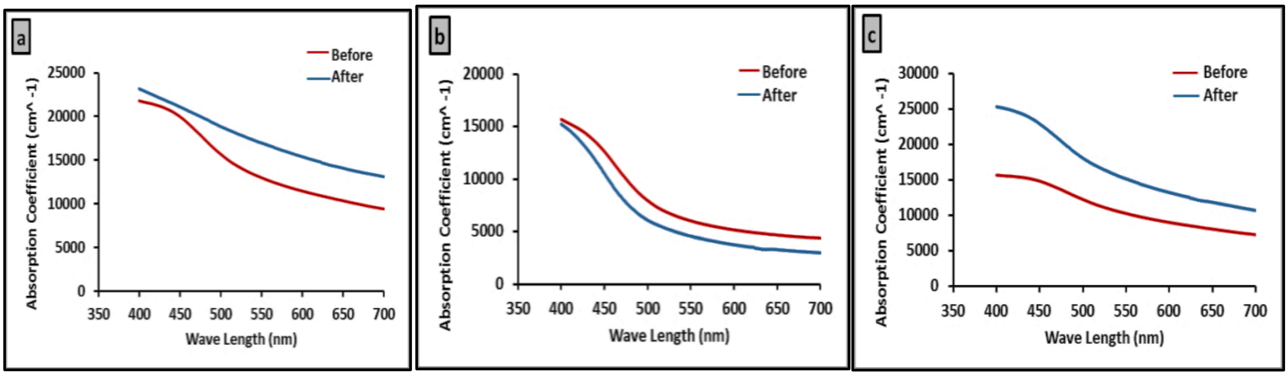

Figure 11. Absorption coefficient of CdO thin films at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

The values of refractive index (n) was received for CdO thin films from eq.3; it is the ratio of the velocity of light in the vacuum to its velocity in the medium (19):

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

Symbol (k) is the coefficient of inactivity, which represents the extinction of the electromagnetic wave in the material, it can be calculated from the following relationship (19):

$$k = \frac{\alpha\,\lambda}{4\pi} \quad \ldots\ldots\ldots\ldots\ldots 4$$

It depends on the wavelength (λ) as well as the coefficient of absorption (α), so it depends on the material type. Figs 12, 13 show the curves of (n) and (k) respectively as functions of wave length, and as is evident from eq.3, 4 we see the same changes of reflectivity as well as coefficient of absorption, and it increased by laser irradiation at (0.05, 0.15)M as in reference (13). This is due to the major contribution of electronic transition and this may lead to a significant change in the optical parameter.

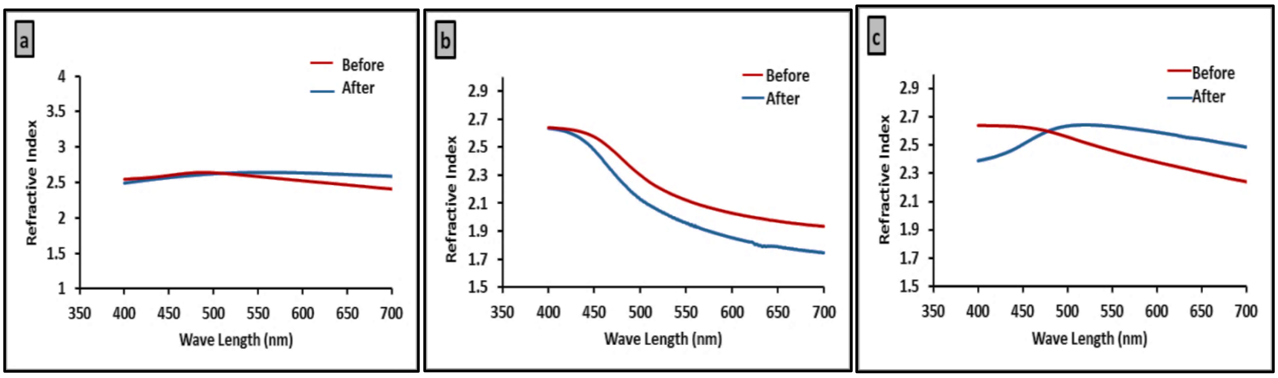

Figure 12. Refractive index of CdO thin films at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

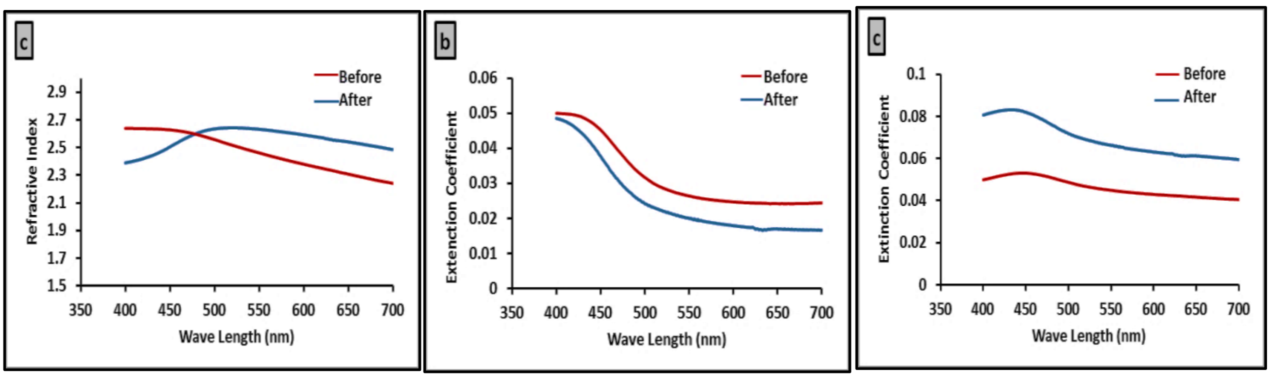

Figure 13. Extinction coefficient of CdO thin films at concentrations: (a) 0.05M, (b) 0.1M , (c) 0.15M

The real and imaginary dielectric constants (showed in figs 14, 15 respectively) can be accounted by counting the refractive index. Electrical insulation constant symbolizes the potential for polarization of the material. Eqs.5, 6 give the constants of real dielectric (ε_r) and imaginary dielectric (ε_i) (19) :

$$\varepsilon_r = n^2 - k^2 \quad \ldots\ldots\ldots\ldots 5$$

$$\varepsilon_i = 2n\,k \quad \ldots\ldots\ldots\ldots 6$$

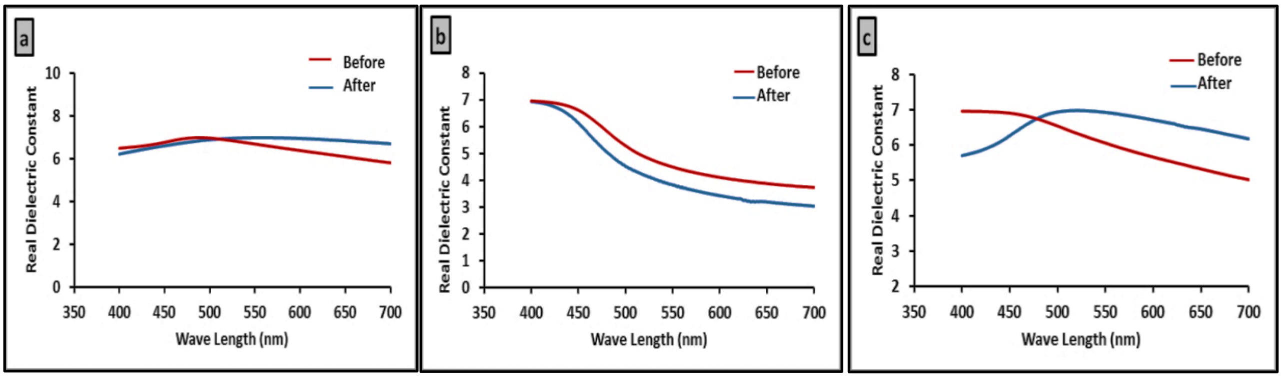

Figure 14. Actual dielectric constant of CdO at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

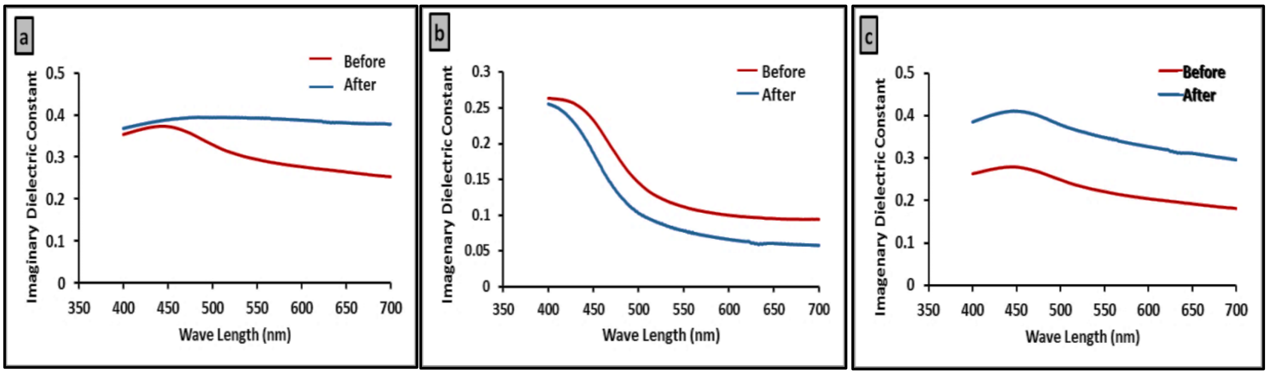

Figure 15. Imaginary dielectric constant of CdO thin films at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

Fig 16 gives the curve of $(\alpha h\upsilon)^2$ as a function of photon energy to determine direct energy gap of (CdO) thin films, (h) is Plank constant, (υ) is frequency. Variation in band gap energy with laser irradiationis observed as in reference (7). These figures show that the values of the energy gap decreased before CO_2 laser irradiation at concentrations (0.05, 0.15)M consistent with the reference (13), but energy gap value increases those irradiated thin films at 0.1M concentration consistent with the references (6,14,20) .This difference may be due to the topical levels of some of the prepared samples.

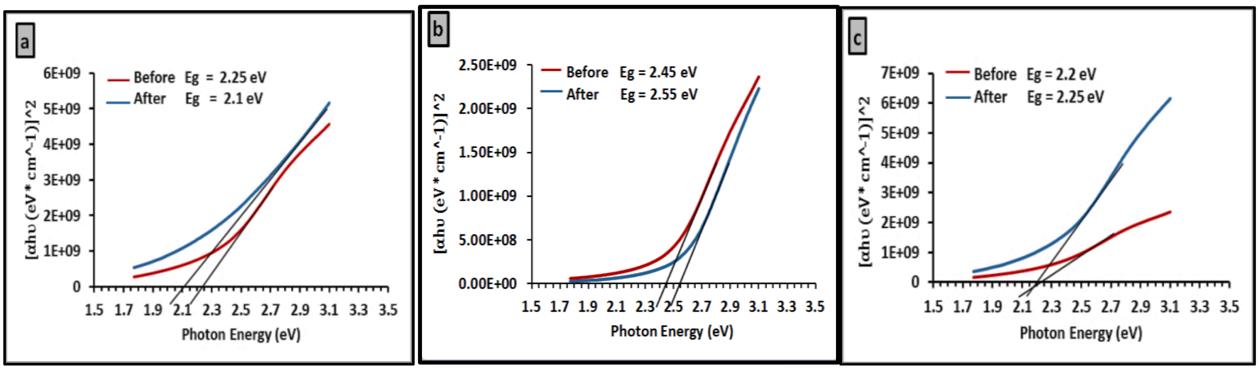

Figure 16. Energy gap of CdO at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M

The energy gap values of the irradiated thin films were also obtained through the fluorine spectrum, which can be obtained from the equation (21):

$$\lambda = \frac{12.4}{E_g} \quad \ldots\ldots\ldots\ldots 7$$

Table 1 is summarized the optical constants and energy gap for CdO before and after irradiation by CO_2 laser with the concentrations (0.05, 0.1 and 0.15) M where the comparison between before and after ideation of the optical constants gives us the maximum of them. In general, during laser irradiation, the samples got enough vibration energy that converted to bulk heating and the defects were gradually reduced. The reduction of defects decreases the density of localized states in the band structure, consequently increasing the optical band gap. These results indicate that the optical properties of these samples were sensitive to radiation and can be modulated under the influence of laser light.

PL spectra show appearance of a broad band extending (22), where its measurement can yield information about band gap energies of nanostructures that can be turned by varying their sizes and the energetic positions of the electronic states in the band gap. On the other hand, a wide bang gap semiconductor material is ideal for studies of trap states, it could be due to localized states or types of defects such as vacancies different, interstitial atoms and dangling bonds.

As it is similar to what was obtained through absorption spectrum. From the observation of this spectrum of irradiated thin films, we find that it is shifted towards high wavelengths as shown in Fig 17.

Table 1. The optical constant and energy gap of CdO before and after irradiation by CO_2 laser

Concentration	Absorption Coefficient (cm^{-1})		Refractive Index		Extinction Coefficient		Real Dielectric Constant		Imaginary Dielectric Constant		Energy Gap (eV)	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
0.05M	21799.56 (at 400 nm)	24444.04 (at 365 nm)	2.641786 (at 488 nm)	2.64 (at 552 nm)	0.072155 (at 437 nm)	0.075762 (at 469 nm)	6.974832 (at 488 nm)	6.984048 (at 313 nm)	0.373123 (at 443 nm)	0.39405 (at 509 nm)	2.25	2.1
0.1M	15684.84 (at 400 nm)	16728.99 (at 355 nm)	2.638488 (at 400 nm)	2.64 (at 330 nm)	0.049952 (at 400 nm)	0.048842 (at 390 nm)	6.959123 (at 400 nm)	6.984255 (at 348 nm)	0.263594 (at 400nm)	0.257822 (at 390 nm)	2.45	2.55
0.15M	15653.76 (at 400 nm)	26705.59 (at 325 nm)	2.638234 (at 400 nm)	2.64 (at 501 nm)	0.053062 (at 449 nm)	0.083125 (at 432 nm)	6.957793 (at 400 nm)	6.975497 (at 520 nm)	0.279082 (at 446 nm)	0.410766 (at 446 nm)	2.2	2.25

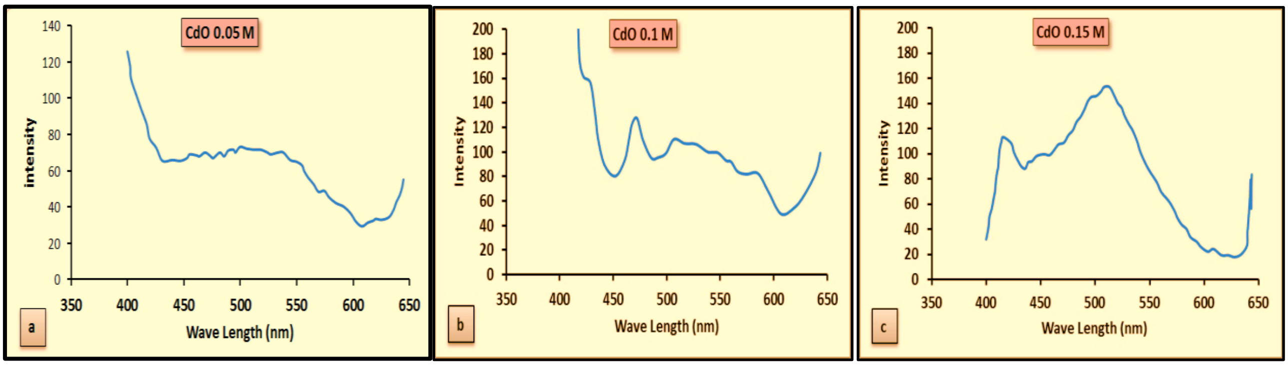

Figure 17. **Fluorine spectrum of irradiated CdO thin films at concentrations: (a) 0.05M, (b) 0.1M, (c) 0.15M**

Conclusions:

CO_2 laser to irradiate CdO thin films is used to improve some of surface topography and optical characteristics of them for various processing enforcement, where laser irradiation increases uniformity and surfaces homogeneity of the prepared thin films .The curves forms of all the characteristics and optical constants of irradiated CdO thin film show the same conduct of change with wavelength changes at (0.05, 0.15)M concentrations, but they differ for those at 0.1M concentration .The results show that these thin films have a direct energy gap, and they also show that prepared at (0.1M) concentration is the best for the transition. The results of the PL measurementare similar to those obtained from the absorption spectrum.

Conflicts of Interest: None.

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تأثير التشعيع بليزر CO_2 على طبوغرافية السطوح والخواص البصرية لأغشية CdO الرقيقة

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الخلاصة:

في هذا البحث تم ترسيب اغشية اوكسيد الكادميوم (CdO) على قواعد زجاجية بطريقة الرش الحراري الكيميائي (CSP) بالتراكيز (0.05، 0.1، M(0.15، ثم تم تعريضها لأشعة ليزر (CO_2) بالطول الموجي (µm10.6) وبقدرة (W1) . بينت نتائج فحوصات مجهر القوى الذرية تجانس سطوح اغشية (CdO) الرقيقة وان تأثير التشعيع بالليزر ادى الى تقليل كل من خشونة السطوح وكذلك ارتفاعات القمم الحبيبية مما يدل على زيادة انتظام وتجانس هذه السطوح. وتم دراسة الخواص البصرية لمعرفة مدى تأثير اشعة الليزر. وقد بينت النتائج ان طيفي الفلورة والامتصاص تزاح نحو الاطوال الموجية العالية مع زيادة التركيز، وقد كانت النفاذية عالية في منطقة الاطوال الموجية العالية، وهناك نقصان في قيم فجوة الطاقة عند التركيزين (0.05، M(0.15 حيث كانت قيمها eV(2.1، 2.25) على التوالي، وازدياد قيمتها لتلك بالتركيز (M0.1) فكانت (eV2.55). بالإضافة الى ذلك فقد تم دراسة خواص بصرية اخرى في هذا البحث ، ونلاحظ بصورة عامة نلاحظ ان قيم الثوابت البصرية للتركيزين (0.05، M(0.15 تزداد بعد التشعيع بالليزر بينما تقل بعد التشعيع عند التركيز ((M0.1 .

الكلمات المفتاحية: اغشية CdO الرقيقة، ليزر CO_2، التشعيع بالليزر، الخواص البصرية، طبوغرافية السطوح.