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Analysis of Structural Parameters and Low Temperature Electrical Conductivity and Thermoelectric Power in Slightly Cu rich p-type CuInSe$_2$ Thin Films

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***Abstract*— The low temperature electrical conductivity and thermoelectric power in reactive evaporated polycrystalline thin films of slightly Cu rich p-type CuInSe$_2$ is explored in detail. X-ray diffraction data was analyzed to deduce the distortion parameter, anion displacement, anion-cation bond lengths and micro-structural parameters of the film. The slightly Cu rich composition of the film was verified from bond length calculations and compositional analysis. The thermo electric power factor of the film was evaluated in view of its use in thermoelectric devices. Moreover, the results of Hall and thermoelectric power measurements were correlated to evaluate the material parameters.**

***Keywords*— CuInSe$_2$, thin films, reactive evaporation, structural parameters, thermoelectric power factor.**

I. INTRODUCTION

The investigation of photovoltaic and thermoelectric properties of ternary compounds belonging to the family of I-III-VI ABC$_2$ chalcopyrite (A= Cu & Ag, B= Al, Ga & In, C= S, Se & Te) has gained renowned interest in the field of materials science research. Among the chalcopyrites, the CuInSe$_2$ (CIS) is an attractive material for researchers because it allows tuning of properties in a desired manner for required applications by means of doping [1]. CIS is a well established stable material used as absorber in thin film solar cells [2]. Solar cells, based on alloys between CuInSe$_2$ and Cu(In,Ga)Se$_2$ have already demonstrated record conversion efficiency which exceed 19.2% [3]. However, literature reports on low temperature electrical conductivity and thermoelectric properties of CIS are very few since it is still a subject of ongoing research.

In the recent years, studies on thermoelectric power of thin films have received much attention since it provides information about the type of carriers, effective mass of carriers, nature of carrier scattering, position of Fermi level, mean free path, relaxation time and other parameters that help in evaluating the suitability of the thin film for possible applications [4]. Hence thermoelectric power measurement is a useful tool that gives an in depth knowledge about the material properties.

Therefore, the present work reports on the low temperature (4-300 K) electrical conductivity and thermoelectric power factor of reactive evaporated slightly Cu rich CuInSe$_2$ thin films, about which there are no reports in literature, to the best of our knowledge. The power factor of the film was calculated in view of its thermoelectric applications. Results of these studies are described and interpreted.

II. EXPERIMENTAL DETAILS

CuInSe$_2$ thin films were prepared by reactive evaporation [5], which is a variant of Gunther's three temperature method [6]. It is based on the principle that for many binary systems there exist a stoichiometric interval with a limited degree of freedom in selecting the individual components and substrate temperature for the formation of a particular compound thin film [7].

In the present work, a conventional vacuum system operated in the range of 10^{-5} mbar was used for the preparation of CuInSe$_2$ thin film. The detailed experimental procedure and the optimized deposition conditions for obtaining good quality CuInSe$_2$ thin films has been described elsewhere [8].

The details on the structural analysis carried out by X-ray diffraction (XRD) and the compositional analysis performed by energy dispersive analysis of X-rays (EDAX) on the as deposited thin film has been discussed in an earlier report [8]. The morphological studies was performed using an AFM nanoscope E Digital Instruments, employed in “contact AFM mode” that uses a silicon nitride cantilever to probe different parts of the film surface. The Hall measurement was carried out at room temperature to determine the carrier transport properties of the film by placing the film in a magnetic field of 8000 G and measuring the current-voltage characteristics using d.c four probe method. The type of conductivity of the prepared film was determined by hot probe method and is found to be of p-type. Thickness of the film was 150nm [8].

The measurement of electrical conductivity and thermoelectric power was carried out in the low temperature range 4-300 K using liquid helium as the coolant. Silver paste was applied at the ends of the film for ohmic contact. The details of the experimental setup and procedure are given in the reference [9].

III. RESULTS AND DISCUSSION

A. Determination of structural parameters

The XRD pattern of as deposited $CuInSe_2$ thin film and the interpretations based on XRD data has already been reported [8]. The crystallite size was calculated using Scherrer formula [10] and was obtained as 52 nm. The microstructural parameters such as dislocation density, number of crystallites per unit area and lattice strain in the film were found as 3.7×10^{10}lines cm^{-2}, $11\times10^{10} cm^{-2}$ and 1.3×10^{-3} respectively [11].

The lattice parameters were calculated as a = 5.79Å and c = 11.68Å. These values agree well with those listed in the JCPDS card (File No. 40-1487). The chalcopyrite $CuInSe_2$ possesses a tetragonal crystal structure. In this structure, each cation A and B is tetrahedrally coordinated by four anions C and each anion C is coordinated by two A and two B cations. Thus there are two cation sublattices and in the equilibrium condition the anion is found to be slightly displaced toward one cation, thereby leading to unequal bond lengths $R_{AC} \neq R_{BC}$ [12], where R_{AC} represents Cu-Se bond length and R_{BC} represents In-Se bond length.

In chalcopyrites, the anions are displaced from their ideal tetrahedral sites by an amount u called anion displacement parameter and it is given by [13]

$$u = \frac{1}{2} - \frac{1}{4}\left(2\eta^2 - 1\right)^{1/2} \qquad (1)$$

The unit cell is tetragonally distorted by a parameter η called distortion parameter given by [12]

$$\eta = \frac{c}{2a} \qquad (2)$$

where a and c are lattice constants.

Using the rule of conservation of tetrahedral bonds, the values of η and u of the prepared $CuInSe_2$ were calculated as 1.009 and 0.246 respectively [14]. The observed decrease in u from that of the equilibrium value of 0.248 in $CuInSe_2$ was explained as due to the slight increase in Cu content in the films (Cu = 25.75%, In = 23.87% and Se = 50.38%) from that of stoichiometric composition, which was quite evident from the EDAX spectrum explained in an earlier report [8]. The increase in Cu content will increase the charge concentration on Cu-Se bond simultaneously producing a shortening of Cu-Se bond length. Since u is proportional to the difference in squares of (Cu-Se) and (In-Se) bond lengths [12], a decrease in Cu-Se bond length lowers u value. Bond lengths were calculated as R_{AC} = 2.501Å and R_{BC} = 2.528Å using Eq. (3) and Eq. (4)

$$R_{AC} = a\left[u^2 + \left(1+\eta^2\right)/16\right]^{1/2} \qquad (3)$$

$$R_{BC} = a\left[(u-1/2)^2 + \left(1+\eta^2\right)/16\right]^{1/2} \qquad (4)$$

As per the bond length calculations, $R_{AC} < R_{BC}$, which means that the anion Se is slightly displaced towards the cation Cu and away from cation In resulting in a slightly stretched unit cell. The values of R_{AC} and R_{BC} thus obtained were compared with the calculated values of R_{AC} (2.500Å) and R_{BC} (2.514Å) for $CuInSe_2$ from the JCPDS card (File No. 40-1487) and it agrees with our interpretation that in the prepared compound, Se atoms are slightly displaced toward the Cu atoms, which was in conformity with the results of EDAX analysis [8] where a slightly increased atomic percentage of Cu was observed. The bond-length mismatch δ [12] was estimated as -0.136(Å)^2 using Eq. (5)

$$\delta = R_{AC}{}^{2} - R_{BC}{}^{2} \qquad (5)$$

The EDAX spectrum [8] was further analysed to confirm the slightly Cu rich nature of the film. Based on EDAX studies, the deviations from stoichiometric composition of $CuInSe_2$ were described by two parameters proposed by Groenik and Janse [15]. These parameters were Δm and Δs given by Eq. (6) and Eq. (7) and they determine the deviations from molecularity and stoichiometry respectively.

$$\Delta m = \frac{[Cu]}{[In]} - 1 \qquad (6)$$

$$\Delta s = \frac{2[Se]}{[Cu] + 3[In]} - 1 \qquad (7)$$

The deviations of these parameters from zero indicate

1. $\Delta m > 0 \rightarrow$ Cu rich films, $\Delta m < 0 \rightarrow$ In rich films
2. $\Delta s > 0 \rightarrow$ excess of selenium, $\Delta s < 0 \rightarrow$ deficiency of selenium.

The value of Δm and Δs was found to be 0.08 and 0.03 respectively, suggesting that the prepared film is slightly Cu rich with an excess of selenium, consistent with EDAX spectrum [8].

B. Morphological analysis

The 2D and 3D atomic force micrographs of the sample with scan size 1µm are shown in Fig. 1 and Fig. 2 respectively. Scan rate is 10.172 Hz.

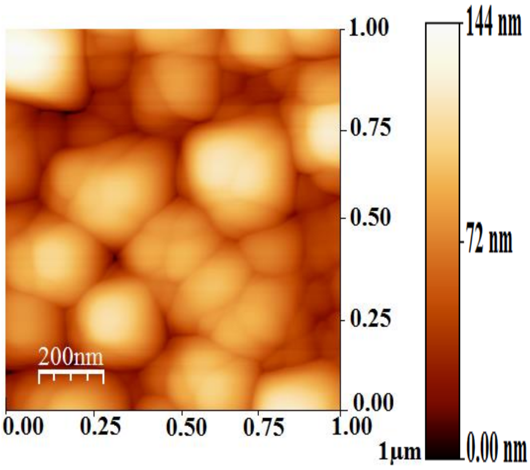

Fig. 1 The 2D AFM of $CuInSe_2$ thin film

It was evident from 2D AFM that a large number of particles were aggregated together to form a superstructure of clusters with grain size ≈ 160nm.

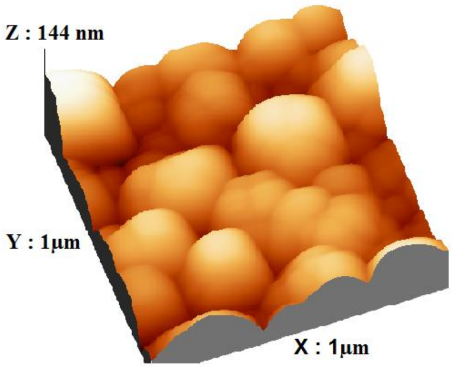

Fig. 2 The 3D AFM of $CuInSe_2$ thin film

The root mean square (RMS) value of surface roug ness of the film determined from 3D AFM was found to be 23nm. Thus AFM topography revealed that the overall film surface was significantly smooth.

C. Low temperature electrical conductivity and thermoelectric power measurements

The p- type conductivity of the film was verified from Hall measurements. The film showed a hole concentration $p \approx 6.2\times10^{16}cm^{-3}$, hole mobility $\mu_h \approx 10.5cm^2V^{-1}s^{-1}$ and electrical conductivity $\sigma \approx 0.1\Omega^{-1}cm^{-1}$ at room temperature.

Fig. 3 shows the variation of electrical conductivity with temperature of a typical $CuInSe_2$ thin film.

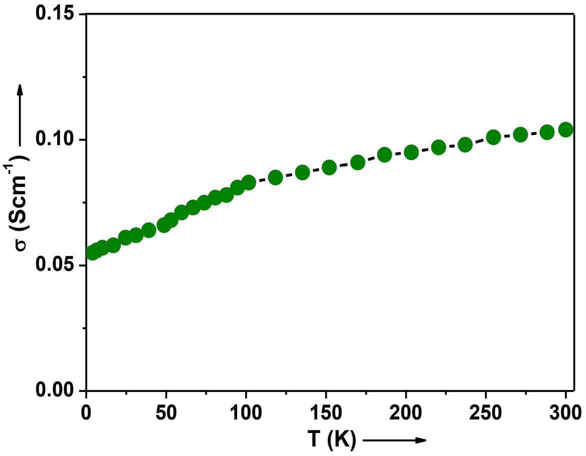

Fig. 3 Variation of electrical conductivity with temperature of a typical $CuInSe_2$ thin film.

The decrease in electrical conductivity with decrease in temperature reveals the semiconducting nature of the film.

Fig. 4 shows the variation of thermoelectric power or seebeck coefficient (S) with temperature of a typical $CuInSe_2$ thin film. The positive values of S indicate that the as prepared thin films were of p-type.

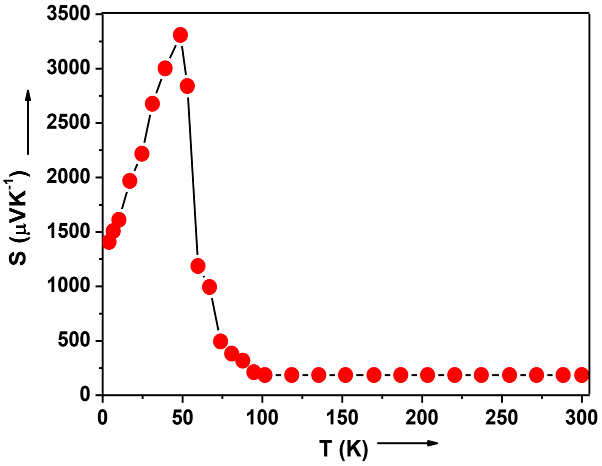

Fig. 4 Variation of seebeck coefficient with temperature of a typical $CuInSe_2$ thin film.

The Fermi level position was determined to be located at 0.02eV above the valence band and the value of A was obtained as 3/2, which indicates ionized impurity scattering [16]. The effective mass of holes m_h^* was determined as 0.07 m_0, where m_0 is the rest mass of electron [16]. The calculated value of effective density of states above valence band edge $N_V \approx 4.6\times10^{17}cm^{-3}$ was found to be very much greater than the value of carrier concentration obtained from Hall measurements. This confirmed the semiconducting nature of the film [17]. Moreover, the relaxation time (τ) and mean free path (λ) were estimated as 4.2×10^{-16}s and 0.12nm respectively. This indicates that the chances of interaction of phonons with grain boundaries in polycrystalline thin films are high.

Fig. 4 shows that in the temperature range 300-100 K, the seebeck coefficient (S) is ≈ 184μVK^{-1}. However, as the temperature was lowered from 100 K, S showed a sudden and sharp increase and reached upto ≈ 3309 μVK^{-1} at 48K. This rapid increase in S was explained as due to the phonon drag on charge carriers that results from the interaction of phonons with mobile charge carriers [18]. In addition, it is interesting to note that below 48K, S showed a sudden drop. This is because 48K is about one fifth of Debye temperatue (θ_D) of $CuInSe_2$ [19]. Below $\theta_D/5$, the number of phonons available for drag is less and this results in a decrease in S [16]. The observed value of S ≈ 1407 μVK^{-1} at 4K for the prepared film, are typical values of efficient materials used for thermoelectric applications [20].

Therefore, in view of the potential of the prepared $CuInSe_2$ thin film for thermoelectric applications, the thermoelectric power factor was evaluated. The thermoelectric power factor is one of the key factors that determine the efficiency of a material for thermoelectric applications and it is given by [21]

$$\text{Thermoelectric power factor} = S^2\sigma \qquad (8)$$

where S is the Seebeck coefficient and σ is the electrical conductivity.

Fig. 5 shows the variation of thermoelectric power factor with temperature of a typical $CuInSe_2$ thin film.

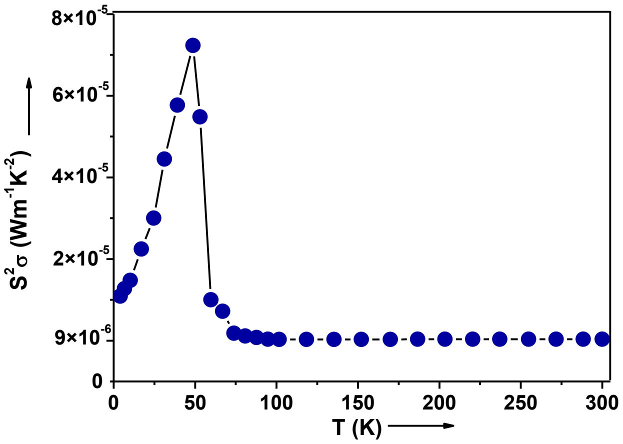

Fig. 5 Variation of thermoelectric power factor with temperature of a typical $CuInSe_2$ thin film.

As observed from Fig 5, the value of thermoelectric power factor of the film was found to vary from 10^{-5} to $10^{-7} Wm^{-1}K^{-2}$ in the measured temperature range, attaining a maximum of ≈ $7.2x10^{-5} Wm^{-1}K^{-2}$ at 48K. These values are somewhat low compared to that of good thermoelectric materials (≈ 10^{-3}–$10^{-5} Wm^{-1}K^{-2}$), but comparable to those reported for some of the potential thermoelectric materials such as Bi_2Se_3 [22], $CuAlO_2$ [23] and $Nd_{2-x}Ce_xCuO_4$ [21] that are recently being developed. This provides an overwhelming optimism for the chalcopyrite $CuInSe_2$ to be considered as a possible candidate for thermoelectric applications, on further enhancement of its power factor by the optimization of carrier concentration [21] through nanostructuring and electronic band engineering.

IV. CONCLUSIONS

The electrical conductivity and thermoelectric properties of reactive evaporated slightly Cu rich thin films of $CuInSe_2$ was studied in detail. The interpretations based on bond length calculations and compositional analysis confirmed the slightly Cu rich nature of the film. The temperature dependence of electrical conductivity and seebeck coefficent revealed the semiconducting nature of the film. The reasonably high value of seebeck coefficient ≈ 1407 μVK^{-1} at 4K and thermoelectric power factor ≈ $10^{-5} Wm^{-1}K^{-2}$ at 4 K of the film, suggests its potential application in the field of low temperature thermoelectrics, on further optimization.

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