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Effect of Thickness on Structural and Electrical Properties of $CuAlS_2$ Thin Films Grown by Two Stage Vacuum Thermal Evaporation Technique

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Abstract**—**This work studies the effect of thickness on structural and electrical properties of $CuAlS_2$ thin films grown by two stage vacuum thermal evaporation technique. $CuAlS_2$ thin films of thicknesses 50nm, 100nm and 200nm were deposited on suitably cleaned corning 7059 glass substrate at room temperature (RT). 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 at the temperature of 673K. The structural properties of the films were examined by X-ray diffraction (XRD) technique while electrical properties of the specimens were studied using four point probe method. The XRD studies revealed that the films are of crystalline in nature having tetragonal structure. The variations of the micro-structural parameters, such as crystallite size (D), dislocation density (δ), and micro-strain (ε), with film thickness were investigated. The results showed that the crystallite sizes increase as the thickness of the film increases. The dislocation density and micro-strain decreases as the thickness increases. The resistivity (ρ) of $CuAlS_2$ film is found to decrease with increase in film thickness, which is related to the increase of carrier concentration with film thickness. Thus thicker films exhibit the lowest resistivity and high carrier concentration, implying these are the most conductive films. Low electrical resistivity and high carrier concentration are widely used as the essential components in various optoelectronic devices such as light-emitting diode and photovoltaic cells.

Keywords**—**Crystalline, $CuAlS_2$, evaporation, resistivity, sulfurisation, thickness.

I. Introduction

TERNARY compound $CuAlS_2$ is an inexpensive and promising material for its technological applications such as in opto-electronics and photovoltaics. In opto-electronics, it can be used as a light emitting diode (LED) for various electronic applications because of its wide band gap energy [1], [2]. In photovoltaic, because of its optical and structural properties the wide gap ternary $CuAlS_2$ crystalline thin films, could be expected as new alternative Cd-free buffer layer [3], [4]. $CuAlS_2$ can also be used as a selective window coating because of its high absorption coefficient in the ultraviolet region of electromagnetic spectrum [1]. It possesses a wide direct band gap of about 3.5 eV which satisfies the band gap requirement for transparent conductive materials (TCMs) [5]. Its exciton binding energy (70 meV) is greater than that of most other ultraviolet emitting materials such as ZnO (60 meV), ZnS (39 meV) and GaN (21 meV) [5].

A number of methods such as Chemical bath deposition CBD [1], [2], Iodine transport [6], Spray pyrolisis [7]-[9] etc., have been used for the deposition of $CuAlS_2$ thin films, but however, these deposition methods have some draw backs. Among the above mentioned methods, two stage vacuum thermal evaporation method is the technique expected to produce high quality crystalline films for the reason that it is a contamination free method since the deposition is usually carried out in a vacuum environment. The great potential of two stage vacuum thermal evaporation method in achieving quality crystalline films [10] and the fact that very scarce or no attempts have been reported in the literature on the growth of $CuAlS_2$ thin films by this technique has motivated us to employ it.

In the present investigation, an attempt has been made to produce highly textured $CuAlS_2$ nano thin films on glass substrates using two stage vacuum thermal evaporation technique. The effect of thickness on the structural and electrical properties has been investigated.

II. Experimental

All the chemicals used (copper, aluminum and sulfur) for the deposition of $CuAlS_2$ 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 $CuAlS_2$ 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.

A. Growth of $CuAlS_2$ Thin Films

$CuAlS_2$ thin films were prepared by two stages described by [11]. 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 $CuAlS_2$. A metallic precursor with Cu-Al bi-layer structure was prepared

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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 $CuAlS_2$ in an elemental sulfur vapor at a temperature of 673K at ramp rate of 10^0/minute, the dwell period was set to one hour and sulfur was allowed to diffuse into the samples at the rate of 4.4Sccm using Argon as a carrier gas.

B. Characterizations

In order to investigate the crystallographic properties of $CuAlS_2$ thin films , X-ray diffraction analyses were carried out using PANALYTICA XPERT PRO Diffractometer with Cu-Kα radiation (λ = 1.54056Å). 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 20^0-80^0 with a scan speed of 2^o/min, step size of 0.2000^o and scan step time of 1.10 seconds for all deposited thin films.

To measure electrical resistivity four wires (or probes) have been attached to the test sample. A constant current was made to flow through the length of the sample through the two outer probes. If the sample has any resistance to the flow of electric current, then there will be a drop of potential or (voltage) as the current flows along the sample, for example between the two inner wires (or probes). The ratio of the voltage drop (V) from the two inner probes to the applied current (I) measured from the two outer probes by the computer which was connected to the four point probe meter, sheet resistance data was generated.

C. Formulation of Structural Parameters

The grain sizes **D** were calculated through the Scherer's formula [12]:

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

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 CuKα radiation.

The Dislocation density of thin films **δ** was calculated by employing **Williamson** and Smallman's relation [7]:

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

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 [13]:

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

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

D. Formulation of Electrical Resistivity

According to [14] for very thin semiconductor layers, it is preferable to use a sheet resistance,

$$\rho_s = R_S \text{ x } t \quad (\Omega - cm) \quad (4)$$

III Results and Discussion

A. XRD Results

Figs. 1-3 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 $2\theta \sim 28^0$ while the second peak appeared at $2\theta \sim 48^0$. On comparing with ICDD (card no. 01-074-7042) and reported values of [5] and [15], the first peak observed at $2\theta \sim 28^0$ was identified to be belonging to $CuAlS_2$ chalcopyrite structure with the (112) preferred orientation; while the second peak observed at $2\theta \sim 48^0$ designated to (220) orientation also belongs to $CuAlS_2$ chalcopyrite structure. It is clear in these 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 $CuAlS_2$ 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 interdiffusion of sulfur at a moderate temperature leading to formation of crystalline film during sulfurisation process.

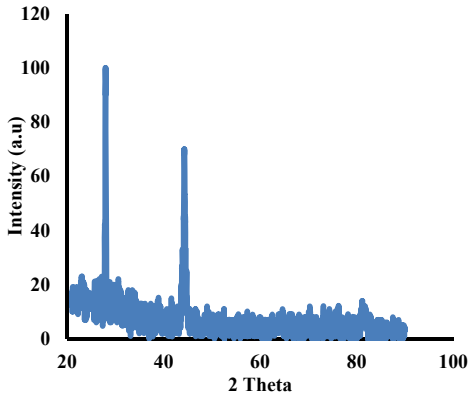

Fig. 1 XRD patterns for 50nm sample

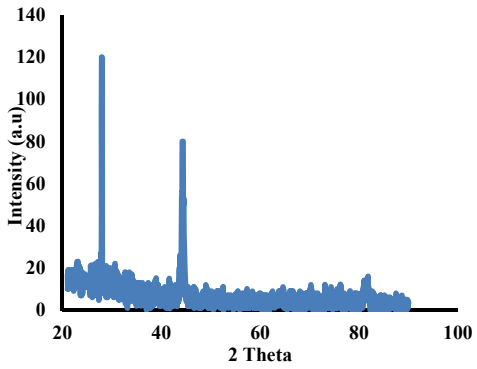

Fig. 2 XRD patterns for 100nm sample

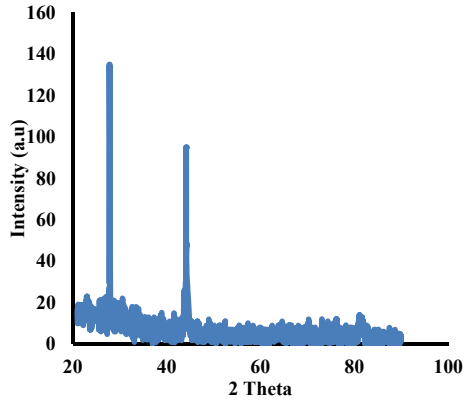

Fig. 3 XRD patterns for 200nm sample

B. Structural Parameters

Table I display the lattice parameters for samples of thicknesses 50nm, 100nm and 200nm grown at room temperature, and each sulfurised at 673K. Figs. 4-7 show the graph of the grain size, dislocation density, micro strain and FWHM as a function of thickness for the samples. It is observed from Table I and as demonstrated in Fig. 4, that for all the films the grain size D increases with increases in film thickness. From calculation, it is shown 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.

It is also seen in Figs. 5 and 6 that as in Table I, 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. Our calculated values of dislocation density δ and micro strain ε are close to those reported by [8], [17], [18]. A similar result but for Nickel Oxide thin films has been reported by [19].

In the same manner from Fig. 7 it is observed that 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].

TABLE I
STRUCTURAL PARAMETERS OF $CuAlS_2$ THIN FILMS

Sample (nm)	D (nm)	δ x10^{14} lines/m^2	ε x10^{-3}	FWHM
50	80.3	1.55	4.31	0.0015
100	115.15	0.75	3.01	0.0014
200	149.1	0.45	2.53	0.0013

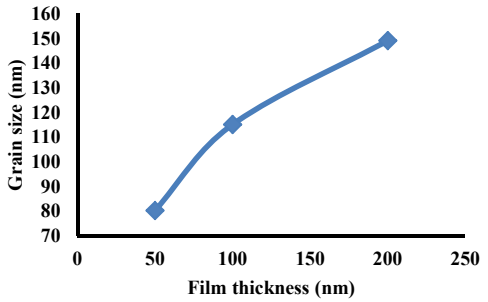

Fig.4 Grain size as a function of film thickness

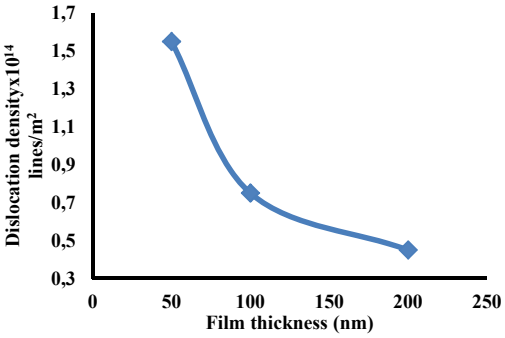

Fig.5. Dislocation density as a function of thickness

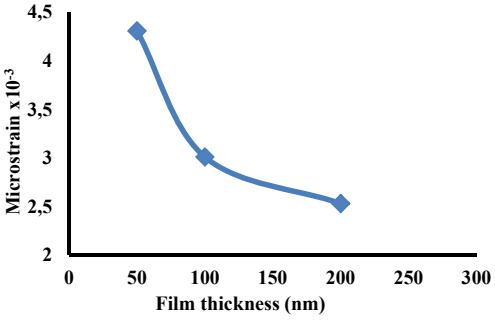

Fig.6 Micro strains as a function of film thickness

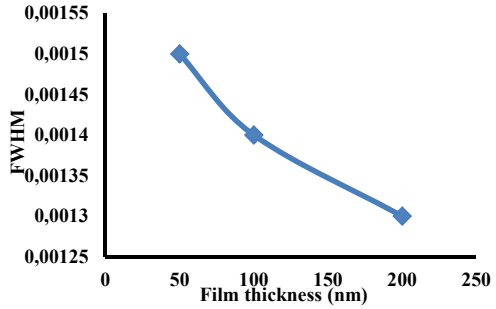

Fig. 7 FWHM as a function of film thickness

C. The Effect of Thickness on Resistivity of Thin Films

The effect of thickness on resistivity for thin films deposited at room temperature and sulfurised at 673K is displayed in Table II and illustrated in Fig. 8. As can be observed, the electrical resistivity decreases with increase in film thickness under all conditions, which is related to the increase of carrier concentration with film thickness. A resistivity of $4.3x10^{-5}$, $3.3x10^{-5}$ and $2.5x10^{-5}$Ω-cm respectively was exhibited by 50nm, 100nm and 200nm $CuAlS_2$ thin films. A low resistivity for thicker films (200nm and 100nm) could be attributed to surface scattering and the increase in carrier concentration. For thinner films (50nm), more defects act as scattering centers which results in the formation of trapping states capable of trapping carriers and thereby immobilizing them. This reduces the number of free carriers available for electrical conduction. Also after trapping the mobile carriers, the traps became electrically charged, creating a potential energy barrier, which impeded the motion of carriers from one crystallite to another, thereby reducing their mobility. It is observed that a very high resistivity was observed for a film thickness of 200nm, which decreases, rapidly with the decrease of thickness. Similar trend was observed by [21]-[27] on ZnTe, ZnO, Sb_2S_3, CuS, ZnO, Al doped ZnO and $CuAlS_2$ thin films respectively.

TABLE II
RESISTIVITY OF $CuAlS_2$ THIN FILMS

Sample thickness (nm)	Resistivity ρ x 10^{-5} Ω-cm
50	4.3
100	3.5
200	2.1

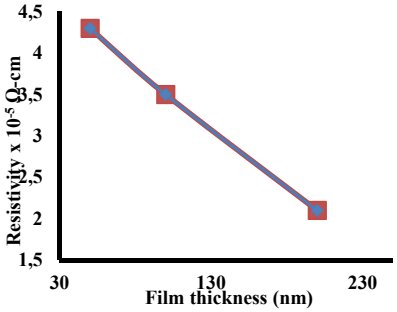

Fig. 8 Resistivity as a function of film thickness

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