Influence of the Annealing Temperature on optical Properties of (CuInSe₂) Thin Films

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Abstract
The Influence of annealing temperature on the optical properties of (CuInSe₂) thin films was studied. Thermal evaporation in vacuum technique has been used for films deposited on glass substrates, these films were annealed in vacuum at (100°C, 200°C) for (2 hours). The optical properties were studied in the range (300-900) nm. The obtained results revealed a reduction in energy band gap with annealing temperature. Optical parameters such as reflectance, refractive index, extinction coefficient, real and imaginary parts of the dielectric constant, skin depth and optical conductivity are investigated before and after annealing. It was found that all these parameters were affected by annealing temperature.

Key words: CuInSe₂ thin films, optical properties, vacuum thermal evaporation, annealing temperature.
Introduction
Semiconducting thin films have been extensively studied for a long time due to their significant role in modern science and technology. CuInSe$_2$ (CIS) semiconductor thin film has recently received much attention as an absorber layer in solar cells owing to its excellent optical and semiconducting properties[1]. It has a direct band gap around (1.0 eV), high optical absorption coefficient (>10$^5$ cm$^{-1}$) [2,3], and reasonable work function, high long-term stability and largest efficiency in solar cell applications[4], photo detectors and light emitting diodes[5].

In order to meet the cost-effective large area requirement for CuInSe$_2$ production, there is continuous research into new processing techniques which are favourable for large scale deployment[6]. The most common methods for preparing of CIS thin films on glass substrates are sputtering, molecular beam epitaxy (MBE) and electrodeposition (ED) [7].

In this work, the optical properties of (CIS) thin films was studied extensively at two different annealing temperatures.

Experimental details
Copper indium diselenide thin films have been deposited by using thermal evaporation in vacuum technique (10$^{-6}$ Torr) on to well cleaned glass substrates by using ultrasonic path. The weighed high purity (99.999 %) elemental copper, indium and selenium are taken in a pure cleaned quartz ampoule of diameter (10 mm) and length (65 mm) under vacuum.

Using a CuInSe$_2$ ingot as the source material. The elements for the ingot were mixed and sealed in quartz ampoules under vacuum. The ampoules were heated at temperature (1200 C°) over (24 hours), and then cooled to room temperature. The thickness of the films was measured by using the weight methods. The accuracy of thickness measurements was (200 nm). These films were annealed in vacuum at (100C°, 200C°) for (2 hours). Optical transmission spectra of CuInSe$_2$ films have been recorded from (300 nm) to (900 nm) wavelength using a double beam (UV/VIS) (Shimadzu Corporation Japan) at room temperature.

Results and Discussions
Fig. (1) shows the spectral distribution of transmittance for the as deposited and annealed CuInSe$_2$ films at (100C°, 200C°) for (2 hours), in the wavelength range (300-900) nm.

In the spectral region, transmittance of annealed films at (200 C°) is lower than that for as deposited and annealed films at (100 C°). Decreasing the transmittance for CuInSe$_2$ might be due to increase scattering of photons by crystal defects, and the free carrier absorption of photons contributed to the reduction in optical transmittance, or might be due to increase of the crystallite size. The increased roughness of the annealed thin films contributed to the drastic decrease of optical transmittance [8], from this figure it is observed that the transmittance decreases at the low wavelength region, which is the spectral region of fundamental absorption, in this region the incoming photons have sufficient energy to excite electrons from the valence band to the conduction band and thus these photons are absorbed within the material to decrease the transmittance. For this reason, this region carries the information of the band gap of the material [7].

Fig. (2) shows the reflectance spectrum of as prepared CuInSe$_2$ films and the films annealed. The reflectance after annealing became lower than that before annealing.

The following relation could be used for calculating the absorption coefficient ($\alpha$) [9]:

$$\alpha = \frac{2.303 A_o}{t}$$  \hspace{1cm} (1)

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Where \((A°)\) is the absorbance and \((t)\) is the film thickness.

Fig. (3) shows the absorption coefficient \((\alpha)\) of annealed by two temperatures \((100 °C, 200 °C)\) and as deposited \(\text{CuInSe}_2\) films versus Wavelength, all films show higher absorption on the shorter wavelength side \((\alpha > 10^4 \text{ cm}^{-1})\). From this figure \((\alpha)\) (annealed films at \(200 °C) > \alpha\) (annealed films at \(100 °C) > \alpha\) (films as deposited), this might be attributed to the increase of defect states which leads to increase absorption coefficient. Absorption of photons creates electron-hole pairs. In turn, the field of such pairs may modify the electronic structure and hence of optical properties of \(\text{CuInSe}_2\) films [10].

The energy band gaps of these films were calculated with the help of the absorption spectra. To determine of the energy band gap, we plotted \((\alpha hf)^2\) versus photon energy using the relation [11]:

\[
\alpha hf = B(hf - E_g)^n
\]  

(2)

in which \((B)\) is a constant, \((E_g)\) is the energy band gap and \((n)\) is the \((\frac{1}{2})\) and \((2)\) for the allowed transition being direct and indirect, respectively.

Fig. (4) shows a plot of \((\alpha hf)^2\) as a function of photon energy. The energy band gap was shifted from \((1.35 \text{ eV})\) to \((1.33 \text{ eV})\) and \((1.312 \text{ eV})\) due to annealing. This may be the cause for the increase in band tail width, and then decreases energy band gap. And the Fig. (5) shows the relation between energy band gap \((E_g)\) and annealing temperature for \(\text{CuInSe}_2\) films.

Refractive index \((n°)\) is one of the fundamental properties for an optical material, because it is closely related to the electronic polarizability of ions and the local field inside materials. The refractive index \((n°)\) is related to the optical reflectance \((R)\) by the following relation [12]:

\[
n° = \left[\frac{4R}{(R-1)^2} - k°\right]^{1/2} - \frac{R+1}{R-1}
\]

(3)

Where \((k°)\) is the extinction coefficient.

The behavior of refractive index is nearly similar to the reflectance, we can observe from Fig. (6) the refractive index \((n°)\) decreases with annealing temperature.

The extinction coefficient \((k°)\) is directly proportional to the absorption coefficient \((\alpha)\) by using the relation [13]:

\[
k° = \frac{\alpha \lambda}{4 \pi}
\]

(4)

Where \((\lambda)\) is the wavelength of the incident photon.

Fig. (7) Shows the variation in extinction coefficient \((k°)\) as a function of the wavelength, it can be noticed that the extinction coefficient increases with annealing temperature.

The variation of the real \((\varepsilon_r)\) and imaginary \((\varepsilon_i)\) parts of the dielectric constant values versus wavelength for \(\text{CuInSe}_2\) films before and after annealing are shown in Fig. (8) and Fig. (9). The behavior of real \((\varepsilon_r)\) part of the dielectric constant is similar to that of refractive index \((n°)\) because the smaller value of \((k°^2)\) compared with \((n°^2)\) [14]:

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\[ \varepsilon_r = n^2 - k^2 \]  

while the imaginary (\( \varepsilon_i \)) part of the dielectric constant mainly depends on the extinction coefficient (\( k^o \)) values, which are related to the variation of absorption coefficient [14]:

\[ \varepsilon_i = 2n^o k^o \]  

The real and imaginary parts of the dielectric constant indicate the same pattern and the values of real part are higher than imaginary part [15].

It is useful to define a characteristic “skin” thickness that is subjected to an appreciable density of optical energy. The skin depth (\( \chi \)) can be determined by using the relation [16]:

\[ \chi = \frac{\lambda}{2 \pi K^o} \]  

Fig. (10) shows the variation of skin depth (\( \chi \)) as a function of wavelength for CuInSe\(_2\) films. At wavelength shorter than (700 nm), the skin depth for three films has approximately the same values, this might be due to equal probability of absorption at this spectral region. At wavelengths greater than (700 nm), the reduction in amplitude occurs after passing a larger distance, then the skin depth will be large. The skin depth decreases with annealing temperature, this might be due to increase the probability of absorption as the annealing temperature increase.

The optical conductivity (\( \sigma \)) of the films depends directly on the wavelength (\( \lambda \)) and absorption coefficient (\( \alpha^2 \)). With the aid of the Drude formula [17]:

\[ \sigma = \left( \frac{\alpha^2 \varepsilon_0 \lambda}{4 \pi} \right) \]  

where (c) is the velocity of light, (\( \varepsilon_0 \)) is the permittivity of free space (\( \varepsilon_0 = 8.85 \times 10^{-12} \) C/N.m\(^2\))

Fig. (11) shows the variation of optical conductivity (\( \sigma \)) as a function of wavelength for CuInSe\(_2\) films.

From the curves, the effect of annealing temperature is increasing of optical conductivity. Under wavelength (700 nm), high absorption of thin film behavior is due to the photon-atom interaction leading to higher carrier concentration. This effect increases the optical conductivity [18].

**Conclusions**

CuInSe\(_2\) thin films have been prepared successfully by thermal evaporation in vacuum technique. It was found that the annealing temperature is an important role in the evolution of CuInSe\(_2\) properties.

The heat treatment changes the optical properties under investigation in this study. The results show that the (\( E_g \)) is (1.35 eV) before annealing and (1.33 eV) after annealing in (100 C°) and (1.312 eV) after annealing in (200 C°).

The film annealed at (200 C°) is a good optical properties (lower transmittance, reflectance, energy band gap, refractive index, real part of the dielectric constant and skin depth, and a larger absorption coefficient, extinction coefficient, imaginary part of the
dielectric constant and optical conductivity), it can be used as an absorber layer in the fabrication of thin film solar cells.

References
Figure No. (2) : Reflectance (R) versus wavelength for CuInSe$_2$ films

![Graph showing reflectance (R) versus wavelength for CuInSe$_2$ films.](image)

Figure No. (3) : Absorption coefficient ($\alpha$) versus wavelength for CuInSe$_2$ films

![Graph showing absorption coefficient ($\alpha$) versus wavelength for CuInSe$_2$ films.](image)

Figure No. (4) : Energy band gap ($E_g$) versus photon energy for CuInSe$_2$ films

![Graph showing energy band gap ($E_g$) versus photon energy for CuInSe$_2$ films.](image)
Figure No. (5) : Energy band gap ($E_g$) versus annealing temperature for CuInSe$_2$ films.

Figure No. (6) : Refractive Index ($n_o$) versus wavelength for CuInSe$_2$ films
Figure No. (7) : Extinction Coefficient ($k_o$) versus wavelength for CuInSe$_2$ films.

Figure No. (8) : real ($\varepsilon_r$) part of the dielectric constant versus wavelength for CuInSe$_2$ films.
Figure No. (9) : Imaginary ($\varepsilon_i$) part of the dielectric constant versus wavelength for CuInSe$_2$ films

Figure No. (10) : Skin depth ($X$) versus wavelength for CuInSe$_2$ films.
Figure No. (11) : Optical conductivity ($\sigma$) versus wavelength for CuInSe$_2$ films.
تأثير درجة حرارة التلدين في الخصائص البصرية لأغشية CuInSe۲

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الخلاصة
إن تأثير درجة حرارة التلدين في الخصائص البصرية لأغشية CuInSe۲ (الرقيقة) تم دراسته. طريقة التخمير الحراري في الفراغ استخدمت في تحضير الأغشية البصرية على قواعد زجاجية. هذه الأغشية تم التلدين في الفراغ بدرجة حرارة (200, 100) °C ، لمدة ساعتين. درست الخصائص البصرية بمدبدي (900-300) nm. ان النتائج المستحصلة أن قوة الالام تتأثر بدرجة حرارة التلدين. المعاملات البصرية مثل الانكسارية، معامل الانكسار، معامل الخضود، ثابت العزل بجزئي الحقيقي والخيالي، عمق الاختراق والتوصلية الضوئية حسب قدر التلدين. وجد أن هذه المعاملات كايفة قد تتأثر بدرجة حرارة التلدين.

الكلمات المفتاحية : أغشية CuInSe۲ ، الخصائص البصرية ، التخمير الحراري في الفراغ ، درجة حرارة التلدين.