International Journal of Physics, 2016, Vol. 4, No. 3, 59-63
Available online at http://pubs.sciepub.com/ijp/4/3/3

DOI:10.12691/ijp-4-3-3

Effect of Annealing by CO2 Laser on Structural and Optical Properties of CuO Thin Films Prepared by Sol – Gel Method

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Abstract Laser heat treatment is one of the important industrial applications of laser and being studied at the present time as a substitute for conventional thermal annealing. In this research (CuO) thin films have been deposition on a glass by (Sol - Gel / Spin Coating) technique and annealed by two ways, the first one using a convection oven, where they were annealing with three temperatures (400 °C, 500 °C, 600 °C) for one hour, and the second way using a continuous (CO2) laser with (10.6 µm) wavelength and (10 W) power and three intervals (10 min, 15 min, 20 min), were studied structural and optical properties of membranes prepared by both ways to determine the effect of laser annealing on them, and the results of (XRD) tests showed that these membranes with the structural of multi-crystalline monoclinic type and increase the degree of oven annealing temperature, as well as increasing the duration of the laser annealing lead to increased volumes of granular membranes rates. The results of the (AFM) tests to the topography of the surfaces of the membranes to be of crystalline uniformity and homogeneity superficially good, especially for laser annealed membranes. The results of optical examinations of these membranes showed that they having high permeability, especially in the regions of the visible spectrum and the near-infrared and increased with increase the degree of oven annealing temperature and the duration of laser annealing, and less energy gap of these membranes values with increase the temperature degree of annealing or increase of laser annealing time. In addition to this, the optical properties studied in this research included absorbance, reflectivity, refractive index, coefficients of absorption and extinction, and real and imaginary dielectric constants.

Keywords: *Annealing, Co2 Laser, CuO thin films*

Cite This Article: Khalil Ibrahim Mohammed, Awatif Sabir Jasim, and Sahar Naji Rashid, “Effect of Annealing by CO2 Laser on Structural and Optical Properties of CuO Thin Films Prepared by Sol – Gel Method.” *International Journal of Physics*, vol. 4, no. 3 (2016): 59-63. doi: 10.12691/ijp-4-3-3.

1. Introduction

Laser is one of the most important inventions of the twentieth century and continues to evolve in various fields and applications [1], since the first laser system manufacturing in the early sixties and the areas of the 2 use of laser is on the rise [2], and among the various applications is laser materials treatment, such as laser annealing process [3]. The oven heat treatment is using for annealing and production of nano-crystals, and laser annealing technique is promising technology for this purpose, where used several types of lasers different in wavelengths including carbon dioxide laser (CO2 laser) [4] which is characterized by a small amount of power with the good quality of consumption came out suitable for annealing [5]. Laser annealing has become one of the topics that have attracted the attention of researchers at the present time [6]. Copper oxide (CuO) semiconductor material is called scientifically (tenorite) or (cupric), one of the stable oxides, is characterized as a brown powder near to black odorless [7] no dissolving in water or bases [8], also features owning non-toxic nature, the possibility of availability, low cost of production [9,10], the quality of electrical and optical properties [10], is one of the most important materials used in optoelectric applications, when it is material known as (TCO) [9], has a wide variety in photoelectric devices applications [7], in the energy sources and diodes link (pn-junction) etc. [11]. Thin film technology has contributed significantly to the study of semiconductors and gave a clear idea of many of the physical properties as well as chemical [12]. To study the characteristics of the semiconductor it became necessary to make a thin film does not exceed the thickness of a few microns [13], and in this paper adoption of carbon dioxide laser in addition to the convection oven for anneal (CuO) thin films prepared rotational by spin coating which is one of (sol - gel) technique methods, and study the structural and optical properties of them.

2. Experimental

In this paper glass bases were used to precipitate membranes on them, they have been cleaned to be free of impurities or plankton by washing the samples with plain water and then cleaned with nitric acid diluted (HNO3) and washed with distilled water lukewarm with put them on magnetic stirrer for (10 min) and then put them in acetone after that they dried and placed in ethanol for (10 min) and dried to be ready to the deposition on them. Copper acetate dehydrate high purity have been used for the preparation of (CuO) thin films, were prepared from the solution concentration (0.2 M) dissolving (1.597 g) of copper acetate in (30 ml) of ethanol (purity of 99.99%), were mixing the solution using magnetic 3 stirrer device for an hour at (60°C) to complete the melting process, and in the meantime added to this mixture component of a solution of (0.84 g) of (diethanolamine) dissolved in (10 ml) of ethanol and operates as installed, has added drip and after this product is covered solution in the volumetric vial was developed and leave it for a period of (24 hour) to obtain a homogeneous solution, then deposited membranes copper oxide on the glass bases by placing the samples to spin coating device basis by using the rotational speed (3000 rpm) for a period of (30 sec), drying temperature was (100°C) for (10 min) and then submitted to the (150°C) for (10 min) and other, were obtained on a number of thin-film layers precipitated by six layers where this deposition process repeated for each layer of them, all membranes have been annealed in two ways:

1- Conventional Thermal Annealing: by useing thermal oven to anneal thin films at three temperatures (400°C, 500°C, 600°C) for one hour.

2- Rapid Thermal Annealing: by useing CW-CO2 laser device of type (engraving machine) with (50 W) power and (10.6 μm) wavelength, which can be increased by the energy resulting from control by changing the power inside tube laser, the power annealing (10 W) in three interval (10 min, 15 min, 20 min), where installed the current index in the device at (5 mA) to reach the power (10 W), and the distance is measured between the laser source and the sample is equal to (48.5 cm), the laser spot of the sample was (0.5 cm).

Thickness measuring of the thin films was by microscope using pro axel program where the sample was set in a certain way so that its edge was under the microscope, and using suitable lens magnification power to observe membrane layer formed on the glass base by the computer screen, with using the computer program it had been identified by two points opposite on the edges of the membrane by the index and install the reading taken pixels unit, which represents the difference between the desired membrane thickness, and repeating the process three or more times at different distances from the edge of the membrane and taking the rate we got approximate thickness membrane unit pixel which can be converted to the nanometer unit using the following relationship:

$$1\mu\text{m} = \text{pixel} / 50.205 \qquad (1)$$

Where (1 μm = 1000 nm). After completion of the annealing process, was chosen best membranes that have been obtained to conduct structural 4 and optical tests on it to see the effect of the conditions used in the preparation of this research by using synthetic tests two techniques:

1- X–Ray Diffraction (XRD): to study crystal structure of annealed thin films by study x-ray pattern, used)XRD-6000(device type.

2- Atomic Force Microscope (AFM): to study topographic of thin films surfaces, used (AA 3000 SPM) device type.

Optical tests had been done by (UV spectrophotometer) which included absorbance and transition at (190–1100 nm) wavelength range.

3. Results and Discussion

a- Structural Results

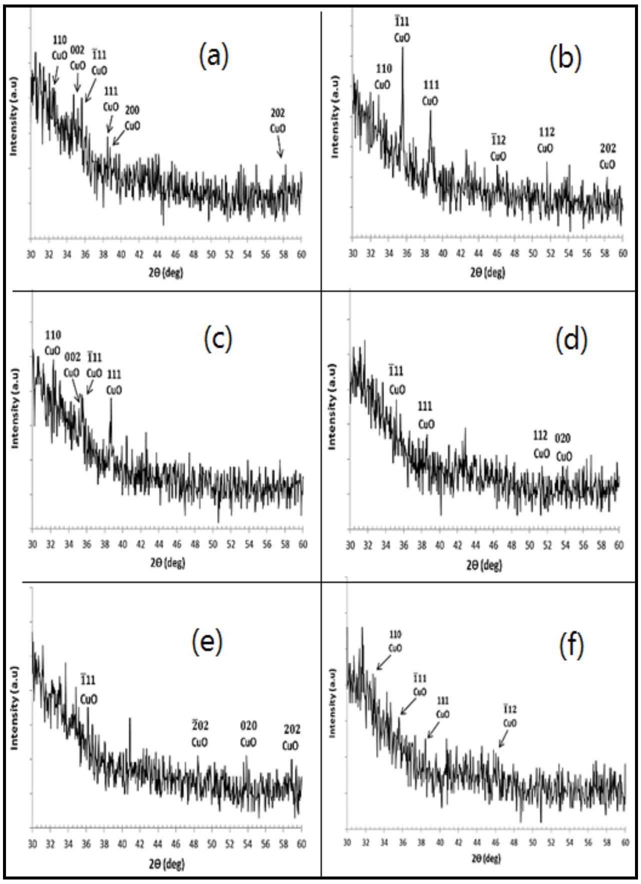

Figure 1. X-ray diffraction scheme of the copper oxide thin films which annealed:(a) by oven at (400 °C), (b) by oven at (500 °C), (c) by oven at (600 °C), (d) by laser for (10 min), (e) by laser for (15 min), (f) by laser for (20 min)

XRD results showed the multi crystalline monoclinic type of CuO thin films which had annealed by oven or by laser, agree with previous researches, and approximately corresponding with American standard for testing materials card (ASTM), card number (05-0661). In the furnace annealing case as in the Figure (1- (a, b, c)) there is emergence of peaks diffraction in both preference directions $(\bar{1}11)$ and (111) in addition to the levels (110), (002), (200), $(\bar{1}12)$, (112) and (202) with differentiation in membranes where different appearance and disappearance of some of them in grades annealing used for heat, while in laser annealing case as in the figures (1-(d, e, f)), there is no certain preferential direction, but there are different diffraction peaks which their appearance and isappearance depends on the duration of laser annealing, they are $(\bar{1}11)$, (111), (112), (020), $(\bar{2}02)$, (202), (110) and $(\bar{1}12)$ as well as the emergence of some of peaks at a number of angles that do not belong to the installation of crystalline material used because of laser high energy laser, this means that the high energy of laser led to formation of effective dispersion centers which have been working to create a sniper levels at grain boundaries working on the sniper charge carriers and freeze in place, especially since annealing was in the air and thus affect the structural properties of the membrane.

Increase in the degree of furnace annealing temperature led to increase particle size, as well as increasing the duration of laser annealing led to similar results in terms of improving the degree of crystallization of the material and narrow diffraction peaks and increase the granular size, since the increase of time annealing with high energy lead to increased temperature and thus increasing the particle size membranes. It noted some of the shapes in the above, we find in spite of the appearance of the material diffraction peaks but they look like random and this means that they have acquired the crystalline state in part of annealing process, the reason for this may be that the preparatory conditions have not had the opportunity to part of the atoms of the material to arrange themselves should also be to get to the case of long-term arrangement for all parts of the article.

The obtained results for the topography of the surface membranes also showed (CuO) that the membrane surfaces of uniformity crystalline and homogeneity superficial good as in the Figure 2- (a, b, c, d, c, e, f)), has resulted in increased oven annealing temperature to reduce distractions resulting in membranes within the preparation conditions in this research, while these deviations did not appear in the case of laser annealing where the surfaces of the membranes form more regularly.

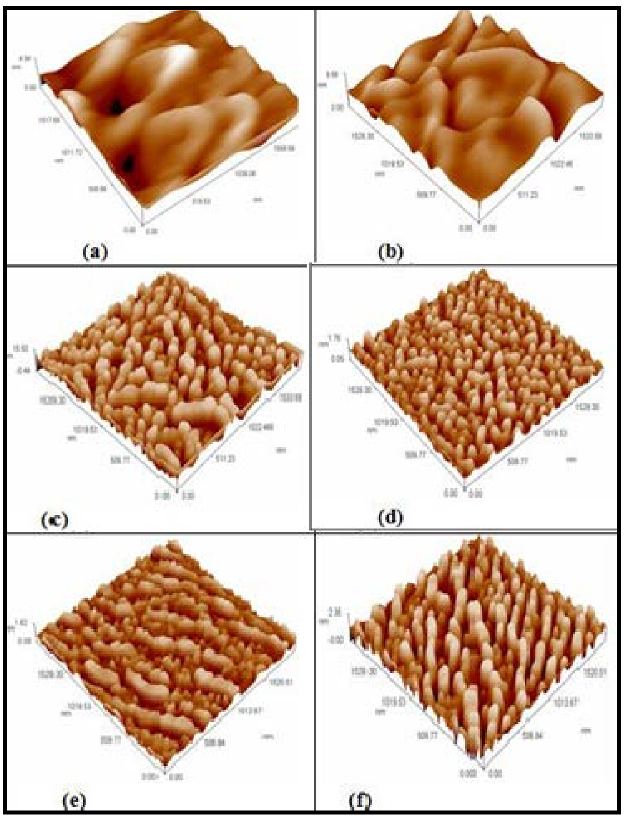

Figure 2. AFM image of copper oxide thin films which annealed: (a) by oven at (400 °C), (b) by oven at (500 °C), (c) by oven at (600 °C), (d) by laser for (10 min), (e) by laser for (15 min), (f) by laser for (20 min)

b- Optical Results

The results showed that the transition of CuO thin films increases with the degree of oven annealing temperature, this is consistent with the results of previous research where up to high levels in the visual areas and infrared, note that the values less when annealing at (500 °C) especially in the visible region, due to the deviation in these membranes at this annealing degree according to (AFM) results. As well as the effect of increasing the duration of laser annealing is similar to the effect of increasing the degree of annealing temperature on the spectrum transition, and an increase in the duration laser annealing led to the improvement of crystallized material, as in Figure 3-a,b, and show a strong response to the many types of solar cells as well as many applications as a result of high transition, and exhibits the spectrum absorbance behavior opposite to the transition spectrum as in Figure 4-a,b.

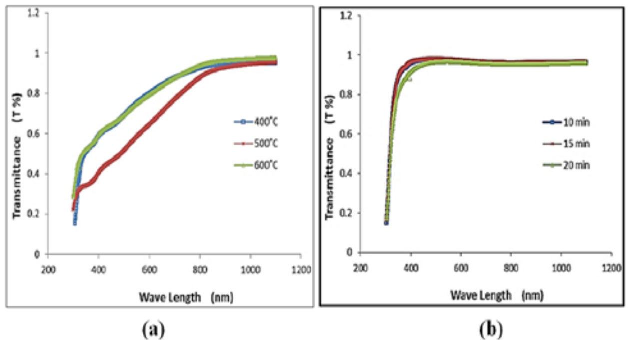

Figure 3. Transition spectrum of CuO thin films: (a) furnace annealing (b) laser annealing

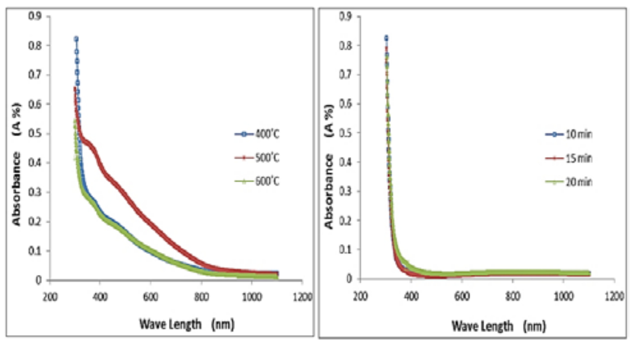

Figure 4. Absorbance spectrum of CuO thin films: (a) furnace annealing (b) laser annealing

In figure 5-a,b we find the increased reflectivity for a particular range of wavelengths as a result of a decrease of transition, then the curve begins to decrease at higher wavelengths with the observation that the rates decrease with increasing degree of annealing temperature, it may be due simplex in the form of curves difference to the different nature of the surfaces, we also find that the effect of laser annealing is similar to the effect of furnace on reflectivity spectrum, noting that the decline curve, up wavelength faster than in the case annealing oven may be due to the high power laser led to the irregular surfaces of the membranes, which led to the similarity of the behavior of the curve for all the times of annealing. In general, the reflectivity be few at energies least of (Eg) and peak appearance in the reflectivity curve is when the value of the wavelength corresponding to the value of the energy gap. We find a slowly increase of absorption coefficient (equation 2) with photon energy increase and then there is a rapid increase at the absorption edge for a certain extent of energies, and laser annealing led to increase the value of a simple than in the case of oven annealing as shown in Figure 6-a,b.

$$\alpha = 2.303A/t \tag{2}$$

Where (A) represents the absorbance and (t) the thickness of thin film.

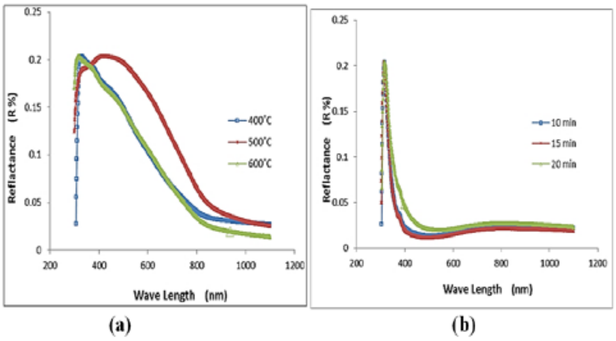

Figure 5. Reflectance curve of CuO thin films: (a) furnace annealing (b) laser annealing

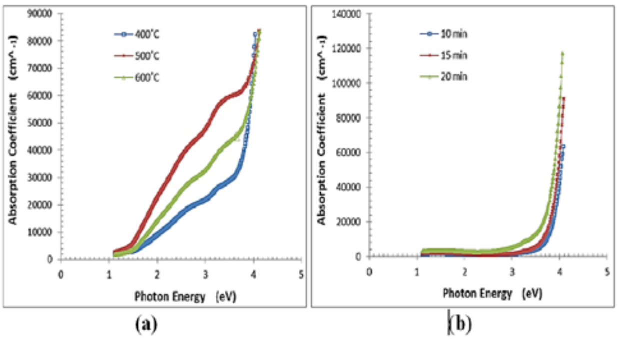

Figure 6. Absorption coefficient as a function of photon energy of CuO thin films:(a) furnace annealing (b) laser annealing

The results showed that the electronic transition is allowed direct type and that the energy gap slightly decreases with increasing oven temperature annealing and values range between (3.75 eV - 3.5 eV) where its value at (500 °C) is at less value because the absorbance at this degree is high. As well as an increase for laser annealing range values between (3.9 eV - 3.8 eV) as shown in Figure 7-A,B.

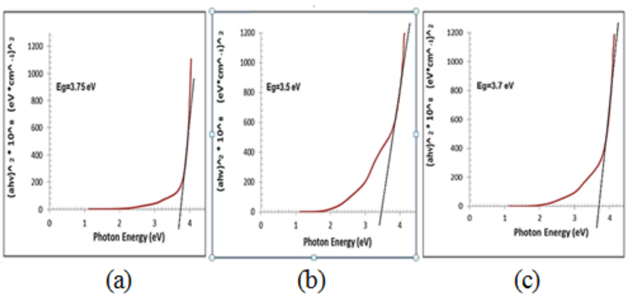

Figure 7A. Allowed direct energy band gap of CuO thin films furnace annealed at: (a) 400°C, (b) 500°C, (c)600°C

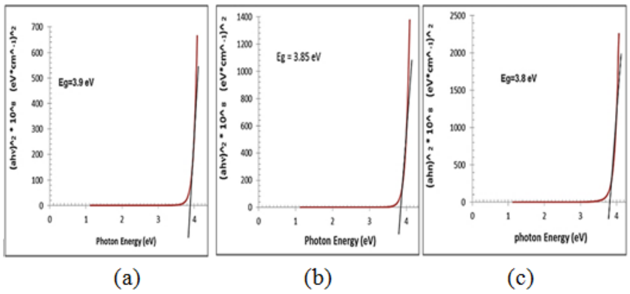

Figure 7B. Allowed direct energy band gap of CuO thin films laser annealed at: (a) 10 min, (b) 15 min, (c) 20 min

The results also showed, as shown in Figures (8-a,b) the change in the refractive index (equation 3) is similar to the (R) change, where little value is at few energies (high wavelengths) and then rise to larger value 9 of its at energy which equal to (Eg) and decreases then, and at all temperature annealing noting the emergence of meanders in curves due to the different nature of the surfaces of membranes, we find that the laser annealing leads to the same results with a note almost meanders curved disappearance has been attributed to high-energy of laser that led to the increase smoothness and irregular surfaces of the membranes.

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

Where (R) represents reflectivity and (K) coefficient of extinction. From figures (9-a,b) we find that the extinction coefficient curve (equation 4) is similar to the (α) curve, and the value be larger in the case of laser annealing than its in the case of oven annealing with note irregular shape of the curves in the laser annealing case.

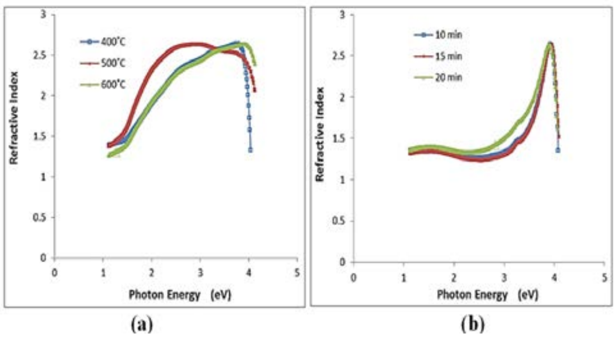

Figure 8. Refractive index as a function of photon energy of CuO thin films: (a) furnace annealing (b) laser annealing

$$k = \frac{\alpha\lambda}{4\pi} \tag{4}$$

Where (λ) represents wavelength. And from figures (10-a,b) we find that the real dielectric constant change (equation 5) is similar to the change of (n), where (εr) can be calculated from the refractive index, while the change of dielectric imaginary constant (equation 6) is similar to the change of (α) with a decrease in the values of (εi) at the end of the curve at high energies and this behavior is more pronounced in the case of laser annealing with the observation that increasing the duration of laser annealing led to increased values as shown in Figure 11-a,b.

$$\varepsilon_r = n^2 - k^2 \tag{5}$$

$$\varepsilon_i = 2nk \tag{6}$$

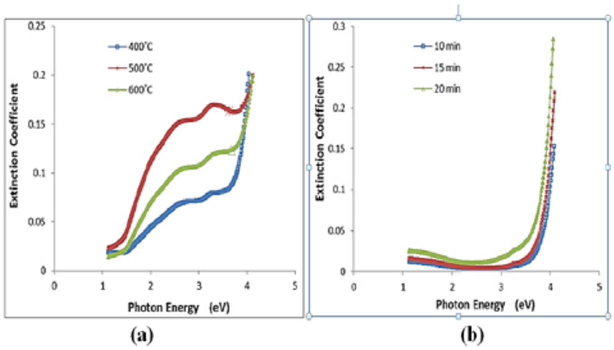

Figure 9. Extinction coefficient as a function of photon energy of CuO thin films:(a) furnace annealing (b) laser annealing

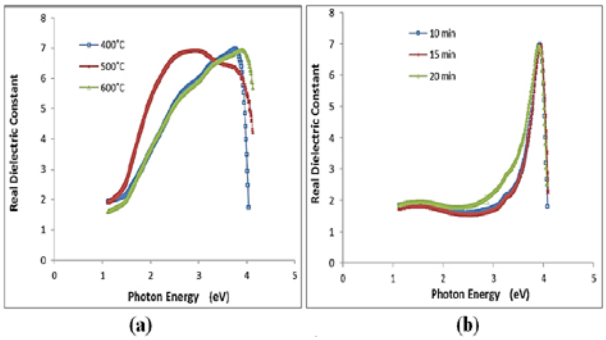

Figure 10. Real dielectric constant as a function of photon energy of CuO thin films:(a) furnace annealing (b) laser annealing

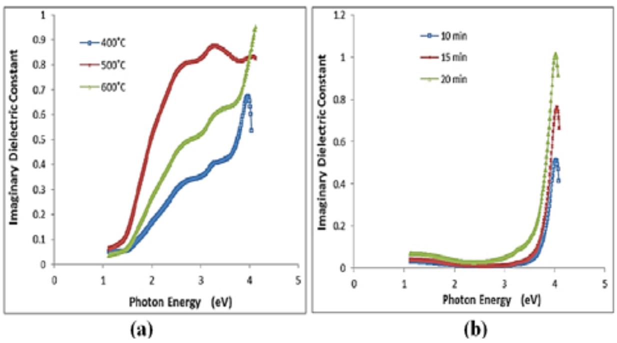

Figure 11. Imaginary dielectric constant as a function of photon energy of CuO thin films:(a) furnace annealing (b) laser annealing

In general by observed the figures that represent the optical parameters of (CuO) membranes furnace annealed, find little difference in form of curves as a result of simple deviation indicated by the results of (AFM), while laser annealing shows homogeneity and irregular forms of curves.

4. Conclusions

1. We can use CO2 laser for annealing and get an approximately similar results to those which obtained by furnace annealing, at the prepared conditions of this paper, in relative little time.
2. Structural results showed that CuO thin films are multi crystalline monoclinic type, and the increase of degree of furnace annealing temperature, as well as laser annealing interval time, lead to enhancing crystallization. Results also showed that the homogenously of membranes surfaces is increasing with increase of furnace annealing temperature, as well as laser annealing interval time.
3. 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 the values of energy gap decrease at increase of furnace annealing temperature, as well as laser annealing interval time, when the thin films defects will decrease and the transition will increase.

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