

Investigation of Bath Temperature Effect on Properties of Copper Aluminium Selenide (CuAlSe₂) Films.

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ABSTRACT

CuAlSe₂ films have been prepared by chemical bath technique on microscopic glass slide from an aqueous solution bath containing CuCl₂.2H₂O, AlCl₃.6H₂O and Sodium selenosulfate in which EDTA was used as complexing agent. The bath temperature was varied in the range 313-353K and it seems to be one of the most important parameters affecting the properties of the films. The films deposited at 313K -353K were polycrystalline. The x-ray diffraction analysis showed the CuAlSe₂ samples with chalcopyrite structure and preferred orientation along (111) plane. The influence of bath temperature on CuAlSe₂ film was investigated and the optical analysis revealed an increase in absorbance with increasing bath temperature. The band gap energy was increased from 2.2 eV to 2.5eV as the bath temperature was increased from 313K to 354K. The optical properties were found to be dependent on bath temperature.

Keywords: chalcopyrite, thin films, nanocrystalline, CuAlSe₂, chemical bath deposition, band gap energy.

1. INTRODUCTION

Extensive research has been carried out recently to grow various kinds of ternary semiconductor thin films because of their potential application in the area of solar cells, optoelectronic devices, photoconductors, sensor and infra red detector devices. Ternary compounds had been studied for efficient solar energy conversion materials [1]. Ternary semiconductor chalcopyrites are being studied intensively due to their application in optoelectronic devices and solar cells [2]. CuAlSe₂ belongs to chalcopyrite family.

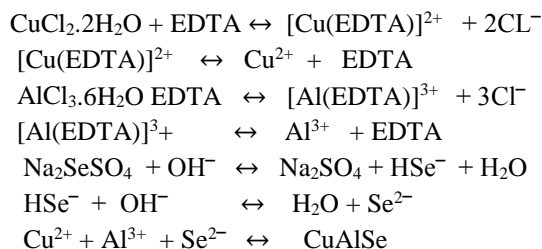
Few researchers have worked previously on CuAlSe₂ thin films using different preparation processes. Pulse electro deposition technique was used by [3] to synthesize CuAlSe₂ films on TCO substrate. A two stage process: e-beam evaporation of Cu and thermal evaporation of Al in a vacuum chamber have been used by [2] to deposit CuAlSe₂ thin films. However, no references have been found on the synthesis of CuAlSe₂ on glass substrate by chemical bath deposition.

In the present work, CuAlSe₂ thin film was synthesized on glass substrate by using chemical bath deposition (CBD) technique. CBD is a simple and low cost technique which has been used to grow several ternary semiconductors [3]. Ternary compounds of CuAlSe₂ thin films were prepared from an aqueous solution containing CuCl₂, AlCl₃ and freshly refluxed Na₂SeSO₄ at constant pH. The ethylene-diamine tetra-acetate (EDTA) was used as a complexing agent. The influence of bath temperature on the chemical bath deposited films was investigated.

2. MATERIALS AND METHODS.

The deposition of CuAlSe₂ thin films on glass slides was carried out using chemical bath deposition technique. Microscopic glass slides were used as the substrate during the deposition process which were previously degreased in trioxonitrate (v) acid (HNO₃) for 48hours, cleaned in water with detergent, rinsed in distilled water and dried in air. The HNO₃ treatment caused the oxidation of the halide ions in glass slides thereby introducing functional groups called nucleation and epitaxial centres for the growth of the films hence yielding highly adhesive and uniformly deposited films. The reaction bath for the deposition of CuAlSe₂ contained 3ml of 1.0M CuCl₂.2H₂O, 3ml of 0.5M AlCl₃.6H₂O, 1ml of 0.1M EDTA, 2ml of freshly refluxed Na₂SeSO₄ (0.5M), 3ml of 14M ammonia and 48ml of distilled water which were added in that order and allowed for 1 hour deposition time. The pH after the mixtures were thoroughly stirred came to 8.2. The selenide source, sodium selenosulfate was prepared in our laboratory by refluxing 100ml of 1M sodium sulphite and 4g of selenium powder for about 2 hours in a vessel which is connected to a Lieberg condenser such that the vapour given out are cooled back to liquid and fall back into the reaction vessel. The vessel was vigorously heated, to thermally accelerate the reaction to the solvent's boiling point. During deposition process, cations and anions which are present in the solution react with each other and became neutral atoms, which either precipitate spontaneously or very slowly in the bath. Fast precipitation, implies that thin films cannot form on the substrate immersed in the solution. But if the reaction is slow, which the complexing agent like

EDTA, TEA could achieve, then thin solid films of neutral atoms could form on the substrate. EDTA was the complexing agent used in this work to slow down the precipitation action and enables the formation of CuAlSe₂ films. The step wise reactions involved in the complex formation and film deposition processes for CuAlSe₂ are:



Selenide ions are released by the hydrolysis of sodium selenosulphate but Cu²⁺ and Al³⁺ ions form complex ions by combining with EDTA in pH of 8.2. The [Cu(EDTA)]²⁺ and [Al(EDTA)]³⁺ complexes adsorb on the glass, then a heterogeneous nucleation and growth take place by ionic exchange of S²⁻ ions. This process is known as ion-by-ion process and this is how CuAlSe₂ film was deposited on glass substrate.

3. Characterization

The deposited films were characterized using an X-ray MD -10.3 mini diffractometer with CuK α radiation wavelength of 1.5406Å. It determines the number of peaks(s), angle, counts, D-space and relative intensity of the diffraction peaks. It does this with the help of software data base supplied by the International Centre of Diffraction Data (ICDD). An Olympus BH2-UMA microscope at 100 x magnifications was used to examine and produce photomicrographs of the samples. The optical absorption spectra were obtained in the wavelength range of 340-1100nm by using a Janway 6405 UV-VIS model of the spectrophotometer. The optical properties investigated were absorbance and transmittance which were used to calculate other optical properties. These optical properties and band gap of the films were obtained from equations given in literature [4] while the optical thicknesses were calculated by optical methods [5].

4. RESULTS AND DISCUSSIONS.

4.1 Structural analysis:

The structure and identification of phases is studied with the help of an X-ray diffractometer using CuK α radiation ($\lambda = 1.5406\text{\AA}$). Figure 2 shows the x-ray diffraction patterns of CuAlSe₂ films prepared at bath temperatures 313K, 333K and 353K respectively. The formation of polycrystalline ternary compound CuAlSe₂ films with chalcopyrite structure and preferential orientation along the (111) are obtained in all cases. When the bath temperature is increased to 333K (60°) and 353K (80°), the number of peaks and their intensity also increased. The average crystallite size in the (111) plane direction has been estimated to be 9.5nm according to the Scherrer's Formula [6] :

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is the crystallite size in nm, λ is the X-ray wavelength in nm, θ the diffraction angle and β the Full Width at Half Maximum (FWHM) of the diffraction peak. The peak list details of XRD patterns of CuAlSe₂ film samples prepared at different bath temperatures are shown in table 1.

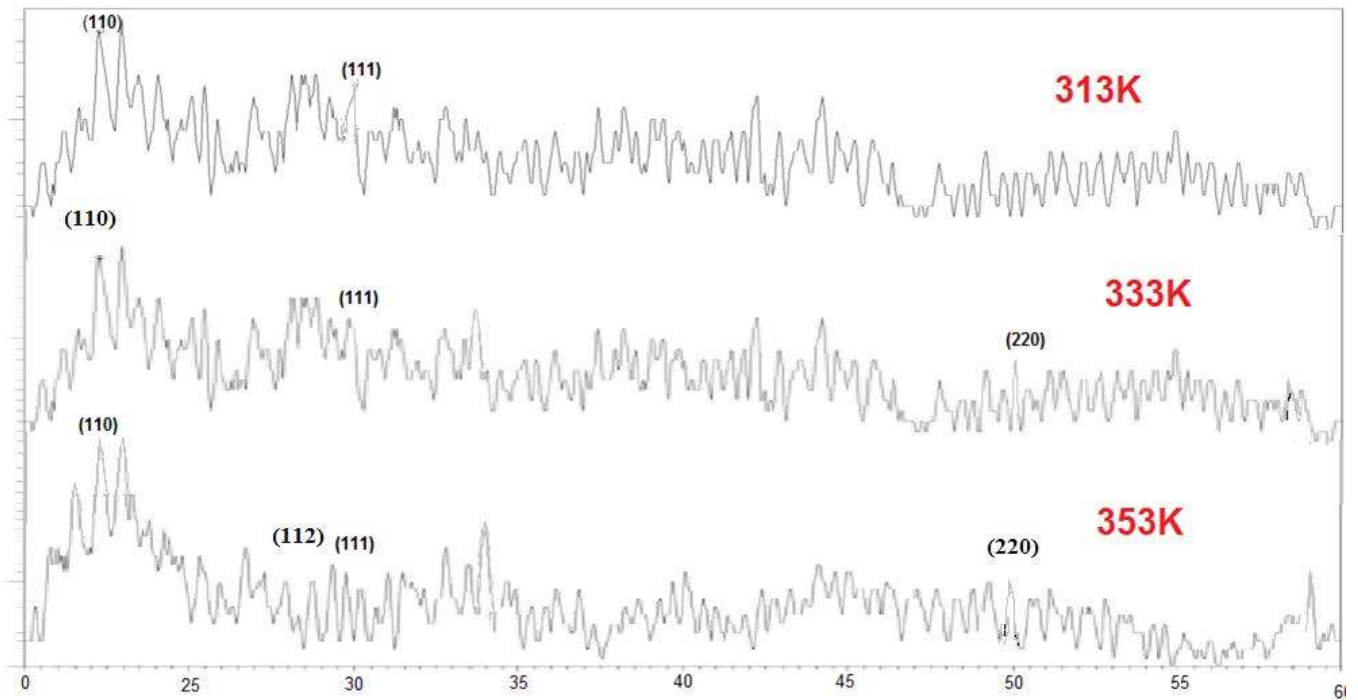


Fig 1 X-ray diffraction patterns of CuAlSe₂ films deposited at varying bath temperatures of 313K, 333K and 353K

Table 1:

No of Peaks	2θ °	h k l	D-spacing (Å)	Rel. Intensity	FWHM (°)	Crystal size (nm)
2	22.3	110	3.99	90	1.0	9.21
	30.0	111	2.96	93	1.0	9.35
3	21.5	110	4.13	90	0.5	21.3
	30.0	111	2.96	93	1.0	9.35
	50.1	220	1.82	92	1.0	9.95
4	21.7	110	4.09	54	0.5	21.33
	28.0	112	3.10	54	1.0	10.24
	30.0	111	2.96	93	1.0	9.35
	50.1	220	1.82	92	0.5	21.3

From the table the strongest peak for the deposited CuAlSe₂ films occurred at 2θ ≈ 30° with d-spacing ≈ 2.96 Å. It indicates that the preferred orientation lies along (111) direction. Average crystallite sizes of 9.28nm, 13.53nm and 15.33nm respectively were obtained for films grown at temperatures 313K, 333K and 353K. This shows that the crystallite size is directly dependent upon the bath temperature.

4.2 Surface morphology:

Surface morphology of CBD CuAlSe₂ films on glass substrates at different bath temperatures was studied. A systematic analysis was carried out at x100 magnification using Olympus optical microscope. Image-J for microscopy image Analysis

[7] software was used to analyse and determine the average particle size of the films from the micrograph images of figure 2. The average particle sizes of 5.7, 9.5 and 4.3 nm were obtained for films grown at 313K, 333K and 353K respectively. Also, close observations reveal no clear particular morphology on the surfaces of CuAlSe₂ film prepared at 313K. But some traces of buckled particles are evident. This may be associated with improper decomposition of precursor's salts. The bath temperature film prepared at 333K has nanograins packed closely to each other indicating good adhesiveness and uniform deposition over the substrate. Also, large coarse aggregates of CuAlSe₂ were missing. This indicates that the precursor is completely decomposed to form crystalline film. The particle size is found to be 9.5nm which is comparable with that of the calculated value from XRD studies. Films deposited at 353K show well defined grains randomly oriented on the substrate. Each grain shows the coalescence of nanometer sized crystallites. The surface shows presence of voids. This indicates that the film is not well adherent and uniformly coated on the substrate.



Fig.2 Micrograph images of CuAlSe₂ films grown at temperatures 313K, 333K and 353K.

4.3 Optical Absorbance and Transmittance Studies.

The optical properties of CuAlSe₂ films were studied using Uv-Vis-Nir spectrophotometer in the wavelength range of 340-1100nm. Fig 3 shows the variation of optical absorbance of the CuAlSe₂ thin films as a function of bath temperature. The spectra clearly indicate that lower wavelengths correspond to maximum absorption compared to higher wavelengths. This makes the film a good window layer for solar cell application. The absorbance of the films produced in the visible region indicates the possibility of these materials being used in the photoelectrochemical cells. The figure shows that there is an increase in the optical absorption with increasing bath temperature which is caused by the free carrier absorption corresponding to the increase in the conductivity[8]. Also, the increase in absorbance with bath temperature may be due to the enhancement in film thickness. Generally, thicker films have more atoms present hence more states are available for the photon energy to be absorbed [9 and 10].

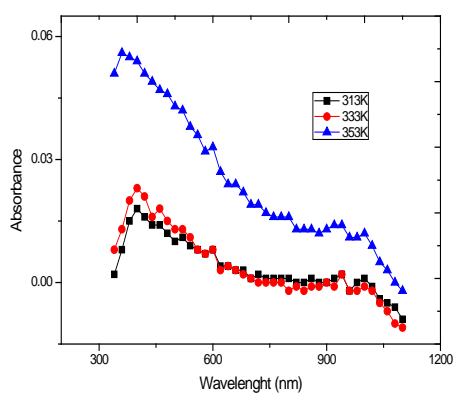


Fig 3 Absorbance spectra of CuAlSe₂ thin films.

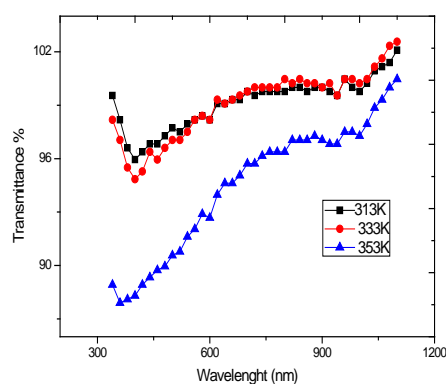


Fig 4 Transmittance spectra of CuAlSe₂ thin films.

Fig 4 reveals the spectral transmittance of CuAlSe₂ films obtained at temperatures 313K, 333K and 354K. The maximum transmittance was observed at VIS -NIR regions. The high transparency in the VIS and NIR regions is a consequence of the wide band gap of the film [11]. Also, there are no appropriate electronic transitions possible so transmission is very high in these regions. The decrease in percentage transmittance with increasing bath temperature may be due to the crystallization of the films. This is consistent with the x-ray diffraction study in figure 1. In addition, the decrease in transmittance may be due to the increase in film thickness with bath temperature, which leads to light scattering losses. As the film thickness increases, the grain size also increases, which in turns results in increase in surface roughness of the films. Thus, the optical transmittance of CuAlSe₂ films decreases with increasing bath temperature. Similar results was reported by [12].

Figure 5 shows the $(\alpha h\nu)^2$ versus $h\nu$ plots of CuAlSe₂ thin films deposited for bath temperatures of 313K (40°), 333K (60°) and 353K (80°). It is clear from the graph that, in the visible region there is no significant change in the band edge by increasing the bath temperature from 60° – 80°. This implies that the basic crystal structure is not changed. The linearity of the plots indicates that the material is of direct band gap. The increase in bath temperature varies the energy band gap from 2.2eV to 2.5eV. These values closely agree with 2.4eV and 2.5eV reported by [2 and 12], 2.5-2.75 eV reported by [13] respectively. The film deposited at larger temperature has higher band energy while the film deposited at low temperature indicates lower band energy value. The increase in the band gap with increasing bath temperature can be viewed as increasing the energy of the electrons in the materials. The result showed that there is a shift in band gap towards high energy which may be due to transformation to crystalline phase taking place at high deposition temperatures. In general, the increase in bath temperatures lead to the decrease in disorder and defect density in the structure which results to increase in the optical band gap. The band gap values exhibited by the films are ideal for photovoltaic application. Thus, this suggests that the optimized bath temperatures are ideal for obtaining good chalcopyrite CuAlSe₂. The optical band gap was found to depend upon bath temperature.

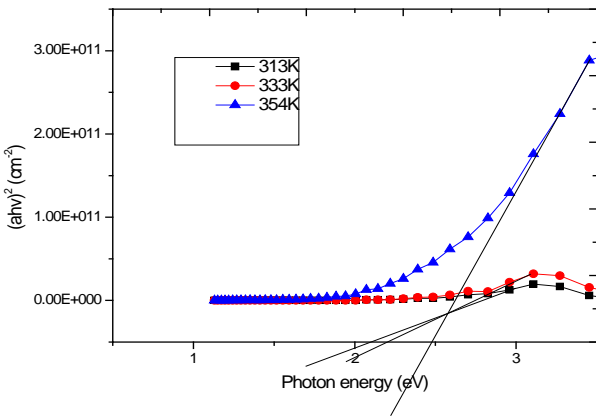


Fig 5 Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CuAlSe₂ film deposited at varying bath temperatures.

Table 1 Optical band gap values of CuAlSe₂ thin films deposited at different bath temperatures

Bath temperature (K)	Band gaps, E _g (eV)	Thickness (nm)
313	2.20	1.05 × 10 ⁻⁷
333	2.40	2.04 × 10 ⁻⁷
353	2.50	2.10 × 10 ⁻⁷

CONCLUSION

The structural and optical properties of CuAlSe₂ films, deposited at different bath temperatures were investigated. XRD strong peaks were observed for films of higher bath temperatures. Number of peaks and their intensities increased as the temperature increases. Optical band gap increases with the increase of bath temperature.

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