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Optical and Morphology Properties of Cu_2Se at Different Temperatures by Thermal Evaporation

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Abstract

A low-cost thermal evaporation deposition technique has been used for the preparation of Cu_2Se thin films on glass substrates at RT with a thickness of 500 nm. Structural and optical properties of these films were investigated. Structural characterization of the films was done using X-ray diffraction XRD analyses, atomic force microscopy AFM was used for the morphological characterization of the film samples, and UV-Vis spectroscopy was also used for the characterization of the samples. The films have been treated at different temperatures (403, 453 &503) K for 1 hour. X-ray diffraction (XRD-with wavelength 1.54 A) study of these films suggests a cubic structure and has prominent (220) orientation. And AFM analysis, it is evident that Cu_2se films are polycrystalline, and that crystallite size and average grain size for films after annealing were increasing. The optical absorption coefficient (α) of the films was determined from absorbance spectra in the range of wavelengths (400-1100) nm. The deposited films showed transmittance (~18%) and a direct band gap of about 2.2 eV. The structure and the optical properties of the films may find practical applications in the field of renewable energy.

Keywords: Cu_2Se thin film, Thermal evaporation technique, Energy gap, XRD, Optical parameters.

1. Introduction

Copper selenide is a widely investigated and important I-VI semiconductor utilized in the industry of photovoltaic cells, thermoelectric converters, solar cells, superionic conductors, photodetectors, electro-conductive electrodes, microwave shielding coating, sensors and photothermal conversion etc. (1, 2) Copper selenide is a semiconducting material, which has electrical and optical properties suitable for photovoltaic application, and it is more interest due to its nature (3, 4), the possibility of optical band gap tuning, less toxicity and earth abundance (5, 6). It has many phases and structural forms: stoichiometric α-Cu_2Se, Cu_3Se2, CuSe, and $CuSe_2$, as well as non-stoichiometric Cu_2−xSe (7). The formation of these compositions depends on the method of preparation, and they exist in different crystallographic forms such as cubic, hexagonal (8, 9), orthorhombic (10), tetragonal, and monoclinic (11, 12). Due to the availability of different kinds of compositions, the band gap of copper selenide is not well-defined. Several authors have reported that copper selenide

possesses a direct band gap in the range of 1.9–2.3 eV and an indirect band gap in the range of 1.2–1.7 eV (13,14). The direct band gap is always preferred over the indirect one, due to reasons of momentum conservation and fast response (15). Many methods have been developed to prepare Cu_2Se thin films, including vacuum evaporation (VE) (16),
magnetron sputtering (17), electrodeposition (18), chemical solution processes, and spin-coating (19). Among these, VE is a mature thin-film preparation technique commonly used to prepare large-area and uniform thin-film materials. Up to now, there are two ways to prepare Cu_2Se thin films using VE. One is to evaporate Cu_2Se powder (or pellets) directly onto the substrates, the other is to co-evaporate Cu and Se using two separate evaporation sources (20). Researchers are in constant search to explore the vast number of applications provided by this compound due to its excellent properties (21). In the present investigation, semiconducting copper selenide thin films have been deposited at room temperature and annealed at (403, 453, and 503) K onto glass substrates using the thermal evaporation deposition technique. The paper deals with a Study of the structural, visual properties of Cu_2Se thin film and annealing effect at different temperatures (403-453 503) K, on these properties of the film prepared by the thermal evaporation method. The results are discussed and compared with the reported data.

2. Materials and Methods

Cu_2Se alloy was synthesized from high purity (99.99%) Cu_2 and Se, mix these elements and put them in an evacuated tube of quartz when a pressure of ($2*10^{-5}$ mbar), heated up to (1000 K), in electric oven for one hour then the alloy left to cool to room temperature. Observation of the structure by X-ray diffraction (XRD). Deposition of thin films Cu_2Se by vacuum thermal evaporation in glass substrates at R.T with (500+-20) nm thickness, then annealing at (403, 453, and 503) K in an electric furnace for 60 minutes. X-ray diffraction was used to examine the compound formation used to study the structure of these films by detailed 2Θ from 20° to 80 °with an interval of 0.05°, Scherer's Formula was used to calculate the crystalline size of the films (22)

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

where 0.9 is the shape factor and B(FWHM). is the width of the diffraction peak at half maximum intensity. Θ is the reflection angle, and λ is the wavelength of the X-rays (23).
The surface morphology, roughness and Grain Size of Cu_2Se were shown to be affected by annealing temperature using atomic force microscopy AFM (24), the optical properties of thin film prepared, transmission and absorption spectrums in the range between 400 to 1100 nm has been noted, lambert law and Tauc equation have been used to determine the absorption coefficients α and the energy gap (Egopt) respectively from absorption spectrum (25, 26). Tauc formula,

$$\alpha h\nu = B\,(h\nu - E_g^{\ opt})^{1/r} \quad (2)$$

Where, B: a constant inversely proportional to the amorphousness of material.
hν : the photon energy (eV).
Eg^{opt} : the optical energy gap (eV) .
r: constant and may take values 2, 3,1/2, 3/2
depending on the material and the type of optical transition. direct or indirect (27), and the absorption coefficient can be calculated from the equation:

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

were
A: the optical absorbance

t: the film thickness

[refractive index (n_o), and extinction coefficient (k)] (26). By using the following equations:

$$n_0 = \left[\frac{4R}{(1+R)^2} - k^2\right]^{\frac{1}{2}} + \left(\frac{1+R}{1-R}\right) \quad (4)$$

The Extinction coefficient, k (imaginary part of the refractive index), which is related to the exponential decay of the wave as it passes through the medium

$$K=\frac{\alpha\lambda}{4\pi} \quad (5)$$

Where λ: is the wavelength of the incident radiation (20, 28).

The reflectance (R) is calculated by: (29)

$$R = 1\text{-}T\text{-}A \quad (6)$$

Where T is transmittance and A is absorbance.

3. Results and discussion

The crystals prepared using the vacuum thermal evaporation deposition technique were characterized by X-ray diffractometry, and the results are given in **Figure 1**. The results were in good agreement between the calculated and measured interplanar spacing (d) values and also in agreement with the values of the crystalline diffraction angles, as shown in **Table 1.** Were peaks (111), (220), and (311) corresponding to 2θ equal to 26.8876, 44.5621, and 52.75 as compared with the standard values in ASTM cards no. (00-046-1129) The structure of copper selenide is cubic, and the preferred orientation is at the 220 plane.

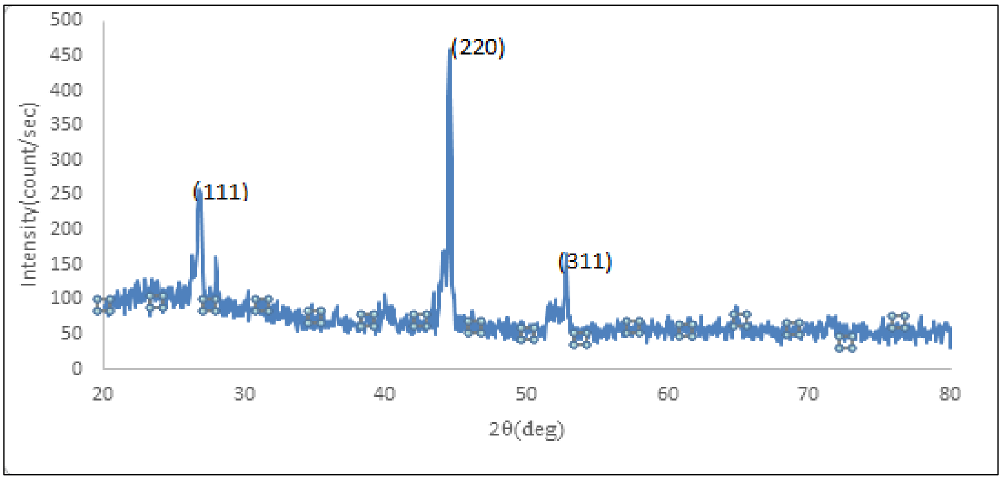

Figure 1. X-ray diffraction pattern of Cu_2Se alloy.

The X-ray diffraction parameters interplanar spacing (d), Miller indices (hkl), crystalline size (C.S), intensity of dislocation, ε Macrostrain, number of crystal defects, and lattice constant for Cu_2Se alloy are listed in **Table 1.**

Table 1. Structural parameters of Cu_2Se alloy

2θ (stand) (degre)	**2θ (exp.) (degre)**	**d (stand) Å**	**d (exp.) Å**	**hkl**	**FWHM (deg.)**	**Crystalline Size (C.S) (nm)**	**δ*10^15(m^-2) =1/(C.S)^2**	**N =t/c.s^3**	**$\varepsilon=\frac{B\ COS\theta}{4}$**
26.425	26.887	3.370	3.3132	111					
43.915	44.562	2.060	2.0316	220	0.1792	50.044	0.3993	$3.9894*10^{-3}$	0.0414
51.909	52.75	1.760	1.733	311					

Results of X-ray diffraction showed that the compound's thin film (Cu2Se) is poly-crystalline with a cubic type, where the prepared thin film contains many crystal peaks and crystal directions (hkl). X-ray results showed an improvement in crystal composition; it also possesses a polycrystalline structure, cubic type, with crystal growth appearing at crystal direction 220 for all different temperatures. The crystal volume increases as the annealing temperatures increase, and the dislocations decrease. Also, the number of crystals N decreases because the crystal size increases with almost fixed lattice constants, due to system regularity, and the inverse proportionality between the dislocation and the crystallite size with increasing annealing temperature. This is due to the FWHM of the main peaks decreasing as shown in **Table 2**. From **Figure 2.** the angles of diffraction creeps towards the few values, and again it increases in 503K, which indicates it is the optimum annulling, and the intensity of the polycrystalline peaks (2θ = 44.68°(220), 39.84°(220), 25°(111), 44.68°(220), increases with increasing the annealing temperature due to re-arrange distances in crystal structure, with increased crystallization by high annulling temperature, which is due to decreases strain. The results confirmed that the Cu_2Se system and also the crystallinity of the compound are improved with annealing; however, the nature of the compound's crystal structure does not change and remains cubic.

Table 2. Structural parameters of Cu_2Se film at different temperatures.

Cu_2S film	2θ (stand) (degree)	2θ (exp.) (degree)	D (stand) Å	D (exp.) Å	d hkl	FWHM (deg.)	Crystalline Size (nm)	$\delta\times10^{-3}$ (lines/nm^2)	$N\times10^{15}$ (disL/cm^3)	$\varepsilon = \beta \cos\theta / 4$
At R.T	43.9154	39.8267	2.060	2.26161	220	0.5324	25.4575	1.543	0.0303	0.0814
	26.4258	26.9012	3.370	3.31160	111					
	43.9154	44.6647	2.060	2.02722	220					
	51.9092	49.8831	1.760	1.82874	311					
At 403K	43.9154	44.7092	2.060	2.02351	220	0.5177	40.4542	0.6083	7.5015×10^{-3}	0.0511
	51.9092	49.8519	1.760	1.82775	311					
	26.4258	26.9012	3.370	3.31160	111					
At 453K	43.9154	44.7092	2.060	2.02351	220	0.5170	41.3321	0.584	7.0812×10^{-3}	0.0501
	51.9092	47.8567	1.760	1.90933	311					
	51.9092	51.3759	1.760	1.77781	311					
	26.4258	25.0450	3.370	3.55627	111					
At 503K	43.9154	44.6891	2.060	2.02617	220	0.2075	45.3386	0.5349	6.1852×10^{-3}	0.0479
	51.9092	49.9083	1.760	1.82852	311					
	26.4258	26.9237	3.370	3.3073	111					

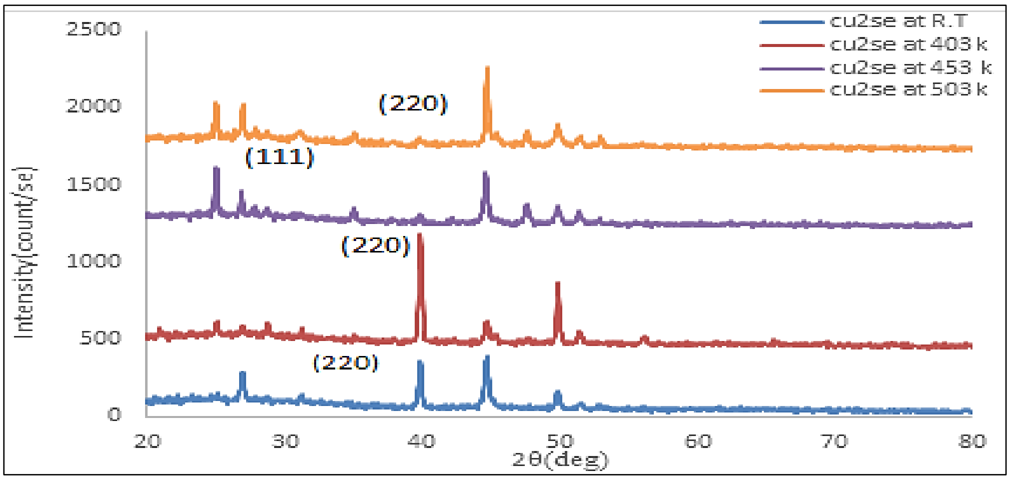

Figure 2. Cu_2Se film with different annealing temperatures.

Atomic Force Microscopy (AFM) analysis provides information on grain size, roughness, and square root rate, as well as 3D images of the compound's surface at different temperatures. As in **Table 3** and **Figure 3.** The grain size increases as the annealing time increases, and the roughness of the surface and r.m.s. Decreases, especially at the degree of annealing (453k). Indicates the uniformity of the surface and its homogeneity with nanoscale dimensions.

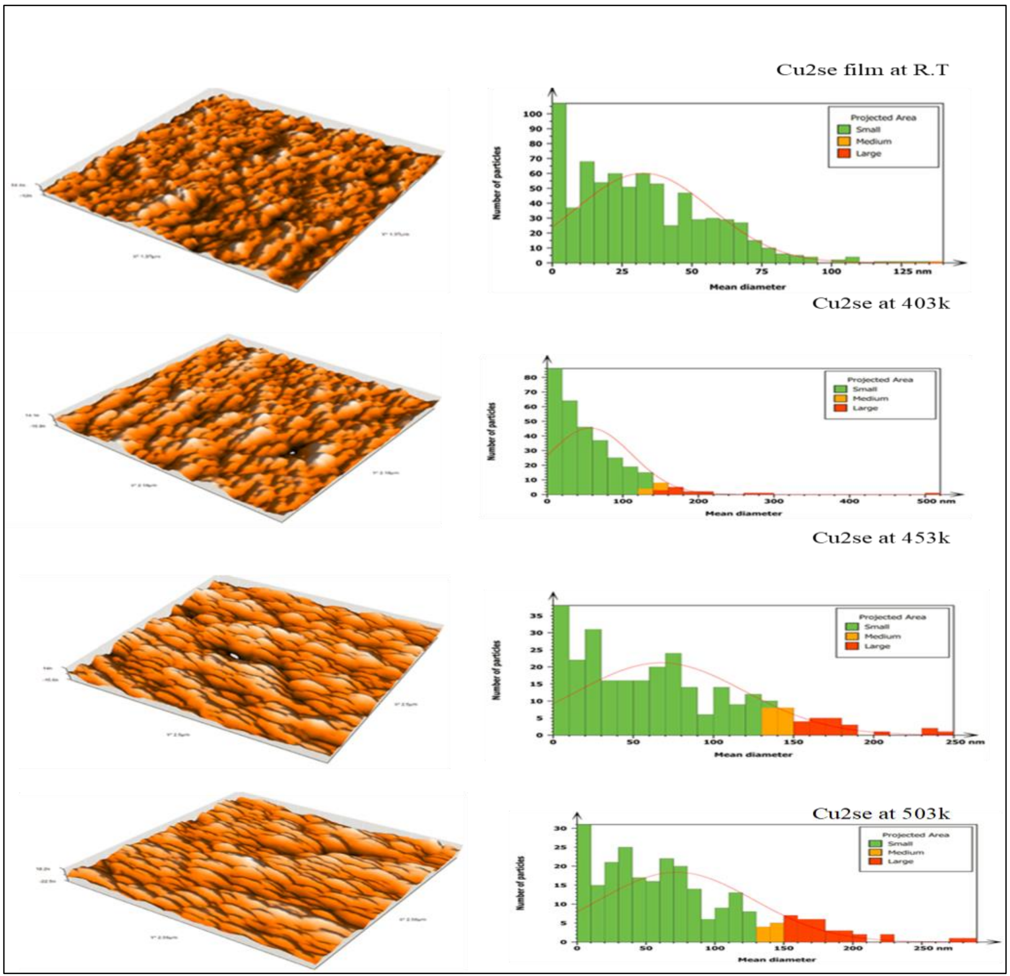

Figure 3. AFM descriptions of Cu_2Se at R.T and Ta (403,453and 503) K.

Table 3. The grain size, roughness average and Root mean square of Cu_2Se at R.T and Ta (403,453 and 503) K

sample	Green size (nm)	S_q root mean square height (nm)	Sa arithmetic mean height (nm)
Cu_2Se film	32.69	14.99	12.12
Cu_2Se at 403k	56.77	8.266	6.691
Cu_2Se at 453k	67.35	7.064	5.709
Cu_2Se at 503k	72.12	8.238	6.486

The spectra of transmittance and absorbance in the spectral area as shown in **Figure 4** were determined in relation to wavelength. at thickness 500 nm for Cu_2Se film in room temperature and an annealing (403, 453 and 503) K. 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 films at (403, 453 and 503) K. The figure shows the effect of raising the annealing temperature on the transmittance and absorbance of the film, were the absorbance of the film decreases with an increase in the annealing temperature towards longer wavelengths, especially between (550 to 1000) nm. The opposite of this is transmittance, which increases with increasing annealing temperature within the same range (550-1000) nm.

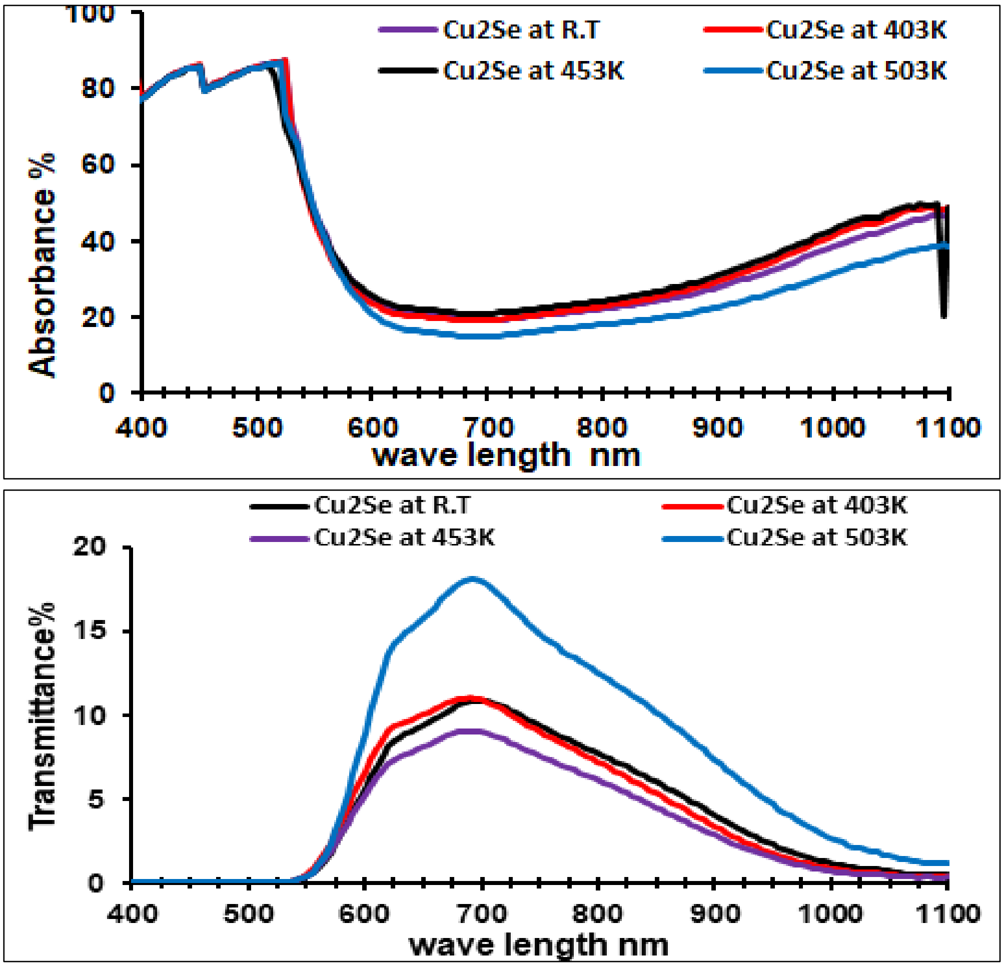

Figure 4. Absorbance and transmittance spectra of Cu_2Se at room temperature and the annealing (403, 453 and 503) K.

The lowest absorbance at a temperature of 503K is 15% at 695 nm, indicating a decrease in the energy gap (30). The energy gap (Eg) was calculated through the intersection of the photon energy axis with the curve (αhv)2 by a straight line, as illustrated in **Figure 5.**

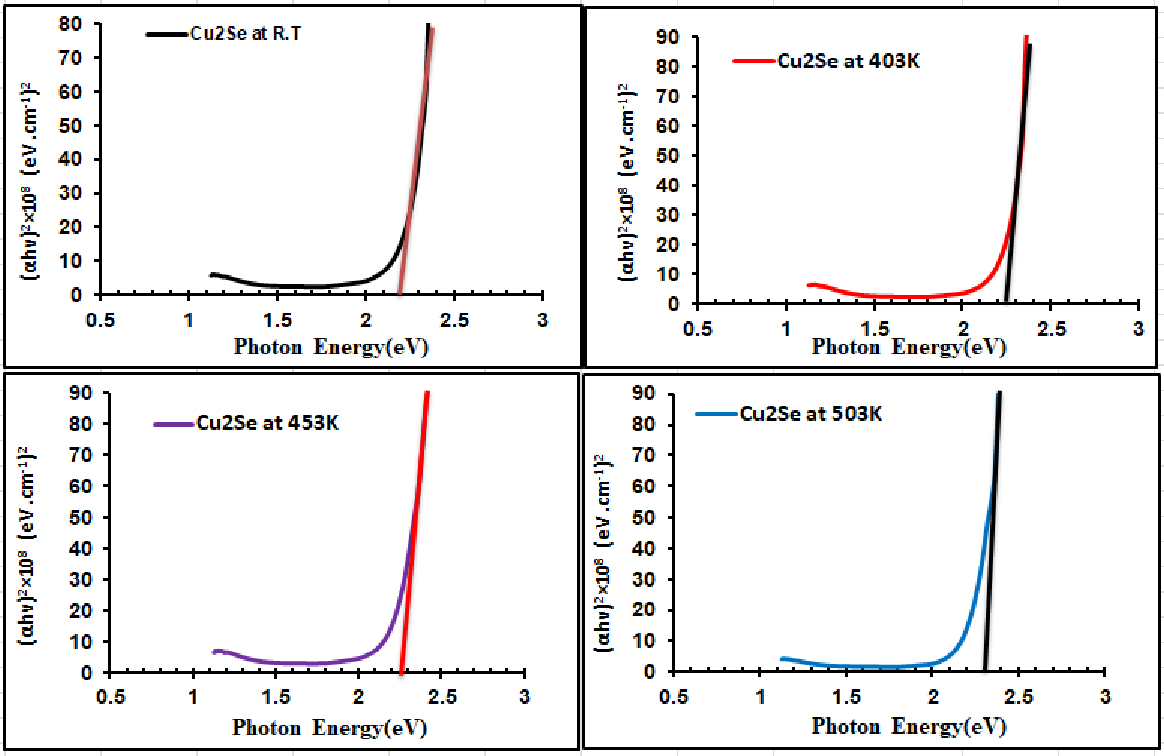

Figure 5. $(\alpha h\nu)^2$ with photon energy of Cu_2Se in R.T and Ta (403, 453, and 503) K.

The energy gap values range from 2.2-2.3, as it increases as the annealing temperature rises to 403 K, then a very slight increase to a temperature of 503 K because the temperature difference is not large enough. This result is consistent with (13,14) despite the different preparation conditions. **Figure 6** shows the reflectivity as a function of the wavelength of the compound at different temperatures. It was calculated using **Equation 7**. It was found that the difference in their behavior appears at high wavelengths, approaching 900 nm. The reflectivity decreases with an increase in the annealing temperature, then it increases at the annealing temperature of 503 K.

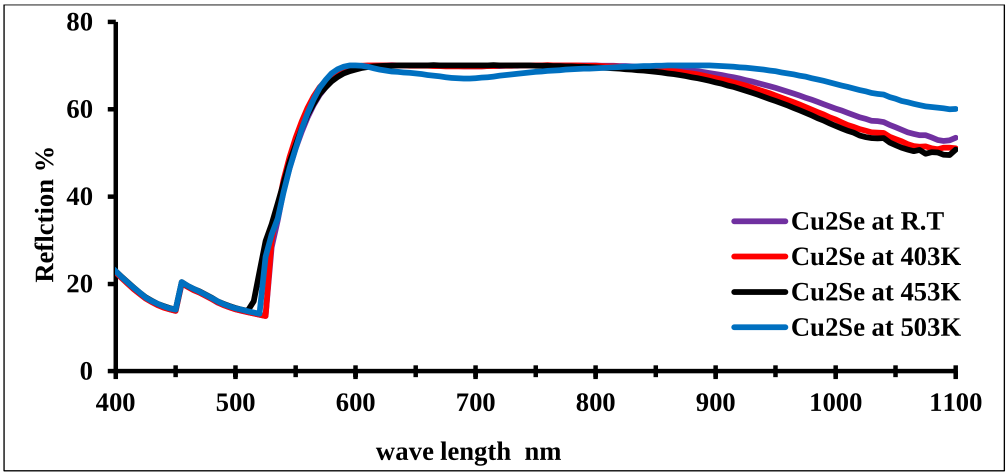

Figure 6. Reflection with wavelength of Cu_2Se in R.T and Ta (403, 453, and 503) K.

It depends on the absorption coefficient according to **Equation 5**. It is clear from **Figure 7** that the extinction coefficient decreases when the wavelength is between 500-600 nm (photon energy 1-2 eV), and increases when the wavelength up to 650nm (photon energy 2-2.5 eV). This behavior is similar for different annealing temperatures.

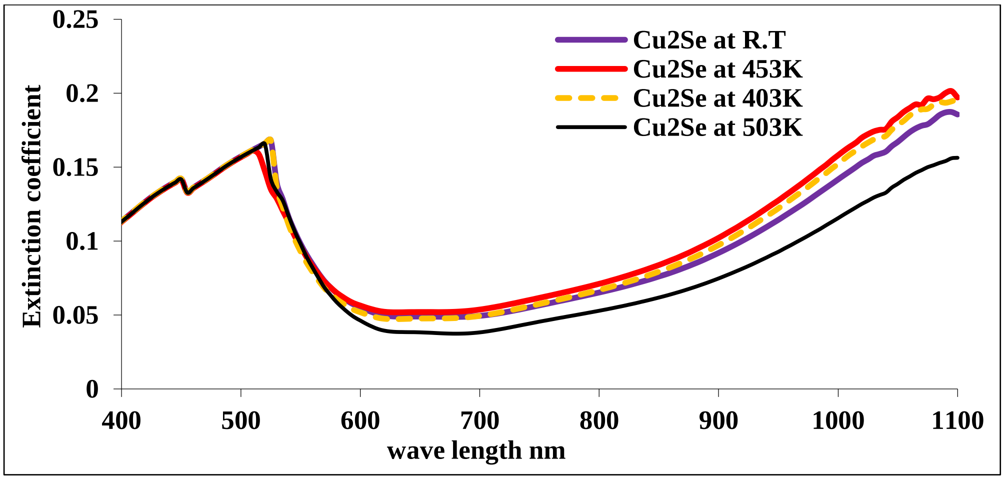

Figure 7. The extinction coefficient varies with the wavelength of Cu_2Se thin film in R.T. and Ta (403, 453, and 503) K.

The behaver of the refractive index (n), calculated from Equation (4). and as a function of the wave length for Cu_2Se film at different temperatures is shown in Figure 8, it is approximately the same behaver of the reflection because it depends on it, were increases at wave length from 520-610 nm then decreases for high wave length, the behavior is similar for all temperatures except a little difference at 503K were it has the lowest value of the refractive index at the wavelength 700nm, and the highest value of refractive index at the wavelength 600 nm.

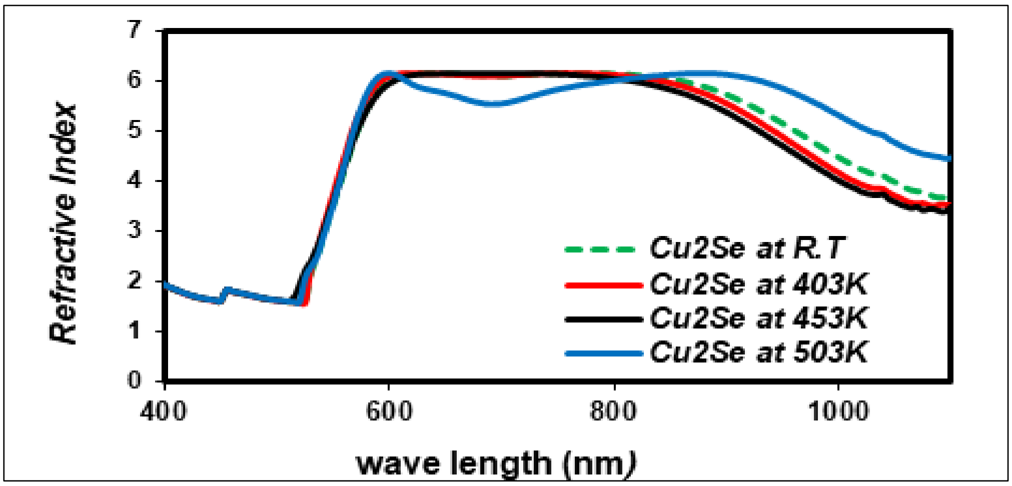

Figure 8. Refractive index varies with wavelength of Cu_2Se thin film in R.T. and Ta (403, 453, and 503) K**.**

The α is non-linear with wavelength. A maximum of 10^4 cm^{-1} absorption coefficient is observed at 520 nm. It is within the wavelength of the visible region. The absorption coefficient of the film at all temperatures prepared increases with wavelength up to 600 nm, also from absorbance values where the α values are observed ($\alpha > 10^4$ cm^{-1}), which means the type of transition promising occurs is directly allowed, as shown in **Figure 9.**

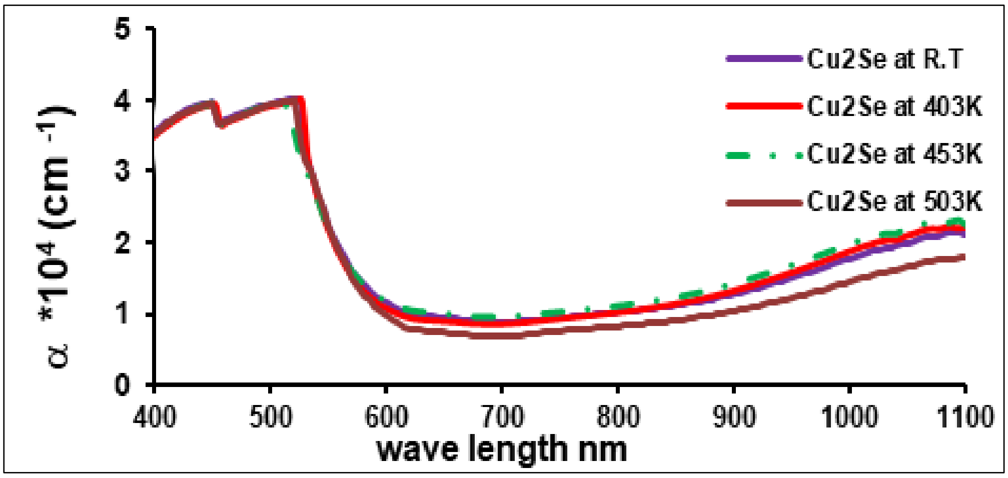

Figure 9. Absorption coefficient varies with wavelength of Cu_2Se thin film in R.T and Ta (403, 453, and 503) K.

4. Conclusion

When the material enters the range of nano dimensions, it presents interesting and unique properties that are different from the bulk material. In this work, we have prepared pure Cu_2Se films by the thermal evaporation method. The structural analysis shows that the Cu_2Se film has a cubic structure, indicating that annealing modifies the crystalline structure. The morphological studies revealed spherical-shaped particles for Cu_2Se and uniform. The optical absorption study of the pure Cu_2Se shows good optical absorption. Thus, the present study suggests that our reports will encourage further investigations on this material for photovoltaic performance and promote their potential industrial application.

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Conflict of Interests

Conflict of Interest. The authors declare that they have no conflicts of interest.

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None.

Ethical Clearance

The project was approved by the local ethical committee at the University of Baghdad

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