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Structural and Current-Voltage Characterization of $CuAlS_2$ Thin Films.

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Abstract

The structure of $CuAlS_2$ has been a subject of conflicting interest. Many researchers have reported different forms of this material. Consequently, this research study is geared towards obtaining the structure through the pyrolysis of the precursor already reported by Damisa and co workers.On the other hand, the current-voltage analysis showed that the film deposited at 450 ℃ is non-ohmic which suggest a semiconducting behavior of the film which could prove useful in the design of optoelectronic devices.

Keyword: Precursor, structure, $CuAlS_2$,non-ohmic, pyrolysis

1. INTRODUTION

$CuAlS_2$is a chalcopyrite structure which is the simplest, noncubic ternary analog of the well known binary II-IV zinc blende structure with a tetragonal space group ($I\bar{4}2d{=}D_{2d}^{12}$). This chalcopyrite compounds are derived from the group IV class of tetrahedrally bonded semiconductors which states that there must be an average number of four valence electrons per atoms however, to maintain an electron-to-atom ratio of four, the chalcopyrite structure were derived from the binary phases by ordered substitution of other group atoms. This ordered arrangement of the metal atoms (or cations) leads to the formation of the tetragonal superlattice. This implies that the $CuAlS_2$ can be envisioned as the ternary analogue of the binary ZnS (II-VI) [1]. However, obtaining the structure has been a subject of dispute by many researchers. Alwan and Jabber [2] reported an amorphous nature of the material at deposition temperature between 200 and 300 ℃. Also in the study of Duclaux *et al*. [3] they reported no formation of the crystal structure of the material. This may be due to the active aluminium in the matrix of the $CuAlS_2$ thin films [4,5] which result in the formation of low quality thin films of the $CuAlS_2$ and ultimately affect the structure of the material. Furthermore the $CuAlS_2$ in thin film form have` been grown by other techniques [6-15] with various incoherent discussions on the structure. In an attempt to solve this dispute, a single solid source precursor of Cu-Al-dithiocarbamate was prepared and deposited using metal organic chemical vapour deposition technique (MOCVD) thus, leading to the formation of the $CuAlS_2$ thin films at 420 and 450℃[16]. Upon characterization by X-ray diffraction, we observed the formation of the crystal structure of the $CuAlS_2$ thin film with preferential orientation at (112) planes whose intensity increases at higher deposition temperature of 450℃. In addition, this study reports the current-voltage (i-v) analysis of the material using four point probe technique. Until recently, a clear characterization of the i-v of the material has not been reported.

2. Experimental procedure

The preparation of the precursor and subsequent deposition to yield the desired copper aluminium sulphide thin films has been reported by Damisa *et al*. [16]. However, the films were characterized with X-ray diffraction for structural properties using a D8 Advance diffractometer operated with a tube voltage of 40kV and tube current of 40mA with software PDF database 1999 attached. The whole procedure was carried out using a $CuK\alpha$ radiation with a wavelength of 1.5406 Å. The current-voltage characteristics of the films were carried out using a JandelRM2 four point probes techniques. It was made in such a way that the voltage across the transverse distance of the films and the corresponding values of the current were measured using silver paste to ensure good ohmic contact to the films. The four point probe was connected to current supply and the inner probes to a volts meter. As current flows between the outer probes, the voltage drop across the probes is measured.

3. **Results and Discussion**

3.1.**Structural analysis**

Figs. 1a and 1b shows the XRD spectrum of the deposited films. For 420℃, the intense peaks occur at diffraction angle 2θ = 29.325° and 33.890° corresponding to (112) and (200) planes belonging to the $CuAlS_2$ crystal structure.

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Other peaks were observed with diffraction angles at 2θ = 27.217º, 32.247 º, 35.678º and 38.733º corresponding to (420), (134), (423) and (174) planes respectively belonging to the chalcocite (Cu_2S) crystal structure.However, for films deposited at 450 ℃ intense peaks occur at diffraction angle 2θ = 29.310 º and 32.287 º corresponding to (112) and (200) planes belonging to the $CuAlS_2$ crystal structure. Other peaks were also observed with diffraction angle at 2θ = 35.631º and 38.780º corresponding to (423) and (174) planes respectively belonging to the chalcocite (Cu_2S) crystal structure. Although, Alwan and Jabbar [2] opined that the deposited films are amorphous at room temperature, 200 and 300 ℃deposition temperatures. In this study, at deposition temperatures of 420 and 450 ℃, the deposited films are found to be crystalline.

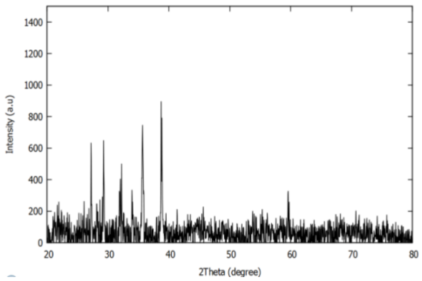

Fig. 1a XRD pattern for films deposited at 420 ℃

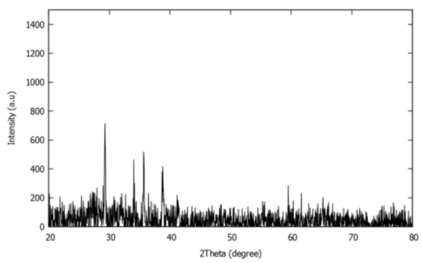

Fig. 1b XRD pattern for films deposited at 450 ℃

The reduction in the number of peaks and intensity level of the chalcocite structure together with increase in the intensity level of the (112) planes of the $CuAlS_2$ structure shows that the material becomes more crystalline as the deposition temperature increases. This we believe is due to the re-arrangement of the mobile atoms which also preferentially grows on the (112) planes. To give further information about the crystallinity of the films, some structural parameters were calculated. The inter-planar spacing d was calculated using equation (1) [17]

$$d = \frac{\lambda}{2\sin\theta} \qquad (1)$$

where λ is the incident wavelength and θ is the Bragg's angle.
The grain size was calculated from the Debye-Scherrer's equation given by equation (2) [17]

$$D = \frac{0.94\lambda}{\beta\cos\theta} \qquad (2)$$

whereβ is the full wave at half maximum (FWHM). The dislocation density was calculated from equation [18]

$$\delta = \frac{1}{D^2} \qquad (3)$$

The micro strain is given by the Wilson's equation (4) [18]

$$\varepsilon = \frac{\beta\cos\theta}{4} \qquad (4)$$

The results obtained together with the film thickness are displayed in Table 1. It can be seen clearly from Table 1 that the grain size, D increases while the full wave at half maximum (FWHM), β decreases at higher deposition temperature and film thicknesses which suggest increase in the crystallinity of the films [8]. Other parameters such as dislocation density, δ and micro strain, ε exhibits a decreasing trend with the deposition temperature and film thickness which consequently leads to decrease in the inter-planar spacing , d and ultimately leads to reduction of the stacking fault in the films [8,13]. The increase in grain size can be attributed to the coalescence of small crystals. The atom mobility also increases as the deposition temperature increase which further confirms that crystallinity of the films increases as the temperature increases. [19].

Table 1: Film thickness and structural parameters of $CuAlS_2$ thin film

Temperature (℃)	Film thickness (nm)	d (Å)	D (Å)	β (°)	δ ($\times 10^{13}$) (lines m^{-2})	ε ($\times 10^{-4}$)
420	534	2.77 3.05	440.45 --	0.20 --	30.64 --	6.34 --
450	541	2.64 3.04	571.30 --	0.15 --	2.18 --	1.69 --

3.2. Current-voltage analysis

Figs. 2a and 2b shows the current-voltage behavior of the deposited films. For 420℃, our obtained results shows that the film possess a non-linear characteristics suggesting that the material is ohmic in nature. However, the films deposited at 450℃, has a non-ohmic characteristics suggesting a semiconducting behavior of the films. This ohmic and non-ohmic behavior of the films may be related to the thickness of the films as thinner films exhibits the lowest resistivity and high career concentration implying that the films with thinner thickness are the most conductive.

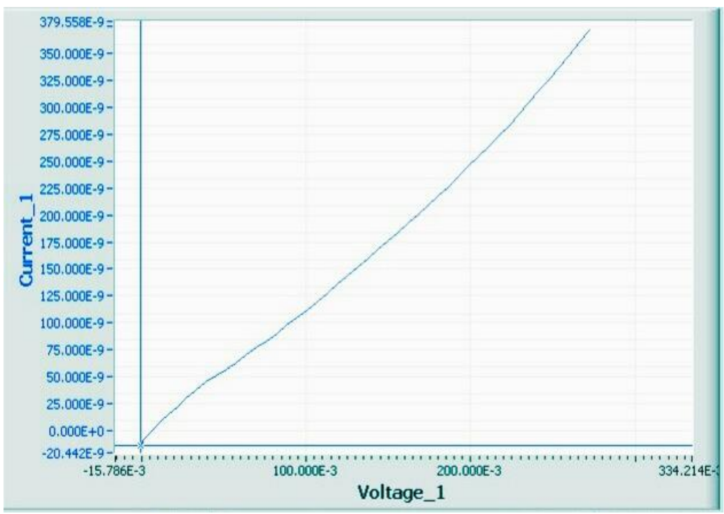

Fig.2a Current-Voltage characteristics of $CuAlS_2$ thin film at 420 ºC

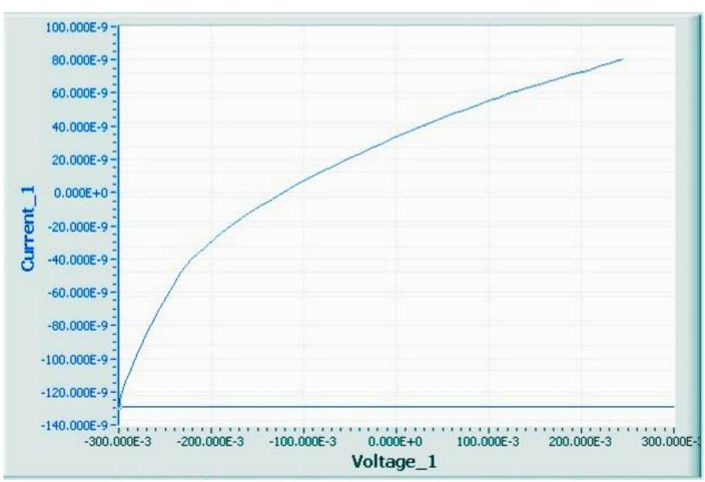

Fig.2b Current-Voltage characteristics of $CuAlS_2$ thin film at 450 ºC

4. Conclusion

We have studied the growth of $CuAlS_2$ thin films at 420 and 450 ℃. We conclude that it is possible to obtain the crystal structure of the $CuAlS_2$ thin films at that deposition temperature and that the crystallinity of the material increases as the deposition temperature increases. We also obtain a semiconducting behavior of the film at deposition temperature of 450 ℃ from our study, which suggest that the material can find application in optoelectronic devices.

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