

THE EFFECT OF THICKNESS ON STRUCTURAL PROPERTIES OF CuAlS_2 THIN FILMS BY THERMAL EVAPORATION TECHNIQUE

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ABSTRACT

In this work, CuAlS_2 thin films of different thickness were deposited on corning 7059 glass substrate by two stages. In the first stage Cu-Al precursors were grown at room temperature by thermal evaporation and in the second stage Cu-Al precursors were converted to CuAlS_2 thin films by sulfurisation under sulfur atmosphere. The structural properties studied by means of XRD revealed that the films were of crystalline nature having tetragonal structure. For all the films the preferential orientation is (112), while the other orientation like (220) was also observed in the films depending upon the thickness of the films. The values of lattice constants, **a** and **c** agree strongly with ICDD data. Similarly, micro strain, dislocation density and grain size were found to be thickness dependent.

Keywords: Thermal Evaporation, Sulfurisation, Film Thickness, Copper Chalcopyrite.

INTRODUCTION

Due to the growing interest in alternative energies, photo-voltaic has become an active field for research. Today's commercial solar cells are predominantly fabricated on the basis of crystalline silicon. However, to be used efficiently in solar cells, silicon needs to be refined to 99.999% purity^[1]. Although Silicon solar cells have produced high efficiencies, high processing costs make it unsuitable for large scale requirements. Moreover, because silicon is an indirect band-gap material, larger thickness is needed to absorb the incident sunlight. Because of these drawbacks associated with silicon, the PV industry started looking for inexpensive efficient PV cells of new semiconductors in thin film form.

The main advantage of thin film solar cells (TFSC) is that they will eventually have lower cost because:

- i. Approximately hundred times thinner layers than Si are needed
- ii. They may be deposited on low cost substrates like glass, metal foils and plastic
- iii. They may be deposited by a number of inexpensive deposition techniques.

In all thin film solar cells the primary p-n heterojunctions occurs between the absorber layer and the window layer. The window layer allows the light to pass through it and travel to the absorber layer. No photocurrent is generated in the window layer. It is preferable that the semiconductor used as absorber layer be of direct band gap material^[2].

Cu-chalcopyrite semiconductor materials otherwise I-III-VI₂ compound semiconductors such as CuAlS_2 , CuGaS_2 , CuAlSe_2 , and CuInS_2 to name a few are used as layers in hetero-junction solar cells. These materials exhibit a direct band gap in the range between about 1 and 3.5 eV and absorb the sunlight within a layer of a few microns thickness due to their high absorption coefficients of almost 10^5cm^{-1} and they crystallize in the tetragonal structure^[1]. The ternary

compound CuAlS₂ is a promising material for its technological applications such as in Opto-electronics and photovoltaic. In opto-electronics, it can be used as a light emitting diode (LED) for various electronic applications because of its wide band gap energy^{[3], [4]}. In photovoltaic, because of its optical and structural properties the wide gap ternary CuAlS₂ crystalline thin films could be expected as new alternative Cd-free buffer layer^{[5], [6]}. CuAlS₂ can also be used as a selective window coating because of its high absorption coefficient in the ultraviolet region of electromagnetic spectrum^{[3], [4]}.

Up to now, a number of methods have been performed to produce CuAlS₂ films, including, metal decomposition,^[7] horizontal Bridgman method^[8], Iodine transport,^[9] Single source thermal evaporation^[10], Chemical bath deposition, (CBD)^{[4], [3]}, and Spray Pyrolysis,^[11]. In this work, we have succeeded in depositing CuAlS₂ films on glass substrate by two stage thermal evaporation technique. The great potential of thermal evaporation such as scalability and controllability drove us to choose it as the deposition technique.

EXPERIMENTAL

All the chemicals used (copper, aluminum and sulfur) for the deposition of CuAlS₂ thin films were 4N grade. Corning 7059 glass was used as substrate. Deposition of Cu-Al alloys was performed by using EDWARDS FL 400 thermal evaporator which was equipped with SQC 310 Deposition controller. A molybdenum boat was used to evaporate Cu thin films and tungsten coils was used for deposition of aluminum placed at a distance of 10cm from the glass substrate. Deposition of CuAl thin film was carried out at room temperature, RT. Cu-Al precursors were converted to CuAlS₂ thin films by sulfurisation/annealing using SVG 2610 BASE horizontal diffusion furnace which was equipped with mini sulfur furnace. The sulfurisation/annealing were carried out at the temperature of 673K.

In order to investigate the crystallographic properties of CuAlS₂ thin films, X-ray diffraction analyses were carried out using PANALYTICA XPERT PRO Diffractometer with Cu-K α radiation ($\lambda = 1.54056\text{\AA}$). The X-ray tube was typically operated at a voltage of 45 kV and a current of 40 mA. XRD patterns were recorded in the range of 20⁰-80⁰ with a scan speed of 2⁰/min, step size of 0.2000⁰ and scan step time of 1.10 seconds for all deposited thin films.

Growth of CuAlS₂ Thin Films

CuAlS₂ thin films were prepared by two stages described by^[12]. Stage one involve sequential deposition of Cu and Al layers on glass substrate to form Cu-Al precursor and stage two sulfurisation of this precursor to convert it to CuAlS₂. A metallic precursor with Cu-Al bi-layer structure was prepared on glass substrate by vacuum thermal evaporation of 4N grade copper and aluminum in a sequential mode. Molybdenum boat was used as source for the deposition of copper and tungsten coils was used for deposition of Aluminium. Samples of Cu-Al films of different thicknesses (50nm, 100nm and 200nm) were deposited at room temperature (RT). The thickness of the thin films was controlled by using a quartz crystal thickness monitor.

Conversion process of the Cu-Al thin films grown using the method described above was carried out by annealing Cu-Al thin films to CuAlS₂ in an elemental sulfur vapour at a temperature of 673K at ramp rate of 10⁰/minute, the dwell period was set to one hour and sulfur was allowed to diffuse into the samples at the rate of 4.4Scm using Argon as a carrier gas.

Formulation of Structural Parameters

The grain sizes **D** were calculated through the Scherer's formula ^[13]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where; β is full width at Full width half maximum (FWHM) of the preferential plane, θ is Bragg angle and λ is the wavelength of CuK α radiation.

The Dislocation density of thin films δ was calculated by employing Williamson and Smallman's relation ^[11]:

$$\delta = \frac{n}{D^2} \quad (2)$$

Where n is a factor which equals unity giving minimum dislocation density and D is the grain size.

The micro strain (ϵ) developed in thin films was calculated from the relation ^[14]:

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

Where β =FWHM (Full width at half maximum intensity and θ is the Bragg's angle

The lattice parameters **a** and **c** value for tetragonal crystallographic system was computed from the following equation using *hkl* parameters and the inter planer spacing, d

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (4)$$

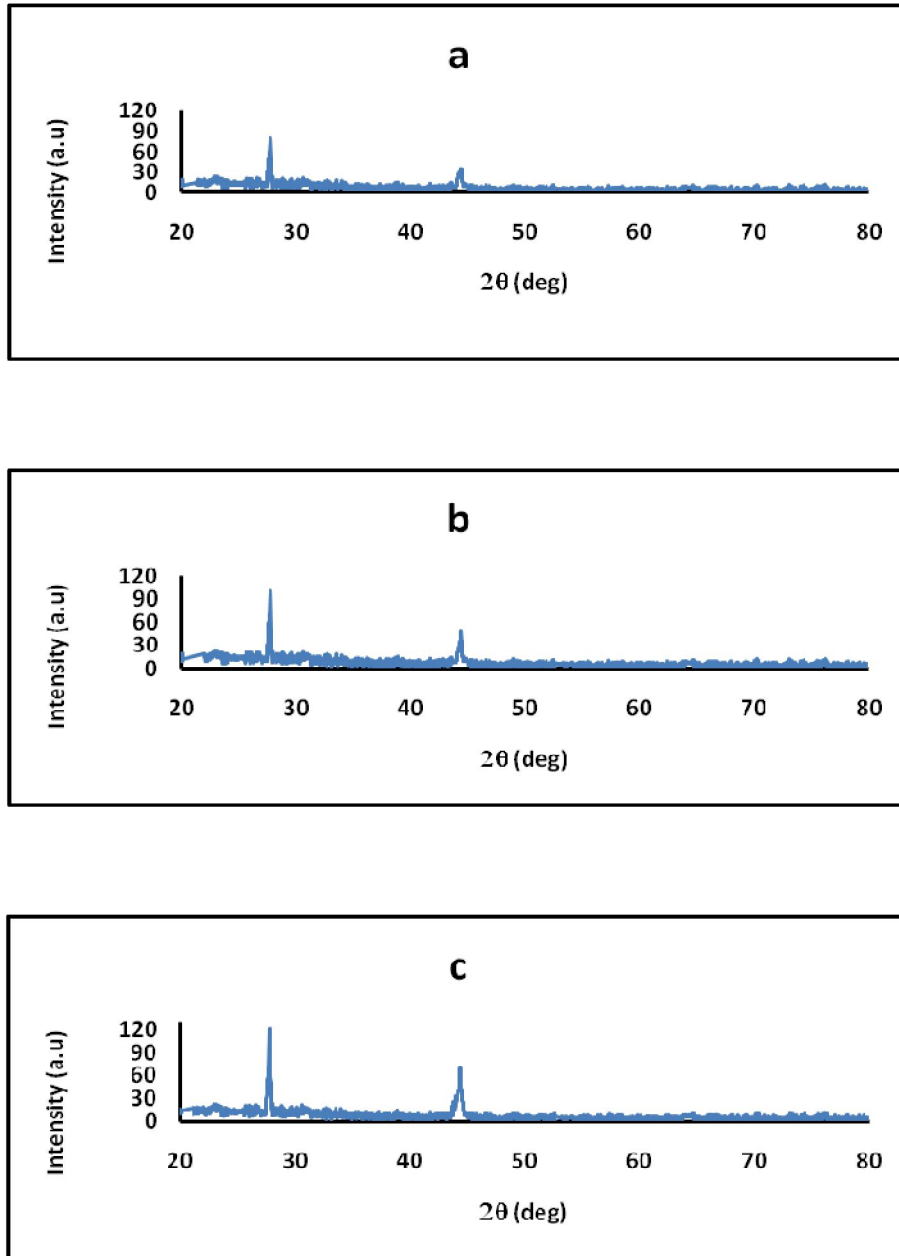
RESULTS AND DISCUSSION

XRD Results

Fig. 1a, 1b, and 1c depict XRD patterns for samples of thicknesses 50nm, 100nm and 200nm respectively grown at room temperature and sulfurised at 673K. It is revealed that films were characterized by two main crystalline peaks; the first peak appeared at $2\theta \sim 28^\circ$ while the second peak appeared at $2\theta \sim 48^\circ$. On comparing with ICDD (card no. 01-074-7042) and reported values of ^[5] and ^[15], the first peak observed at $2\theta \sim 28^\circ$ was identified to be belonging to CuAlS₂ chalcopyrite structure with the (112) preferred orientation; while the second peak observed at $2\theta \sim 48^\circ$ designated to (220) orientation also belongs to CuAlS₂ chalcopyrite structure.

It is clear in the figures that, at all thicknesses there is no variation in peak position. On the hand, there is increase in intensity with increase in film thickness. The peak intensity for 50nm, 100nm and 200nm were found to be 80, 100 and 120 respectively suggesting that the crystallinity of the films is closely related to the film thickness. The low peak intensity observed in a thinner CuAlS₂ film could be associated with an incomplete growth of the crystallites as only few atomic layers of disordered atoms constitute the bulk of the film.

However, ^[13] attributed this to contribution from inter-diffusion of sulfur at a moderate temperature leading to formation of crystalline film during sulfurisation process.



**Fig. 1: XRD Patterns for Samples Grown at Room Temperature and Sulfurised at 673K
(a) 50nm (b) 100nm (c) 200nm**

Structural Parameters

Table 1.0 display the lattice parameters for samples of thicknesses 50nm, 100nm and 200nm grown at room temperature, and each sulfurised at 673K. Figures 2,3,4,5 shows the grain

size, dislocation density, micro strain and FWHM respectively for thin films deposited with thicknesses 50nm, 100nm and 200nm.

It is observed from the table and as demonstrated in fig. 2, that for all the films the grain size D increases with increase in film thickness. From calculation, it is known that the grain sizes for 50nm, 100nm and 200nm are 80.3nm, 115.2nm and 149.1nm respectively. In other words, the 200nm thin film has the largest grain size, and hence should exhibit the most crystallinity. This theoretical consideration has been supported by our investigation. We now attempt to explain this observation in some detail.

It is felt that for the thicker films, there are several atomic layers grown; thereby creating greater chance of gain in thermal energy which could enhances their restructuring that lead to enlargement of grain size and reduce defects. According to ^[16], the increase in particle size could also be due to the merging of the smaller particles into larger ones and is as a result of potential energy difference between small and large particles.

Our calculated values of dislocation density δ and micro strain ϵ are close to those reported by ^[8], ^[17] and ^[18]. It is also seen in figures 2 and 4 that as in Table 1, the dislocation density δ and micro strain ϵ values decreases exponentially with increase in film thickness. This is because increase in film thickness leads to reduction in the interplanar spacing and thus minimize the stacking fault (irregularity in the planar stacking sequence of atoms) in the films. A similar result for Nickel Oxide thin films has been reported by ^[19].

In a similar manner FWHM decrease as film thickness increase; implying that as thickness increase thin films becomes more crystalline. This is attributed to the relaxation of the misfit strain, as the film thickness increases, the misfit strain decreases resulting in better crystallinity ^[20].

The lattice constants a and c in table 1 agree well with the standard values. It has been noted that defects changes the lattice constants ^[21]. Thus small deviation from the ideal value is a clear indication that the defects in the films are minimal.

Table 1: Structural Parameters of CuAlS₂ Thin Films

Sample (nm)	Sulfurisation Temp. (K)	Lattice Constants				D (nm)	$\delta \times 10^{14}$ lines/m ²	$\epsilon \times 10^{-3}$	FWHM
		a		b					
		Calc. ICDD	5.33	Calc. ICDD	10.44				
50	673	5.56		10.6		80.3	1.55	4.31	0.0015
100	673	5.47	5.33	10.52	10.44	115.15	0.75	3.01	0.0014
200	673	5.67		10.48		149.1	0.45	2.53	0.0013

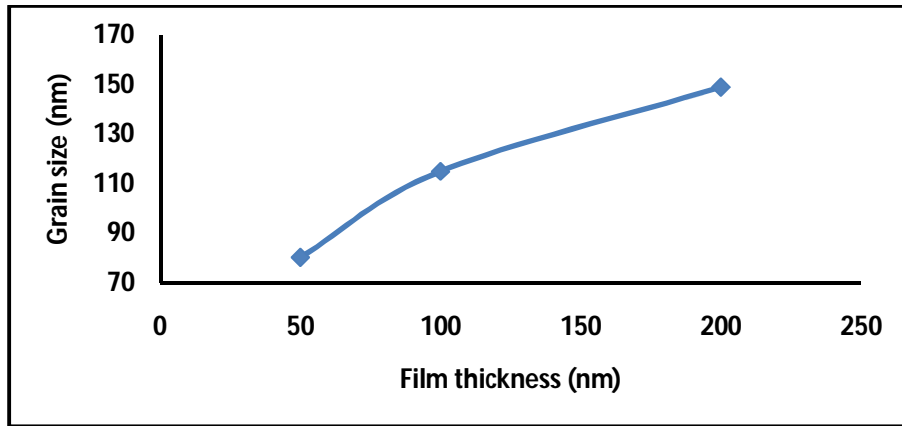


Fig. 2: Grain Size as a Function of Film Thickness

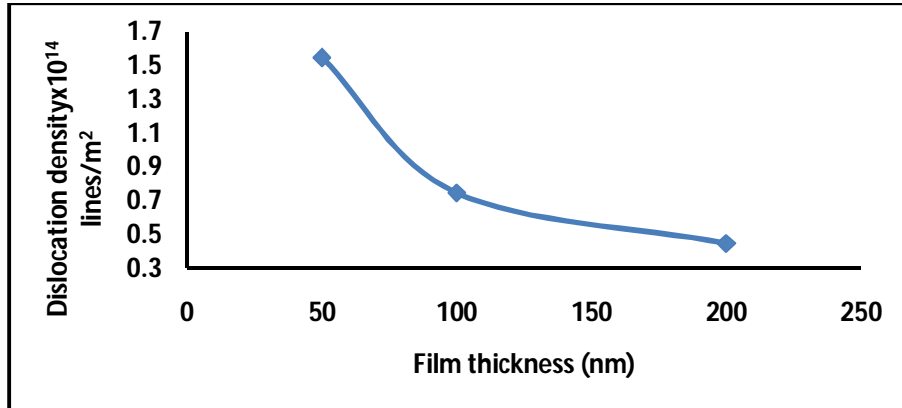


Fig.3: Dislocation Density as a Function of Sulfurisation Temperature

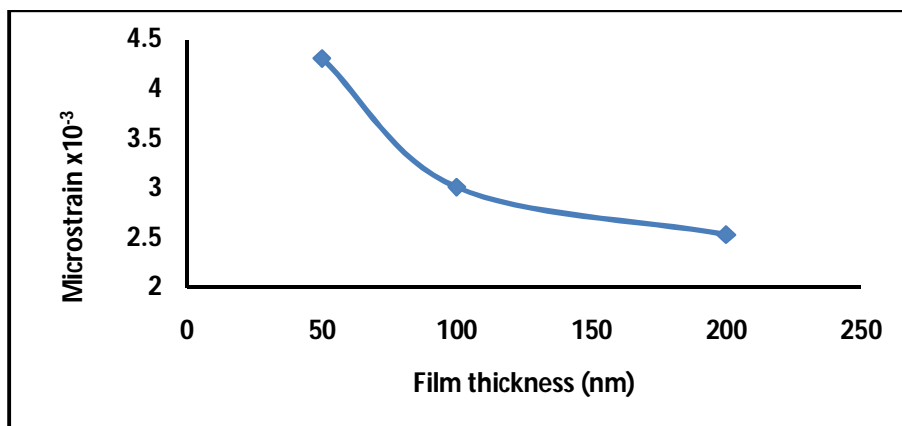


Fig. 4: Micro Strains as a Function of Film Thickness

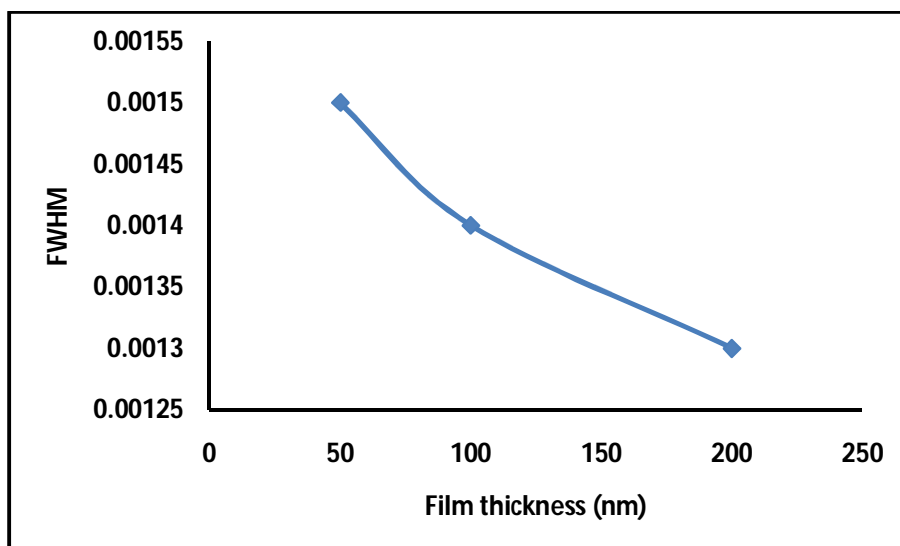


Fig. 5: FWHM as a Function of Film Thickness

CONCLUSION

The deposition of CuAlS_2 film was successfully carried out on a corning glass substrate (glass slide) at room temperature using two stage vacuum thermal evaporation techniques. XRD characterizations reveal that film thickness has a great influence on the structure of films. It was discovered that the crystallinity of the grown films increase with increasing film thickness. Similarly, lattice parameters were found to depend largely on thickness of the film: the grain size D of the thin film increases with increasing film thickness, while micro strain (ε), dislocation density (δ), and FWHM (β) were found to decrease appreciably with increasing film thickness implying that the thicker samples are less strained and crystalline especially at high sulfurisation temperature (673K). This work would benefit the fabrication and investigation of optoelectronic and photovoltaic devices.

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