Structural, optical and electrical properties of spray pyrolytically deposited thin films of CuInS_2

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Abstract. CuInS_2 is a promising chalcopyrite semiconducting material for solar cell fabrication. Using aqueous solutions of cupric chloride, indium trichloride and thiourea, we deposited thin CuInS_2 films on glass at 350°C and studied their structural, optical and electrical properties. From the XRD pattern the chalcopyrite structure of these films was confirmed. The films were polycrystalline. The grain size estimated from scanning electron micrographs was found to be of the order of $1\ \mu\text{m}$. Resistivity of the film was measured for temperatures ranging from 77 to 473 K. Band gap values were determined from optical transmission data. Hall mobility and carrier concentration at room temperature were calculated using Van der Pauw–Hall method.

Keywords. CuInS_2 thin films; chalcopyrite semiconductors.

1. Introduction

CuInS_2 is a member of the I–III–VI₂ family of chalcopyrite semiconductors with a band gap of 1.55 eV and hence has been predicted to yield photocells of efficiency (Meese *et al* 1975) between 27% and 32%. CuInS_2 photocells have shown 15% efficiency (Tell and Thiel 1979). Solar cells of CuInS_2 thin film homo-junction produced by vacuum evaporation with efficiency up to 3.62% have been demonstrated by Kazmerski and Sanborn (1977). Many research groups have investigated the properties of this compound in the form of a single crystal. There is a need for systematic evaluation of the variables associated with the production of CuInS_2 thin films so that electrical, optical and structural characteristics can be easily understood and controlled for device applications.

Different techniques of thin film deposition such as double-source method (Kazmerski *et al* 1975), flash evaporation (Hwang *et al* 1980a; Neumann *et al* 1981), r.f. sputtering (Hwang *et al* 1980c) and chemical vapour technique (Grindle *et al* 1979; Hwang *et al* 1980b) have been used and structural, optical and electrical properties of the thin films studied. Hiroyoshi and Kazuo (1984) used spray pyrolysis for depositing CuInS_2 films and studied structural, optical and electrical properties above room temperature, while Rajaram *et al* (1983) studied the conductivity of spray pyrolytically deposited films of CuInS_2 at room temperature.

The study of electrical properties at low temperatures gives information about the various mechanisms responsible for conduction in thin films. We have chosen the economical and convenient method of chemical spray pyrolysis for deposition of thin CuInS_2 films and studied structural, optical and electrical properties of as-deposited films up to liquid nitrogen temperatures. Thickness of the films was measured by using a Michelson interferometer. The grain size was determined by SEM. The absorption edge analysis was carried out using transmittance vs wavelength data on a Hitachi spectrophotometer (model 330 UV-VIS-NIR). Hall mobility and carrier

concentration at room temperature were determined by using Van der Pauw–Hall method. The conductivity type of the film was determined by hot-probe method.

2. Film preparation

Aqueous solutions of cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), indium trichloride (InCl_3) and thiourea (H_2NCSNH_2) were used to prepare the films on hot glass substrates. Stock solutions of 0.02 M of each of the above compounds was prepared in double distilled water. The chemicals used were of AR grade. Prior to use in deposition, the molarity of each solution was first reduced to 0.003 M and then the solutions were mixed together in the ratio 1:1:3.2 by volume. Excess sulphur is necessary to obtain CuInS_2 films. Deposited films show sulphur deficiency if the ratio of the solutions is 1:1:2. Excess sulphur (in the form of thiourea) is used in order to remove this deficiency (Rajaram *et al* 1983). Biological glass slides (1.30 mm thick), were used as substrates. The temperature of the substrate, measured by a pre-calibrated thermocouple was maintained at 350°C , which was the most suitable for the production of CuInS_2 thin films. The solution mix was sprayed at 12 kg/cm^2 pressure. The distance between the sprayer nozzle and substrate was 30 cm. The rate of flow was maintained at 3.5 ml/min. The glass sprayer was mechanically moved to and fro during spraying to avoid formation of droplets on the hot substrate and to ensure instant evaporation.

3. X-ray study

Figure 1 shows the X-ray diffraction pattern for as-grown films of CuInS_2 . Cu K_α radiation with wavelength of $1.542 \text{ \AA}$ was used. A pronounced diffraction peak corresponding to the 112 plane indicates preferred orientation as the direction of the 112 plane is least energy oriented for tetragonal systems. The other prominent peaks, corresponding to the 200, 211, 220, 204, 312, 400 and 424 planes, are also present. The positions of the peaks 112, 220, 200, 116/312 tally with those of the diffraction peaks obtained by Samann *et al* (1986) for r.f. sputtered films of CuInS_2 and those obtained by Hiroyoshi and Kazuo (1984) for spray pyrolytically deposited films. However, the intensity order in our XRD pattern is slightly different. The above four

Figure 1. X-ray diffraction spectrum of as-deposited CuInS_2 thin films on glass substrate.

Figure 2. Scanning electron micrograph of the as-deposited thin films of CuInS_2 on glass substrate.

peaks are attributed to chalcopyrite phase of CuInS_2 (Hiroyoshi and Kazuo 1984; Samann *et al* 1986). The positions of the other peaks obtained in our XRD pattern tally with ASTM data for tetragonal phase of CuInS_2 . The lattice parameters a and c calculated from the above diffraction peaks are $5.524 \text{ \AA}$ and $11.104 \text{ \AA}$ respectively. The standard values of a and c for single crystals (ASTM No. 27–159) are $5.523 \text{ \AA}$ and $11.141 \text{ \AA}$ respectively. The values for our sprayed films therefore differ from the standard values by $0.001 \text{ \AA}$ and $0.036 \text{ \AA}$ respectively. The value of tetragonal distortion ($\Delta = 2 - c/a$) was found to be negative, and equal to -0.01031 , indicating built-in dilation ($c > 2a$) rather than compression. In general in I–III–VI₂ compounds it is observed that $c < 2a$, which means compression (Shay and Wernick 1975).

Figure 2 shows the scanning electron micrograph of the as-deposited thin film of CuInS_2 . The grain size varies from $0.5 \mu\text{m}$ to $1.0 \mu\text{m}$.

4. Optical study

The optical transmission (T) of the film was measured at room temperature using a Hitachi spectrophotometer (model 330 UV-VIS-NIR). Transmission was recorded for the wavelength range $400\text{--}1600 \text{ nm}$ of the incident beam. Figure 3 shows transmission (T) vs wavelength (λ) for a film of thickness $0.15 \mu\text{m}$.

The absorption coefficient (α) at various wavelengths for a sample of thickness t is given by the relation

$$\alpha t = \ln(I_0/I), \quad (1)$$

where I_0 and I are the intensities of incident and transmitted radiation respectively. It is seen from figure 3 that interference effects can be neglected for films deposited on a thick non-absorbing substrate. The values of absorption coefficient (α) at various wavelengths were calculated from the transmission curve using relation (1) above.

Figure 4 shows the graph of $(\alpha h\nu)^2$ against $h\nu$, for $h\nu \leq 2.0 \text{ eV}$, the region in which the graph is linear. This linear relation indicates that the direct allowed transition described by the relation

$$\alpha = (A/h\nu)(h\nu - E_g)^{1/2} \quad (2)$$

Figure 3. Transmission T as a function of the wavelength λ of the as-deposited CuInS_2 films on glass substrate (thickness of the film, $t = 0.15 \mu\text{m}$).

Figure 4. Plot of $(\alpha hv)^2$ against incident photon energy ($hv \leq 2.0 \text{ eV}$).

is probably responsible for the absorption process. The band gap (E_g) determined from the intercept (by extrapolation) on the hv axis was 1.43 eV. This result is in fairly good agreement with those of Rajaram *et al* (1983) and Hiroyoshi and Kazuo (1984), who reported band gap values of 1.44 eV and 1.38–1.43 eV respectively for spray pyrolytically deposited films. However, Pamplin and Fiegelson (1979) obtained a band gap value of 1.3 eV for similar films. Neumann *et al* (1981) studied the optical properties of flash evaporated CuInS_2 thin films and obtained an energy gap of 1.524 eV at room temperature. The optical band gap value obtained by us (1.43 eV) is smaller than that of a single crystal (Shay and Wernick 1975), which is 1.55 eV.

Using this value of band gap (E_g) and slope of the curve (A), absorption coefficient

Figure 5. Plot of $(\alpha_2 hv)^2$ against incident photon energy ($h\nu \geq 2.0$ eV).

was calculated for $h\nu \geq 2.0$ eV. We find that this calculated absorption coefficient is always less than the observed optical absorption coefficient for $h\nu \geq 2.0$ eV. This can only be explained if we assume the presence of an additional absorption process. We denote the absorption coefficient for $h\nu \leq 2.0$ eV by α_1 and the absorption coefficient due to the additional process (for $h\nu \geq 2.0$ eV) by α_2 ; α_2 is given by the relation

$$\alpha_2 = \alpha_{\text{exp}} - \alpha_{\text{cal}}.$$

Figure 5 shows $(\alpha_2 hv)^2$ plotted against $h\nu$ for $h\nu \geq 2.0$ eV. It is observed that the graph is a straight line up to $h\nu = 2.82$ eV, with an intercept of value 2.44 eV, indicating the presence of a second direct allowed transition. On the same lines if α_3 is calculated for $h\nu \geq 2.82$ eV, the graph of $(\alpha_3 hv)^2$ vs $h\nu$ is a straight line and gives an intercept at 2.71 eV. Neumann *et al* (1981) studied the optical properties of thin CuInS₂ films produced by flash evaporation method. They found that the direct optical transitions corresponding to 1.524, 2.81 and 3.04 eV were present. Our values are 1.43, 2.44 and 2.71 eV and are smaller than the values obtained by Neumann *et al* (1981). According to Shay and Wernick (1975) all sulphides and selenides of Cu and Ag with In, Ga or Al have direct energy gaps, probably due to transitions from copper-d-band to the lowest conduction band minimum.

5. Electrical properties

Conductivity of the film, as determined by the hot probe method, was of *p*-type. The resistivity was determined for two different ranges of temperature. Range (a) was from 300 K to 473 K and range (b) was from 77 K (liquid nitrogen temperature) to 273 K. The resistivity in range (a) was measured at atmospheric pressure and in range (b) at 10^{-2} torr, 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.

Figure 6 shows the Arrhenius plot of conductivity vs inverse temperature of as-deposited film for the above temperature ranges. Three distinct regions of conductivity

Figure 6. Arrhenius plot of conductivity of as-deposited CuInS_2 thin films (temperature range 77 K to 473 K).

are seen. Activation energies calculated for these three regions are 200 meV, 52 meV and 8 meV, for the temperature ranges 300–473 K, 160–250 K and 90–125 K respectively.

To study the conduction mechanism and the defect states one has to determine the resistivity in the region of very low temperature. As the temperature is lowered, the deeper levels can be progressively frozen out (Tuttle *et al* 1988). The Arrhenius plot can yield the different levels which are responsible for the different donor, acceptor mechanisms. Change in the carrier mechanism is indicated by change in the slope of the curve. As the films are not intentionally doped, intrinsic defects are expected to be present.

The activation energy of 200 meV obtained in our experiment may be due to deep acceptor level. The activation energy obtained by Hiroyoshi and Kazuo (1984) for this range of temperature was 310 meV for spray pyrolytically deposited CuInS_2 films, annealed for 2 h at 500°C in vacuum. They have reported an increase in the height of the peak at an angle of 27.9° which indicates that vacuum annealing does not decompose the compound but enhances crystallization. To find the effect of annealing in vacuum, our film was annealed for 90 min at 400°C. The $\ln(\sigma)$ vs $1/T \times 10^3$ graph (figure 7) gives two different activation energies. The activation energy for the range 473 K to 500 K was obtained as 350 meV, which is slightly more than that obtained by Hiroyoshi and Kazuo (1984). For the temperature range 300 K to 473 K, the activation energy was 150 meV, which is nearly the same as that obtained by Ueng and Hwang (1989). They have reported activation energy of 145 meV for the

Figure 7. Arrhenius plot of conductivity of CuInS₂ thin films after vacuum annealing for 1.5 h at 400°C (temperature range 300 K to 500 K).

single crystal and attributed it to antisite defects of indium on copper sites (In_{Cu}). Lange *et al* (1985) also have identified activation energy of 145 meV from luminescence data and attributed it to the defect states of indium occupying copper site.

It has been suggested (Tell *et al* 1972; Migliorato *et al* 1975) that in CuInS₂/Se₂ (Cu-III-VI₂) ternary compound Cu and In vacancies act as acceptor levels. As Cu participates very weakly in covalent bond formation, Cu vacancies are more probable than In vacancies. For these vacancies in CuInS₂, many workers (Lahlou and Masse 1981; Masse *et al* 1981; Masse 1984) have reported activation energies of the order of 45 meV to 50 meV. An activation energy of 52 meV obtained in our investigation is in fairly good agreement with this value and therefore may be attributed to Cu vacancy.

In addition to bulk conductivity, grain boundary conduction should also be taken into account while explaining the electrical behaviour of polycrystalline films at low temperatures. At low temperatures the effect of grain boundary is predominant when the grain size is small. The atoms at the grain boundary are disordered. There are a large number of defects due to incomplete atomic bondings. These form the trapping states and charge carriers are trapped and immobilized. The traps become electrically charged and give rise to potential barriers (Seto 1975). The conductivity temperature relation for such an effect was derived by Seto (1975). To verify whether the grain boundary effect is present, a graph of $\ln(\sigma T^{1/2})$ vs $1/T \times 10^3$ was plotted in the temperature range 150–300 K (figure 8). This plot is a straight line, which indicates the predominance of grain boundary effect in this temperature range.

Figure 8. Plot of $\ln(\sigma T^{1/2})$ vs inverse temperature showing grain boundary effect.

It appears that the observed activation energy (52 meV) may be due to the copper vacancies inside the grain or/and the formation of trapping states at the grain boundaries.

At very low temperature, all the trap states are filled and conduction occurs through the variable range hopping of the electrons in the localized states (Mathur *et al* 1983) at the Fermi level. Greaves (1973) derived an expression for the conductivity for variable range hopping (VRH) model applicable at low temperature as

$$\sigma T^{1/2} = C \exp(-T_0/T)^{1/4}, \quad (3)$$

where C and T_0 are constants and T_0 is related to the density $N(E_F)$ of localized states by

$$T_0 = 16\alpha^3/k N(E_F), \quad (4)$$

where α^{-1} is a measure of the spatial extension of the wave function $\exp(-\alpha x)$ associated with the localized states. The plot of $\ln(\sigma T^{1/2})$ vs $T^{-1/4}$ for as-deposited film is indicated in figure 9 for the temperature range 90–125 K. The slope of this plot gives the value of T_0 , which comes out to be 9.872×10^3 K. Taking (Ambegaokar *et al* 1972; Mott and Davis 1979; Dawar *et al* 1984) $\alpha^{-1} = 10 \text{ \AA}$, the value of $N(E_F)$ was determined by using relation (4), which comes out to be $1.884 \times 10^{22} \text{ eV}^{-1} \text{ cm}^{-3}$. Dawar *et al* (1984) reported the values of T_0 and $N(E_F)$ for evaporated CuInTe_2 thin films. The values of T_0 reported by them are of the order of 10^3 to 10^2 and that of $N(E_F)$ of the order of 10^{20} to 10^{23} . Our values for CuInS_2 thin films are of the same order of magnitude. The obtained value of $N(E_F) \simeq 10^{22}$ is too large for a semiconductor. It appears that some correction to the assumed value of α^{-1} is necessary. The straight line nature of the plot indicates the validity of hopping conduction mechanism, with activation energy 8 meV. Similar mechanism was operative for flash evaporated (Sridevi and Reddy 1986) and spray pyrolytically deposited (Tembhurkar and Hirde 1992) CuInSe_2 thin films, with low activation energy at the same temperature range.

Figure 9. Plot of $(\sigma T^{1/2})$ versus $T^{-1/4}$ showing hopping conduction in CuInS_2 thin films.

6. Hall mobility and carrier concentration at room temperature

Hall coefficient at room temperature was determined by using Van der Pauw–Hall technique (Putley 1960). The Hall mobility and carrier concentration were calculated. Hall mobility at room temperature was found to be $6.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This result is in fairly good agreement with that of Kazmerski *et al* (1975) who reported a value for Hall mobility of $8.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, Tell *et al* (1972) reported a value of $15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a single crystal.

The carrier concentration given by the relation

$$p = \frac{1}{|eR_H|}$$

comes to be $2.33 \times 10^{19} \text{ cm}^{-3}$, which is in good agreement with the value obtained by Hiroyoshi and Kazuo (1984).

7. Conclusion

It was observed that *p*-type CuInS_2 polycrystalline thin films can be deposited by spray pyrolysis. The structure is predominantly chalcopyrite with grain size of the order of $1 \mu\text{m}$. The films have preferred orientation along 112 direction. Three direct allowed transition at 1.43, 2.44 and 2.71 eV were observed. The above room temperature investigation of resistivity reveals acceptor levels at 350 meV and 150 meV. Below room temperature copper vacancies inside the grains or/and formation of trapping states at the grain boundaries play a major role in conduction. At very low temperature hopping conduction appears to be operative.

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References

- Ambeagaokar V, Halperin B I and Langner J S 1972 *Phys. Rev.* **34** 2612
- Dawar A L, Kumar A, Mall R P and Mathur P C 1984 *Thin Solid Films* **112** 107
- Greaves G N 1973 *J. Non-Cryst. Solids* **11** 427
- Grindle S P, Smith C W and Mittleman S D 1979 *Appl. Phys. Lett.* **35** 24
- Hiroyoshi O and Kazuo M 1984 *Jap. J. Appl. Phys.* **8** 965
- Hwang H L, Tu C C, Maa J S and Sun C Y 1980a *Sol. Energy Mater.* **2** 433
- Hwang H L, Tseng B H, Sun C Y and Loferski J J 1980b *Sol. Energy Mater.* **4** 67
- Hwang H L, Cheng C L, Liu L M, Lin Y-C and Sun C Y 1980c *Thin Solid Films* **67** 83
- Kazmerski L L, Ayyagiri M S and Sanborn G A 1975 *J. Appl. Phys.* **46** 4865
- Kazmerski L L and Sanborn G A 1977 *J. Appl. Phys.* **48** 3178
- Lahlou N and Masse G 1981 *J. Appl. Phys.* **52** 978
- Lange P, Neff H, Fearheiley M L and Bachmann J 1985 *J. Electronic Mater.* **14** 6
- Masse G, Lahlou N and Butthi C 1981 *J. Phys. Chem. Solids* **42** 449
- Masse G 1984 *J. Phys. Chem. Solids* **45** 1091
- Mathur P C, Sharma R P, Renuka S, Saxena P and Kotnala R K 1983 *J. Appl. Phys.* **54** 3913
- Meese J M, Manthuruthil J C and Locker R D 1975 *Bull. Am. Phys. Soc.* **20** 696
- Migliorato P, Shay J L, Kasper H M and Wagner S 1975 *J. Appl. Phys.* **46** 1777
- Mott N F and Davis E S 1979 *Electronic processes in non-crystalline material* (Oxford: Clarendon Press)
- Second edition
- Neumann H, Horig W, Schumann B, Kuhn G, Savelev V and Lagzdonis J 1981 *Thin Solid Films* **79** 167
- Pamplin B and Fiegelson R S 1979 *Thin Solid Films* **60** 141
- Powder Diffraction File, Joint Committee on Powder Diffraction Standards, International Center for diffraction Data, Swarthmore, PA, Card 27-159
- Putley H 1960 *Hall effect and related phenomenon* (London: Butterwords)
- Rajaram P, Thangaraj R, Sharma A K, Raza A and Agnihotri O P 1983 *Thin Solid Film* **100** 111
- Samann A N Y, Wasim S M, Hill A E, Armour D G and Tomlinson R D 1986 *Phys. Status Solidi (a)* **96** 317
- Seto John Y W 1975 *J. Appl. Phys.* **46** 5247
- Shay J L and Wernick S H 1975 *Ternary chalcopyrite semiconductors: growth, electronic properties and applications* (Great Britain: Pergamon Press)
- Sridevi D and Reddy K V 1986 *Indian J. Pure and Appl. Phys.* **24** 392
- Tell B, Shay J L and Kasper H M 1972 *J. Appl. Phys.* **43** 2469
- Tell B and Thiel F A 1979 *J. Appl. Phys.* **50** 5045
- Tembhurkar Y D and Hirde J P 1992 *Thin Solid Films* **215** 65
- Tuttle J R, Albin D, Goral J, Kennedy C and Nouff R 1988 *Solar Cells* **24** 67
- Ueng H Y and Hwang H L 1989 *J. Phys. Chem. Solids* **50** 1297