Study of Structural and Optical Properties of Cu2OThin Film Prepared by Rapid Thermal Annealing Using Nd-YAG Laser

Muhanad A. Ahmed[1*], Mohammed M. Sabri[2], Hind Q. Mohammad[3]

Abstract

In this paper, we reported the preparation of a thin film of Cu2O of a thickness of about 200 nm on a glass substrate using rapid thermal annealing by Nd-YAG pulse laser. The x-ray diffraction (XRD) results showed that the prepared Cu2O thin film is polycrystalline and the crystal structure is cubic with the planes of (111) and (200) are dominated. In addition, the optical measurements showed that the spectral permeability of the prepared thin film is high (73 % - 90 %) in visible and infrared (IR) regions and also the thin film has a high absorbance as a function of the incident wavelength in the ultraviolet (UV) region. The energy gap of the Cu2O thin film, on the other hand was also measured and it was found that it is 2 eV with allowable direct transition. It was also found that the rapid thermal annealing technique resulted in an increase in the particle size of the Cu2O and a decrease in the value of the energy gap of the latter, while annealing at 300 oC resulted in entirely Cu2O to CuO transformation and eventually an enhancement in the properties of the prepared thin film.

Key Words: Ultraviolet (UV), Ultra-high Vacuum (UHV), Pulsed Laser Evaporation (PLD), Infrared (IR).

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Introduction

Deposition using pulsed laser technique has become a widely used technique in recent years due to several factors. For instance, the energy source is outside the deposition chamber, the deposition rate is high and, hence obtaining an ultra-thin film. In addition, focusing the laser beam on a part of the sample is possible and no need to irradiate the whole sample. Finally, an ultra-high vacuum (UHV) is available in this technique with the possibility to evaporate more than one material [1-3]. Usually, pulsed laser evaporation (PLD) technique is used in crystalline films preparation. The first laser system was manufactured in early 60s in the last century and since then the applications of laser were expanded and it has been used to evaporate materials that cannot be evaporated using other techniques [4-9]. The laser absorption by the material is essential in order to laser-matter interaction being performed and this absorbance is the source of the energy in the material. This source will then give the indication to what happen to the material when irradiated by laser beam. Copper oxide (Cu_2O) thin film is one of the most important materials that have many optical and electronic applications [10-12]. It is used in solar energy, especially in the optical-thermal solar compounds. These applications require a material of a high efficiency, a suitable range of stability and a high absorbance in the visible wavelength region and these requirements are all available in the Cu_2O thin film.

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Copper oxide (Cu_2O), on the other hand has positive conductivity and has a low energy gap value [13,14] and also a variety of detectors are made of this thin film. It has been demonstrated that polycrystalline thin films are semiconductors and have importance in the production of electronic and electro-optical devices due to the high absorbance coefficient and low-cost manufacturing. Finally, Cu_2O is odorless not toxic material, has a light-brown color and has an optical absorbance coefficient that makes it convenient in the manufacturing of thin films solar cells [15-17].

Experimental Part

In this work, we deposited a thin film of Cu_2O of a thickness of about 200 nm on a glass substrate of dimensions of 7 cm × 2.5 cm using deposition technique by Nd-YAG pulse laser (manufactured by Siemens) of a wavelength of 1.06 μm operating at 700 mJ and pulse range of 10 nm. The evaporation system consists of a bell jar made of Pyrex of a thickness of 1 mm, a diameter of 320 mm and a height of 20 cm. The vacuum system, on the other hand consists of a rotary mechanical pump of type Edward, in which the minimum vacuum value obtained using this pump was 10^{-3} torr.

The experimental part consists of the following measurements:

X-ray diffraction (XRD)

In order to investigate the phases of the prepared thin film, x-ray diffraction technique of a type Philips PW 1050 and an x-ray of a wavelength of 1.93728 Å of a source of Fe-Kα was used.

The surface topography

In order to analyze the surfaces of the prepared thin film, a reflected optical microscopy of type Leit3-Metallax of a magnification of 600x was used.

Optical Measurements

Here, we measured the optical constants and the value of the energy gap of the Cu_2O thin film. We measured the spectral permeability and absorbance of the prepared thin film by using a spectrometer of type UV-VIS-NIR-Double beam spectrophotometer.

Annealing

Thermal annealing of the prepared Cu_2O thin film was performed using a halogen lamp of a power of 1000 W at different temperatures of 100 °C, 200 °C and 300 °C at a fixed time of 3 min.

Results and Discussion

This section was divided into two sub-sections of structural measurements and of optical measurements.

Structural measurements

The x-ray diffraction results showed that the prepared Cu_2O thin film is polycrystalline. Fig. 1 shows the x-ray diffraction spectrum of the un-annealed Cu_2O.

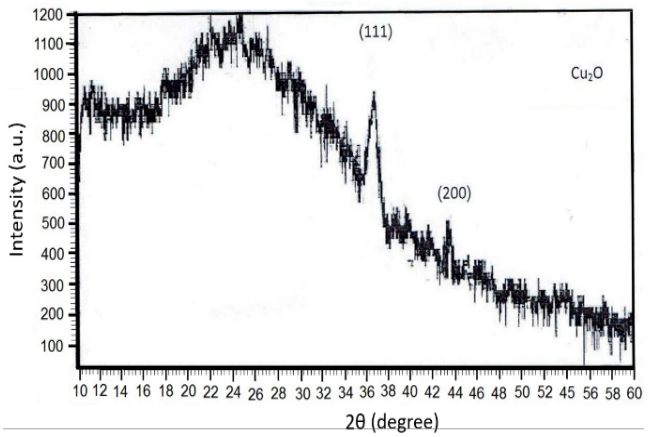

Fig. 1. XRD spectrum of the un-annealed Cu_2O

It is clear that the two dominated planes are (111) and (200)[17]. However, after performing the annealing process for 3 min at 100 °C, the increase in the growth of the planes was observed (See Fig. 2) and this increase was continued when the thin film was annealed at 200 °C and the appearance of new planes ((111) and ($\overline{111}$)), which indicates that the Cu_2O thin film started to transform into CuO (See Fig. 3). The Cu_2O was entirely transformed into CuO when annealed at 300 °C [18-20] as shown in Fig. 4. The reason beyond this transformation was the oxygen diffused inside the Cu_2O thin film which resulted in an interaction between the oxygen and the thin film [21] as illustrated in the following formula:

$$2CU_2O + O2 \longrightarrow 4CUO \quad (1)$$

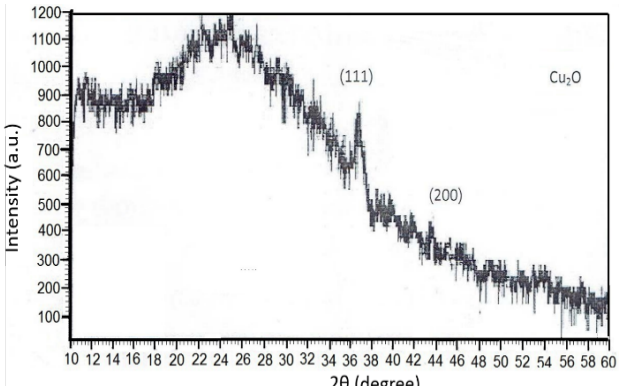

Fig. 2. XRD spectrum of the annealed Cu_2O at 100 °C

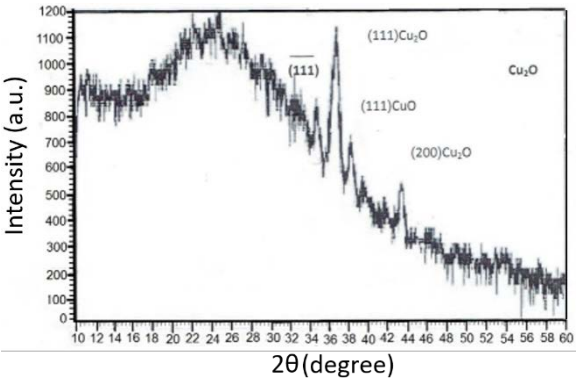

Fig. 3. XRD spectrum of the annealed Cu_2O at 200 °C

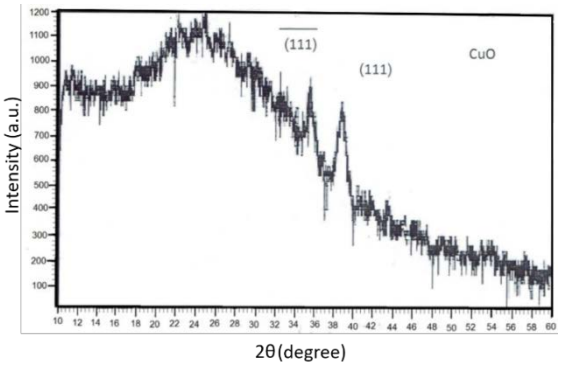

Fig. 4. XRD spectrum of the annealed Cu_2O at 300 °C showing the fully transformation into CuO

Table 1. Shows the summary of the x-ray diffraction results for un-annealed and annealed Cu2O at different temperatures

Table 1. X-ray diffraction data for un-annealed and annealed Cu_2O thin film at various temperatures along with that for CuO

Sample	2θ	T (°C)	*hkl*
Cu_2O	36.7 43.8	27	(111) (200)
Cu_2O	36.7 43.8	100	(111) (200)
Cu_2O	34.9 36.7 38.1 43.8	200	$\overline{(111)}$ $\overline{(111)}$ (111) (111)
CuO	34.9 38.1	300	$\overline{(111)}$ (111)

The un-annealed Cu_2O thin film has an average particle size of about 17 nm, while the particle size has increased to 25 nm when the thin film was annealed at 300 °C and this was another reason beyond the crystal phase transformation of Cu_2O to CuO. In addition, the height of the peaks has increased while the width was decreased, and this give an indication of an increase in the particle size of the Cu_2O thin film [21].Fig. 5 shows anoptical microscope topographic image of the un-annealed Cu_2O thin film. The homogeneity of the thin film is clear, while the obvious spots are from the preparation of the thin film by laser technique evaporation. The figure also shows that the color of the Cu_2O thin film is light-brown.

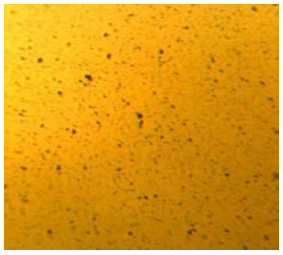

Fig. 5. An optical microscope micrograph for the un-annealed Cu_2O film at a magnification of 600 (600x)

Fig. 6 shows the surface of the annealed Cu_2O thin film at 100 °C – 300 °C. It is indicated that by increasing the annealing temperature, the homogeneity of the thin film will be increased and hence the particles will be distributed more regularly, and the thin film will be more packed and freer of defects [22].

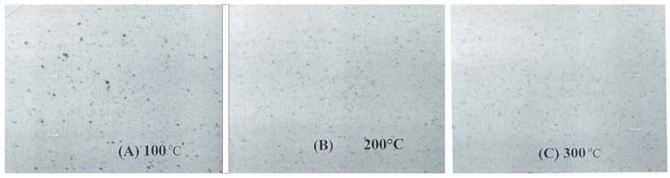

Fig. 6. Optical microscope micrographs for the annealed Cu_2O at (A) 100 °C, (B) 200 °C and (C) 300 °C

In order to further confirm the homogeneity of the prepared thin film, atomic force microscope (AFM) was used (See Fig. 7). From this figure, the nano structure of the prepared Cu_2O thin film and the three dimensionality (3D) of the film are obvious. In addition, by this technique, we succeed in measuring the thickness of the thin film, which was 200 nm.

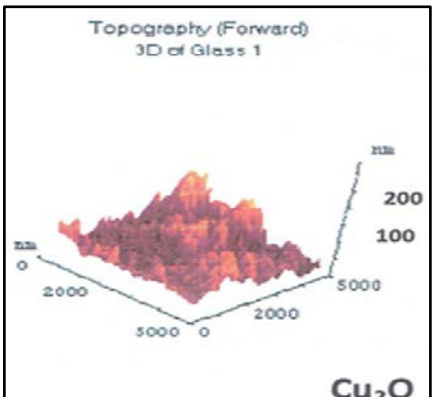

Fig. 7. Atomic force microscopy (AFM) image for the Cu_2O thin film

Optical Measurements

Fig. 8 shows the optical permeability (transmittance) of the un-annealed Cu_2O film as a function of the incident wavelength. It is clear that the permeability increases with increasing the wavelength (400-900 nm). The optical permeability of the film is then depending on the crystal structure of the material and the thickness of the film.

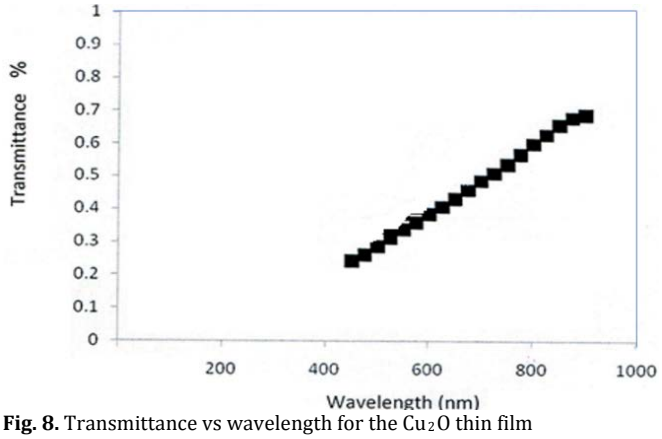

Fig. 8. Transmittance vs wavelength for the Cu_2O thin film

Fig. 9, on the other hand shows the permeability of the annealed Cu_2O film at different temperatures (100 °C, 200 °C and 300 °C). It is obvious that by approaching to the near infrared region, the film's permeability increases with increasing the wavelength along with increasing the permeability with increasing the annealing temperature. The better permeability to the Cu_2O film will be at 300 °C due to the fact that with increasing the annealing temperature the size of the volatile and deposited materials on the film will be decreasing and therefore, the fast annealing process will increase the optical permeability[21,23].

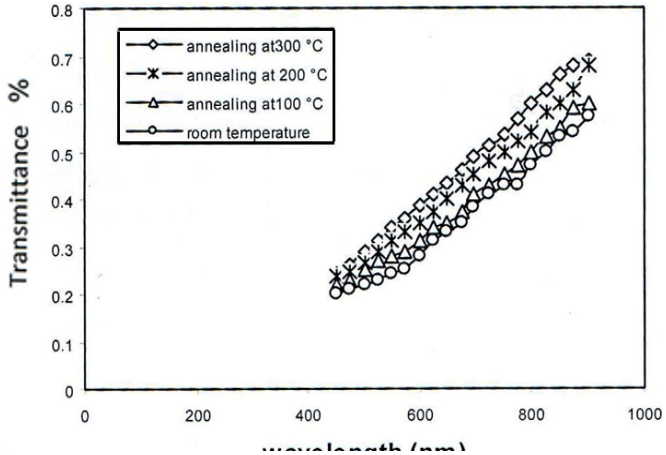

Fig. 9. Transmittance vs wavelength for the annealed Cu_2O thin film at various temperatures

Fig. 10 shows the absorbance spectrum (A) of the un-annealed and annealed Cu_2O film at different temperatures as a function of the incident wavelength (λ). It can be seen that the value of the absorbance decreases with the increase in the wavelength and there is a slight decrease in the value of the absorbance in the low energy region (long wavelengths), while the value of the absorbance quickly decreases in the high energy region (short wavelength).

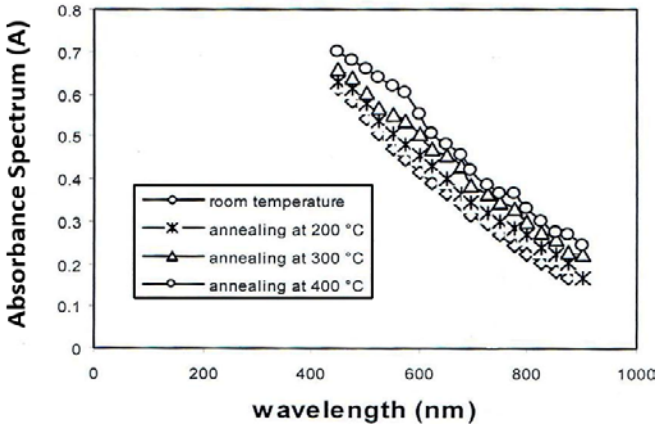

Fig. 10. Absorbance spectrum (A) as a function of the wavelength for the un-annealed and annealed Cu_2O thin film at different temperatures

It is obvious that the optical absorbance will be decreased as a result of increasing the annealing temperature of the Cu_2O and also as a result of increasing the permeability. For instance, the leaser value of the optical absorbance when the temperature is 300 °C. The value of the absorbance coefficient signifies the ability of the film to absorb the energy of the incident radiation. The relationship between the intensity of the transmitted light (I_x) and the intensity of the incident light (I_o) is:

$$I_X = I_0 e^{-xt} \quad (2)$$

t: the film's thickness.

α: the absorbance coefficient and it is a

wavelength's function (cm $^{-1}$).
After simplifying the above equation, we get:

$$\alpha\, t = 2.303\ (I_n \frac{I_0}{I_X}) \qquad (3)$$

The term ($\log\frac{I_0}{I_X}$) is the absorbance of the film. The intensity of the incident radiation is logarithmically decreasing and then the absorbance coefficient (α), which represents the decreasing ratio in the radiation energy within the material will be given as [24]:

$$\alpha = \frac{2{\cdot}303\ A}{t} \qquad (4)$$

It has been confirmed that the Cu2O thin film has a direct energy gap and the allowable direct absorbance is dominated and the value of the absorbance coefficient is [25,18]:

$$\alpha = A[h\nu - Eg]^{1/2} \quad (5)$$

In which (A) is constant and (*Eg)* is the energy gap. The value of is about 8.5 × 10^4 cm^{-1} at a wavelength of 620 nm. The wavelength can be found from the following formula:

$$\lambda_c(\mu m) = \frac{1{\cdot}24}{E_g(eV)} \qquad (6)$$

Fig. 12 shows the absorbance coefficient (α) for the un-annealed and annealed Cu_2O film as a function of the incident photon energy ($h\nu$). From the figure, it is clear that the value of the absorbance coefficient is greater than 10^4 cm^{-1} for a range of energies between 1.4 – 2.8 eV and this value increases with the increase of the photon energy and this will be benefit for the occurrence of direct electron transitions within the aforementioned energy ranges. The absorbance coefficient of about 7.3×10^4 cm^{-1} at a photon energy of 2.8 eV for the prepared Cu_2O film will be decreased to about 6×10^4 cm^{-1}at the same photon energy (2.8 eV) and at a temperature of 300 ^{o}C. This is obvious in Fig. 11 in which by increasing the annealing temperature, the absorbance coefficient decreases as a result of the decrease in the absorbance.

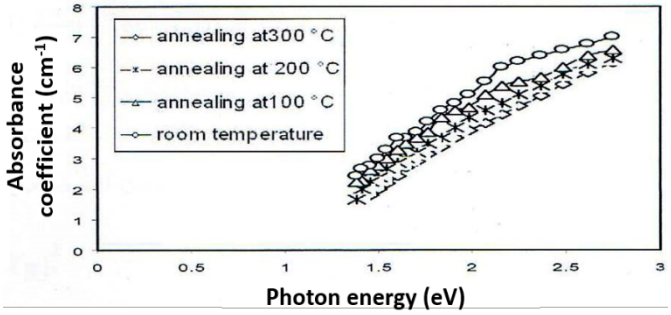

Fig. 11. The relationship between absorbance coefficient and photon energy for the un-annealed and annealed Cu_2O thin film at different temperatures

In addition, the value of energy gap (E_g), which depends on the crystal structure of the material can be measured by knowing the value of the absorbance coefficient and the incident photon energy. Figs. 12 and 13 shows the relationship between the square of the absorbance coefficient value $((\alpha\, h\nu))^2$ and the incident photon energy ($h\nu$) for un-annealed and annealed Cu_2O thin film at 300 ^{o}C, respectively. The value of the energy gap of the Cu_2O film of about 2 eV [8] has been decreased to about 1.7 eV [26] when the Cu_2O film was annealed at higher temperature (here at 300 ^{o}C) as shown in Fig. 14. This value of the energy gap is too close to that of CuO, which confirm that the Cu_2O film was fully transformed to CuO at this temperature (300 ^{o}C) as proven by XRD data.

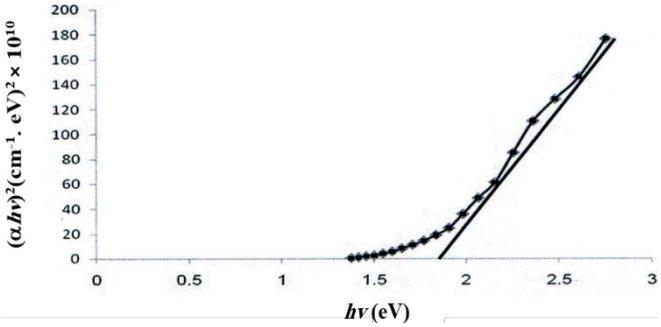

Fig. 12. The relationship between the square of the absorbance coefficient value $((\alpha\, h\nu))^2$ and the incident photon energy ($h\nu$) for the un-annealed Cu_2O thin film

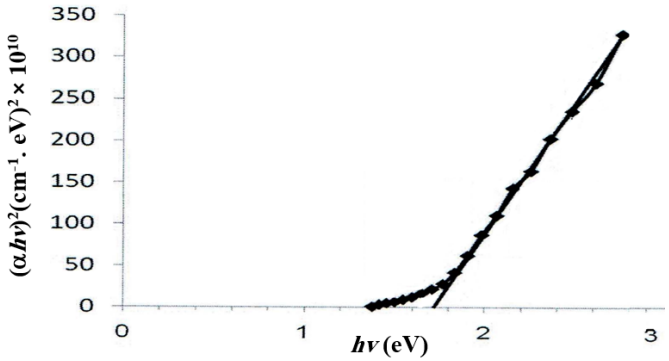

Fig. 13. The relationship between the square of the absorbance coefficient value $((\alpha\, h\nu))^2$ and the incident photon energy ($h\nu$) for the annealed Cu_2O thin film at 300 ^{o}C

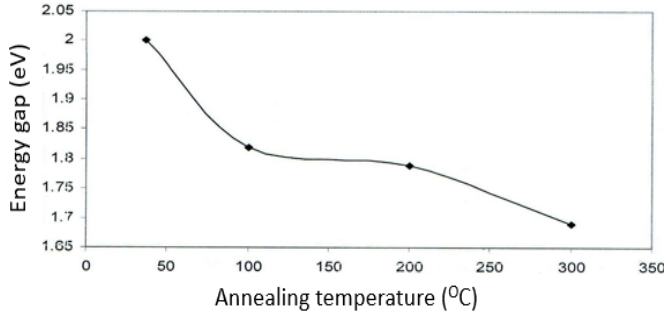

Fig. 14. The value of energy gap as a function of annealing temperature for the Cu_2O thin film

On the other hand, refractive index (n) and damping index (k) through the absorbance and transmission of the Cu_2O film have also been calculated. Fig. 15 shows the refractive index as a

function of the photon energy of the Cu_2O film. From this figure, it is clear that the nature of the refractive index curve is similar to that of the reflection due to the relation between these two. The value of refractive index for the Cu_2O film is 2.65, as shown in Fig. 15. Furthermore, this figure also shows the effect of the rapid annealing on the value of refractive index of the Cu_2O film in which this value was slightly decreased with the increase of the annealing temperature as a result of the decrease in the reflectivity with the increase in the annealing temperature.

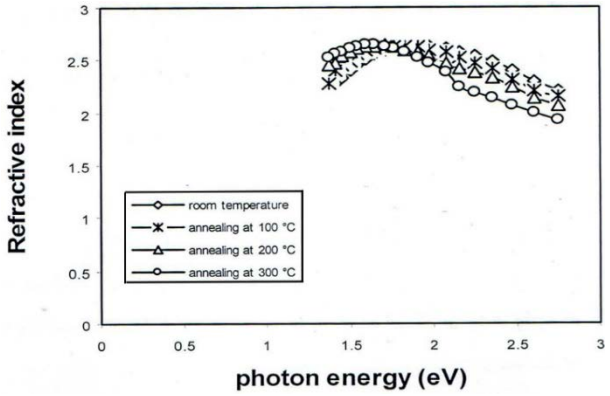

Fig. 15. The relationship between the refraction index (n) and the incident photon energy ($h\nu$) for the un-annealed and annealed Cu_2O thin film at various temperatures

The damping index (k) represents the amount of the energy absorbed by the thin film and represent the imaginary part of the complex refractive index and can be given by:

$$n_1 = n_o - ik \quad (7)$$

n_1 is the real refractive index, n_0 is the imaginary refractive index and k is the damping index. In addition, the relationship between the damping index (k) and the absorbance index (α) can be given by:

$$K = \frac{\alpha\lambda}{4\pi} \quad (8)$$

Fig. 16 shows the changes in the damping index (k) as a function of the photon energy of the Cu_2O film. It is clear from the figure that the damping index increases with the increase in the photon energy (1.4 – 2.3 eV) as a result of the increase in the value of the absorbance coefficient, which occurs due to the electronic transition between valence band and conduction band. On the other hand, it has been noticed that the value of damping index is constant at the range of energies of 2.4 – 2.7 eV as a result of the fixed value of the absorbance coefficient at this range of energies. The figure also shows the increase in the value of damping index with the increase in the annealing temperature. This effect is due to the decrease in the value of the dielectric constant (the real and the imaginary parts).

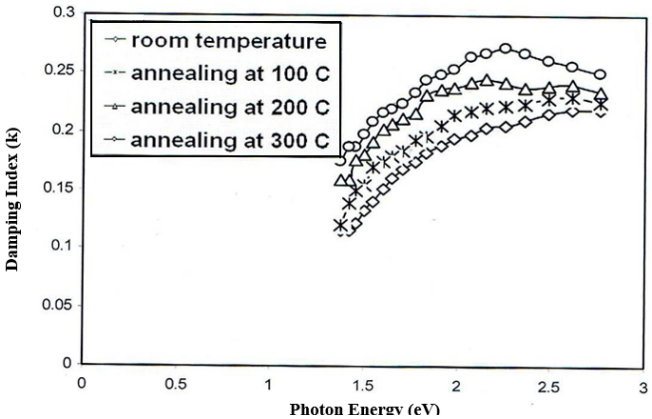

Fig. 16. Damping index (k) vs photon energy for the un-annealed and annealed Cu_2O thin film at different temperatures

The relationship between the dielectric constant and the damping index is shown in the following:

$$\varepsilon_1 = n_0^2 - k^2 \quad (9)$$

$$\varepsilon_2 = 2n_o k \quad (10)$$

In which $\varepsilon_1$is the real dielectric constant,$\varepsilon_2$is the imaginary dielectric constant and k is the damping index.

The interaction between the light and the charges of the media is due to the absorbance of the energy in the material and this will lead to the polarization process for the media charges. This polarization is usually known as a complex dielectric constant (ε). Figs.17 and 18 show the changes in the real part of the dielectric constant as a function of the photon energy of the Cu_2O film and the changes in the imaginary part of the dielectric constant as a function of the photon energy of the Cu_2O film, respectively. In the former figure, it is shown that the behavior of the curve is similar to the behavior of the refractive index. This part of the dielectric constant is also called dielectric loses factor and this refers to the lose in the energy of the electromagnetic wave when its electric compound tries to direct the dipoles in the material to the incident field of the wave. When the dipoles try to respond to the incident wave, their bonds with the atoms impede this response and this will lead the dipoles to drop behind the electric compound of the field in terms of the phase and this will lead to the loss in the power. The latter figure, on the other hand shows that the behavior of the curve is somewhat similar to the behavior of the damping coefficient.

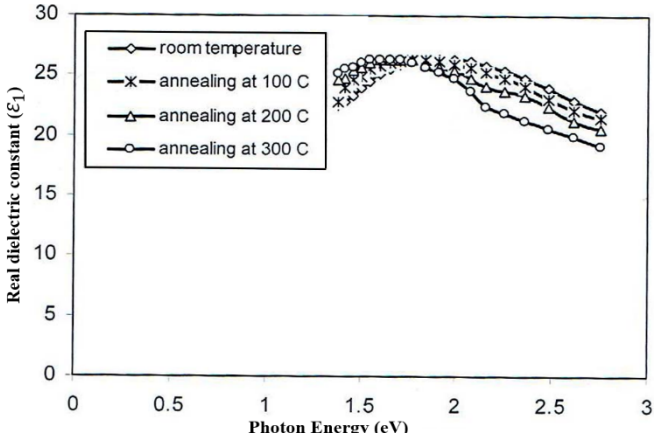

Fig. 17. The real dielectric constant and photon energy for the un-annealed and annealed Cu_2O thin film at different temperatures

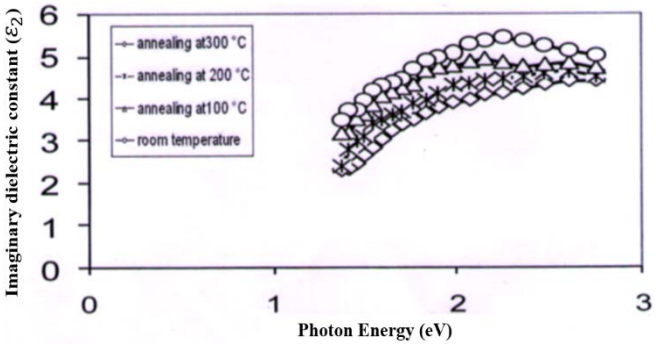

Fig. 18. The imaginary dielectric constant and photon energy for the un-annealed and annealed Cu_2O thin film at different temperatures

The rapid annealing has a great impact on the real and imaginary parts of the dielectric constant, as by the increase in the annealing temperature, an atomic rearrange will occur and this will result in an arrangement in the localized state. This will result in an increase in the conductivity of the material and a decrease in the real dielectric constant. The localized state rearrangement in the energy gap has a great impact in the decrease of the real dielectric constant in a less manner relative to the decrease in the imaginary dielectric constant. The dielectric loses, on the other hand refer to the regularity in the free carriers as dipoles due to the electric polarization.

Conclusion

In this research, we succeeded in preparation a polycrystalline Cu_2O thin film by thermal evaporation process using laser technique. The prepared thin film has only allowable direct electronic transitions. In addition, the value of the energy gap of the prepared Cu_2O thin film was found to be about 2 eV. It has been also concluded that the value of the energy gap was decreased as a result of increasing the annealing temperature. The rapid annealing was also of a great impact on the properties of the prepared Cu_2O thin film in which it resulted in an increase in the optical permeability and decrease in both the absorbance and the reflection. In addition, the rapid annealing resulted in a decrease in the optical constants such as absorbance coefficient, refractive index and both parts of dielectric constant (real and imaginary parts), while an increase in the damping index was observed. Finally, at the temperature of 300 ^oC, theCu_2O thin film was entirely transformed into the CuO thin film.

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