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SOME PHYSICAL PROPERTIES OF SPRAY PYROLYTICALLY DEPOSITED CuInSeS THIN FILMS

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Abstract

Ternary compound semiconductor CuInSeS film has been deposited spray pyrolytically using aqueous solution containing $CuCl_2$, $InCl_2$, (H_2NCSNH_2) and SeO_2. Structural characterization of the deposited film has been carried out using X-ray diffraction technique. The chalcopyrite structure of the film was confirmed with 112 preferred orientations. The films were polycrystalline. The resistivity of the film was measured for temperature ranging from 77 K to 473 K. The activation energy values were calculated from the Arrhenius plot. In the low temperature region conduction takes place through variable range hopping mechanism. The Hall mobility and carrier concentration at room temperature were calculated using the Van der Pauw-Hall method.

Keywords: - Spray pyrolysis, CuInSeS thin films, X-ray diffraction, Electrical Properties.

1. Introduction

The I-III-IV_2 chalcopyrite materials are most promising candidates for applications such as photovoltaic power generation system (1). The chalcopyrite semiconductors such as CuInSeTe, CuInSeS and CuInSeTe have been receiving a great deal of attention for their potential use in solar cells. The compound $CuInSe_{1-x}Te_x$, $0<x<1$ has studied by Quinter and wooley (2) and leon et al (3). According to their study there is always a solid-solution phase along all the composition range 0 to 1.They also found that all the phases have chalcopyrite type unit cell. The chalcopyrite materials have a direct band gap and extremely high absorption coefficient of $10^{-5}cm^{-1}$, light weight, radiation-resistance, large minority carrier diffusion length, stable electro-optical properties

and good thermal stability (4, 5). The highest conversion efficiency of 19.9% was demonstrated for Cu(InGa)Se_2-based thin film solar cells with small area (<cm^2) (6). The characterization of CIS thin films depends on native defects such as deviation of stoichiometry and therefore reduction of the stoichiometry deviation during fabricating CIS thin films is required. In this group of compound all the phases have chalcopyrite type unit cell with c/a = 2 therefore a more structural and transport investigations of CuInSeTe, CuInSeS and CuInSeTe compound have been considered necessary. There are several method to prepared CIS thin films such as DC or RF magnetron sputtering (7), chemical vapour deposition (8), Electro deposition (9), vacuum evaporation, flash evaporation and spray pyrolysis (10, 11, 12).

Spray pyrolysis is a simple inexpensive method specially for substances which have water soluble salts. So we have used this method to obtain CuInSeS thin films on glass substrate. In this paper we reported some physical properties of CuInSeS thin films.

2. Preparation of Sample

The CuInSeS thin films were deposited on highly clean glass substrates. Aqueous solution of 0.02 M $CuCl_2 2H_2O$, Indium tri-chloride ($InCl_3$), thiourea and selenium dioxide prepared in double distilled water, proportion of each solution was adjusted in the ratio 1:1:2.1:2.1 for spraying the mixture so as to obtain the desired CuInSeS thin films. The temperature of the substrate was maintained at 350^oC and was measured by pre-calibrated copper-constantan thermo-couple. The spray rate was maintained at 3.5 ml/min and spraying was done in air at 12 kg/cm2 pressure. Thickness of the films was measured by Michelsen-interferometer. The thickness so obtained was of the order of 0.1653 μm. The electrical conductivity σ was measured by four –probe method. The Hall voltage measured with the usual precautions reversing both the

magnetic and current direction. The X-ray power diffraction patterns were recorded using Cu K_α radiation on Philips X-ray diffractometer with wavelength 1.542 Å.

3. Structural Study

Fig.1 shows the X-ray diffraction (XRD) pattern of as deposited CuInSeS thin films. All diffraction peaks can be easily indexed and confirms the dominantly chalcopyrite structure of the films to a tetragonal phase .The value of lattice parameter a and c determined from the XRD pattern of polycrystalline films are 5.626 Å and 11.353 Å respectively. These values are slightly less than those reported for thermal evaporation under vacuum of 10^{-5} torr (13). The value of tetragonal distortion (Δ=2-c/a) was found to be negative and equal to -0.01831, indicating built-in dilation (c >2a) rather than compression. In general in compounds it is observed that c >2a, which means compression reported by shey and wernick (14). The peak height and position for CuInSeS are in good agreement with the data reported for the bulk materials (2, 3, 15). The high intensity of reflection from 112 planes indicates the preferred orientation along the (112) direction. A similar preferred orientation along the 112 direction has also been reported by Padam (16) and Kazmerski et al (17) for chalcopyrite $CuInSe_2$ thin films.

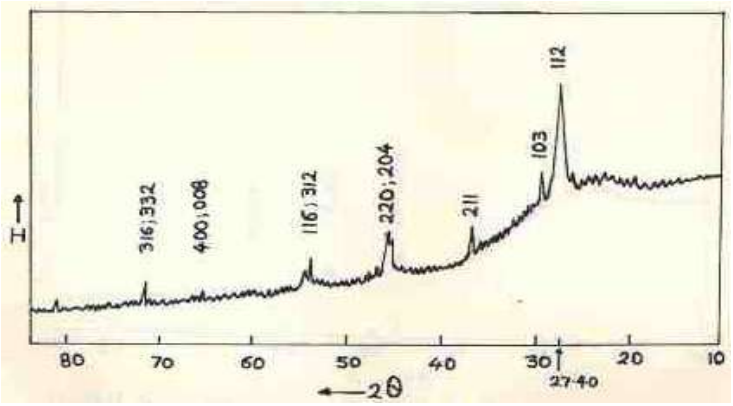

Fig.1. X-ray diffraction spectrum of as-deposited CuInSeS

4. Electrical properties

The temperature dependence of the electrical conductivity of CuInSeS thin films in the range 77 K to 473 K as shown in fig.2. The conductivity of the films, as determined by the hot probe method, was p-type. The conductivity of the films increases with increasing temperature, but increase in slow in the low temperature region upto 273 K. Above the temperature 273 K conductivity increases linearity. The resistivity for range 300 K to 473 K is measured at atmospheric pressure. The resistivity for range of temperature between 77 K to 473 K is measured at 10^{-2} torr pressure for which a four probe arrangement together with the sample film was enclosed in a specially prepared stainless steel container, which was immersed in a liquid nitrogen bath.

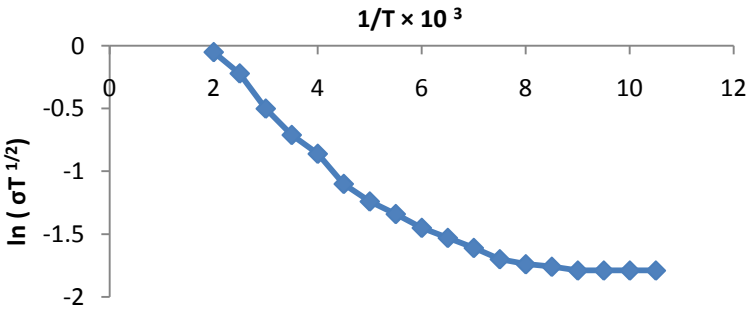

Fig. 2. Arrhenius plot of conductivity of conductivity of CuInSeS thin Films

Three distinct regions of conductivity are seen in the Arrhenius plot. The activation energies calculated for these three regions are 66 meV, 48 meV, and 3 meV, for the temperature ranges 300 K -473 K, 160 K -250 K and 90 K -125 K respectively. This suggests that there are three types of conduction mechanism that contribute to the conductivity. The change in the carrier mechanism is indicated by the change in the slope of the curve. The conductivity exhibit at higher temperature range 300 K to 473 K in accordance with the relation,

$$\sigma (T) = \sigma_0 \exp (-E_a/kT) \quad (1)$$

where, E_a - is the activation energy and k is the Boltzmann constant

In the low temperature range 77 K to 300 K, the conduction takes place through variable range hopping mechanism this can be verified in accordance with the relation (18),

$$\sigma \alpha \exp (-T_0/T^{1/4}) \quad (2)$$

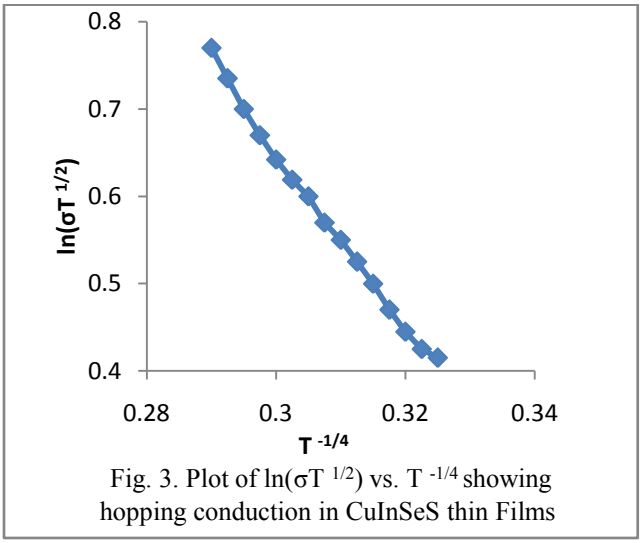

Fig. 3. Plot of $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ showing hopping conduction in CuInSeS thin Films

The plot of log ($\sigma T^{1/2}$) again $1/T^{-1/4}$ shown in fig.3 which was found to be a linear. The activation energy calculated for this region to be 3 meV, which appears to be due to variable range hopping conduction. This result are in good agreement to soliman (13) by evaporated thin films. Dawer et al (21) studied the electrical conductivity of thermally evaporated polycrystalline thin films of $CuInTe_2$ in the range of temperature from 77 K to 300 K. They observed that the hopping conduction below 200 K. Similar mechanism can also be present in $CuInSe_2$ (18)/ $CuInTe_2$ (19) polycrystalline films. Similar results with E_a= 3meV for flash evaporated $CuInSe_2$ thin films have been reported by Sridevi and Reddy (20). Soliman (13) reported that the presence of Se or S content in the compounds reveals that the carrier activation energy is reduced that the grain boundary scattering contribution is reduced

significantly. In low temperature the T_0 is related to the density $N(E_F)$ of localized states by the relation,

$$T_0 = 16\ \alpha^3/kN(E_F) \quad (3)$$

Where α is the measure of the spatial extension of the wave function exp (-αx) associated with the localized states. For a very low temperature range that is 90 K -125 K, the activation energy is 3meV which appears to be due to Variable Range Hopping conduction Mechanism. The slope of the plot (fig.3) gives the value of T_0 which comes out to be 1.011×10^3 K. Taking $\alpha^{-1}= 10^{-1}A^0$, the value of $N(E_F)$ were determined using equation (3) which comes out to be 1.8604×10^{22} $eV^{-1}cm^{-3}$.This result also in good agreement to soliman (13) by evaporated thin films.

5. Hall mobility and carrier concentration at room temperature

At room temperature the Hall coefficient was determined by using Van der Pauw-Hall technique (22).The Hall mobility and carrier concentration were calculated. The Hall mobility at room temperature was found to be 1.95 cm^2 $V^{-1}S^{-1}$ which is of the same order as that reported by soliman (13) by evaporated thin films.

6. Conclusion

We conclude that CuInSeS polycrystalline thin films can be prepared by spray pyrolysis. Structure of the films has been investigated by X-ray diffraction technique. The structure is predominantly chalcopyrite type unit cell with a = 5.626 Å, c = 11.353 Å. The films have preferred orientation along the 112 direction. 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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