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Influence of Annealing on the Morphology and Optical Properties of Chemically Fabricated Amorphous CuSe Thin Films

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ABSTRACT

Thin films of CuSe have been deposited on glass slides from alkaline bath employing chemical bath deposition method. Films were annealed at 573k to study their properties. Both the as-deposited and annealed films were found to be amorphous which was detected by the SEM microscopy and confirmed by the X-ray diffraction. The optical properties were studied in the wavelength range 320nm – 900nm. Peak values of 96.10%, 46.43% were observed for absorbance and reflectance which increased on annealing while transmittance decreased. Average values of refractive index which ranged between 2.14 – 2.62 increased to 2.16 – 3.33 on annealing. As-deposited band gap which ranged between 2.35ev and 2.60ev were found to reduce on annealing to the range 2.10ev – 2.40ev. Films could be used as absorber materials in solar cells and as window layer in photovoltaic cells. The high refractive index qualifies them for use in optoelectronic devices.

KEYWORDS: *Amorphous, Annealing, band gap, Copper selenide, deposition*

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I. INTRODUCTION

Copper selenide (CuSe) is a semiconductor chalcogenide compound whose preparation and study has attracted the interest of researchers because of its potential applications in the fabrication of photovoltaic devices. It exhibits p-type conduction due to copper vacancies [1] and is very useful as absorber [2] or window [3] layers in heterojunction solar cells and also as radiation filters [4]. CuSe has a wide range of stoichiometric compositions with different crystallographic forms for each composition.

Thin film materials exhibit crystalline or amorphous nature depending on their deposition conditions. Films with amorphous nature also have optical properties that are of potential applications in various areas of technology [5]. Thin films are annealed in order to investigate the effect of service environment on their properties which may deteriorate or improve on annealing. CuSe which was hexagonal at room temperature, transited to orthorohmbic at 48^{o}c and to hexagonal at 120^{o}c [4]. The band gap of CuSe is not well defined because of the wide variety of stoichiometric forms, presence of high density dislocations and defects and quantum confinement effects [6]. Band gap values of 1.39ev – 2.40ev have been reported by [4,7-8]. Different deposition methods have been employed to fabricate thin films of CuSe. They include sputtering [9], vacuum evaporation [10], electrophoretic deposition [11], spray pyrolysis [12] and chemical bath deposition [CBD] [7-8, 13]. Of all the techniques mentioned, CBD was employed to fabricate the films of CuSe because of its simplicity, cheapness, convenience, ease for large area deposition and possibility of yielding results comparable to sophisticated methods. The as-deposited films were annealed to a temperature of 573k in order to investigate their properties. Thin films were subjected to structural, microstructural and Uv-vis-spectrophotometric analysis.

II. MATERIALS AND METHODS

Copper selenide thin films were deposited on glass substrates using chemical bath deposition technique. The source of Cu^{2+} was $CuS0_4.5H_20$ while the source of selenide ion Se^{2-} was solution of sodium selenosulphate prepared by refluxing 8g of selenium powder mixed with 25g of anhydrous sodium sulfite in 200mls of distilled water at 90^{o}c for 6hrs [14-15]. This gave 0.4m of sodium selenosulphate [Na_2Se0_3] solution. Thin film can be achieved only if the ionic product of Cu^{2+} and Se^{2-} is greater than the solubility product [K_{sp}] of the compound. This is aided by the use of ammonia solution which served as a complexing agent which slows down the reaction so that Cu^{2+} and Se^{2-} released in the solution can condense on the substrate to form the film.

Chemical bath deposition of CuSe was carried out in a 50mls beaker in which were placed 5mls of 0.5M $CuS0_4.5H_20$, 1ml of 13.4M ammonia solution, 6mls of 0.4M Na_2Se0_3 and 35mls of distilled water. The mixture was vigorously stirred for few seconds at a pH of 8. Previously, degreased and cleaned glass slides were placed vertically in the chemical bath at different bath variations. The coated slides were brought out after deposition, rinsed with distilled water and dried in air. Five samples with varying bath conditions were prepared as shown in table 1.

Table I Preparation of Copper Selenide (CuSe) thin films

Reaction bath	**Deposition time (hrs)**	**$CuS0_4.5H_20$**		**Ammonia soln**		**Na_2Se0_3**		**H_20**
		mol (m)	**vol (ml)**	**mol (m)**	**vol (ml)**	**mol (m)**	**vol (ml)**	**vol (ml)**
J_1	6	0.5	5	13.4	1	0.4	6	35
J_2	7	0.5	5	13.4	0.5	0.4	6	35
J_3	8	0.5	5	13.4	1	0.4	6	35
J_4	9	0.5	5	13.4	0.5	0.4	6	35
J_5	8	1.0	2.5	13.4	0.5	0.4	6	30

Film J_5 was used to study the structure of as- deposited and annealed film. The thin films were characterized as-deposited and then annealed to a temperature of 573k and re-characterized using Avantes double beam spectrophotometer, model 2048 Ava soft 7.1 for absorbance-transmittance - reflectance spectra, a Vecco Dektak 150 stylus surface profiler for thickness measurement. The structural and morphological analysis were carried out using X-ray diffractometer (PANALYTICAL) with Cukα (1.54 A) at a scanning range of 20^o-90^o, and a TM 3000 Tabletop Microscope (HITACHI).Rutherford Backscattering Spectrometry(RBS) was used for the elemental composition. The absorbance-transmittance and reflectance were used to calculate the absorption, extinction coefficients α, k and the refractive index (n) from mathematical relations given by [16-17]. The band gap energy was calculated using relations given by [18].

III. RESULTS AND DISCUSSION

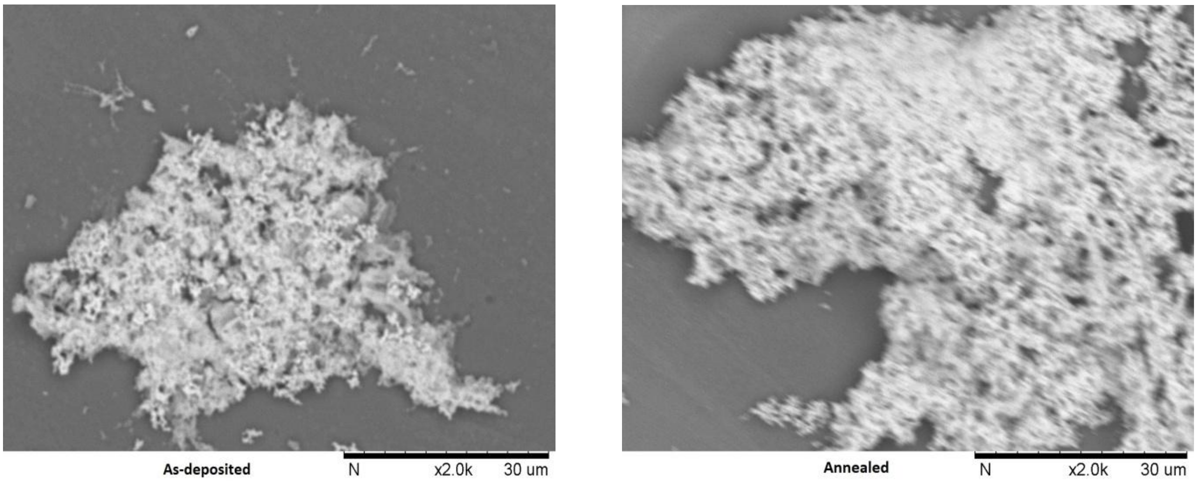


Figure 1: SEM Micrographs of CuSe Thin Films

Figure 1: Shows the SEM micrographs of as-deposited and annealed CuSe thin films. The as-deposited film surface is not homogenous and contains irregular agglomerated features with surface roughness. These features were highly magnified on annealing and tend to spread all over the film surface showing increase in amorphousness with annealing.

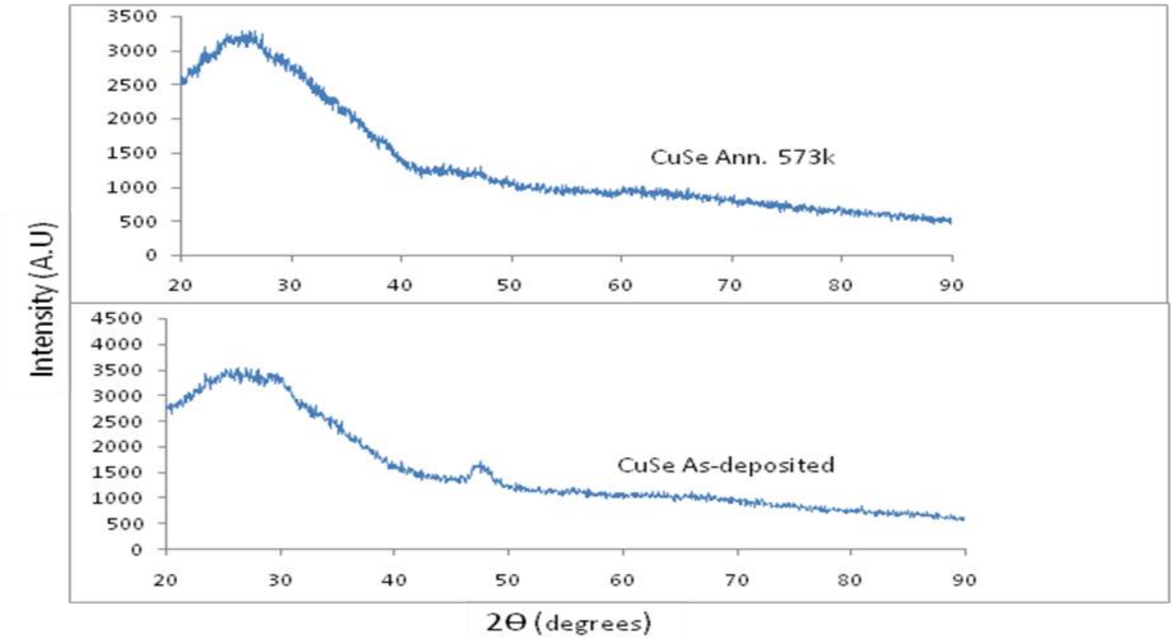


Figure 2: X-ray diffraction studies of CuSe thin films

The X-ray diffraction pattern shows that no well defined peak was found and no well defined plane was obtained for both as-deposited and annealed CuSe films. The amorphous nature of the film samples was confirmed by the X-ray diffraction technique as no sharp peaks were obtained, even after annealing at 573k. This may be due to low temperature deposition.

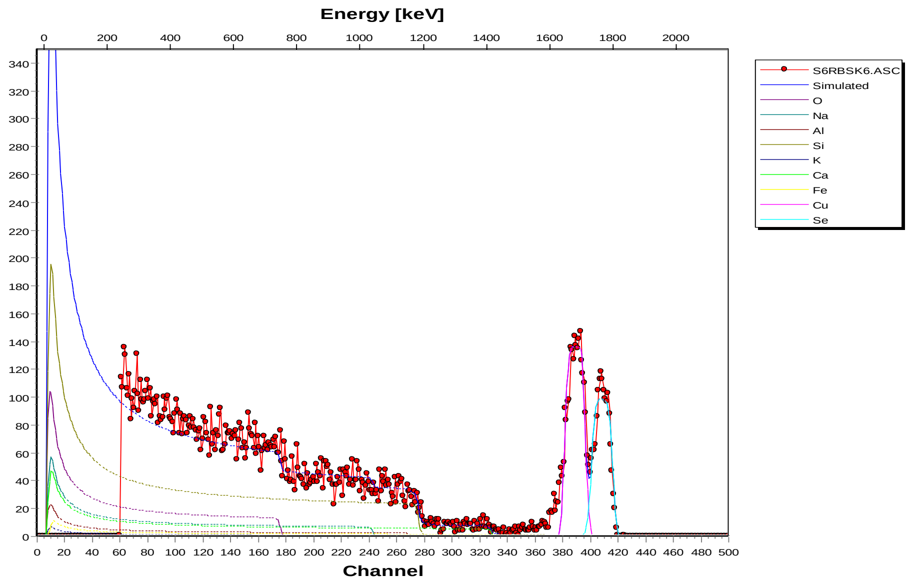


Figure 3: RBS Analysis for CuSe thin films

From figure 3, the RBS analysis shows the number of backscattered helium ions which are plotted against their energies. The composition of CuSe and substrate from RBS analysis is displayed in table 2. The average atomic percentage of Cu and Se is 65.25% : 34.75% showing that the samples are Cu rich. Presence of O_2, Si, Na, Fe, etc is due to substrate. Thickness of the films deposited ranged between 0.25μm and 0.60μm.

Table 2: Composition of CuSe and substrate from RBS analysis

CuSe	Cu	Se	O	Si	Na	Fe	Al	Ca
Sample	65.25%	34.75%	-	-	-	-	-	-
Substrate	-	-	56.0%	28.0%	12.6%	0.52%	0.53%	1.83%

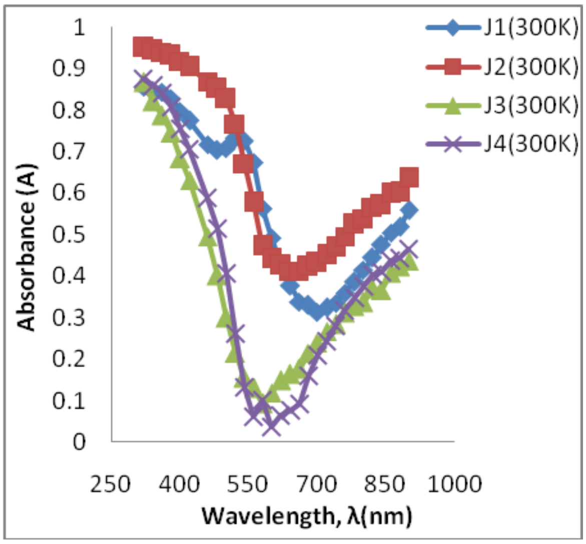


Figure 4a

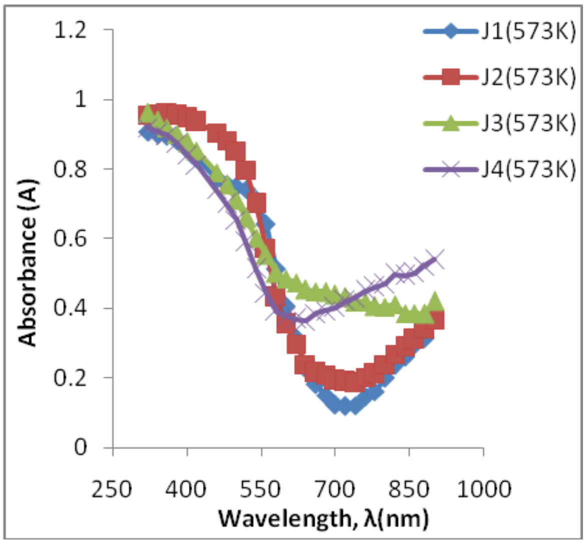


Figure 4b

Absorption spectra for CuSe thin films

Figures 4(a, b): Show the absorption spectra for the as-deposited and annealed CuSe films. The as-deposited films showed very high absorption in the UV region with highest peak of 95.10%. In their annealed state, all the films showed greater increase in absorbance with highest peak of 96.1% by film J_2 in the UV. Increase in absorbance with annealing showed the presence of more states within the band gap for photon absorption. Annealing therefore produced a good absorber. This is in line with report of [19] on absorption of CuSe.

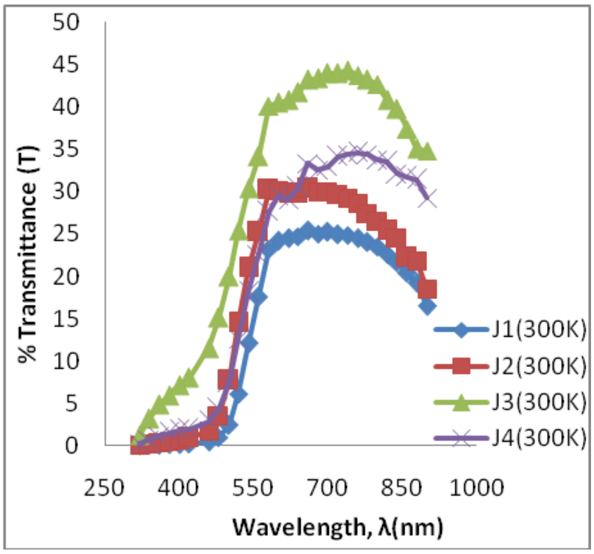


Figure 5a

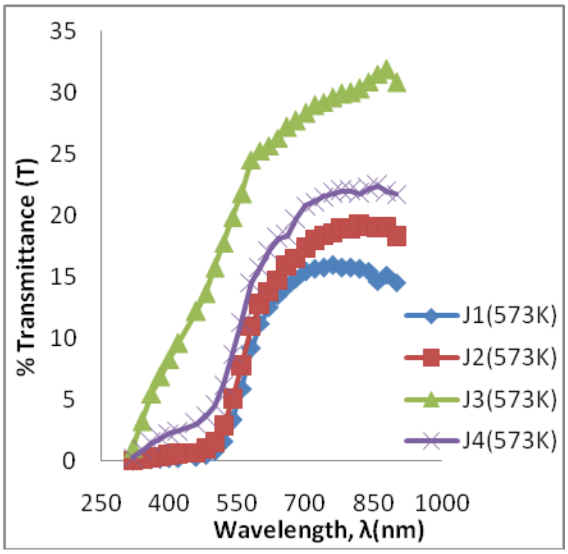


Figure 5b

Transmittance spectra for CuSe thin films

Figures 5(a, b): Show the transmittance curves for as-deposited and annealed films. Highest peak of 42.65% at 800nm was noted for the as-deposited films J_3 while the annealed films showed a decrease in transmittance with highest peak of 31.88% at 880nm by J_3.

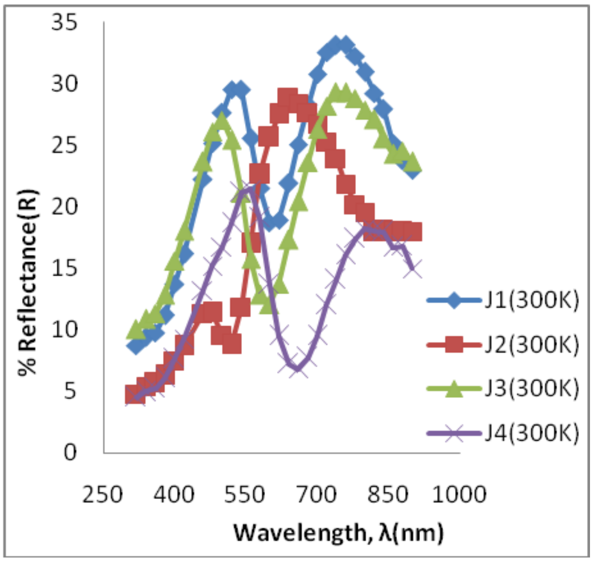


Figure 6a

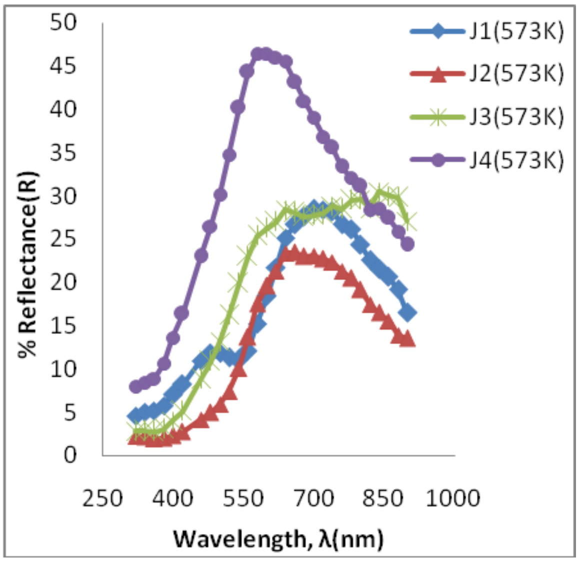


Figure 6b

Reflectance curves for CuSe are shown in figures 6(a, b). The curves for as-deposited films showed interference peaks with points of minima and maxima. Peak values range between 18.66% and 33.14%. For the annealed films, the prominent points of minima and maxima disappeared and gave smoother curves with consistent increase and decrease in values. Film J_4 showed highest peak reflectance of 46.43% at 600nm which was higher than the as-deposited.

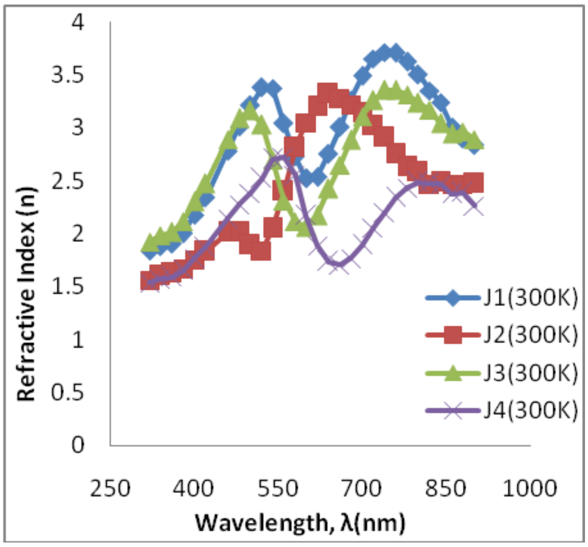


Figure 7a

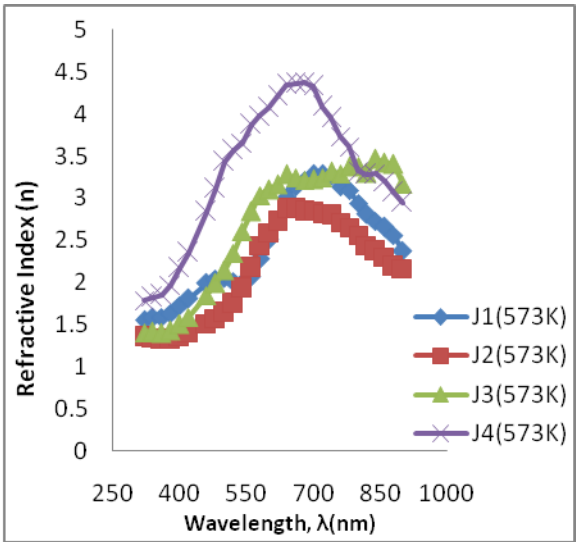
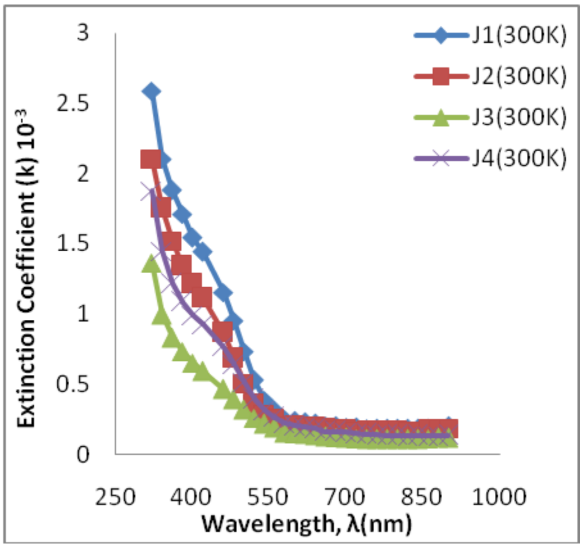


Figure 7b

Variation of refractive index with wavelength for CuSe thin films

The variation of refractive index n with wavelength is shown for as-deposited and annealed films in figures 7(a,b). The annealed curves show increase in refractive index with wavelength between 560nm and 820nm. Average values for the as-deposited films range from 2.14-2.62 while for the annealed films it is between 2.16 and 3.33. The increase in n values is due to annealing. The as-deposited values fall within the range of 1.5-2.5, 1.7-2.6 reported by [8, 13] for CuSe at room temperature. The high values of refractive index qualify CuSe films to be used in optoelectronic devices.



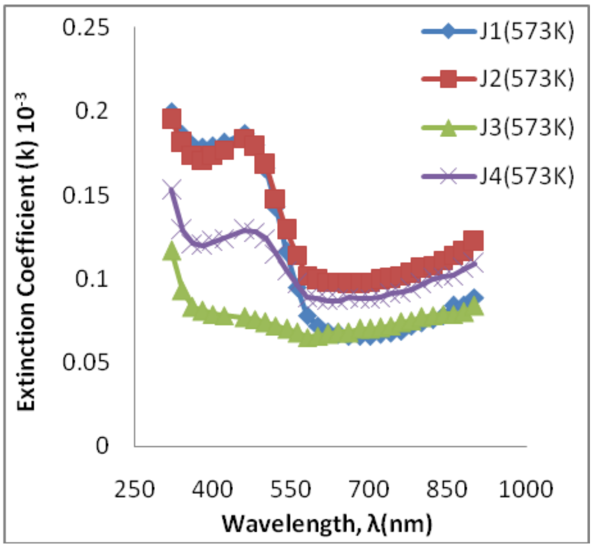


Figure 8a **Figure 8b**

Plot of extinction coefficient against wavelength for CuSe thin films

Figures 8(a, b) show the plots of extinction coefficient against wavelength. It is observed that as-deposited films showed constant decrease with wavelength from the Uv region. However, the annealed films showed points of minima and maxima with a general decrease in values. A peak value of k = 2.589 x 10^{-3} was observed for as-deposited film J_1 and a minimum of 0.179 x 10^{-3} while when annealed, the peak and minimum values dropped to 0.2 x 10^{-3} and 0.066 x 10^{-3} respectively. This shows the annealing effect on CuSe films.

The direct energy gap, E_g of the films were studied using the stern equation [18]

$$\alpha = \frac{[A\,(E_g - h\nu)]^{n/2}}{h\nu} \quad ----\quad 1$$

Where α is the absorption coefficient,
hν is the photon energy
E_g is the band gap energy
n is 1 for direct transition and 4 for indirect transition

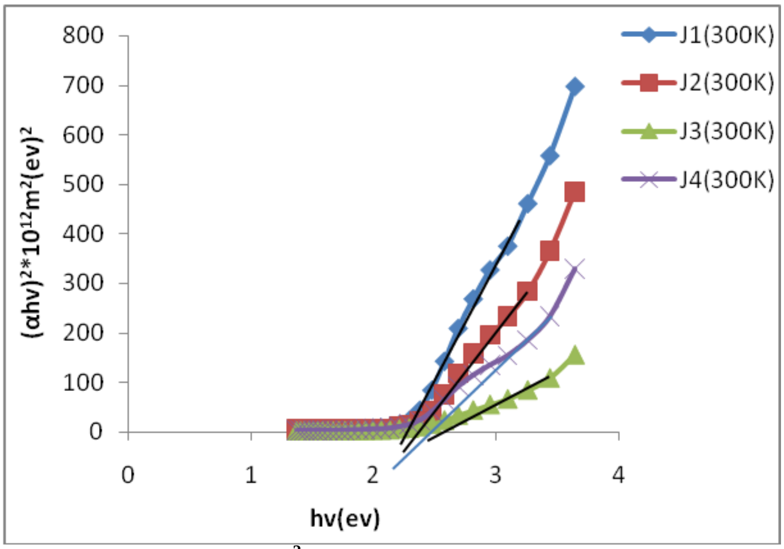


Figure 9a: Plot of $(\alpha h\nu)^2$ and hν for as-deposited CuSe thin films

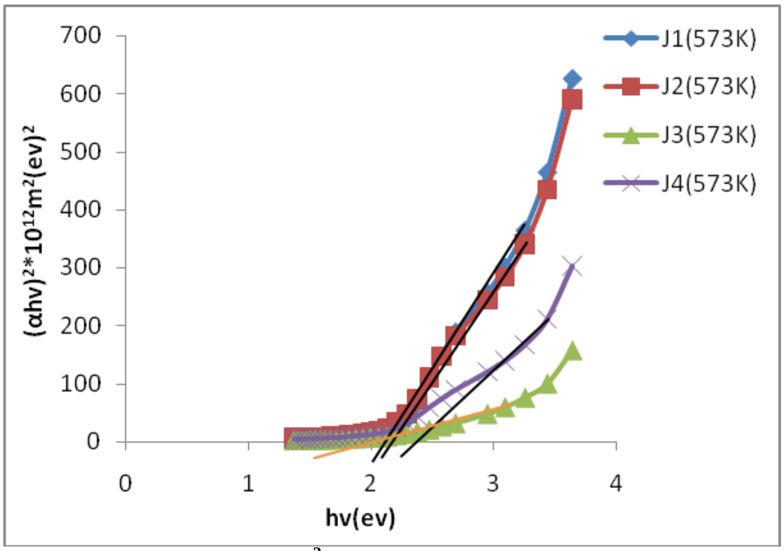


Figure 9b: Plot of $(\alpha h\nu)^2$ and hν for annealed CuSe thin films

The optical band gap for the as-deposited and annealed films were obtained from figures 9(a, b) by the extrapolation of the best fit line between $(\alpha h\nu)^2$ and hν to the intercept hν axis at $(\alpha h\nu)^2 = 0$.

The range of band gap obtained for as-deposited CuSe films varies from 2.35eV-2.60eV while it varies from 2.10eV-2.40eV for the annealed films. The direct band gap was found to decrease on annealing. This is because the as-deposited films were under compressive strain while the annealed films were under tensile strain [20]

This is close to earlier report of [21] with values of 2.20eV-2.13eV for annealed CuSe thin films. A range of 2-29eV-2.36eV was obtained by spray pyrolysis [12], 2.40eV by sputtering [9], and 2.30eV-2.45eV by [13] for as-deposited CuSe films. The values of energy gap being greater than 2eV make the films potential window layer for photovoltaic cells.

IV. CONCLUSION

The influence of annealing on copper selenide thin films has been studied in this work. From the SEM microscopy and X RD analysis the films presented an amorphous behaviour even when annealed at 573k.The RBS analysis confirmed that film contains Cu and Se. Films were found to show higher absorption of 96.10%, reduced transmittance and increased reflectance of 46.43% with annealing. The energy gap in the range 2.10ev - 2.60ev obtained for both as-deposited and annealed films was found to decrease with annealing. The refractive index had higher value as a result of annealing.

Therefore, the fabricated amorphous CuSe thin films are potential absorber materials in solar cell, good candidates for use in optoelectronic devices with high refractive index. With wide band gap, they could be used as window layer for photovoltaic cells.

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