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Some Physical Properties of CuInSeTe thin Films Prepared by Spray Pyrolysis

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Abstract: ***Spray pyrolysis is simple and inexpensive method to depositing thin films on large area. A quaternary compound semiconductor CuInSeTe thin film has been deposited by this method. The tetragonal structure of the films was confirmed with 013 preferred orientations. The films were polycrystalline. The resistivity of the films was measured for temperature ranging from 77 K to 473 K. The activation energy 92 meV calculated from Arrhenius plot for the temperature range 303 to 473 K shows Selenium interstitial act like acceptors. In the very low temperature 77 K to 125 K conduction takes place through variable range hopping conduction mechanism. The Hall mobility and Carrier concentration at room temperature were calculated by Van-der Pauw-Hall Method.***

Keywords: Spray pyrolysis, CuInSeTe thin films, electrical and structural properties.

1. Introduction

I-III-VI_2 quaternary chalcopyrite semiconductors have been receiving a great deal of attention for their potential use in solar cells. In the recent years, solar cells based on $CuInSe_2$ (CIS) are reported to have efficiency around 17 % (1, 2). It is also suggested (3) that solar cells with $CuInTe_2$ (CIT) another members of thin films family that also a band gap around 1 eV, could give similar efficiency. Polycrystalline thin film heterojunction device, such as ZnO/CdS/$CuInSe_2$, should high solar energy conversion efficiency over 14 % (4). Fernadez and Wasim (5) reported solar efficiency of GaAs. $CuInSe_2$ yield 22.6 % interest has increased due to the fact such that such compounds have direct allowed transition (6, 7). The Cu-III-VI_2 thin film is use in solar cell also required knowledge of its optical properties due to its influence in the efficiency.

Preparations of Cu-III-VI_2 thin films have been deposited using various techniques such as elemental co-evaporation (8), flash evaporation (9), electro-deposition (10), and Spray Pyrolysis (11-13).

Spray pyrolysis is simple inexpensive methods specially for substances which are water soluble salts. So we have used this method obtain CuInSeTe thin films on glass substrate. The films have been characterized by X-ray diffraction, activation energy calculated from electrical conductivity, Hall mobility and carrier concentration at room temperature were calculated by Van der- pauw-Hall technique and the results have been presented.

2. Preparation of Samples

Thin films of CuInSeTe prepared by using aqueous solutions of copper chloride, Indium tri-chloride, selenium dioxide and tellurium tetra-chloride of 0.02 M of each in double distilled water. The chemical used were of AR grade. These solutions we have mixed in the ratio 1:1:2.2:2.2 by volume. The excess selenium and tellurium is necessary to obtain CuInSeTe. The films deposited have a selenium or tellurium deficiency of the ratio of solutions taken as 1:1:1:1. The excess selenium or tellurium is used to remove this deficiency (14, 15).

The temperature of the substrate measured by pre-calibrated copper-constantan thermocouple was maintained at 325^0C, which was the most suitable for the production of CuInSeTe thin films. The distance between the sprayer nozzle and substrate was 30 cm. The spraying rate of 3.5ml/min was maintained. The glass sprayer was mechanically move to and fro to avoid droplets on the hot substrate and to ensure instant evaporation.

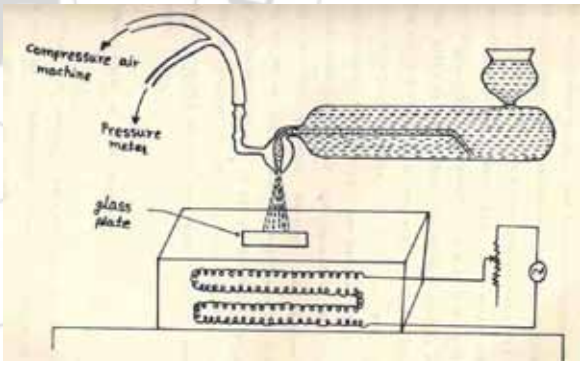

Figure 1: Experimental set up of spray pyrolysis method

3. Results and Discussion

1) Structural Properties

Fig.2 shows the X-ray diffraction pattern of as deposited CuInSeTe thin films. This shows that a polycrystalline nature. All diffraction peaks can be easily indexed and confirms the dominantly chalcopyrite structure of the films to a tetragonal phase. The peak heights and positions for CuInSeTe are in good agreement with the data reported for the bulk materials (16, 17). The lattice parameter a and c determined from the XRD pattern of thin films are 5.980 Å and 12.098 Å respectively. These values are slightly less than those reported for evaporation method (18). The values of tetragonal distortion (Δ = 2-c/a) was found to be negative

and equal to 0.023, indicating built-in dilation c > 2a, which means compression (19).

2) Electrical Properties

The temperature dependence of the electrical conductivity of the polycrystalline CuInSeTe thin films in the range of 77 K to 473 K shown in fig. 2. The conductivity is increases with increasing temperature but the increase is slow in the low temperature region 90 K-125 K. Three distinct regions of conductivity are seen. Activation energies calculated for these three regions are 92, 32 and 2.02 meV, for the temperature range 300 K- 473 K, 160 K- 250 K and 90 K-125 K respectively.

Arrhenius plot can yield the different levels which are responsible for different donor or acceptor mechanisms. The change in the carrier mechanism is indicated by change in the slope of the curve.

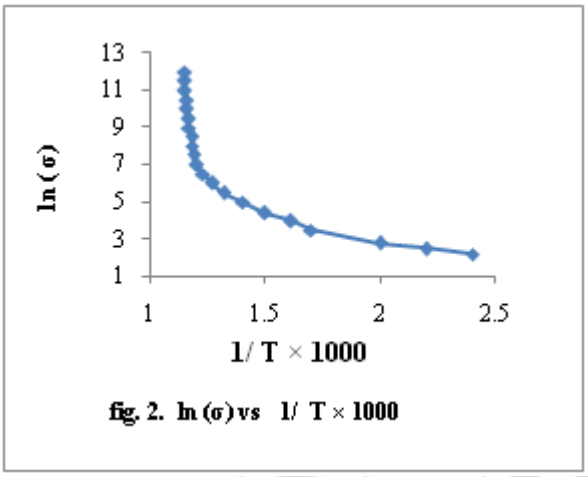

fig. 2. ln (σ) vs 1/ T × 1000

The conductivity of the films are determined by hot probe method, was p- type, hence acceptor-like levels are expected to be present. As the conductivity of the film is p-type, acceptors like levels are expected to be present. Our activation energy of 92 meV may be due to acceptor-like levels produced by selenium interstitials. Husan et al (20) has reported that the activation was 100.00 meV which is in fairly good agreement with our 92 meV activation energy.

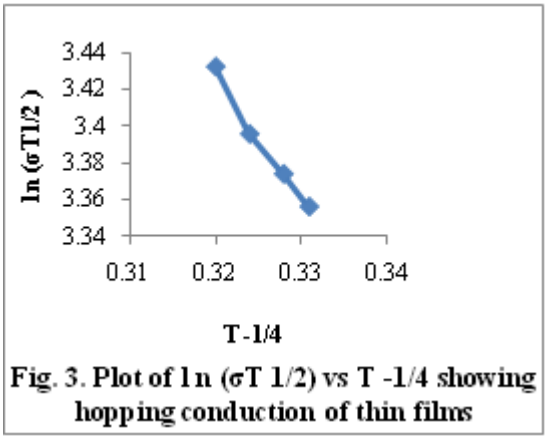

Fig. 3. Plot of ln (σT 1/2) vs T -1/4 showing hopping conduction of thin films

For a very low temperature range i.e 90 K-125 K activation energy is 2.02 meV which appears to be due to variable range hopping conduction. Similar mechanism can also be present in $CuInSe_2$ polycrystalline thin films (21). Fig shows the plot of ln ($\sigma T^{1/2}$) vs $T^{-1/4}$ for this temperature is linear. Similar results with Ea = 4 meV for spray pyrolysis $CuInSe_2$ thin films have been reported by Tembhurkar et al (15).

4. Hall mobility and Carrier Concentration

The Hall coefficient at room temperature determined by using the Van der Pauw-Hall technique (21). The Hall mobility and carrier concentration were calculated. The Hall mobility at room temperature was found to be 0.0493 $cm^2 V^{-1} S^{-1}$ which is of the same order as that obtained by Soliman (18) for vapour fusion method for CuInSeTe thin films. The carrier concentration as calculated from the relation, P = 1/|ρR|, this value comes out to be 1.88 $\times 10^{19} cm^{-3.}$ This value is in good agreement that obtained by Soliman (18) for films prepared by Fusion method.

5. Conclusion

We conclude that p-type CuInSeTe polycrystalline films can be deposited by spray pyrolysis method. The structure is predominantly tetragonal with preferred orientation along the 013 direction. Intrinsic defects may be due to selenium interstitial, acceptor- like levels, 92 meV above the valance band. The grain boundary effect also appears to be present at low temperature. At very low temperature a variable range Hopping conduction mechanism appears to be operative.

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