Study the optical properties of $CuInS_2$ non stoichiometric thin films prepared by chemical spray pyrolysis method

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Abstract

Effect of [Cu/In] ratio on the optical properties of $CuInS_2$ thin films prepared by chemical spray pyrolysis on glass slides at 300^oC was studied. The optical characteristics of the prepared thin films have been investigated using UV-VIS spectrophotometer in the wavelength range (300-1100 nm). The films have a direct allow electronic transition with optical energy gap (E_g) decreased from 1.51 eV to 1.30 eV with increasing of [Cu/In] ratio and as well as we notice that films have different behavior when annealed the films in the temperature 100^oC (1h,2h), 200^oC (1h,2h) for [Cu/In]=1.4 . Also the extinction coefficient (k), refractive index (n) and the real and imaginary dielectric constants (ε_1, ε_2) have been investigated.

Key words

films $CuInS_2$, optical properties of $CuInS_2$ thin films, chemical spray pyrolysis

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دراسة الخصائص البصرية للأغشية الرقيقة $CuInS_2$ الغير متكافئة المحضرة بطريقة الرش الكيميائي الحراري .

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الخلاصة

تم دراسة تأثير النسبة [Cu/In] على الخصائص البصرية لأغشيه $CuInS_2$ الرقيقة المرسبة على شرائح زجاجية بطريقة الرش الكيميائي الحراري عند درجة حرارة الأساس $300\ ^oC$ وقد تم دراسة الخصائص البصرية للاغشية المحضرة باستخدام مطياف (UV-VIS) ضمن مدى الأطوال الموجية (300-1100nm). ولقد وجدت إن هذه الاغشيه تمتلك فجوة طاقه مباشرة تقل من 1.51eV إلى 1.30eV مع زيادة النسبة [Cu/In]. كذلك تسلك فجوة الطاقة سلوك مختلف عندما تم تلدين النسبة[Cu/In]=1.4 بدرجات حرارة 100 درجة سيليزية و200 درجة سيليزية ولزمن ساعة واحدة وساعتين. كما تم دراسة معامل الخمود (k) ومعامل الانكسار (n) وثابتي العزل الكهربائي الحقيقي (ε_1) والخيالي (ε_2) .

Introduction

$CuInS_2$ is one possible candidate in the family of I-III-VI_2 type compounds for the photovoltaic applications due to its direct band gap of 1.5eV and high absorption coefficient. The spray pyrolysis method is a widely used process to produce large-area metal oxide thin films and it also seems attractive for depositing low-costfilms of ternary compounds [1, 2]. The properties, such as high optical absorption coefficient and band gap energy of 1.5eV, have raised researchers' interest in $CuInS_2$ thin films used as an absorber layer in solar cells [3,4]. The growth and material properties of $CuInS_2$ films prepared by spraying on glass substrates have been investigated by different authors [5]. The supersaturate structure has the advantages, such as an easy and reliable encapsulation and that only one cover glass is needed for the solar cell module reducing the overall fabrication costs[4,5]. The effect of the growth temperature on the structure of I-III-VI_2 type films prepared by spray pyrolysis is studied in many works [1]. A variety of techniques have been applied to deposit CuInS2 thin films, such as single source evaporation, co evaporation from elemental sources, sulfurisation of metallic precursors, diffusion of Cu and S into In_xS precursor, electro deposition and spray pyrolysis. A multisource evaporation technique has resulted in the best ternary compound solar cells on the basis of $CuInSe_2$. This technique results also in high prices of the cell and converted energy. Other inherently less expensive thin film deposition techniques cannot provide accurate and reproducible compositional control of deposited films. Additional heat and chemical treatments are required to improve the qualities of thin films [6].

The optical properties of sprayed $CuInS_2$ films depend on the preparation conditions as growth temperature and ion ratio of Cu/In in spraying solution are under the study.

Experimental

$CuInS_2$ thin films prepared by chemical spray pyrolysis on micro glass slides .firstly, the glass slides were cleaned with detergent water and then dipped in acetone. Spray solutions were prepared by mixing 0.1M aqueous solution of $[Cu(NO_3)_2.3H_2O]$, $[In(NO_3)_3]$ and Thiourea $[CS(NH_2)_2]$ and the Copper Indium molar ratio in the solution was varied as (Cu/In= 0.5,0.8,1.0,1.2,1.4). After that the amount of solution for each experiment were mixed using a magnetic stirrer. Automated spray solution is transferred to the hot substrate kept at the normalized deposition temperature of 300 ºC with the help of carrier gas. Filtered air is used as carrier gas, the flow rate of which is normalized to ~3ml/min. To avoid excessive cooling of substrate, spraying was achieved in periods about of 10sec followed by 15sec wait. To deposit films of uniform thickness the distance between the substrate and spray nozzle was kept at 50cm. Thickness measurement of the films has been carried out using weight method which equal to 300 ±20 nm.

UV-VIS spectrophotometer type Jenway 6405 UV/VIS was used to measure the absorptance and transmittance in the wavelength range 300-1100nm, and from these measurements, the optical parameters were calculated. The films with [Cu/In] =1.4 was annealed at temperature of 100, 200^oC for one hours and two hours.

Results and discussion

Optical absorption studies of $CuInS_2$ were carried out in the wavelength (λ) range 200-1100 nm at room temperature. The variation of absorbance with the wavelength for the prepared films in a different value of [Cu/In] ratio is shown in Fig.1.

The absorption coefficient (α) is related with the absorbance (A) through the relation [7]

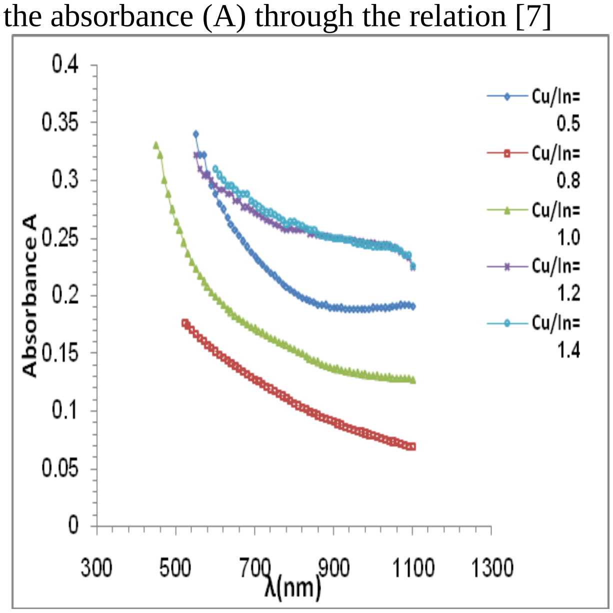

Fig.(1) the variation of the optical absorbance as a function to the wavelength for films prepared in different value of [Cu]/[In] ratio.

$$\alpha = 2.303\frac{A}{t} \qquad (1)$$

where t is the sample thickness.

The optical absorption coefficient (α) for $CuInS_2$ thin films were calculated from Eq.1 . Fig.2 shows the optical absorption coefficient (α) as a function of photon energy (hυ) for the thin films with [Cu]/[In] ratios = 0.5, 0.8, 1.0, 1.2, 1.4. It can be noticed that the values of (α) for all thin films are found to be greater than 10^4 cm^{-1} in the UV- visible region, which means that the films have a direct optical energy gap[7]. This relatively high absorption coefficient is very important because the spectral dependence of (α) can drastically affect the solar conversion efficiency, so that the value of (r) in the imperial following equation equal to 1/2 [8,9] .

$$(\alpha h\upsilon) = c\left(h\upsilon - E_g^{opt}\right)^r \qquad (2)$$

where c is constant.

Also, it can be obtained from this figure that (α) reach a higher values at the ratio of [Cu]/ [In] equal to 0.8, 1.4.

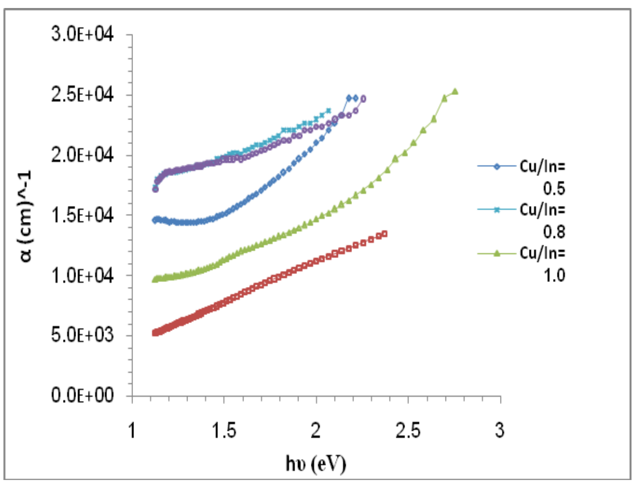

Fig.(2) shown (α) vs. (hυ) for $CuInS_2$ thin films prepared with a different ratio of [Cu]/[In].

Fig.3 shows direct Eg as a function of photon energy for [Cu]/[In] at different ratios. A direct optical energy gap (E_g) can be obtained from Fig.3 for the different [Cu]/[In] ratios. It can be seen that (E_g) decreases with increasing of the ratios as shown in Table1. A possible reason for this phenomenon is carrier degeneracy in $CuInS_2$ due to continuous distribution of defect state this result is in a good agreement with H Bouzouita's result[10].

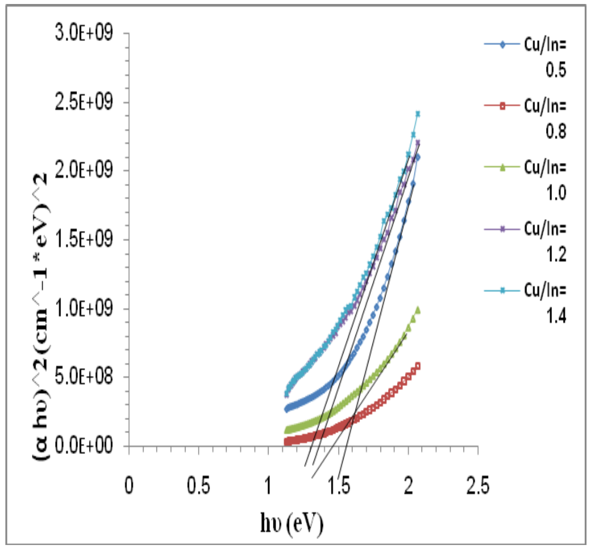

Fig.(3) The optical energy band gap(E_g) for $CuInS_2$ thin films prepared with a different ratio of [Cu]/[In].

Table1: Decreasing the band gap with increasing [Cu]/ [In] ratio.

Sample	Cu/In	Band
1	0.5	1.55
2	0.8	1.50
3	1.0	1.45
4	1.2	1.34
5	1.4	1.30

The effect of annealing temperature in different times (T=100°C for 1and 2 hours, T=200°C for 1 and 2 hours) on the prepared films at [Cu]/ [In] = 1.4 are shown in Fig.4. This figure obtained that E_g decreases with increasing of annealing for both temperature (100 and 200) °C for all thin films. This phenomenon may be cased by the varied in grain size due to the re crystallization processes [11].

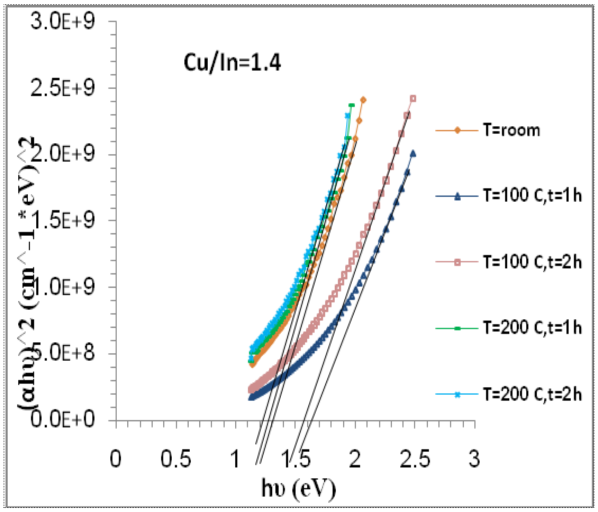

Fig.(4) The optical energy band gap for annealing $CuInS_2$ films at [Cu]/[In]=1.4.

The value of extinction coefficient are calculated using the following relation [12]

$$K = \frac{\alpha \lambda}{4\pi} \qquad (3)$$

where λ is the wavelength of the light.

Fig.5 shows the plot of K vs. hυ for $CuInS_2$ thin films at different ratios of [Cu]/[In] .It is cleared from this figure, that the behavior of K is not systematic .The films of [Cu]/[In] with the ratio of 0.5 show decreases of K with increasing of hυ and until 1.5eV and after this value K will increased with increasing hυ. For [Cu]/[In]=0.8,1.0, Fig.5 shows that an increasing in the K with increasing of hυ, in the same figure we can see that when [Cu]/[In]=1.2,1.4 ,K value deceased with increasing of hυ.

The refractive index (n) was calculated using Eq.4 [12].

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K^2\right]^{\frac{1}{2}} \qquad (4)$$

where R is the reflectivity.

The variation of n vs hυ is shown in Fig.6. In general, we can observed that the value of n increases with increasing of hυ. Also, by increasing the ratio of [Cu]/ [In], the refractor index increases this means that

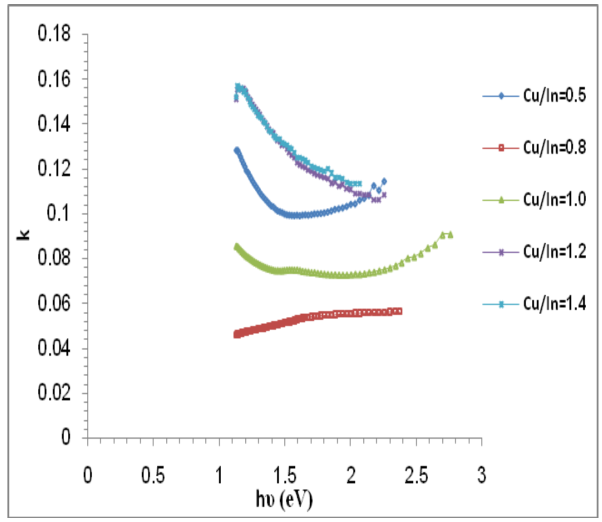

Fig.(5) The extinction coefficients(k) vs. (hυ) for $CuInS_2$ thin films prepared with a different ratio of [Cu]/[In].

the behavior of film polarization different with each treatment , where n depends on material polarization and with increasing the polarization, velocity of light decreases so that n is changed . The polarization depends on crystalline and grain size of this film .The maximum value of n equal to 2.64 is occurred at ratio of (1.4) of [Cu]/[In] film, as shown in Fig.6 .

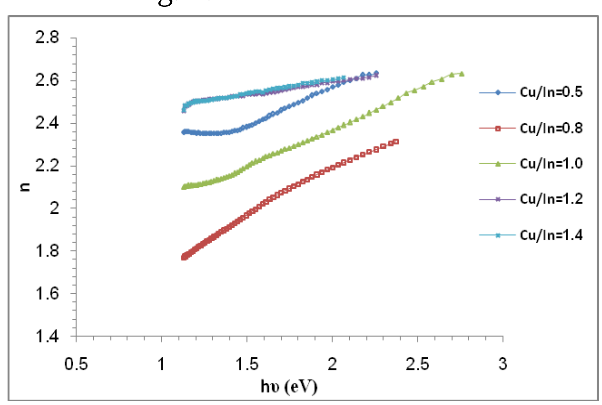

Fig.(6) The refractive index(n) vs. (hυ) for $CuInS_2$ thin films prepared with a different ratio of [Cu]/[In].

Real and imaginary parts of dielectric constants were determined using the following equations [13].

$$\varepsilon_1 - n^2 - k^2 \quad (5)$$

$$\varepsilon_2 = 2nk \quad (6)$$

The plots of real (ε_1) and imaginary (ε_2) dielectric constant of [Cu]/ [In] thin films at different ratios are illustrated in Fig.7 and 8, respectively. Fig.7 shows that the three curves of [Cu]/[In]=0.5,1.2,1.4 are intersect at a maximum value of ε_1 equal to 6.8 at photo energy equal to 2.1eV energy and the behavior of each one different with respect to before and after intersect point as shown in Fig.7.

Also the behavior of ε_1 with hυ was similar to that of refractive index. The real dielectric gives the indication about the polarizability of matter. Fig.8 shows the behavior of ε_2 with hυ. It can be observed that behavior of ε_2 is similar to that of K.

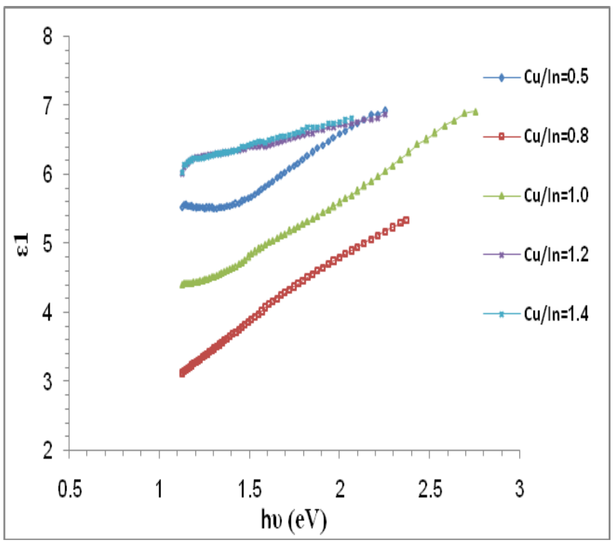

Fig.(7) The real dielectric constant(ε_1) vs. (hυ) for $CuInS_2$ thin films prepared with a different ratio of [Cu]/[In].

Conclusions

$CuInS_2$ thin films have been deposited by spray pyrolysis technique on glass substrate .The films obtained were uniform and had good adherence to the substrate. The optical studies indicated that films exhibit direct band gap which is changed with changing of [Cu]/ [In] ratio. The optical constant such as K, n, ε1 and ε_2 are discussion.

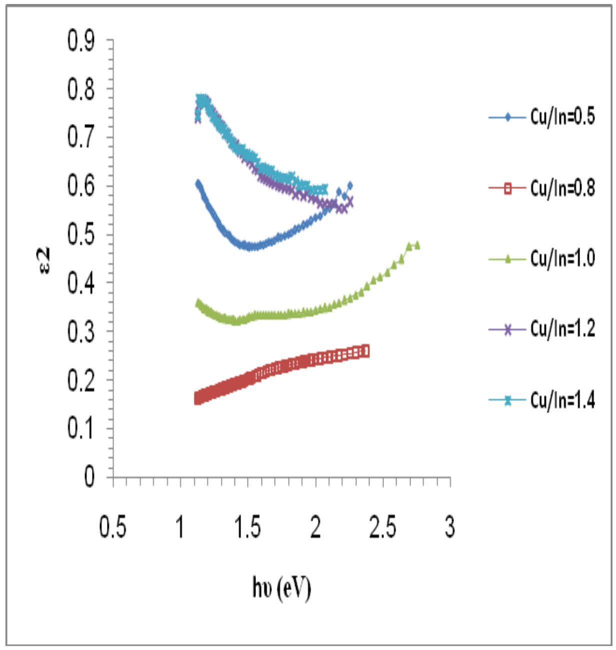

Fig.(8) The imaginary dielectric constant(ε_2) vs. (hυ) for $CuInS_2$ thin films prepared with a different ratio of of [Cu]/[In].

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