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Study the Interaction of CO₂ Laser with ZnO Thin Films and Its Effect on Its Topographic and Optical Properties

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ARTICLE INFO.

Keywords: laser irradiation, CO₂ laser, laser interaction with material, ZnO thin films.

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ABSTRACT

In this work, the effect of the laser on the material was studied through the interaction of carbon dioxide (CO₂) laser radiation with zinc oxide (ZnO) thin films, where laser irradiation is one of the most important industrial applications which have been studied in several researches and are still in continuous development. ZnO thin films were deposited on glass substrates by chemical spray pyrolysis (CSP) method with concentrations (0.1 and 0.2)M, then exposed to CO₂ laser radiation at (10.6 μm) wavelength and (1 W) power. The topography of these thin films and the optical properties were studied before and after irradiation to show the effect of laser radiation. The irradiation clearly reduced the granular volume of thin films prepared with concentration (0.1 M). The results of the optical tests of these thin films showed that they had high transmittance especially in the high wavelength range, and an increase in the value of the energy gap of those irradiated with concentration (0.1 M), in addition, the other optical properties which have been studied in this paper included both absorbance, reflectivity, as well refractive, absorption and extinction parameters, and both of real and imaginary dielectric constants.

Introduction

Laser materials processing is an enabling technology in many industries, the most prominent are semiconductor technology, flat panel display production, solar cell technology and medicine. Typical laser based processes are welding, cutting, drilling, annealing and laser irradiation [1]. A lot of research work is underway on the effect of laser irradiation, annealing, etc. on optical and structural properties of material [2].

Thin film technology has contributed significantly to the study of semiconductors and gave a clear idea of many of the physical as well as chemical properties [3], and metal oxide thin films have received great attention in the recent years owing to their special characteristics in optical properties in the area of optoelectronics [4]. The methods of preparing thin films developed with the development of the world and the progress of science and became highly accurate in the determination of thickness and homogeneity of the thin film, and the methods of measurement were developed, as well as, devices which used in the manufacture of thin films and its

privileges and applications [5]. In recent years, 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], and among the most important of these oxides is zinc oxide (ZnO) [8,9]. It is a semiconductor hexagon (II-VI) [10], characterized by being a cheap and easy to prepare, relatively abundant, stable chemical and non-toxic, it can be easily neutralized by many other materials [11], does not dissolve in water but dissolves easily in acids and bases [8], has direct and wide band gap (3.4 eV) [9]. ZnO thin film presents investigation in optical, acoustical and electrical properties which can be useful in applications in the fields of electronics, optoelectronics and sensors [9,10]. Variety of techniques have been reported to prepare (ZnO) using different techniques, and the technique of thermal spraying is a useful alternative to traditional methods

that have been widely used for more than two decades. This method has advantages, easy to use, low cost and low production loss, allowing access to a large surface thin film. The production of thin films in this way is more uniform in size and composition than the powder produced by other methods. The disadvantage of this method is that the thin films are not easily formed, islands may form on the base or deform the thin film so that careful attention should be paid to the sediment, use with soluble materials only and do not use alloys or powder directly [12]. In the present work, ZnO thin films have been prepared using chemical spray pyrolysis (CSP) method and then irradiated by CO₂ laser. The aim of this work is to investigate the effect of laser on the topographic and optical properties of these thin films by studying the interaction of the laser with the material.

Theoretical

Laser applications cover various fields in science and technology including physics, chemistry, biology, electronics and medicine. They are the result of the special properties of laser light (mono-wavelength, temporal and spatial coherent (equal phase in time and place), directivity and brightness), in addition to being a direct result of the understanding of the interaction of laser beams with the material of different types as the most important factor in the development of laser applications. This prompted scientists to study the interaction of laser beams with different types of materials [13]. The penetration of laser radiation in material is a very important process related with the interaction of this radiation with materials and respectively its impact on their structure and properties. For laser treatment of material, the parameters of laser radiation should be precisely controlled [14]. When the laser light falls on any material, changes are made to this material, but the absorption coefficient of this wavelength of the material must be high compared to the reflected light rate. In the case of dark matter there is no penetration and the greater focus is on the absorbed light and reflection. Also, the wavelength varies from the other according to the coefficient of permeability in this article, which is a greater absorption rate and greater penetration of the material. The interactions resulting from the laser with the material are divided into several types:

- Interaction resulting in heating.
- Interaction occurs fusion.
- Interaction occurs evaporation.
- Plasma reaction occurs.

The importance of optical properties is shown when light is interacted with matter through a phenomenon called absorption, which is expressed by the absorption coefficient α [15]. The energy absorbed by the photons allows the transition from the excited state to the ground state [16]. The photon focuses its ability on the target and then the energy is converted to heat, which is distributed to the vicinity by

transport or radiation. The amount of effect depends on the laser's energy, the area exposed to laser light, wavelength, spot size, exposure time and type of material [17].

The material can interact with electromagnetic radiation in multiple ways. When a light beam is incident on a slice of material, in principle, three effects exist which may modify its propagation:

- Reflection and refraction.
- Absorption.
- Scattering.

According to the type of material and the incident wavelength, we can have a predominance of either losses or reflection, absorption or scattering. The optical parameters as the refractive index, the absorption and scattering coefficient depend on the wavelength of the incident light. In particular, the refractive index strongly depends on wavelength in spectral regions of high absorption for the material only [18]. Figure (1) shows the geometry of light propagation.

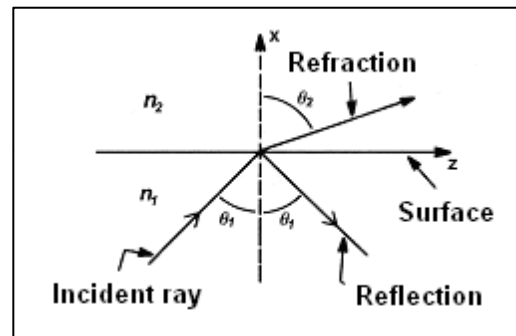


Figure (1): Geometry of light propagation [18]

Refraction occurs when the reflecting surface separates two media of different indices of refraction (n_1 and n_2). The mathematical relation governing refraction is known as Snell's law [18]:

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \dots\dots\dots(1)$$

In order for the laser effect to occur in the material there must be absorption of the laser beam. This absorption is very important for the interaction of the laser with the material, which is a fundamental source of energy within the material, which is the basic source of evidence that the laser beam emitted from the source determines what happens to the laser beams [19]. The thermal interaction term stands for a large group of interaction types, where the increase in local temperature induces the significant parameter change. Depending on the duration and peak value of the material temperature achieved, different effects like thickening, vaporization, carbonization, and melting [18]. In Figure (2) the incident laser pulse heats the target material quickly, this causes a shift in the phase and generates waves of stress in the irradiated target, after which the material begins to melt into the gas phase and this occurs very short time and the plasma is generated. The laser beam will be absorbed by plasma flame, attenuating the intensity of the light incident on the target, Ionization

and plasma ionization. The thermal diffusion depth of the laser pulse (D) can be determined by the following relationship :

$$D = (4N\tau_{las})^{1/2} \dots\dots\dots (2)$$

Where (D) is the thermal diffusion depth, (N) is the thermal diffusion of the material, and (τ_{las}) is the duration of the laser pulse [19].

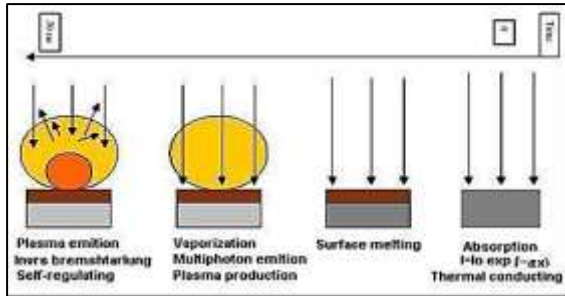


Figure (2): Intraction of laser with the material [19]

Experimental

ZnO thin films were prepared with two concentrations (0.1 and 0.2)M of zinc nitrate dehydrate ($Zn(NO_3)_2 \cdot 6H_2O$) solution with (99%) purity and (297.51 g/mol) molecular weight, where specific quantities of zinc nitrate dehydrate were dissolved according to the concentration required in the distilled water and added a few drops of nitric acid (HNO_3) to prevent the deposition of the solution and then mixed the solution using a magnetic mixer at (5 – 10)min period time to completion of the melting process, and leave the solution for an hour to obtain a homogeneous solution, and then place the solution in the tank of the spray device, the solution was sprayed on heated bases at a temperature (375 °C) in the form of batches within specified time periods, where air is used in this process which is pumped of limits (1.8 bars) and the flow of air through the spray tube helps to separate molecules of solution and get spray as the diameter of the spray tube (0.3 mm) with a flow rate of about (3 ml/min)

and the distance is (28 cm), measured between the end of the spray tube and the base is by using a double rebar. Spraying chemical reactions continue to produce a highly adhesive ZnO thin film on the glass substrate (throw studying x-ray diffraction of these thin films, where it was found that these are multi-crystallization composition returns to ZnO as shown if figure (3)). After that the prepared thin films were irradiated by CO_2 laser (10.6 μm) wavelength and (1 W) power for (15 sec) at (1 m) distance between the sample and laser, and then the topographic and optical tests were done for the prepared thin films before and after radiation to see how laser irradiation affects them, where the topography of the thin films surfaces was conducted by atomic force microscope (AFM), while the optical tests were performed by (UV – visible – IR spectrometer).

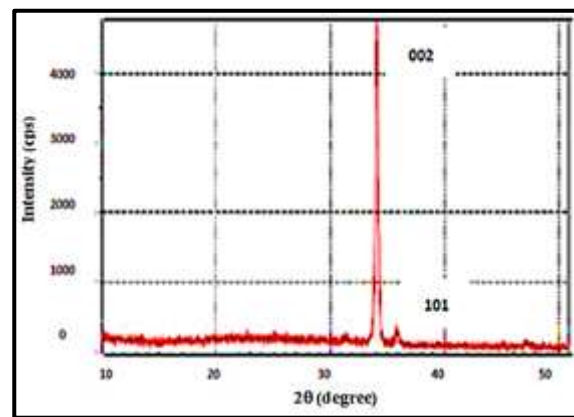


Figure (3): XRD spectrum of prepared ZnO thin films

Results and Discussion

1- AFM Test Results

The obtained results of topography tests of ZnO thin films showed the effect of CO_2 laser radiation on the some structural characteristics of them, were they are shown in the figures (4 – 7).

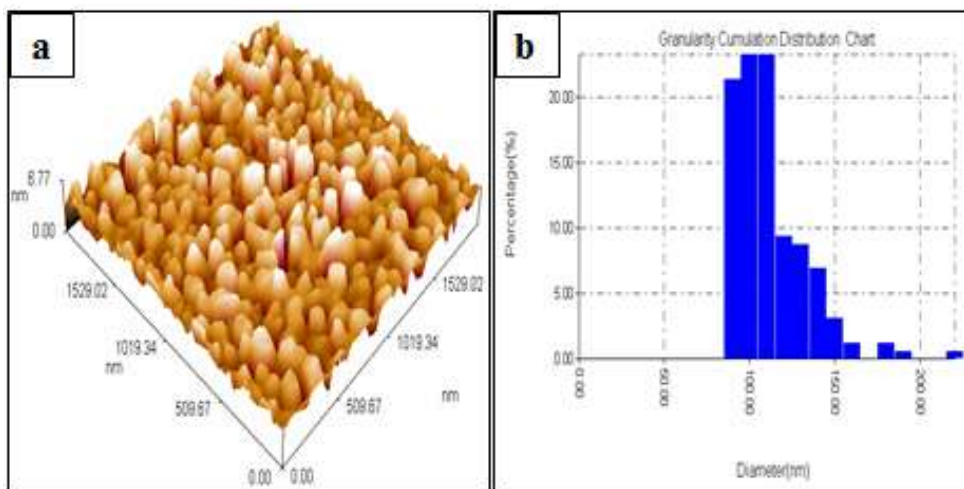


Figure (4): AFM image of ZnO thin film at (0.1 M) before irradiated
 a: 3D, b: Distribution of particle size on the thin film surface

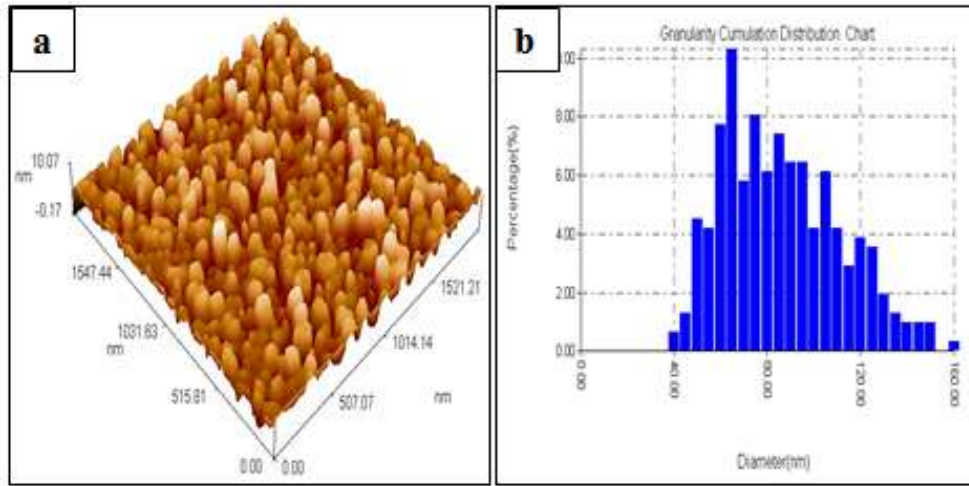


Figure (5): AFM image of ZnO thin film at (0.1 M) after irradiated
 a: 3D, b: Distribution of particle size on the thin film surface

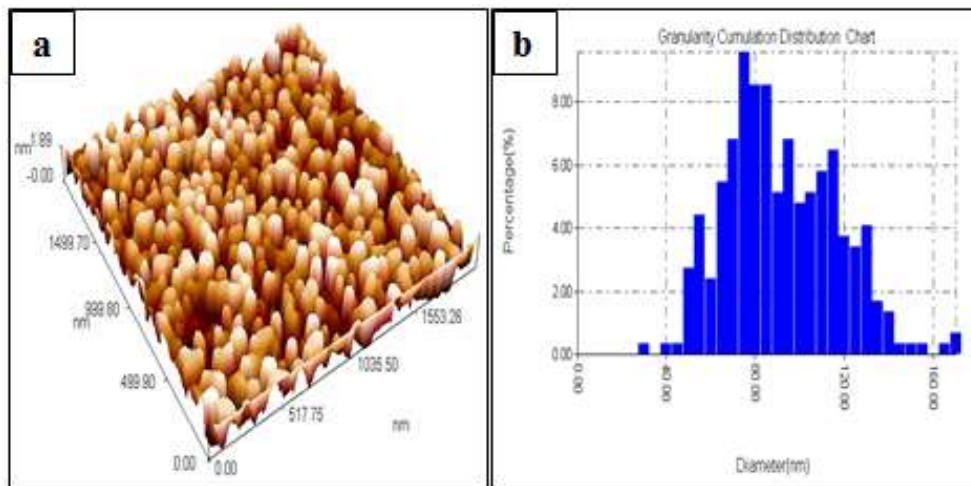


Figure (6): AFM image of ZnO thin film at (0.2 M) before irradiated
 a: 3D, b: Distribution of particle size on the thin film surface

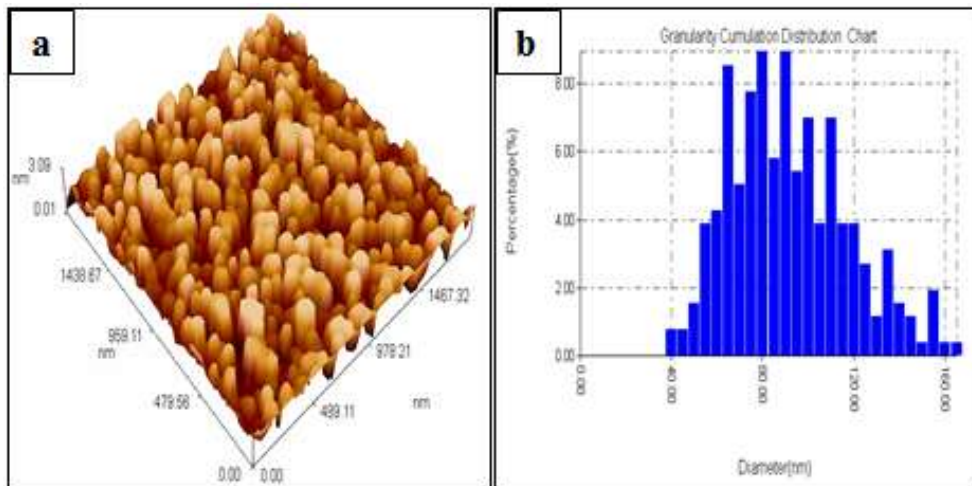


Figure (7): AFM image of ZnO thin film at (0.2 M) after irradiated
 a: 3D, b: Distribution of particle size on the thin film surface

We note that laser irradiation of (0.1M) concentration of thin films significantly reduced granular volume and at the same time decreased their roughness by a clear percentage, the reason is that laser radiation led

to high temperature of the thin film brighten and thus reduce the thickness and small size of granular and at the same time led to regularity of the surface, these results are in agreement with reference [5]. While

laser irradiation effect was lower than that of the (0.2M) concentration of thin films, were change in particle size was lower compared with the first concentration, laser irradiation of this concentration of thin films grow up particle size and regulate the surface and reduce the roughness, where there is increasing in the thickness of thin film and thus increase the particle size due to increase in concentration, these results are in agreement with reference [3]. These can be seen in the table (1):

Table (1): Results of AFM tests of ZnO thin films

Case	Concentration (M)	Average Diameter (nm)	Roughness Average (nm)
Before Irradiation	0.1	107.3	0.927
	0.2	83.89	1.31
After Irradiation	0.1	89.21	0.444
	0.2	89.32	0.557

2- Optical Test Results

The obtained results of optical tests of ZnO thin films showed the effect of CO₂ laser radiation on the optical properties of them.

• Absorbance, Transmittance & Reflectivity:

Absorbance spectrum of ZnO thin films as a function of photon energy showed increase in absorbance values (A) for both (0.1 and 0.2)M concentrations in high energies region, this means a decrease in its with increase wavelength starting from the visible region which continue in high wavelength regions, and irradiation by CO₂ laser led to a slight decrease in their values (compared to their pre-irradiation) for (0.1M) is more pronounced in the low wavelength ranges and a slight increase for (0.2M), this is due to what was obtained from the structural tests as the intensification of change in this concentration is lower compared to the other one as it shown in the figure (8). On the contrary, the transmittance spectrum of these thin films as in figure (9) shows a decrease at high energy area before and after laser irradiation, where the greater of absorption of the material leads to a lack of its transmittance and vice versa (with relatively a slight increase in its value after irradiation for (0.1M) and decrease for (0.2M)), we can say transmittance (T) increased by increasing the wavelength in both the visible and infrared spectral regions and for both concentrations, so these thin films are of the TCO and show a strong response for many solar cells in addition for many applications due to its high transmittance, note its values of the films with a concentration (0.1M) are higher than those of the (0.2M). In general slight variation in the shapes of the curves that represent the optical parameters may be due to the different nature of the surfaces of these thin films. Figure (10) represents reflectivity spectrum (R) which shows that the behavior of its of these thin films is similar to the behavior of the absorbance spectrum, as they together represent what was lost from the beam as it passed through the material, in general, the reflectivity is low at the lower energies of energy gap (E_g) and the peak

reflected in the reflectivity curve corresponds to the value of the energy gap.

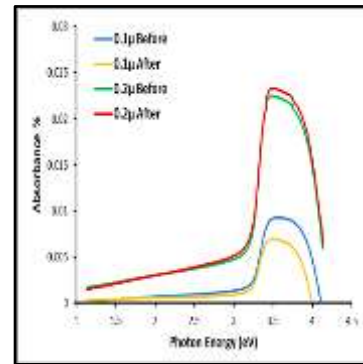


Figure (8): Absorbance spectrum of ZnO thin films

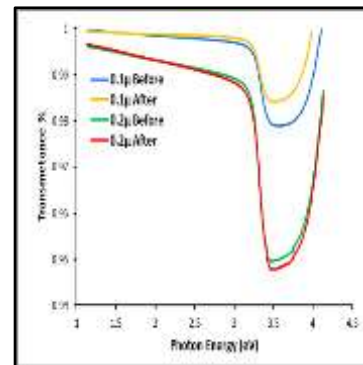


Figure (9): Transmittance spectrum of ZnO thin films

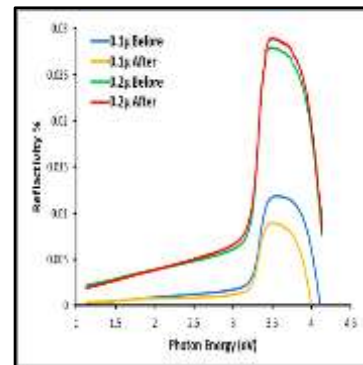


Figure (10): Reflectivity spectrum of ZnO thin films

• Optical Constants:

Figure (11) shows the change in the absorption coefficient values (α) of ZnO thin films with photon energy change, it shows a similar behavior to the absorbance spectra, where absorption coefficient was obtained by the following [3]:

$$\alpha = 2.303 \frac{A}{t} \dots\dots (3)$$

Where (t) is thickness of thin films. From the figure we find (α) is increased slowly by increasing the photon energy and then a rapid increase at the absorption edge which indicates the occurrence of directly electronic transitions, as well we find that laser irradiation led to higher coefficient values of (α) for (0.2M) but less for (0.1M), noting that the increase in concentration mainly led to higher values because the transition decreased by increasing the concentration of these thin films, and that due to the

result of structural tests. The values of (α) of the range before the absorption edge are attributed to absorption by impurities or transitions within the beam and occur at wavelengths where the photon energy falls below (E_g) [20].

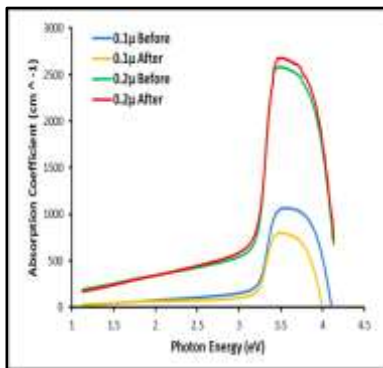


Figure (11): Absorption coefficient of ZnO thin films

The refractive index (n) values were obtained for ZnO thin films from equation (4), which is defined as the ratio between the velocity of light in the vacuum and its velocity in the medium [2]:

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

Where (k) is the extinction coefficient, which is represent the extinction of the electromagnetic wave within the material, and it can be calculated according to the following relationship [2]:

$$k = \frac{\alpha \lambda}{4\pi} \dots\dots\dots (5)$$

Where (λ) represents the wavelength. Figure (12) shows that change (n) is similar to change (R) where its value is low at a few energies (high wavelengths) and then rises to its highest value when the energy reaches a value equal to (E_g). So (K) gradually increases at low energies as in figure (13) and then increases rapidly at the absorption edge due to electronic transitions between the equivalence and conduction bands, we note that laser irradiation for each of them led to increased values for (0.2M) and decreased them for (0.1M) compared of their before irradiation, this is due to the same reason mentioned earlier, since the structural properties of matter affect their optical properties.

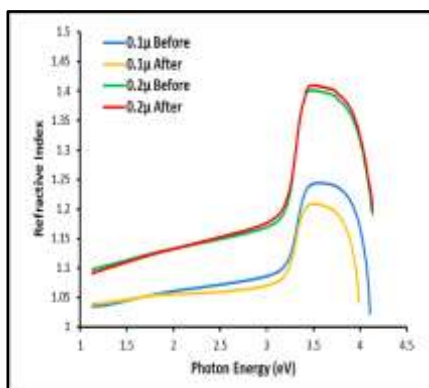


Fig.(12): Refractive index of ZnO thin films

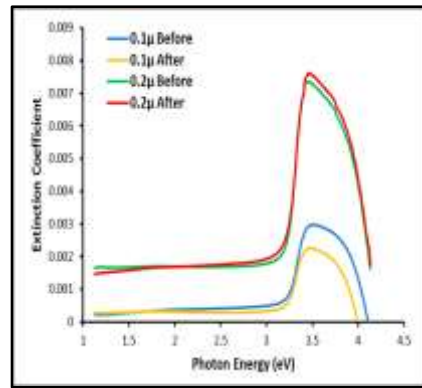


Fig.(13): Extinction coefficient of ZnO thin films

It is noted that the extinction coefficient depends mainly on the wavelength (λ) and absorption coefficient (α) which depends on the quality of the material. The real and imaginary dielectric constants (showed in figures 14 & 15 respectively) can be calculated by calculating the refractive index. The dielectric constant represents the material's polarization potential, which is the material's response to different frequencies with complex behavior, and these materials are polarized due to the increased values of the dielectric constant. The following equations represent real dielectric constant (ϵ_r) and imaginary dielectric constant (ϵ_i) [3]:

$$\epsilon_r = n^2 - k^2 \dots\dots (6)$$

$$\epsilon_i = 2nk \dots\dots (7)$$

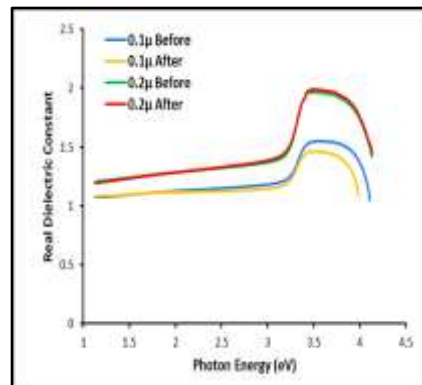


Fig.(14): Real dielectric const. of ZnO thin films

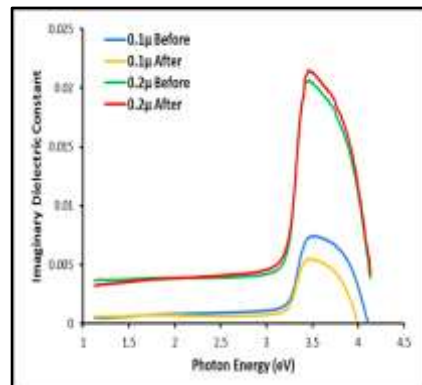


Fig.(15): Imaginary dielectric const. of ZnO thin films

Figure (16) represents $(\alpha h\nu)^2$ curve as a function of photon energy to calculate the direct energy gap of the (ZnO) thin films, where (h) is Plank constant and

(u) is frequency, it is clear from the figure that the values of the energy gap of the thin films have increased its value before the CO₂ laser irradiation at concentrations (0.1M) may be due to the local levels of some of the thin films prepared after irradiated, but energy gap value stayed the same of those irradiated

thin films at (0.2M) concentration, this relates to the transition of these thin films at this concentration as the effect of laser irradiation on them was very simple due to the structural properties of matter affect their optical properties.

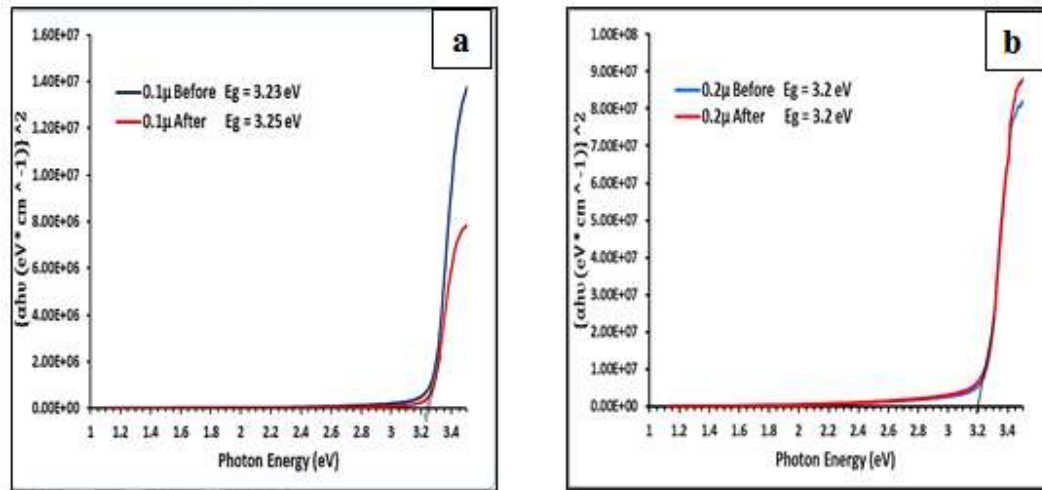


Fig. (16): Energy gap of ZnO thin films with concentrations: (a) 0.1 μ , (b) 0.2 μ

Conclusion

We can use CO₂ laser to irradiate ZnO thin films with the used power in this paper, and it can be tried different power and different exposure to improve optical properties of thin films (get optical effects of laser on the material) for various industrial applications. Laser irradiation reduced the granular size of the thin films prepared by (0.1M) concentration. The curves of the optical parameters of ZnO thin film irradiated show that the effect of CO₂ laser on them was more clear for those at (0.1M) than

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those at (0.2M) concentration. Optical results showed that these thin films have direct electronic transition, where they have just allowed direct energy gaps at the prepared conditions of this paper, and it showed that prepared at (0.1M) concentration are most affected by laser were its value changed from (3.23 eV) to (3.25 eV), while there was no change of its value of this at (0.2M) after irradiated which equal to (3.2 eV), these values are close of the values in some previous researches like the references [8] and [11].

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دراسة تفاعل ليزر CO₂ مع أغشية ZnO الرقيقة وتأثيره على طوبوغرافيتها وخواصها البصرية

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الملخص

في هذا البحث، تمت دراسة تأثير الليزر على المادة من خلال تفاعل أشعة ليزر ثنائي أكسيد الكربون (CO₂) مع أغشية أكسيد الزنك (ZnO) الرقيقة، حيث يعد التشعيع بالليزر أحد أهم التطبيقات الصناعية التي تمت دراستها في العديد من الأبحاث ومازالت مستمرة في التطور. تم ترسيب أغشية ZnO الرقيقة على قواعد زجاجية بطريقة الرش الحراري الكيميائي (CSP) بالتركيزين (0.1 و 0.2)M، ثم تم تشعيعها بليزر CO₂ ذي الطول الموجي (10.6 μm) وقدره (1 W). تمت دراسة طوبوغرافية سطوح هذه الأغشية والخواص البصرية لها قبل وبعد التشعيع لمعرفة تأثير أشعة الليزر. أدى التشعيع بشكل واضح إلى تقليل الحجم الحبيبي للأغشية الرقيقة المحضرة بالتركيز (0.1 M). وأظهرت نتائج الفحوصات البصرية لهذه الأغشية أن لها نفاذية عالية خاصة في مناطق الاطوال الموجية العالية، وزيادة في قيمة فجوة الطاقة لتلك المشعة ذات التركيز (0.1 M)، إضافة إلى ذلك فإن الخصائص البصرية الأخرى التي درست في هذا البحث شملت كلا من الامتصاصية والانعكاسية، وكذلك معاملات الانكسار والامتصاص والخمود، وكلا من ثابتي العزل الكهربائي الحقيقي والخيالي.