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Study of Influence of Sulfurisation Temperature on the Resistivity and Surface Morphology of Thermally Evaporated $Cuals_2$ Thin Films

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ABSTRACT

$CuAlS_2$ thin film samples of equal thicknesses were deposited on corning glass substrate at the same substrate temperature by thermal evaporation method. Samples were subsequently sulfurised at different sulfurisation temperatures. Electrical characterization was performed by using Keithley four point probe meter and morphological characterization was carried out by employing Evoma-10 Scanning electron microscope. It was observed that resistivity decreases as sulfurisation temperature increases. The lowest resistivity was recorded at an elevated sulfurisation temperature and this is related to increase of carriers concentration with increase in sulfurisation temperature. Low electrical resistivity and high carriers concentration are essential components widely used in fabrication of various optoelectronic devices and solar cells. The scanning electron microscopy (SEM) micrographs of the films revealed that size of the crystallite increase with increase in sulfurisation temperature. Increase in crystallite size implies increase in crystallinity of films which also prove the quality of the films.

Key Words: *$Cuals_2$, Thermal Evaporation, Sulfurisation Temperature, Resistivity, Surface Morphology.*

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1. INTRODUCTION

In recent years, one of the two trends in the research activities which try to develop high-efficiency thin film solar cells based on $CuInSe_2$ (CIS) thin film absorbers with the use of CdS-like buffer layers deposited by CBD method is to realize more environmental-friendly device of Cd-free buffer layers [1,2]. I-III-VI_2 compounds are ternary isoelectronic analogs of the II-VI binary compounds. They crystallize in the chalcopyrite structure, which is closely related to that of zinc blend. All these materials have direct band gaps [3]. The wide gap ternary I-III-VI_2 and their polycrystalline thin films alloys, because of their optical and structural properties, could be expected as new alternative Cd-free buffer layers. Furthermore, these compounds could be obtained by a similar physical preparation process as the absorbers' one. $CuAlS_2$ semiconductor is the wide-gap, 2.67 eV [4, 5] belonging to the I-III-VI_2 features. It is well known and proven to be very difficult [6, 7] to grow high quality $CuAlVI_2$ compounds due to the existence of chemically active Al in the matrix. We have succeeded in growing good quality $CuAlS_2$ thin films by using a simple low-cost technique. The purpose of this paper is to present some electrical and morphological characteristics of $CuAlS_2$ films.

2. METHODOLOGY

2.1 Growth of CuAlS2 thin films

$CuAlS_2$ thin films were prepared by two stages:

1) Sequential deposition of Cu and Al layers on glass substrate to form Cu-Al precursor, and
2) Sulfurisation of this precursor to convert it to $CuAlS_2$

2.1.1 Sequential Deposition of Cu-Al Precursor

The deposition of Cu-Al alloy was carried out by using an **EDWARDS FL 400** thermal evaporator equipped with **SQC-310C** deposition controller. The system basically consists of a rotary pump, a vacuum chamber, equipped with substrate holder with heating element, source crucible with embedded thermocouple and heating element, and a shutter placed between source and target. A metallic precursor with Cu-Al bi-layer structure was prepared on glass substrate by vacuum thermal evaporation of 4N grade (by Aldrich) 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 aluminum. Both were inside the vacuum chamber.

By employing the above steps 5 samples of Cu-Al films each of thickness 300nm were deposited at substrate temperature of 573K. The thickness of the thin films was controlled by using a quartz crystal thickness monitor. The post thickness measurement was performed using Profilometer and the thicknesses agree with what was obtained by crystal thickness monitor.

2.3 Sulfurisation of CuAl thin films

In this work sulfurisation process of the Cu-Al thin films was carried out in an elemental sulfur vapor in 4 steps at temperatures of 473K, 573K, 673K and 773K in a horizontal diffusion furnace The furnace consists of sample loader, heater, Argon inlet, and an outlet for argon/sulfur. The furnace was also equipped with external mini sulfur furnace which supply sulfur to the samples kept in the furnace chamber. Prior to sulfurisation samples were inserted into the sulfurisation chamber of the furnace using a long Pyrex cylinder. Nitrogen gas was then passed into the furnace for 30 minutes to flush out the air which might be trapped in the sulfurisation chamber. The heat of sulfur furnace containing elemental sulfur was raised to a temperature of 140 ^{0}C (413K), i.e. above melting point of sulfur 114 ^{0}C (386K) and the diffusion furnace heat was raised to the temperature of 473K, 573K, 673K and 773K respectively at a ramp rate of 10^0/min, the dwell period was set to one hour. Sulfur vapor was allowed to diffuse into the sample chamber by passing Argon (carrier gas) through an argon inlet. The samples were withdrawn from the furnace when it has cooled down to room temperature.

2.4 Characterizations

In order to investigate the electrical resistivity **KEITHLEY 2400** four point probe meter was used. Resistivity has been measured at atmospheric pressure. Four wires (or probes) have been attached to the test sample and 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. According [8] for very thin semiconductor layers, the resistivity ρ_S is expressed in equation (1) as,

$$\rho_S = Rs \, . \, t \qquad (1)$$

Where Rs is the sheet resistance and t is the film thickness.

Surface morphology characterization was carried out by using **EVOMA-10** scanning electron Microscope (SEM).

3. RESULTS AND DISCUSSION

Figure 1.1 depicts the variation of resistivity of samples with the same thickness grown at 573K but sulfurised at 473K, 573K, 673K, and 773K temperatures. It can be seen from table 1.1 that for as grown sample the high resistivity of 6.01 X 10^{-3} Ωcm was exhibited. However as the films were sulfurised at a temperature of 473K, a remarkable improvement in conductivity was observed. This is evident from the fact that the resistivity as low as 1.5×10^{-3}Ωm was recorded. In a similar manner for samples sulfurised at 573K a further drop in resistivity was observed. This condition has lead to the reduction of resistivity to as low as 8.5×10^{-4}Ω-cm. Still when the sulfurisation temperature was raised to 673K the resistivity of the sample depressed to 2.5×10^{-4}Ωcm. In the same trend it can be seen that the lowest resistivity of 0.9×10^{-4} Ωcm was recorded when the sulfurisation temperature was upgraded to 773K.

It is observed that as deposited samples exhibited a high resistivity. The high resistivity may be due to the existence of shallow states in band gap region resulting in formation of both acceptors and donors leading to self-compensation. This may also be ascribed to the amorphous nature of the films. In amorphous structure some electrons are bound in short range by the net non-uniform structure. When the structure of the films becomes crystalline, these electrons are released from the bound. Similar observations have been reported for $CuAlS_2$, ITO and NiO thin films by [9], [10] and [11] respectively. More so, the high values

of resistivity of as deposited films may be due to the presence of disorder, high density of state and structural defects in the film as observed in XRD which renders the films amorphous.

It is observed that resistivity decrease as samples undergo sulfurisation, and continued to decrease with increase in sulfurisation temperature. The decrease in resistivity with increase in sulfurisation temperature is an indication of semiconducting nature of the films. This behavior may be attributed to the incorporation of sulfur atoms that act as donor sites, which in turn increase mobility and carrier concentration, hence decreasing the barrier height at the grain boundaries, resulting in less impedance for the carrier transport. Similar observations have been reported for Cadmium Telluride and tin oxide thin films by [12] and [13] respectively. A wide band gap combined with low resistivity is the crucial requirement of window material in solar cells.

Table 1.1: Resistivity of $CuAlS_2$ thin films Sulfurised at different temperatures.

Sample thickness (nm)	Substrate temperature (K)	Sulfurisation temperature (K)	Resistivity ρ (Ω-cm)
300	573	As deposited	6.01×10^{-3}
300		473	1.5×10^{-3}
300		573	8.5×10^{-4}
300		673	2.5×10^{-4}
300		773	0.91×10^{-4}

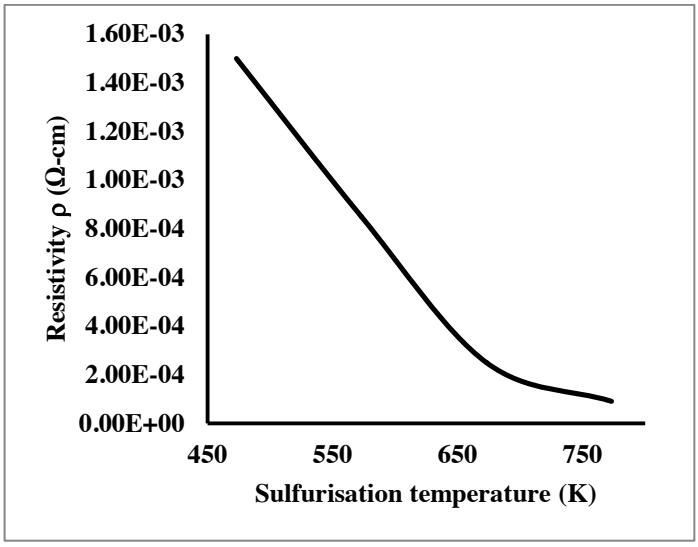
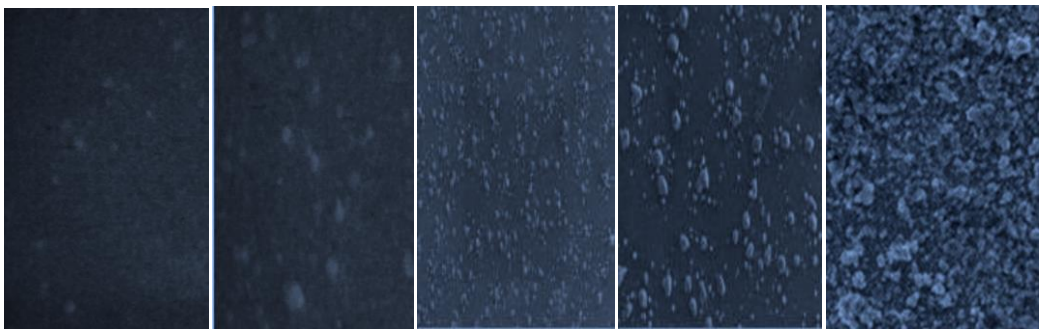


Figure 1.1: Resistivity versus sulfurisation temperature for $CuAlS_2$ films sulfurised at different sulfurisation temperatures

Figures 1.2a-e depicts SEM micrographs of as grown films as well as films sulfurised at the temperatures of 473K, 573K, 673K and 773K respectively. For as grown films, as shown in Figure 1.2a no meaningful spheres or crystallite is observed. But however for films sulfurised at 473K as shown in figure 1.2b it is observed that a few cluster of tiny spheres is distributed over the surface of the film. In a dissimilar manner the number and size of spheres shows a remarkable rise as sulfurisation temperature attain 573K (Figure 1.2c) which confirms improvement in grain size. The random distribution of grains and size suggests a random nucleation mechanism and random orientation of grains show that the grain growth is isotropic [13]. Figures 1.2d and 1.2e demonstrated that as the sulfurisation temperature reaches 673K and 773K respectively, a large number of spheres appeared some of which appeared to be even larger than those formed in Figure 1.2c. This, we believe is an indication of overgrowth of the particles which imply an increase in grain sizes of the films with increase in sulfurisation temperature.



(a) (b) (c) (d) (e)

Figure 1.2: SEM micrographs for $CuAlS_2$ (a) As grown (b) sulfurised at 473K(c) sulfurised at 573K (d) sulfurised at 673K (e) sulfurised at 773K

4. CONCLUSION

The deposition of CuAlS2 film was carried out successfully on a glass substrate (glass slide) at substrate temperature of 573K using two stage vacuum thermal evaporation techniques. The electrical characterizations reveal that sulfurisation temperature has a great influence on the resistivity of films. It was discovered that the resistivity of the grown films decrease with increasing sulfurisation temperature. Similarly morphological characterization showed that crystallite size increases with increase in sulfurisation temperature implying that crystallinity of the films improves at an elevated sulfurisation temperature. These properties exhibited by $CuAlS_2$ thin films make it useful for fabrication of optoelectronic, photovoltaic and light emitting devices.

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