Study the properties of Cu_2Se thin films for optoelectronic applications

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Copper selenide (Cu_2Se) thin films were prepared by thermal evaporation at RT with thickness 500 nm. The heat-treating for (400 &500) K for the absorber layer has been investigated. This research includes, studying the structural properties of X-ray diffraction (XRD) that show the Cu_2Se thin film (Cubic) and has a polycrystalline orientation prevalent (220). Moreover, studying the effect of annealing on their surface morphology properties by using Atomic Force Microscopy AFM. Optical properties were considered using the transmittance and absorbance spectra had been recorded when wavelength range (400 - 1000) nm in order to study the absorption coefficient and energy gap. It was found that these films had allowed direct transition optical band gap which decreases with the increasing effect of annealing, while it increasing with the increase in the annealing temperature at all ratio UV-Visible transmission spectrum. Hall Effect results presented that all thin films have P-type. It is quite possible that the heterojunction (p-Cu_2Se/n-Si) solar cell device is a buried. The illumination current- voltage (I-V) characteristics showed that the solar cell, with (t=500 nm and T=500 K) has highest efficiency (η =1.4 %).

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1. Introduction

Copper (II) selenide is interesting metal chalcogenide belong to compound I_2–VI semiconductor materials suitable for optoelectronic [1] and thermoelectric [2] applications. The copper chalcogenides Cu_2X (X = S, Se, and Te) have photoelectric properties as well as ionic conductivity and applications in solar cells [3]. The phase of Cu_2Se is cubic with lattice parameter a = 5.76 Å, [4,5] with a direct band gap [6] Cu_2Se have corresponding band gaps in the range of (2 - 3) eV [7] behaved as a p-type semiconductor [5,6,8] The Cu_2Se has been produced by using the fallowing methods: hot injection [9,10] Solvo thermal synthesis[11] Chemical vapor deposition [12] electrodeposition [6] chemical bath deposition method [13,14,15] Sb-doped[15] chemical bath deposition with thermal treatment at 200ºC – 400ºC in air and vacuum[16] Magnetron Sputtering[17] Brush plating technique 300 ºC and 500 ºC [18] sputtering[19] The effect of different material doped on Cu_2Se characterization thin films were investigated by various researches such as Bi3+, Cd2+, Na+ - doped Cu_2Se thin Films [20] the influence of Pb doping on the electrical resistivity it found increase when adding Pb doping [21] The effect of doped on Cu_2Se(Bi) displayed strong band gap release at 629 nm, this doping make the Cu_2Se preferable optical media [22] The influence of Na doping on electrica,l structural, and optical properties of Cu_2Se thin film [13] Cu_2Se with Cd^{2+}-doped thin film by the chemical bath deposition technique then prepared films were annealed at 200°C [14] 0.03 Sb-doped Cu_2Se films[15].

2. Experimental

Copper (II) selenide thin film has been deposited through using vacuum thermal evaporation technique ($6*10^{-6}$ Torr) on to well cleaned glass & silicon substrates by using

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ultrasonic path to study its optical, structural, and electrical properties, deposited on a silicon substrate to manufacturing solar cell. The weighed high purity (99.999 %) elemental copper and selenium percentages by weight (2:1) are taken in a pure cleaned quartz ampoule of length (20cm) under vacuum (10^{-4} mbar). Using a Cu_2Se 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 (1100 °C) over (6 hours), and then cooled to room temperature RT. These films were annealed at (400 &500) K for (1 hours). Optical transmission spectra of Cu_2Se films have been recorded from (400 nm) to (1000 nm) wavelength using (UV/VIS) (Shimadzu Corporation Japan) at room temperature.

X-ray diffraction (XRD) using to study the crystal structure of thin films with (λ equal to 1.5418 Å). Crystallite size (C_S) calculate by Scherrer's formula f Cu_2Se thin films:

$$C.S = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where B the full-width at half-maximum of the main peak and the reflection angle is θ [23,24].

We used (AFM technology) to study the nature of the surface topography, determine both surface roughness and grain size.

The optical properties measurements for thin films (Cu_2Se) on glass substrates were found using UV/Visible 1800 spectrophotometer from 400nm to1000nm. The energy gap E_g (eV) calculated from Tauce equation and absorption coefficient α from lambert equation [25,26]:

$$\alpha h\upsilon = C\,(h\upsilon - E_g)^n \quad (2)$$

$$\alpha = 2.303\ A/t \quad (3)$$

The Hall Effect results showed (n or p) type of Cu_2Se thin films have been achieved by Van der Pauw (Ecopia HMS 3000), it is determining mobility and carrier concentrations for Cu_2Se and in thin films.

Heterojunction where synthetic since (p- Cu_2Se /n-Si) which done by the deposition of the composite thin films (Cu_2Se) on (111) single crystal (n-type) silicon.

3. Result and discussion

Figure 1 shows the XRD patterns of Cu_2Se thin film at RT and (400,500) K thickness 500nm it can see from this Figure and Table (1) that the Cu_2Se thin films have the polycrystalline type Cubic structure confined with the standard values in ICDD 00-046-1129 card have three sharp peaks referred to directions (111), (311) and with prefer orientation is (220). From the FWHM values for the (220) peak we can estimate the crystallite size by using Scherrers equation and is observed the crystallite size increased when annealing temperature increase as displays in Tables (1). Note from Table 1 that there is a significant shift in the position of the peaks of the prepared films after the annealing process. The intensities of the peaks increase by increasing the temperature this gives the probability that the crystallization of the films material increases by increasing the temperature.

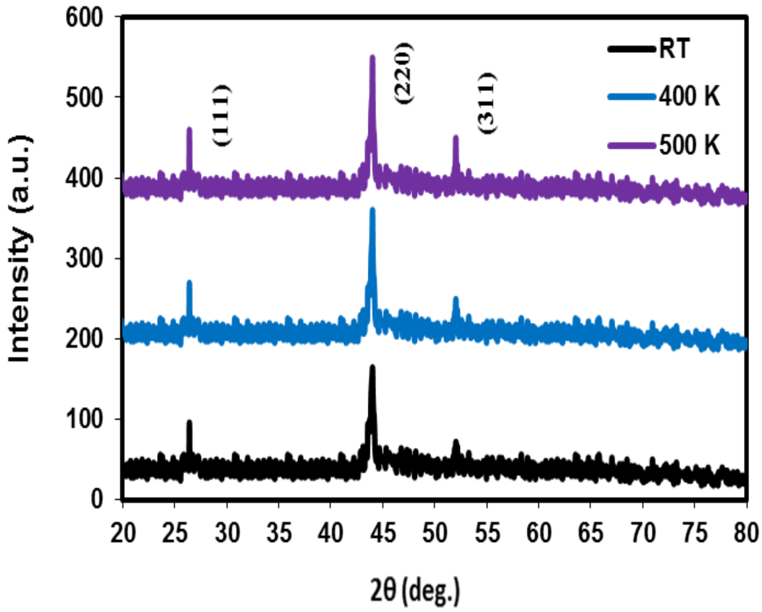

Fig. 1. X-ray diffraction pattern for as deposited and annealed Cu_2Se films.

Table 1. Structural parameters for as deposited and annealed Cu_2Se thin films.

T_a (K)	d_{exp} (Å)	d_{stand} (Å)	$2\theta_{exp}$ (deg.)	hkl	FWHM (deg.)	C.S (nm)
R.T	3.357888	3.37	26.513	(111)	0.3222	27.7891
	2.050177	2.060	44.120	(220)		
	1.755843	1.76	52.021	(311)		
400	3.361748	3.37	26.482	(111)	0.3002	29.87318
	2.030862	2.060	44.562	(220)		
	1.756722	1.76	51.993	(311)		
500	3.367994	3.37	26.432	(111)	0.2566	34.98885787
	2.017251	2.060	44.879	(220)		
	1.760378	1.76	51.877	(311)		

Fig. 2 shows the three -dimensional (3D) of Cu_2Se thin films at RT and (400,500) K. The value of roughness besides the grain sizes are studied. It has been saw that a roughness for surface was equal to (8.89,12.9 and 15.9). The grain size has been find (70,91.89 and 98.72) for at RT and (400,500) K respectively. So the average diameter of Cu_2Se thin films at RT and (400,500) K. (Fig. 2c) is larger than the Cu_2Se thin film (Fig. 2a&b).

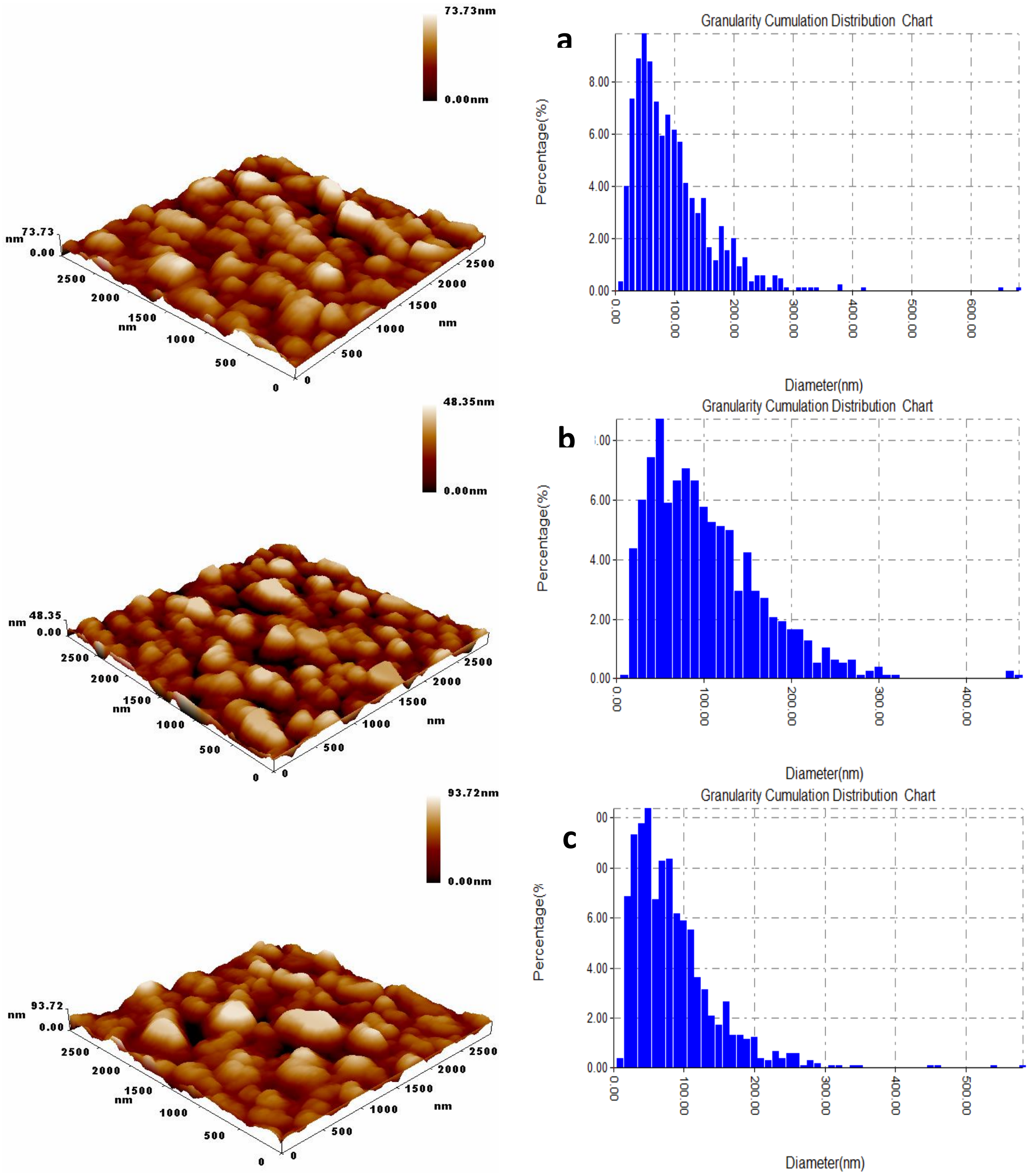

Fig. 2. 3D Atomic force microscopy and Granularity Cumulation Distribution of Cu_2Se thin films at R.T and (400,500) K.

Table 2. The average grain size and roughness for thin films Cu_2Se at R.T and (400,500) K.

Sample	**Avg. Diameter (nm)**	**Roughness average (nm)**	**r.m.s (nm)**
RT	70	8.89	10.9
400 K	91.89	12.9	16
500 K	98.72	15.9	19.9

To determine the effect of annealing of the optical measurements of thin films Cu_2Se as in Fig. 3. The absorbance (A) and transmittance (T) measurements in the range (400–1000) nm. transmittance behaves the opposite of absorbance that the transmittance increasing with increasing wavelength of Cu_2Se while The absorbance decreasing with increasing wavelength of Cu_2Se. The absorption coefficient is an important for calculating the material's ability to light absorption, function of the falling photon energy (hυ) and energy gap (Eg) [27]. Figure 3 show that the absorption coefficient (α) values, that considered using equation (3), high value of α above (10^4) cm^{-1}. The α value increases (from 3.6 to 5) $\times 10^4 cm^{-1}$ as annealing increases, That is mean an increase in absorbance of Cu_2Se films . While the values of band gap decreases from (2.1 to 1.9) eV. The decrease in the values of band gap (Eg^{opt}) may be attributed to the increasing of the absorption coefficient, that is agreement with [7,28].

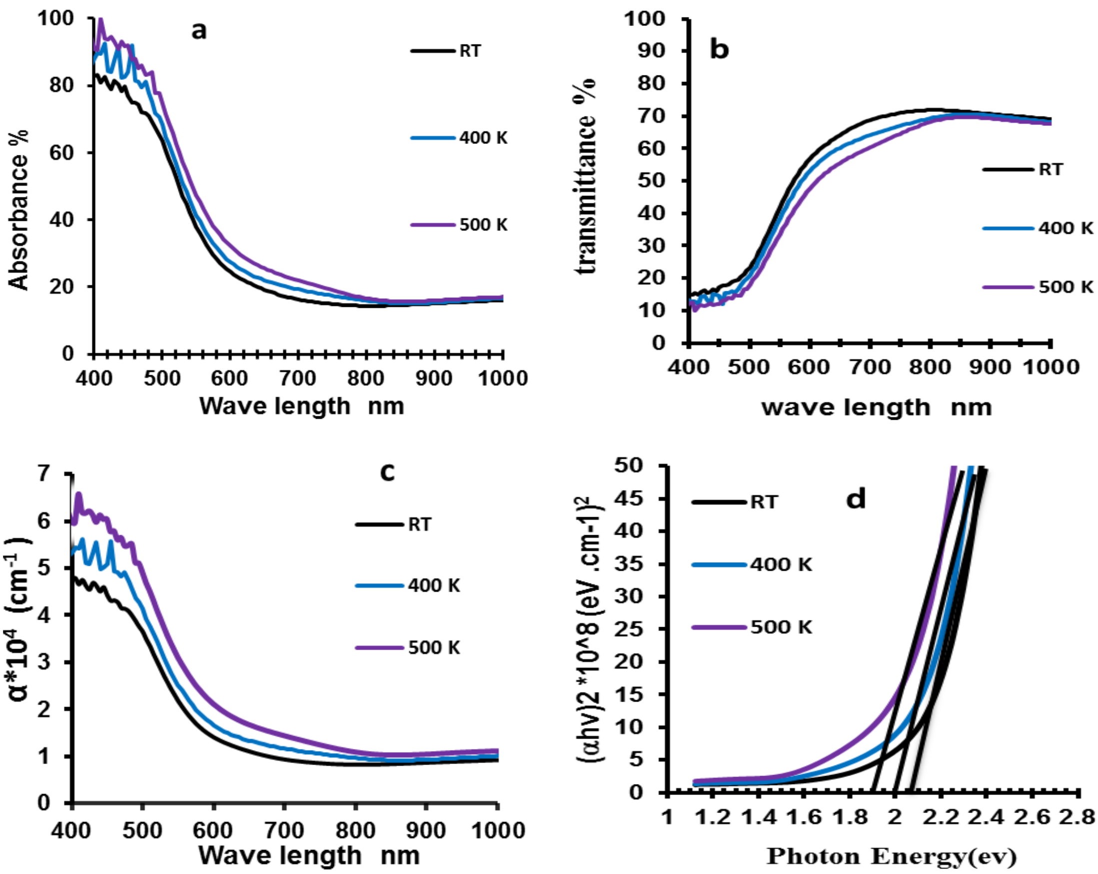

Fig. 3. The absorbance (a), transmittance (b) verse wavelength, (c) absorption coefficient (d) $(\alpha h\upsilon)^2$ for thin films Cu_2Se at R.T and (400,500) K.

Table 3. Direct optical band gap and absorption coefficient (λ=500nm) of thin films Cu_2Se at R.T and (400,500) K.

Sample	RT	400 K	500 K
E_g^{opt} (eV)	2.1	2	1.9
$\alpha \times 10^4\ cm^{-1}$	3.6	4.2	5

The Hall Effect measurement R_H was calculated are listed in Table (4) to determine the type of majority carriers and mobility of the pure (Cu_2Se) at R.T T and (400,500) K. The obtained results displayed that all the thin films were positive confirm that the conducting carriers are of p-type for all the films. This designates that the carriers are holes, our results agree with the study [14]. We can note from this Table decrease in the value of the Hole coefficient (R_H) due to an increase in the carrier concentration for Cu_2Se thin film will due to an increase in the current and voltages passing through the Cu_2Se films, the increased probability of collisions between the carriers lead to decrease in the values of mobility (μH). The highest percentage of the charge carriers when the T equal to 500 K.

Table 4. Hall parameters for of thin films Cu_2Se at R.T and (400,500) K.

Thickness(500 nm)	ρ (Ω.cm)	μ_H (cm^2/V.S)	$N_{A*10^{22}}$ (cm^{-3})	$R_{(H)}$ ($cm^3.C^{-1}$)
RT	**0.1**	**0.000864**	**7.23**	**8.64E-05**
400 K	**0.081300813**	**0.000911**	**8.44**	**7.41E-05**
500 K	**0.064516129**	**0.000476**	**20.36**	**3.07E-05**

The variations of photovoltaic parameters of Cu_2Se at R.T and (400,500) K derived from the current-voltag measurement are listed in Table 5. Figure 4 display the current-voltage (I-V) curves for three devices made from the same Cu_2Se/Si heterojunction with different annealing temperature with illumination. The efficiency is increased with the powers for incident photo (10^2mw/cm^2) for Cu_2Se because the J_{sc} values began to increase that is due to the result of reducing the energy gap value as mentioned in the study of optical properties. However, there is an increase the value of open circuit voltages (V_{OC}) that will increase in concentration of carriers increase the roughness and the absorption coefficient [29].

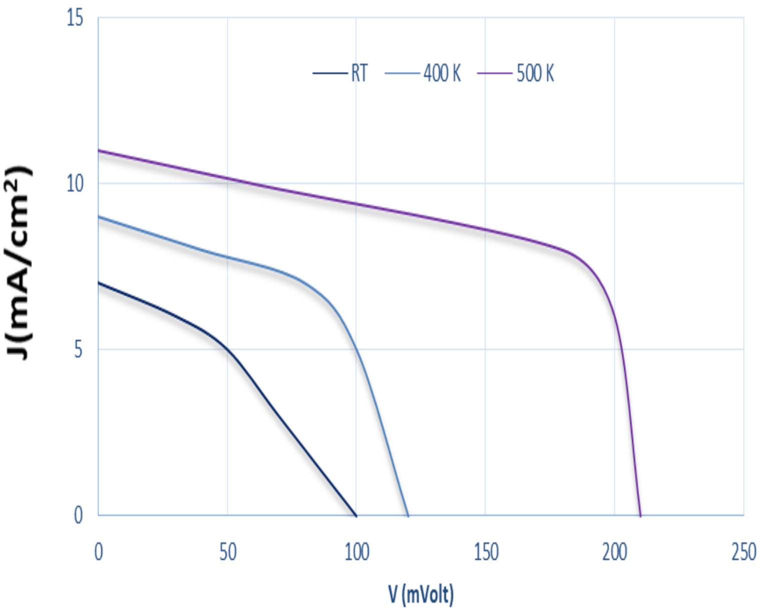

Fig.4. Characteristic of I-V under illumination for Cu_2Se /Si solar cell at R.T and (400,500) K.

Table 5. Light I-V parameters of solar cell for Cu_2Se /Si devices at R.T and (400,500) K.

Thickness(500 nm)	RT	400 K	500 K
Voc (mVolt)	100	120	210
J_{sc} (mA/cm^2)	7	9	11
Vmax (mVolt)	50	80	180
Jmax (mA/cm2)	5	7	8
Fill factor	0.357	0.518	0.623
Efficiency	0.25	0.56	1.44

4. Conclusions

Cu_2Se 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 Cu_2Se properties.

The heat treatments change the optical properties under investigation in this study. The results show that the (Eg) is (2.1 eV) before annealing and (2 eV) after annealing in (400 K) and (1.9 eV) after annealing in (500 K). The film annealed at (500 K) is a good optical properties (lower transmittance, reflectance, energy band gap, and a larger absorption coefficient, it can be used as an absorber layer in the fabrication of thin film solar cells. XRD for alloy and thin films showed that polycrystalline and have the Cubic structure and the (220) direction was prefer orientation. All thin film have p-type conductivity The efficiency increases after annealing, the maximum values of fill factor and efficiency were 0.623 and 1.44 when annealing temperature (500 K).

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