ELECTRICAL PROPERTIES OF THE COMPOUNDS CuInSeTe, CuInSeS and CuInSTeTHIN FILMS

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Abstract

The structure, electrical conductivity and Hall coefficient of CuInSeTe, CuInSeS and CuInSTe thin films were measured in the temperature range from 100-450K. These compounds have been structurally investigated by X-rays diffraction technique. It was found that all the phases of these materials had a chalcopyrite type unit cell with (a=5.94Å, c = 12.13Å) for CuInSeTe, (a = 5.7 Å, c=11.52 Å) for CuInSeS and (a=5.52 Å, c=11.52 Å) for CuInSeS and (a=5.52 Å, c = 11.08 Å) for CuInSTe. It was found that the thin films evaporated at rates from 60 to 80 AS^{-1} had better electrical properties than the films grown at higher evaporation rates. The d.e conductivity and the mobility data were analysed assuming scattering by an ionized impurities.

The calculated values of the carrier concentration were found to be 2.06 x 10^{19}, 9.64 x 10^{17} and 5.5 x 10^{18} cm-3 for CuInSeTe, CuInSeS and CuInSTe thin films respectively.

Introduction

The quaternary chalcopyrite semiconductors (CuInSeTe, CuInSeS and CuInSTe) have been receiving a great deal of attention for their potential use in solar cells.

The quaternary chalcopyrite semiconductors CuInSeTe, CuInSeS and CuInSTe thin films are relatively unknown. The system CuIn (Se_{1-z} Te_z), $0 < Z < 1$ has only been studied by Quintero et al. [1] and Leon et al. [2]. According to their investigation there is always a solid solution phase along all the composition range $0<Z<1$. They also found that all the phases had a chalcopyrite type unit cell with c/a=2

and with a =0.5991 nm for CuInSeTe. Therefore a more structural and transport investigations of the CuInSeTe, CuInSeS and CuInSTe compounds have been considered necessary.

For this reason we have started to study the structure and the transport properties of the compounds CuInSeTe, CuInSTe and CuInSeS thin films.

2. Experimental

Few experiments for growing quaternary single crystals by CVD method has been carried out only Robbins and Lambrecth (1973) [3] and Bodnar et al. (1979, 1980, 1982) [4-6]. Gombia et al. (1984) [7] grew quaternary single crystals by chemical vapour transport technique (CVT) in a closed tube using iodine as a transport agent.

In our case we found that it is convenient to prepare quaternary polycrystalline specimens using diffusion method. Such method is more simple and needed shorter time and will be describe as follows:

All the starting materials used were of 99.99% purity. A two section tube furnace was used for preparing such compounds because the melting points of the reactants differ largely.

The chalcogen (S, Se or Te) was held at a temperature not exceeding half its boiling point to avoid explosion. The Cu and In element always palced in the hot part of the silica tube, were maintained at a temeprature 50°C above the melting point of Cu. In this way reaction took place between vapour of the chalcogen and the melted elements (Cu and In).

After the reaction was completed (revealed by the disappearance of the chalcogen vapour) the temperature of the cold zone of the tube was raised to the same temeprture of the hot zone. To ensure homogeneity of the compound the tube was carefully shaked several times. The temperatutre was kept constant for 2 hours to ensure

compoletion of the reaction and homogeneity of the melt. The temperature of the furnace was then lowered slowly to a vlaue equal to half the value of the melting point of the compound. The tube was then left in the furnce at this temepratute for further homogenisation and annealing for about four days. Finally the sample was gradually cooled down to room temeprature.

Films of these compounds were grown at vairous deposition rates (60-150 $Å s^{-1}$) by evaporating under vacuum (about 5×10^{-6} torr) onto glass substrates. The evaporation rate was varied by changing the source temperature from 800 to 950°C. The substrate was cooled to room temeprature over a period of 6 h in order to fix the structure of the film. The thickness of the film was monitored by using a qaurtz thickness monitor.

The electrical conductivity σ was meausred by the conventional four probe method. The Hall voltage was measured potentiometrically witht the usual precautions of reversing both the magnetic and current direction. All measurements were done under vacuum (10^{-3} torr).

3. Results and Discussion

3.1. Structure

In order to obtain kinematically interpretable intensities for the different reflections we have made X-ray powder diffraction patterns. Single crystal diffraction was not possible with the present materials since the grian size was too small and no suitable single crystals could be separated. Due to the fact that the lattice constnat values for ternary compound family have a range of existence as high as 0.6% we use in our calculation the average values of data reported in the literatures [8]. Typical diffraction patterns of CuInSeTe, CuInSeS and CuInSTe powder are shown in Fig. (1,a,b,c). The peak hights and positions for CuInSeTe are in good agreement with the data reported for the bulck materials [1,2,7].

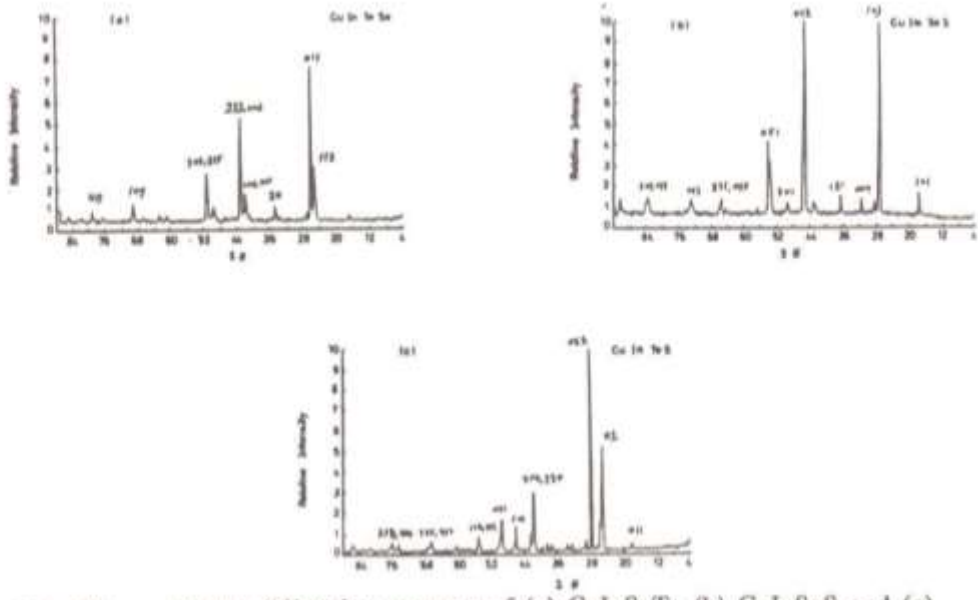


Fig. (1): X-ray diffraction patterns of (a) CuInSeTe (b) CuInSeS and (c) CuInSTe powder samples.

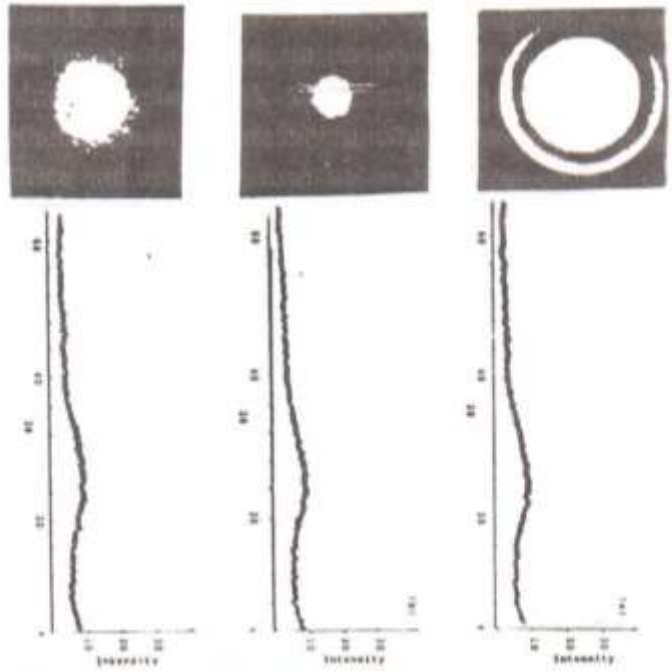


Fig. (2): Tube Excitation Fluoresecne Analysis (TEFA) of CuInSeTe, CuInSeS and CuInSTe bulk and thin films.

The caclualted lattice constant of CuInSeTe, CuInSeS and CuInSTe powder compared with that values for $CuInTe_2$, $CuInSe_2$ and $CuInS_2$ were summarized in Table (1).

Table (1)

Compund	aA	CA	C/a	Ref.
$CuInSe_2$	5.773	11.55	2.001	9
$CuInTe_2$	6.167	12.34	2.00	9
$CuInS_2$	5.517	11.06	2.005	9
CuInSeTe	6.003	-	2.00	2
	5.948	12.13	2.039	present work
CuInSeS	5.711	11.524	2.017	"
CuInSTe	5.525	11.08	2.005	"

The structure and composition of the films were investigated by using X-ray diffractometer (XRD),a diffraction electron microscope (DEM) and tube excitation flourecence analysis (TEFA). An electron microscopic study demonstrated the amorphous structure of the three films (Fig. 2, a,b,c) and there is no evidence for the existance of any crystalline films. Fig. (3, a,b,c) shows the quantitative analysis of the bulk and the amorphous films. From these figures it is clear that all these films have the same materials as well as the bulk compounds.

3.2. Electrical properties

The temperature dependence of the electrical conductivity of the amorphous CuInSeTe, CuInSeS and CuInSTe thin films in the range 100 K up to 450 K is shown in Fig. 4.

It is clear from these figures that the conductivity for all three films have the same behaviour. It increases with increasing temperature, but the increase is slow in the low temeprature region up

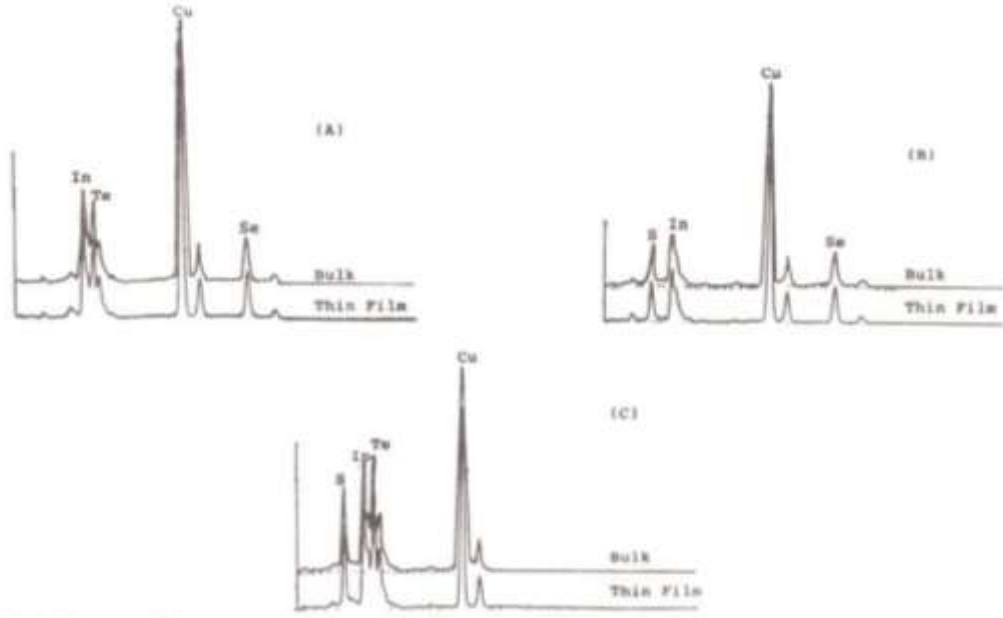


Fig. (3): Electron and diffraction patterns ofCuInSeTe, CuInSeS and CuInSTe thin films.

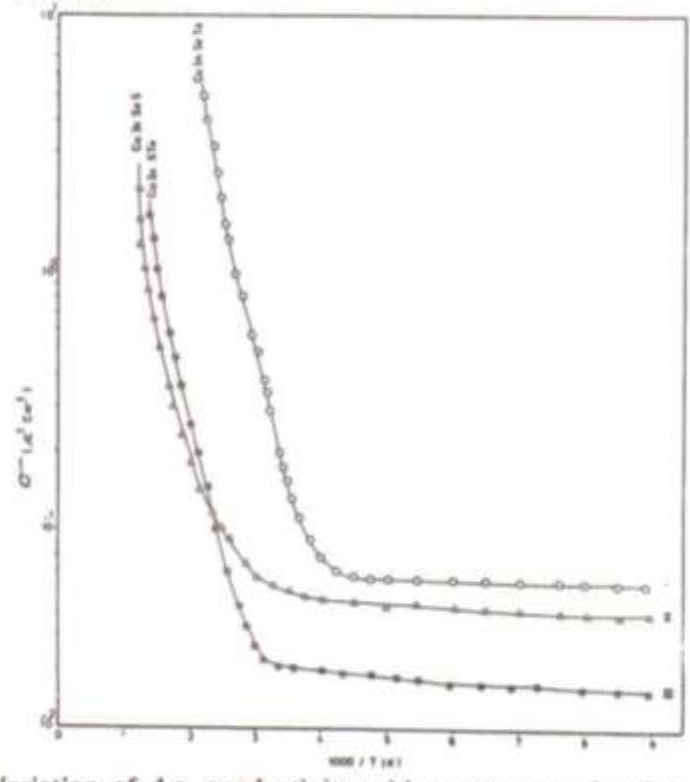


Fig. (4): Variation of d.c. conductivity with temperature for CuInSeTe, CuInSeS and CuInSTe films.

to 200 K. Above 200 K the conductivity incresed linearly. The plot suggests that there are two types of conduction mechanisms that conribute to the conductivity.

The linearity of log σ (T) agaisnt 1/T in the high temperature region (>250 K) indicates that σ (T) in this region exhibits activated behaviour while in he low temperture region σ (T) exhibits non activated behaviour. However, log $[\sigma (T)T]^{1/2}$ can be plotted linearly vs. $T^{-1/4}$ indicating variable-range hopping [10] (VRH) conduction.

At high temperatures (200–450 K) the conductivity exhibits an activation temperautre dependence in accordance with the relation:

$$\sigma (T) = \sigma_o \exp. (-\Delta E/KT) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where Δ E is the conductivity activation energy.

σ_o is the pre-exponental factor includes the charge carrier mobility and density of state.

In the low temperature regioin (100–200 K) conduction takes palce through variable range hopping mechanisms. This can be verified in accordeance with the following relation [10].

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

The plot of log $(\sigma T)^{1/2}$ against $(1/T^{1/4})$ is shown in Figure (5) which was found to be a linear one. This is in good accordance with Mott's VRH process. The calcualted values of To for the three films using equation(2) are shown in Table (2).

The localized states necessary for such a conduction process are a consequence of imperfection associated with the polycrystalline films [11]. It is also well known that in this case To is related to the density of localized state N (E) by the relation [12]

$$N(E) = \frac{10\,\alpha_o^3}{K\,T_o} \qquad \text{.....} \qquad (3)$$

where α_o^{-1} is the spatial extension of the wave function associated with the localized state and To is a measure of the degree of disorder. The calcualted values of N (E) for the three compounds are recorded in Table (2).

The presence of Se or S content in the compounds reveals that the carrier activation energy is reduced. Furher evidence for this reduction is provided by the large values of μ compared with their vlues in the stoichiometric compounds [12-15].

3.3 Hall effects

An investigation of Hall effect has been done on the CuInSeTe, CuInSeS and CuInSTe thin films in the range of temperature 100 K to 450 K. From these measurements, it is clear tht the films of every compound have a constant value of Hall coefficient all over the whole temeprature range, and the calculated values of the current carrier concentration of these films are shown, Table (2).

Hall mobility

The temperautre dependence of the carrier mobility ($\mu = R_H\sigma$) in the range 100 to 450 K for the three compounds thin films is plotted in Fig. (6). It is clear from this figure that the mobility increases first slowly in the temperature range from 100 K up to about 250 K and then rapidly above 250 K. Also it can be seen tht the Hall mobility μ increases linearly above 250 K with rise of temperutre according to the relation:

$$\mu = BT^a$$

where a = 1.15, 2.1 and 1.1 for CuInSeTe, CuInSeS and CuInSTe respectively.

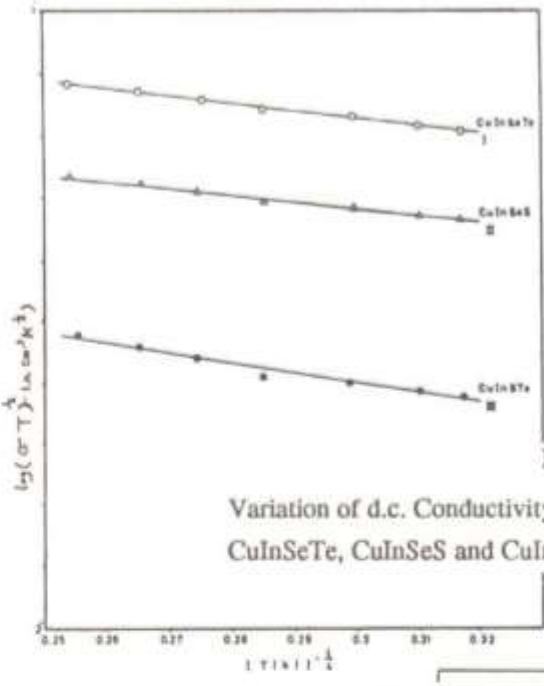
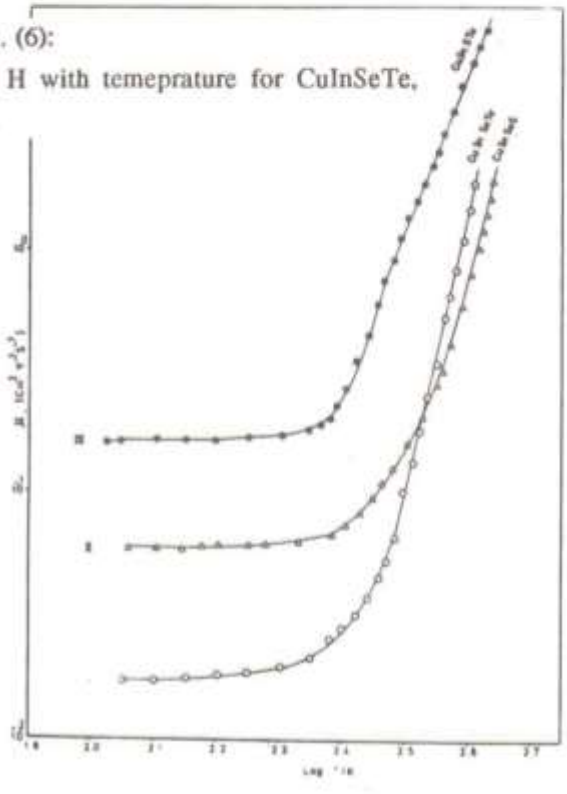


Fig. (5):

Variation of d.c. Conductivity with temperature $(\sigma T)^{1/2}$ Vs. $T^{-1/4}$ for CuInSeTe, CuInSeS and CuInSTe films.

Fig. (6):

Variation of Hall Mobility H with temeprature for CuInSeTe, CuInSeS and CuInSTe films.



The vlaues of a is somewhat differ from 1.5 for scattering of charge carriers on ionized impuity atom [16] i.e. $\mu \alpha T^{1.5}$. This deviation from the 1.5 law may partly arise from the temperature dependence of the effective mass in this temperature range. According to theory the mobility in the case of ionized impurity scattering [16] is given by :

$$\mu = \frac{T^{3/2}}{N\,(m^*)^{1/2}} \qquad \text{.....} \qquad (5)$$

where N is the concentration of the charge carriers.

The Hall mobility of these films are summarized in Table (2).

Table (2)

Sample	E_σ (e.v)	n cm^{-3}	μ_o $Cu^2V^{-1}S^{-1}K^{1/2}$	T_o K	N(E) $ev^{-1}cm^{-3}$	Ref
$CuInTe_2$	0.0625	3.6×10^{17}	2.5×10^{2}	1.13×10^{2}	1.642×10^{24}	12,19
$CuInSe_2$	0.526	6.77×10^{17}	1.0×10^{2}	6.5×10^{2}	2.823×10^{23}	19
$CuInS_2$	0.148	3.046×10^{18}	9.2×10^{2}	4.49×10^{2}	4.134×10^{23}	19
CuInSeTe	0.0406	2.06×10^{19}	8.0×10^{1}	6.86×10^{5}	2.7×10^{22}	present
CuInSeS	0.197	8.50×10^{18}	1.1×10^{2}	1.35×10^{5}	1.37×10^{23}	"
CuInSTe	0.0583	9.64×10^{17}	6.0×10^{2}	2.17×10^{6}	8.57×10^{23}	"

Conclusion :

CuInSeTe, CuInSeS and CuInSTe compounds have been structurally invesitgated by X-rays diffraction technique. All the phases of these materials had a chalcopyrite type unit cell with (a = 5.94 Å, c = 12.13 Å), (a = 5.7 Å, c = 11.52 Å) and (a = 5.52 Å, c = 10.08 Å) for CuInSeTe, CuInSeS and CuInSTe respectivley.

The structure and qualitative analysis of the films have been investigated by using an X-Ray diffractometer, diffrction electron microscope and tube excitatioin flourecence analysis. All the films have an amorphous structure.

Wide variation of the electrical conductivity and the Hall coefficient with the degree of deviation from stoichiometry were observed in CuInSeTe, CuInSeS and CuInSTe thin films.

The mobility data were analysed assuming the scttering due to an ionized impurities. The calculated values of the carrier concentration (n) were found to be 2.06×10^{19}, 9.64×10^{17} and 5.5×10^{18} cm^{-3} for CuInSeTe, CuInSeS and CuInSTe respectively.

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