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Article

Influence of Substrate Temperature on Electrical Resistivity and Surface Morphology of $CuAlS_2$ Thin Films Prepared by Vacuum Thermal Evaporation Method

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Abstract: In this paper the effect of substrate temperature on electrical and morphological properties of $CuAlS_2$ thin films prepared by two stage vacuum thermal evaporation technique have been studied. The electrical resistivity of the films was studied using four point probe method. The surface morphology was examined by employing Evoma-10 Scanning electron Microscope. The resistivity (ρ) of $CuAlS_2$ film is found to decrease with increase in substrate temperature, which is related to the increase of carrier concentration with increase in substrate temperature. Thus films grown at an elevated substrate temperatures exhibit the lowest resistivity and high carrier concentration, implying that these are the most conductive films. Low electrical resistivity and high carrier concentration are widely used as the essential components in various optoelectronic devices and photovoltaic cells. Visual inspection of Scanning electron microscopy (SEM) micrographs of the films showed that crystallite size increase with increase insubstrate temperature.

Keywords: Thermal evaporation, $CuAlS_2$, substrate temperature, resistivity, sulfurisation.

1. Introduction

Today one of the major challenges of the world scientific community is to find a sustainable supply of electrical energy. At present, most of our energy comes from fossil (i.e. coal, liquefied petroleum, oil, natural gas) and nuclear resources. Not only are these sources of energy non-renewable and in dwindling quantities, they are also polluting to the environment (Madelung, 2004). Burning of fossil fuels releases almost 7 billion tons of CO_2 per year, which is the equivalent of 107,700,000 jet airplanes being in the air at once! This harrowing figure is the main cause of environmental problems such as the greenhouse effect and global warming, and has been increasing for the last 50 years (United Nations, 2011). Burning of unrefined coal also results in acid rain, which is directly responsible for large area forest and wildlife destruction as well as soil pollution. These events have stimulated interest in clean renewable energy alternatives. In general these energy systems do not depend on resources, which are limited to our earth, but on the constant radiation of the sun. Alternative sources of energy may be singled out – they include nuclear fission, nuclear fusion, geothermal, wind, hydroelectric, fuel from biomass and the direct conversion of sunlight into electricity by the photovoltaic (PV) effect to mention the most common.

Among these renewable energies, the direct conversion of sunlight by the photovoltaic (PV) is one of the most promising option. Photovoltaic solar power is the most desirable one and holds great potential and promise. Photovoltaic (PV) solar power converts directly the sunlight to electricity by using the photovoltaic effect. Given a no end life of the sun, the power generation is totally non-polluting, i.e., causing no changes to the environment when generating power. Even compared to other renewable energy sources such as wind power and water hydro power, PV solar power holds obvious advantages. Crystalline silicon was first used to produce PV cells (also known as solar cells), and still dominates the PV market nowadays (Madelung, 2004). Due to high cost of production Silicon PV power generation is not competitive in most urban areas where conventionally generated power is readily available. This lays down the background for the extensive research interest in materials suitable for thin film solar cells (TFSC). I-III-VI_2 compounds are particularly good candidates for the formation of the p-n hetero-junction with II-VI group semiconductors because of the similarity between the structures of the two compounds. I-III-VI_2 compounds, especially $CuAlS_2$ thin films have played a major role in thin film PV technology.

A number of methods such as Chemical bath deposition CBD (Okoli et al, 2006, Tariq and Almushtak 2010), Iodine transport (Honeyman 2011), Spray pyrolisis (Illican and Caglar 2007, Caglar and Saliha 2008 and Mujadat et al 2008) etc, have been used for the deposition of $CuAlS_2$ thin films. Among these, two stage vacuum thermal evaporation method is the technique that 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.In this paper, we report the results on the growth of $CuAlS_2$ thin films on glass substrates by two stage vacuum thermal evaporation technique at different substrate temperatures. The aim of the present study is to investigate the effect of substrate temperature on electrical and surface morphology on the prepared $CuAlS_2$ thin films.

2. Materials and Method

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. 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.

2.1. Deposition of $CuAlS_2$ Thin Films

$CuAlS_2$ thin films were prepared by two stages described by Morehetal (2013). Stage one involves 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 on glass substrate by vacuum thermal evaporation of 4N grade copper and aluminum in a sequential mode. This was achieved by placing Copper and Aluminium chips on Molybdenum boat and tungsten coils for evaporation of copper and Aluminium respectively. A set of three samples each of thickness 100nm were deposited at 300K, 373K and 473K respectively and all sulfurised at 573K, another set of three samples each of thickness 100nm were prepared at 300K, 373K and 473K respectively and all sulfurised at 673K. 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 573K and 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.

2.2. 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 to Ogwu et al (2007) for very thin semiconductor layers, the sheet resistance is expressed as,

$$\rho_s = R_s \times t \quad (\Omega - cm)$$

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

3. Results and Discussion

Figure 1 depicts the resistivity for three samples each of thickness 100nm grown at 300, 373 and 473K respectively, and sulfurised at 573K. It can be observedfrom table 1 that the resistivity amounting to 6.01**x** 10^{-3}, 5.77x $10^{-3}$and 5.2 x $10^{-3}\Omega$cm was recorded for three samples respectively. As can be observed the resistivity decreases with increase in substrate temperature. It is observed that resistivity decrease as samples undergo sulfurisation, and continued to decrease with increase in substrate temperature. The decrease in resistivity with increase in substrate temperature is an indication of semiconducting nature and crystallinity of the films. These results are similar to those reported for $CuAlS_2$ and ITO thin films by Moreh and Hamza (2013) and Mohamed et al. (2009) respectively.

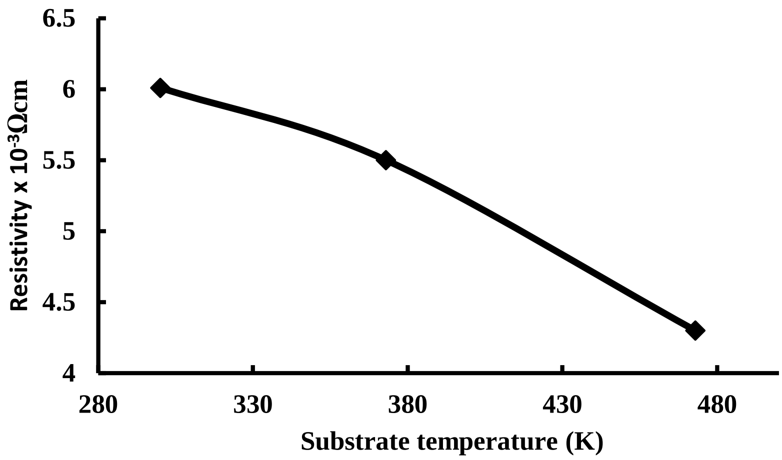

Figure 1: Resistivity versus substrate temperature for $CuAlS_2$ thin film sulfurised at 573K but grown at 300K, 373K and 473K

Figure 2 and as displayed in table 1 shows the resistivity of three samples of $CuAlS_2$ thin films each of thickness 100nm deposited at 573K, 673K and 773K respectively, and all sulfurised at 573K. A remarkable improvement in conductivity was observed over those in figure 2. This is obvious from the fact that the resistivity recorded for the three samples was 4.77x10^{-4}, 3.70x10^{-4} and 2.17x10^{-4}Ω-cm respectively.It is observed that samples grown at an elevated substrate temperature of 773K exhibited the lowest resistivity of 2.17x10^{-4}Ω-cm. This implies that resistivity decrease with increase in substrate temperature. In other words conductivity increases with increase in substrate temperature. Similartendency have beenreported by Buba*et al*. (2010), Arton*et al.* (2007), Fasaki*et al.*(2010), Mansour *et al.* (2010), Jung et al. (2010) on ZnO, ITO, NiO, Cu(In,Ga)Se_2 and Ga doped ZnO thin films respectively. 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. The decreases in resistivity with increase in substrate temperatures may also be due to the fact that at higher substrate temperatures, the extra thermal energy provided by the substrate to the atoms is used by the latter to reach equilibrium positions which bring about micro structural re-arrangement to form crystalline films and it is a known fact that improved crystallinity favors low resistance. Furthermore at high substrate temperature, the mobility sharply increases, which results from the amount of barriers and their potential that traps free carriers and also lowers the activation energies leading to the generation of free carriers. A wide band gap combined with low resistivity is a crucial requirement of window material in solar cells. Thus the low electrical resistivity observed at high substrate and sulfurisation temperatures in $CuAlS_2$ thin films in this work, is the essential property which makes $CuAlS_2$ a potential candidate for use in solar cells and other optoelectronic devices fabrication.

Table 1: Resistivity of $CuAlS_2$ thin films grown at different substrate temperatures and sulfurised at different temperature

FILM THICKNESS (nm)	SUBSTRATE TEMPERATURE (K)	SULFURISATION TEMPERATURE (K)	RESISTIVITY (Ω-cm)
100	300	573K	6.01x10^{-3}
100	373		5.50 x10^{-3}
100	473		4.77 x10^{-3}
100	573	573K	4.30 x10^{-4}
100	673		3.70 x10^{-4}
100	773		2.18 x10^{-4}

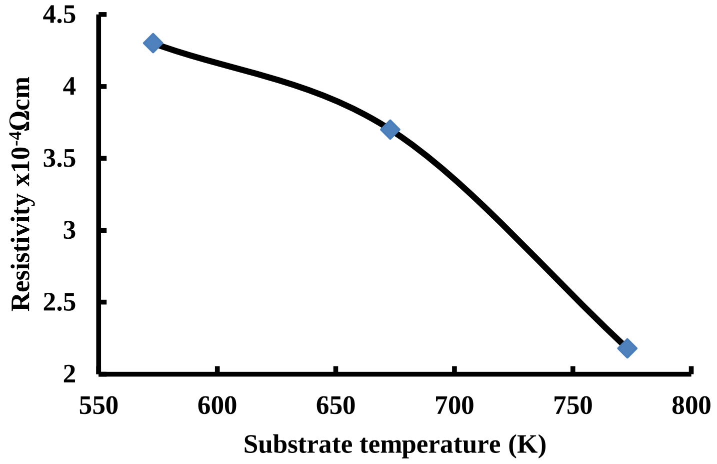

Figure 2: Resistivity versus substrate temperature for $CuAlS_2$ thin films sulfurised at 573K but grown at 573K, 673K and 773K

Figure 3 depicts the micrographs of $CuAlS_2$ thin films deposited at 300K, 373K and 473K respectively but all sulfurised at 573K. It is observed that acluster of tiny spheres are irregularly distributed over the surface of the film. Similarly a lot of empty space isobserved within these clusters. The cluster size shows remarkable rise with substrate temperature whichconfirms improvement in grain size (Ubale et al 2010). The random distribution of grains size suggests a randomnucleation mechanism and random orientation of grains show that the grain growth is isotropic (Al-Gashi et al 2011).

Figure 4 shows the micrographs for three samples grown at substrate temperatures of 573K, 673K and 773K respectively and also sulfurised at 573K.It can be seen that as substrate temperature progresses films becomes more uniform, densely packedand pinhole free, andit shows that the morphology ofthesefilmshas larger number of grain size and arehomogeneously distributed, which indicates the crystalline nature of the film. It can also be observed that a large number of spheres appeared some of whichappeared to be larger than those formed in figure 3. This, we believe is an indication of overgrowth of the particles which implies an increase in grain sizes of the films with increase in substrate temperature.

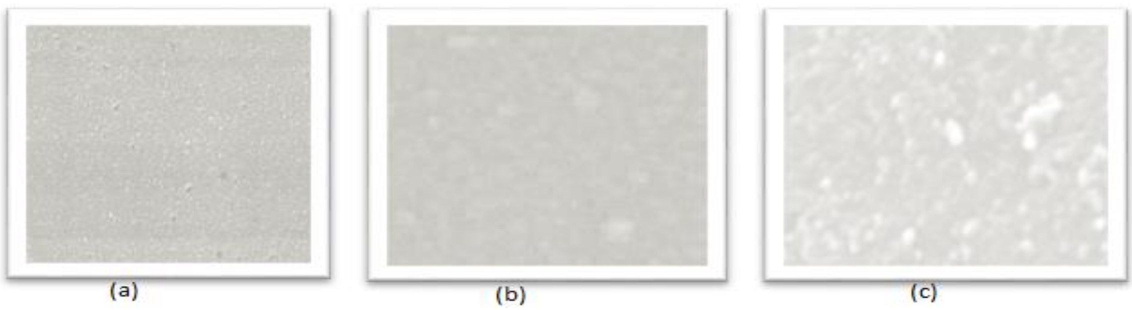

Figure 3: SEM micrographs for films sulfurised at 573K but grown at (a) 300K (b) 373K (c) 473K

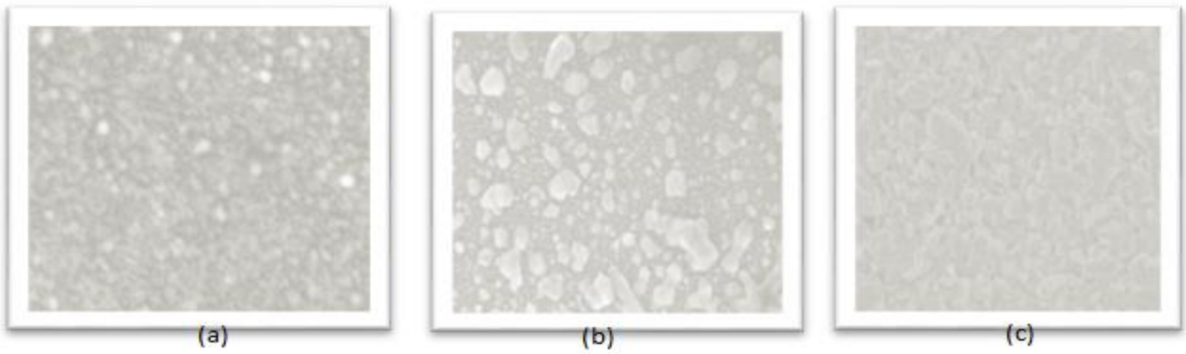

Figure 4: SEM micrographs for films sulfurised at 573K but grown at (a) 573K (b) 673K (c) 773K

4. Conclusion

$CuAlS_2$ thin films were prepared by two stage vacuum thermal evaporation technique. The resistivity (ρ) of $CuAlS_2$ film is found to decrease with increase in substrate temperature, which is related to the increase of carrier concentration with increase in substrate temperature. At elevated substrate temperatures films exhibited lowest resistivity and high carrier concentration, indicating that these are the most crystalline and conductive films. Low electrical resistivityplus high carrier concentration are widely used as the essential components in fabrication of various optoelectronic and photovoltaic devices. From Scanning electron microscopy SEM, when the substrate temperature increases, the morphology ofthesefilms shows larger number of grain size and arehomogeneously distributedanduniform,which indicates the crystalline nature of the film.

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