Annealing effects on the structural and optical behavior of $Cu_2Se_{0.8}Te_{0.2}$ thin film

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Chalcogenide have attracted great interest over the last years due to their thermal, electrical and optical properties. Understanding the crystal structures of chalcogenide is crucial in the hunt for novel materials. In this study, we prepared $Cu_2Se_{0.8}Te_{0.2}$ thin film on a glass substrate using thermal evaporation method and then annealed at different temperatures (403, 453 &503) K to study the effect of annealing on the structure and optical properties of the film, we find that $Cu_2Se_{0.8}Te_{0.2}$ the composition is cubic structural and this is shown by X-ray analyses. And the optical properties improve with different annealing degrees, that is annealing reduces absorption while increasing transmittance, and so we find the optical energy gap increasing by increasing annealing where it is (1.1) eV at room temperature and it becomes (1.7) eV counting the temperature of 503 K. Thus, $Cu_2Se_{0.8}Te_{0.2}$ compound can be adopted as a thin film to further improve the solar cell's photoelectric performance.

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Keywords: Thin films, X-ray diffraction, Cu_2SeTe, Optical parameters, Crystals structure

1. Introduction

Certainly, the primary issues in our modern lives are tied to energy. The question always arises of how can clean and renewable energy be affordable and abundant. The sun is a major source of free, continuous energy for the earth. Solar cells are commonly used to convert energy into electricity [1]. Nowadays copper chalcogenide (Cu2−δX) based compounds (X = Se, S, and Te) have shown outstanding TE performance. [2] This can be directly converted. Because of its ability to convert light into energy and vice versa, it has piqued researchers' curiosity due to its advantages. [3-4] Features include neither mechanical nor chemical processes, nor moving parts, zero emissions, and great durability and reliability, [5] Researchers are very interested in materials like ternary chalcogenide due to their role in electro optic, nonlinear optical and optoelectronic devices, Solar cells optimization efficiency is regarded as the basic element that makes these compounds technologically significant. [6-7] Ternary compounds are semiconductors with a high energy direct band gap, significant non-linearity, poor thermal conduction, broad transparency window, lower melting temperatures, and a tetragonal chalcopyrite crystal structure. [8] Copper chalcogenides have complicated crystal structures that vary depending on a value of Cu deficiency (δ) and production procedure. [9] So the structure is based on examination of X-ray diffraction data. [10] The exact atomic locations for Cu2Se1-xTex are yet unclear, and their TE properties have not been investigated. Thus, a thorough investigation of the crystal structure and TE transport characteristics for Cu2Se1-xTex is still desirable. [11]

2. Experimental

Here we succeeded in preparing $Cu_2Se0.8Te0.2$ alloy through combining the optimum amounts of high purity Cu_2, Se and Te elements (99 .999%) into the evacuation of fused quartz ampoules, heated (1000 K) for one hour, then left to be gradually cooled to room temperature. After the tube opening and extracted the alloy as in Figure 1. Using a mortar and pestle, the resulting ingots were crushed and pulverized into fine powders.

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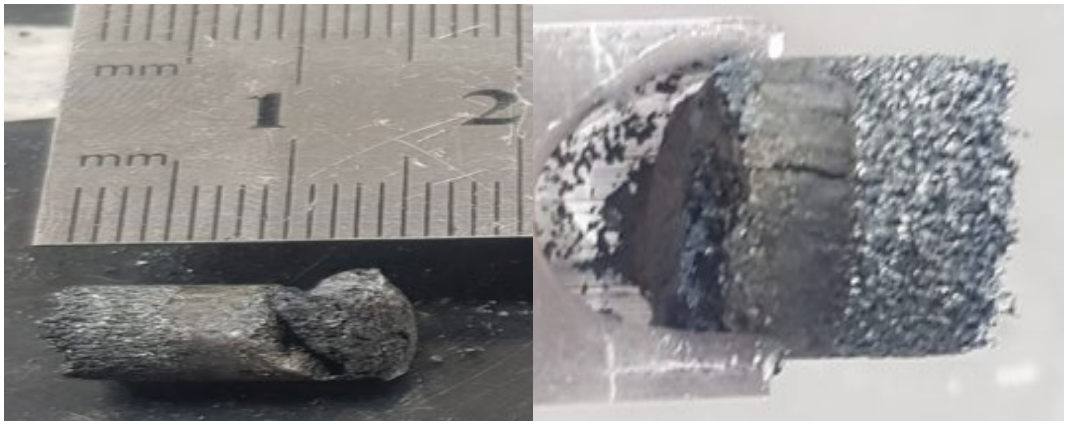


Fig. 1. $Cu_2Se_{0.8}Te_{0.2}$ alloy

Thermal evaporation was used to create $Cu_2Se_{0.8}Te_{0.2}$ thin films on a glass substrate. of the ($2x10^{-5}$) Torr discharge system. Thin film has been annealing with temperatures Ta (403, 453 &503) K. Detailed crystal structures are determined by X-ray diffraction, the position and intensity spectrum versus θ of the Prague angle, using (XRD diffraction Shimadzu6000 with the brass target of wavelength λ = 1.5406 Å, provides information about crystal structure, including phase, multicrystalline, and lattice parameters. The distance between planes, d (hkl), is measured using the Bragg law. The effects of different annealing temperatures on the compound's structure and optical properties have been studied through the data of the AFM Surface Topography Device and UV-Visible 1800spectro photometer examinations - for some optical parameters such as refractive coefficient, absorption, transmission, extinction coefficient, and absorption coefficient through which we calculate the optical energy gap of the thin film.

Our analysis in this study is of the structure and optical properties of the $Cu_2Se_{0.8}Te_{0.2}$. Structure properties we provided based on X-ray diffraction data where Bragg's law was used to calculate the interplaner distance d (hkl) between different planes.

$$n\lambda = 2\, d \sin\theta \tag{1}$$

where
n: order of diffraction.
λ: wavelength of the X-rays.
d: distance between consecutive parallel planes.
θ: angle of incidence.
Scherrer's Formula can be used to compute the average crystal size[12].

$$C.S=\frac{0.94\lambda}{B\cos\theta} \tag{2}$$

where
λ: wavelength for (X-ray).
β: full width at half maximum intensity in radians. [13]

The fundamental absorption, can be used to compute the optical band gap's character and value, which corresponds to electron excitation from the valance to the conduction band, by expression [14-15]

$$\alpha h\nu = B\,(h\nu - Eg)1/r \tag{3}$$

where, depending on the type of semiconductor, B is a constant, hv is the photon energy (eV), eV is the optical energy gap, and r is a constant that can have values of 2, 3,1/2, or 3/2 depending on the kind of optical transition and the material [16] Depending on the type of materials and optical transitions can be classified as either direct and indirect. The formula can be used to calculate the values of the absorption coefficients.

$$\alpha=2.303\frac{A}{t} \tag{4}$$

A: optical absorbance, t: film thickness [17-19]

Optical Constants such as k: extinction coefficient, n refractive index, can be considered by the relations below [20-21]

$$k=\frac{\alpha\lambda}{4\pi} \tag{5}$$

$$n=[\frac{4R}{(R-1)^2}-k^2]^{1/2}-\frac{(R+1)}{(R-1)} \tag{6}$$

3. Result and discussion

Figure (2) shows the XRD pattern of Cu2Se0.8Te0.2 powder, with its polycrystalline structure, was compared to the card. NO.00-046-1129, NO. 270186 and ref. (2), of this compound and its component elements. The Cu2Se0.8Te0.2 is formed in cubic phase and can be trigonal, the dominant phase is the cubic phase and the direction (111).

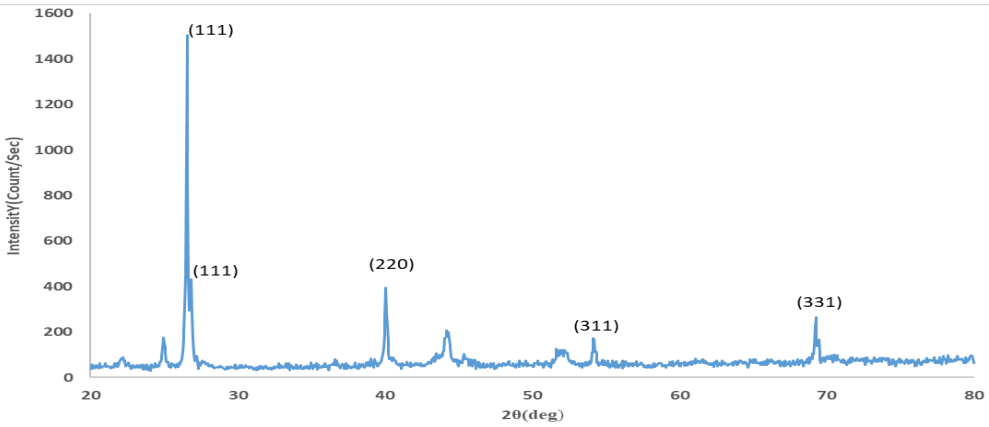


Fig. 2. X-ray diffraction pattern of the $Cu_2Se_{0.8}Te_{0.2}$ as alloy.

Figure (3) show XRD for $Cu_2Se_{0.8}Te_{0.2}$ on glass substrate as thin film at RT and annealed at (403, 453 &503) K when the thickness (500 ± 20) nm, all the samples show in proximity to the single-crystalline form for films have cubic structural, at room temperature the $Cu_2Se_{0.8}Te_{0.2}$ film with main distinguishable peak when 2θ ≈26.8842° with preferred orientation (111) and another peak appear at 2θ equal to 44.6253° with orientation (220),as shown in the figure 3,and it good matched comparison with reference (2).

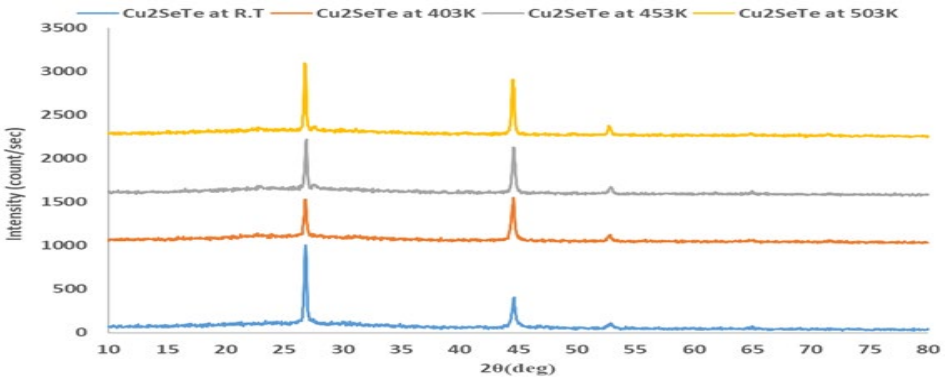


Fig. 3. XRD Pattern for $Cu_2Se_{0.8}Te_{0.2}$ thin film at R.T and Ta= (403, 453 &503) K.

From table (1) and the comparison with the card no. 00-046-1129 show standard value very good matched, the degree of crystalline improve with annealing, which means thisdecreases crystallographic defects in thin film deposition.

FWHM decrease when the annealing temperature increase so the crystal size increase, which is calculated from equation 2.

Table 1. Data of XRD for $Cu_2Se_{0.8}Te_{0.2}$ thin films, at R.T, (403, 453 &503) K.

Temperature	2θ(Std.) (Deg.)	2θ(Exp.) (Deg.)	d(Std.) (A^O)	d(Exp.) (A^O)	hkl	FWHM	C.S (nm)
R.T	26.4258	26.8842	3.370	3.31365	111	0.21630	39.44557
	43.9154	44.6253	2.060	2.02892	220		
403K	43.9154	44.5668	2.060	2.03145	220	0.30770	29.14554
	26.4258	26.8616	3.370	3.31639	111		
453K	43.9154	44.6311	2.060	2.02867	220	0.24830	36.12625
	26.4258	26.9240	3.370	3.30884	111		
503K	26.4258	26.8500	3.370	3.31779	111	0.19350	44.09028
	43.9154	44.5610	2.060	2.03170	220		

Compared to Se^{-2} 198 pm, Te^{-2} ion 221 pm has a bigger ionic radius [2], Therefore, it is expected that when Se is replaced with Te, the unit cell will expand, it is clear that the (111) diffraction become (220) at (403 and 453) K then become (111) at 503K, the diffraction peaks' intensities are increase, small discontinuous jumps at 503 K are observed for Cu2Se0.8Te0.2 These are attributed to the structural chang in the compound. The electronegativity of Cu is 1.90 and Te 2.10, this deference is less than that between Se 2.55 and Cu 1.90 and Cu-Se has a shorter average bond than Cu-Te. Because of the nature of Cu-dominated ionic connections with Se/Te. Atomic-Force-Microscopy (AFM) was utilised to investigate the roughness of the surface nature of thin films, as well as the effect of annealing on their homogeneity and uniformity[22].

Figure (4) shows three-dimensional (AFM) images and two-dimensional photographs of pure thin films at room temperature (without annealing). We see the formation of semi-spherical nanoscale structure. Few hollow parts with homogeneous nature.

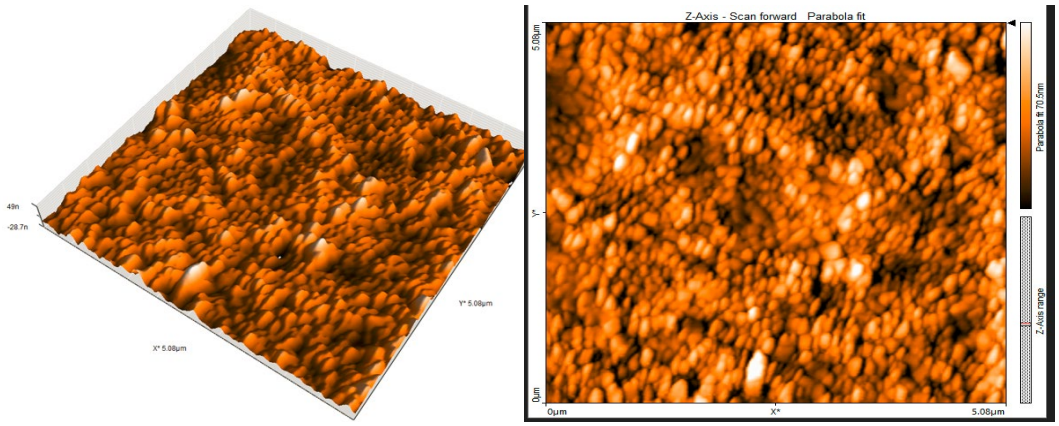
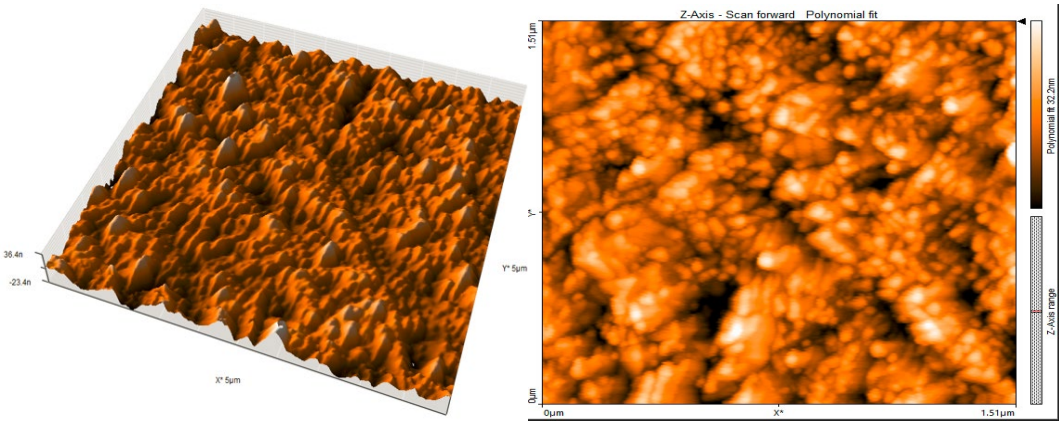


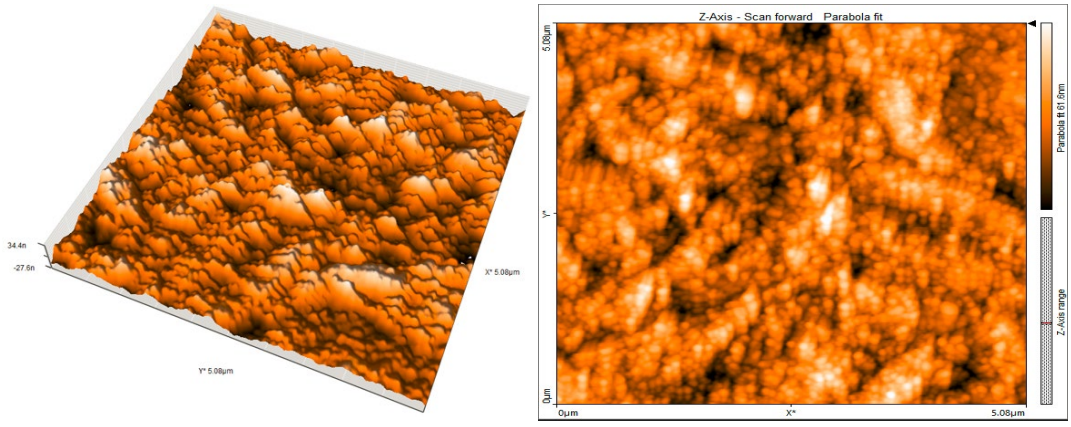
Fig. 4. AFM images of pure $Cu_2Se_{0.8}Te_{0.2}$ thin films at RT.

Figure (5) demonstrates two-dimensional AFM images and three-dimensional of $Cu_2Se_{0.8}Te_{0.2}$ thin film prepared and annealing (403, 453 and 503) K, we observe increases in the green size when the annealing temperature increase, from (39.56nm at 403K to 65.97nm at 503K), but the values of the Sa surface roughness and Sq root mean square are alternate on the surface.

at 403K



at 453K



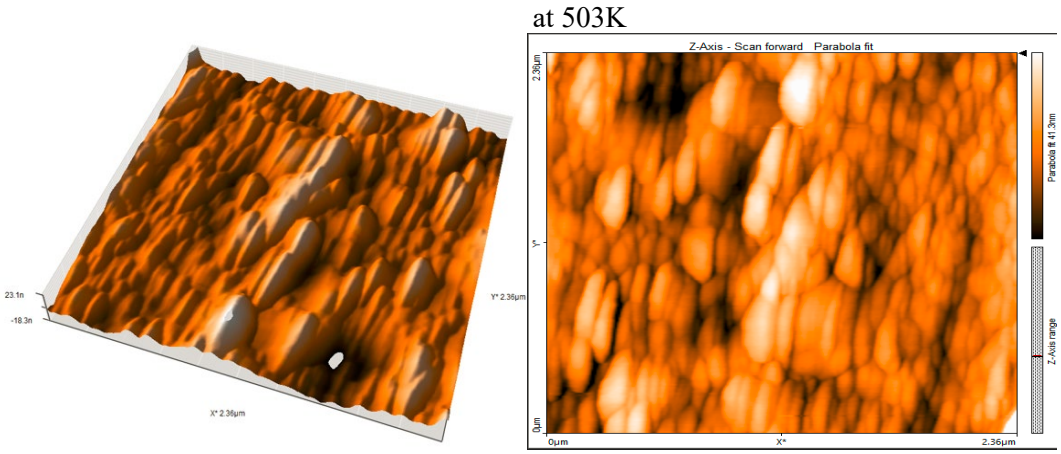


Fig. 5. AFM images of $Cu_2Se_{0.8}Te_{0.2}$ thin films annealing at Ta (403,453 and 503) K.

The spectra of transmittance and absorbance in the spectral area of 300–1100 nm were determined in relation to wavelength. at thickness 500 nm for $Cu_2Se_{0.8}Te_{0.2}$ film in room temperature and an annealing (403, 453 and 503) K as shown in figure. (6). The figure shows the effect of raising the annealing temperature on the formation of thin films, as evidenced by a decrease in the absorption spectrum for the absorption region within the wavelength range from (550 to 1000) nm for the $Cu_2Se_{0.8}Te_{0.2}$ films at (403, 453 and 503) K. By increasing the annealing temperature, the absorption spectrum decreases in the direction of longer wavelengths, indicating a decrease in the energy gap. The opposite is the transmittance spectrum, transmittance increases by Increase annealing temperature [23,24] within the wavelength range from 600 to 900nm, reaching transmittance about to 40% at the wavelength 750 at the Ta equal to 503K.

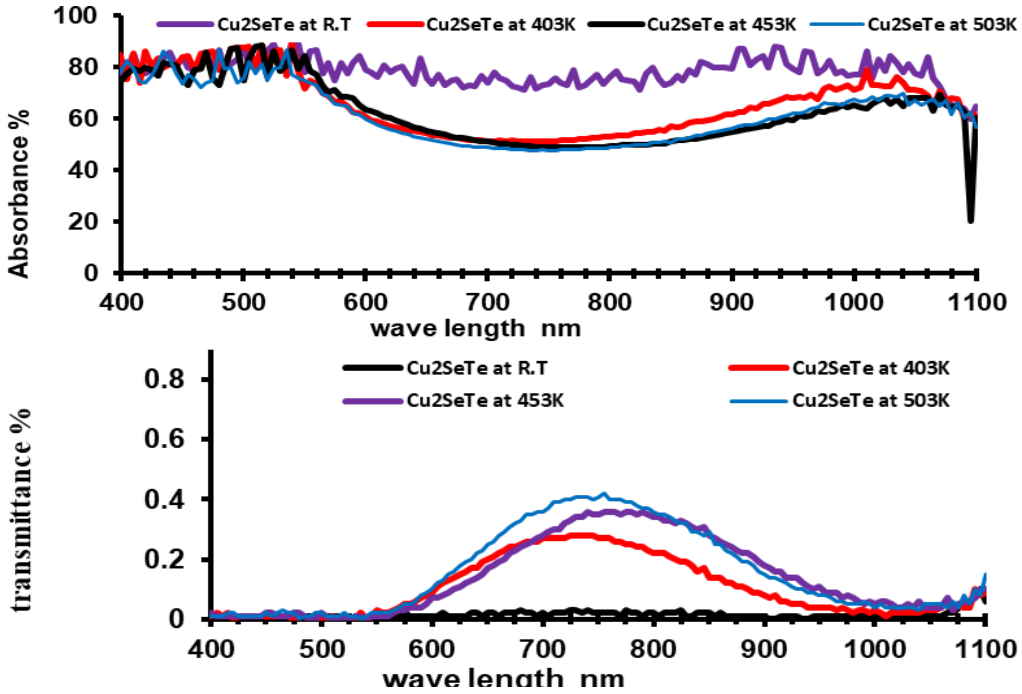


Fig. 6. Absorbance and transmittance spectra of $Cu_2Se_{0.8}Te_{0.2}$ at room temperature and the annealing (403, 453 and 503) K.

The fundamental absorption, which occurs when electrons are excited from the valence to conduction bands, is applied to calculate the energy gap. (Eg) energy gap of $Cu_2Se_{0.8}Te_{0.2}$ thin film is calculated by equation (3).

The energy gap (Eg) was calculated through the intersection of the photon energy axis with curve $(\alpha hv)^2$ by a straight line, as illustrated in Figure (7.)

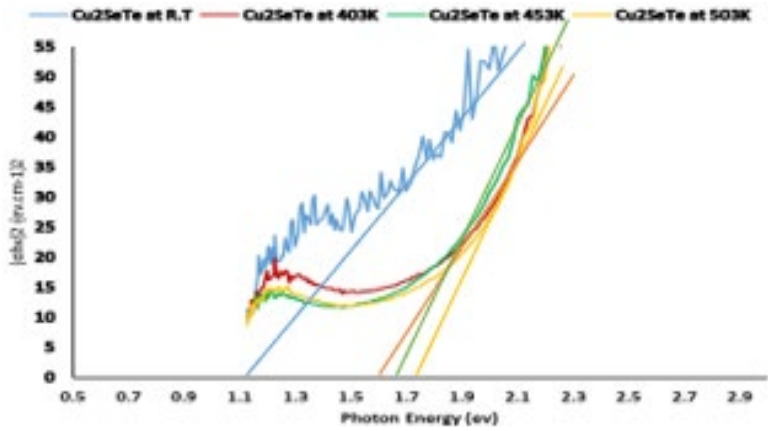


Fig. 7. $(\alpha hv)^2$ with photon energy of $Cu_2Se_{0.8}Te_{0.2}$ in R.T and Ta (403, 453 and 503) K.

The optical energy gap increasing by increasing annealing where it is (1.1) eV at room temperature and it becomes (1.7) eV counting the temperature of 503 K as observed in the table 2.

Table 2. Energy for $Cu_2Se_{0.8}Te_{0.2}$ thin films, at R.T, (403, 453 &503) K.

Temperature	R.T	403K	453K	503K
E_g (eV)	1.1	1.6	1.68	1.7

Figure (8) shows that (α) absorption coefficient values, derived by equation 4, exceeded 10^4 cm^{-1}, indicating an optical transition in an expanded band area. Coefficient absorption values decrease by increase an annealing throw photon energy about 1.2 to 2.4 eV. This behavior is due to variations in the film's crystal structure by annealing at deferent temperature.

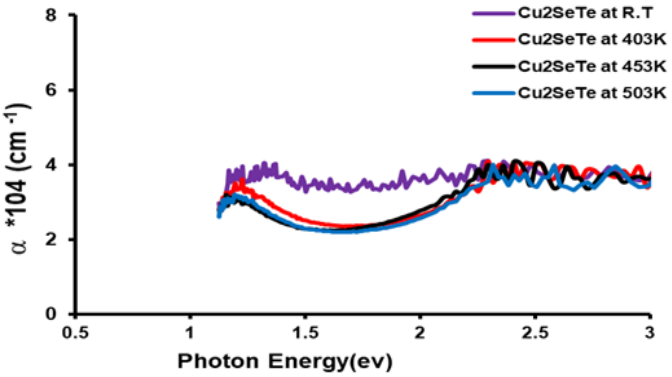


Fig. 8. Variation of absorption coefficient varies photon energy of $Cu_2Se_{0.8}Te_{0.2}$ thin film in R.T and Ta (403, 453 and 503) K.

The change in (n) refractive index in association with photon energy of $Cu_2Se_{0.8}Te_{0.2}$ thin films at R.T and Ta (403, 453 and 503) K. Figure 9 illustrates that n increases with the increase of annealing at the range of photon energy from (1.25 -2.25) eV. This behavior may indicate a decrease in reflection, which affects the refractive index.

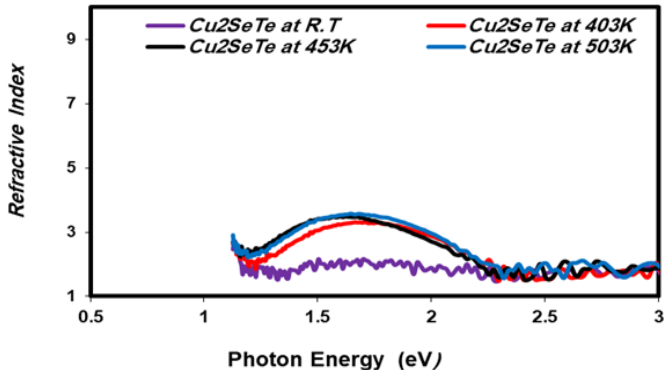


Fig. 9. The refractive index varies varies photon energy of $Cu_2Se_{0.8}Te_{0.2}$ thin film. in R.T and Ta (403, 453 and 503) K.

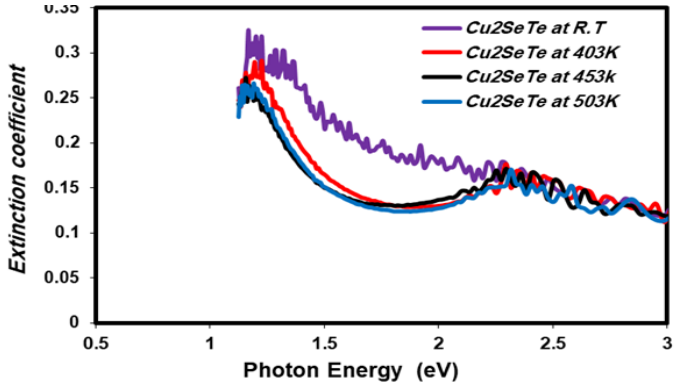


Fig. 10. Extinction coefficient varies with photon energy of Cu2Se 0.8Te0.2 thin film in R.T and Ta (403, 453 and 503) K.

4. Conclusions

The Cu2Se 0.8Te0.2 alloy was successfully produced and used to produce thin film using thermal evaporation. (X-Ray) tests of film showed, that semi single structure and have cubic structural with a preference for orientation in the [111]and [220] directions respectively. The effects of annealing on the optical properties of Cu2Se 0.8Te0.2 thin films are investigated, all thin films demonstrated significant absorption in the visible and infrared bands. Thus, these films are beneficial for optoelectronic devices, such as window layers in solar cells.

References

[1] N. Messeia, M. S. Aidab, A. Attafa, N. Hamania S. Laznek, solar cell efficiency , Vol. 20, No. 2, February 2023, p. 165 - 175; https://doi.org/10.15251/CL.2023.202.165

[2] Kunpeng Zhao, Mengjia Guan, Pengfei Qiu1, Anders B. Blichfeld, Espen Eikeland, Chenxi Zhu1 et al., Journal of Materials Chemistry A , 2018; https://doi.org/10.1039/C8TA01313F

[3] Lisi Huang, Jianzhang Lu, Duowen Ma, Chunmiao Ma, Bin Zhang, Hengyang wang, et al., Facile in situ solution synthesis of SnSe/rGO nanocomposites with enhanced thermoelectric performance.2020, 8, 1394; https://doi.org/10.1039/C9TA11737G

[4] Kunpeng Zhao, Anders Bank Blichfeld, Hongyi Chen, Qingfeng Song, Tiansong Zhang, Chenxi Zhu et al., Enhanced Thermoelectric Performance through Tuning Bonding Energy in Cu2Se1-xSx Liquid-like Materials, 29 2017 6367-6377; https://doi.org/10.1021/acs.chemmater.7b01687

[5] Qi Hao Zhang, Xiang Yang Huang, Sheng Qiang Bai, Xun Shi, Ctirad Uher , Li Dong Chen; Advanced engineering materials 2016, 18, No. 2; https://doi.org/10.1002/adem.201500333

[6] I. Ur Rahmana, M. Khalida, M. Aamera, F. Alia, M. U. Javeda, Q. Rafiq et al., I. Ur Rahmana, M. Khalida, M. Aamera, F. Alia, M. U. Javeda, Q. Rafiq et al., Chalcogenide Letters, Vol. 20, No. 2, February 2023, p. 131 - 144; https://doi.org/10.15251/CL.2023.202.131

[7] Sa. M. Ali, H. K. Hassun, A. A. Salih, R. H. Athabb, B. K. H. Al-Maiyaly, B. H. Hussein, Chalcogenide Letters, 19 (10), 663-671, (2022); https://doi.org/10.15251/CL.2022.1910.663.

[8] R. C. Guptaa, P. Varshneyb, Praveshc, M. Lald, D. Kumare, K. Singh et al., Chalcogenide Letters Vol. 20, No. 2, February 2023, p. 101 - 112; https://doi.org/10.15251/CL.2023.202.101

[9] Kunpeng Zhao, Haozhi Duan, Nunna Raghavendra, Pengfei Qiu, Yi Zeng, Wenqing Zhang et al., Adv. Mater. 2017, 1701148; https://doi.org/10.1002/adma.201701148

[10] Gurudayal Behera, Nanostructured copper selenide: synthesis and characterization, Thesis, 2015

[11] N. A. Alieva, G. G. Guseinov, V. A. Gasymov, Yu. I. Alyev, T. R. Mekhtiev, Inorganic materials Vol. 51 No. 7 2015pp. 726-729; https://doi.org/10.1134/S0020168515070018

[12] B. K. H. Al-Maiyaly, B. H. Hussein, A. A. Salih, A. H. Shaban, S. H. Mahdi, I. H. Khudayer, AIP Publishing, 1968 (1), 1 (2018); https://doi.org/10.1063/1.5039233

[13] I. H. Khudayer, B. H. Hussien, Ibn AL-Haitham J. Pure Appl. Sci., 29 (2), 41(2017).

[14] Bushra H. Hussien, Iman Hameed Khudayer, Bushra K. H. Al-Maiyaly, Hanan K.Hassun, AIP Conference Proceedings, 2437, 020032 (2022);https://doi.org/10.1063/5.0092335

[15] S. N. Sobhi, B. H. Hussein, Ibn AL-Haitham J. Pure Appl. Sci., 35 (3), 16 (2022); https://doi.org/10.30526/35.3.2824

[16] R. H. Athab, B. H. Hussein, Ibn AL-Haitham J. Pure Appl. Sci., 35 (4), 45 (2022); https://doi.org/10.30526/35.4.2868

[17] R. H. Athab, B. H. Hussein, Chalcogenide Letters, 20 (2), 91 - 100 (2023); https://doi.org/10.15251/CL.2023.202.91

[18] Hiba M. Ali, I. H. Khudayer, Ibn AL-Haitham J. Pure Appl. Sci., 36 (2), 147 (2023); https://doi.org/10.30526/36.4.3236

[19] Bushra H. Hussein, Iman Hameed Khudayer, Mohammed Hamid Mustafa, Auday H. Shaban, Progress in Industrial Ecology - An International Journal 13(2), 173 (2019); https://doi.org/10.1504/PIE.2019.10020850

[20] K.L. Chopra & I. Kaur, Thin Film Device Applications, Plenum prss, New York, (1983); https://doi.org/10.1007/978-1-4613-3682-2

[21] B. H. Hussein, H. K. Hassun, NeuroQuantology,18 (5), 77 (2020); https://doi.org/10.14704/nq.2020.18.5.NQ20171

[22] Wesley C. Sanders , Basic Principles of Nanotechnology, Taylor & Francis Group; https://doi.org/10.1201/9781351054423

[23] Athab R H and Hussein B. H., Preparation and study effect of vacuum annealing on structure and optical properties of $AgCuInSe_2$ thin film, Digest Journal of Nanomaterials and Biostructures, 17(4) 1173-1180 197-203, (2022) https://doi.org/10.15251/DJNB.2022.173.1173

[24] Ali, Hiba M., I. H. Khudayer, Chalcogenide Letters, 20(3), 197-203, (2023) https://doi.org/10.15251/CL.2023.203.197