PHOTOVOLTAIC CHARACTERISTICS OF THIN FILMS OF Cu_2SnS_3

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We report for the first time the optical absorption and photovoltaic characteristics of thin films of Cu_2SnS_3. Films obtained by the direct evaporation of the synthesized compound were observed to be deficient in copper, while those grown in an atmosphere of copper vapour were observed to be more stoichiometric. Both sets of films are characterised by indirect and direct absorption edge properties. The indirect absorption edges are at 1.065 and 1.510 eV, while the direct band edges are at 1.658 and 1.770 eV for the copper deficient and stoichiometric films respectively. The stoichiometric film is characterised by p-type semiconducting properties while a Schottky type solar cell developed from it is observed to have potential photovoltaic characteristics.

1. Introduction

Cu_2SnS_3 belongs to a group of compounds represented by the general formula $A_2^I B^{IV} C_3^{VI}$ (superscripts denote group in the periodic table and subscripts the number of atoms). These compounds are the ternary analogues of the widely used binary $A^{II} B^{VI}$ semiconducting compounds [1]. The compound is characterised by a cubic structure [1,2], with a lattice constant of $a = 5.445$ Å. However, unlike the $A^{II} B^{VI}$ analogues, not much is known about the optical properties of thin films of this compound. This paper reports for the first time the absorption properties of thin films of the compound, and the preliminary results on the investigation of the photovoltaic properties of the compound.

2. Experimental

Cu_2SnS_3 powder samples were prepared by melting together in an initially evacuated ampoule a stoichiometric mixture of 99.999% purity samples of Cu, Sn and S. X-ray analysis with a Philips X-ray goniometer (Cu K_α radiation and nickel filter) gave a lattice constant consistent with that reported in the literature [2].

Thin films were prepared by vacuum evaporation of the prepared compound in Edwards high vacuum equipment capable of generating a vacuum of about 10^{-6} Torr. For absorption measurements, films were grown on clean soda glass or quartz substrates maintained at temperatures between 423 and 523 K. X-ray analysis of the

Table 1
Elemental composition of Cu_2SnS_3-like films prepared by two different methods

Element	Type A (at.%)	Type B (at.%)	Expected (at.%)
S	40.911	26.569	28.130
Sn	48.489	34.767	34.707
Cu	10.600	38.664	37.163

films so prepared show that they are polycrystalline, and have essentially the same structure as the base compound. However, an electron-probe microanalysis (JOEL JSM-35 scanning electron microscope with microprobe attachment) showed that the films are deficient in copper as detailed in table 1, and labelled as type A films. The copper content of the films were therefore subsequently improved by using a double evaporation technique, in which the Cu_2SnS_3 powder was evaporated in an atmosphere of copper at a temperature of about 1373 K, at a vapour pressure of about 3×10^{-6} Torr [3]. Such films were found to be much more stoichiometric as also shown in table 1 and labelled as type B films.

Room temperature transmission measurements were made in a Varian 2300 double beam spectrophotometer in the spectral range 350–800 nm. Film thickness was determined with a Talystep instrument (Rank Taylor Hobson).

Schottky type diodes were fabricated by evaporation of an aluminium film, whose thickness ranged between 0.6 and 1.0 µm, on glass slides. This was followed by the deposition of a Cu_2SnS_3 film of dimension 5×6 mm and 3–4 µm thick, on substrates heated to 523 K. The top contact was made of vacuum evaporated indium (~ 0.14 µm thick) which has a solar transmittance of about 70%. Ohmic contact was made to this with very fine silver wire and silver dag. A tungsten halogen lamp with 100 mW/cm² incident radiation was used for the photo I–V measurements with the devices held at about 300 K. The lamp was calibrated with a solar meter (Dodge products, model 776).

3. Results and discussion

3.1. Absorption spectra

Fig. 1 shows the variation of absorption coefficient, α, with wavelength for the copper deficient (type A) and stoichiometric (type B) Cu_2SnS_3 films respectively. The α values were obtained by the direct ratio of the transmitted radiation (T), by two samples of thickness $x = 0.16$ µm and 0.37 µm for type A and $x = 0.173$ µm and 0.325 µm for type B films, which were used in the equation:

$$T_1/T_2 = e^{-\alpha(x_1 - x_2)}.$$

Fig. 2 shows the square root of the absorption coefficient against photon energy for the two sets of films. Plotted in this way, the curves display the well-known
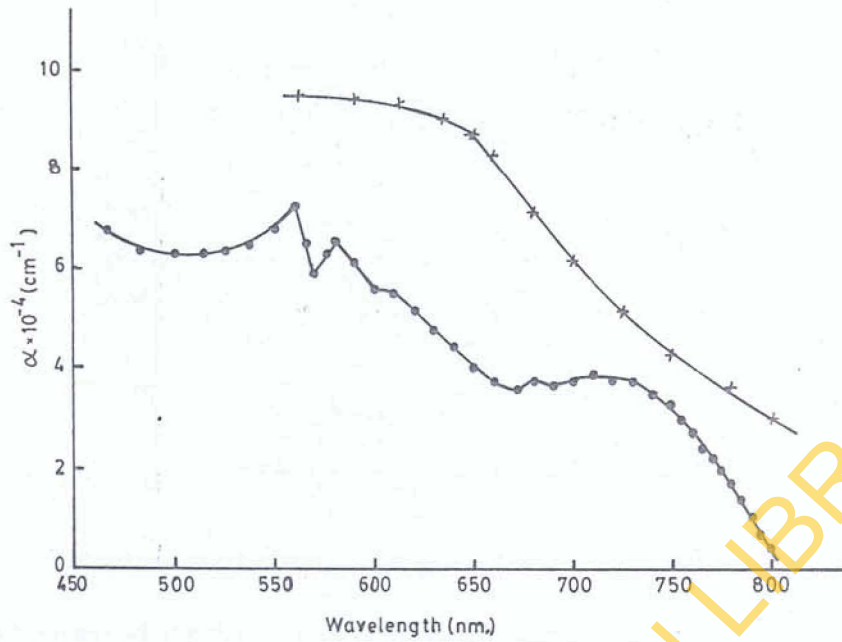
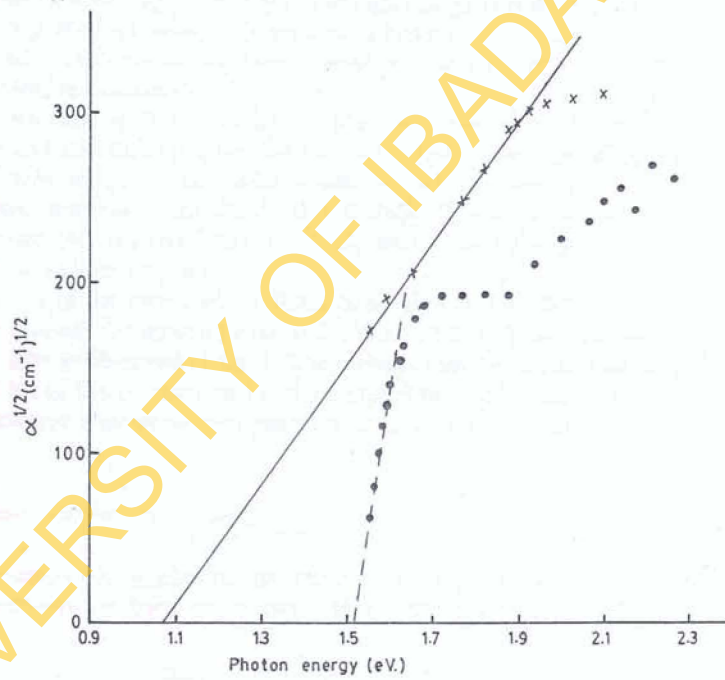Fig. 1. Variation of absorption coefficient with wavelength for type A (×) and B (●) films.

Fig. 2. The dependence of the square root of the absorption coefficient on photon energy (eV) for type A (×) and B (●) films.
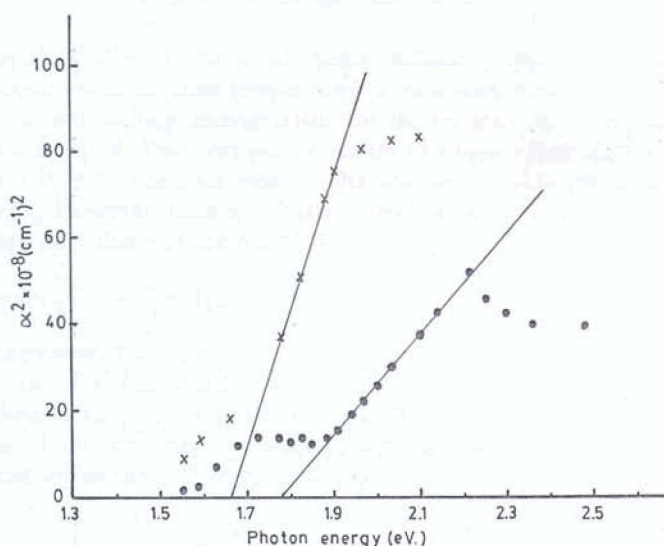
Fig. 3. Variation of α^2 against photon energy for type A ($\times$) and B ($\bullet$) films.

linear dependence associated with absorption at an indirect gap, with corresponding indirect energy gaps of 1.065 and 1.510 eV for type A and B films respectively. However a plot of the square of the absorption coefficient against energy, shows also a linear relationship especially in the high energy regime as shown in fig. 3. This indicates that the high energy absorption in both sets of films may be characterised by direct edge absorptions, with corresponding edges at 1.658 and 1.770 eV for type A and B films respectively.

It is worth noting that both sets of films are characterised by high absorptivity ($\alpha > 10^4$) and also that both the indirect and direct absorption edges are well placed in the visible range of the solar spectrum, which when compared with other photovoltaic materials like Cu_2S and $CuInS_2$ (having absorption edges in this energy range [4]) suggests that Cu_2SnS_3 may also be a suitable candidate for photovoltaic cell development.

The values of the direct and indirect band gaps in type B films are about equal. The well resolved absorption peaks at 2.138 and 2.214 eV are evident in the spectra of type B film as observed in fig. 1. These peaks may be due to transitions to higher energy states in the conduction band generated probably due to spin orbit splitting of the electronic state of the component atoms. This will be further verified in future studies.

3.2. Schottky barrier cells

For the diode configuration, only the behaviour of type B films with stoichiometric compositions has been investigated. Hot probe conductivity type measurements

on such films show them to be p-type semiconducting, while a four point probe resistivity measurement at room temperature gives a resistivity of 1.74 Ω cm.

A typical current–voltage characteristic for the In–Cu$_2$SnS$_3$ contact at $T = 300$ K is as shown in fig. 4. Two sections are easily distinguishable: (i) for $V < 0.25$ V and (ii) for $V > 0.25$ V. These sections are characterised by different current–voltage dependences [5]. However, both are characterised by an exponential relationship of current density on voltage of the form [6]

$$J = J_s\left[\exp(qV/nkT) - 1\right],$$

where the components have their usual meanings.

The diode factor n was calculated to be 1.87 for region I and $n = 3.4$ for region II. These values allow us to speculate (since only data at 300 K are available) that regions I and II are governed by space charge region generation–recombination, and thermionic emission mechanisms respectively [7].
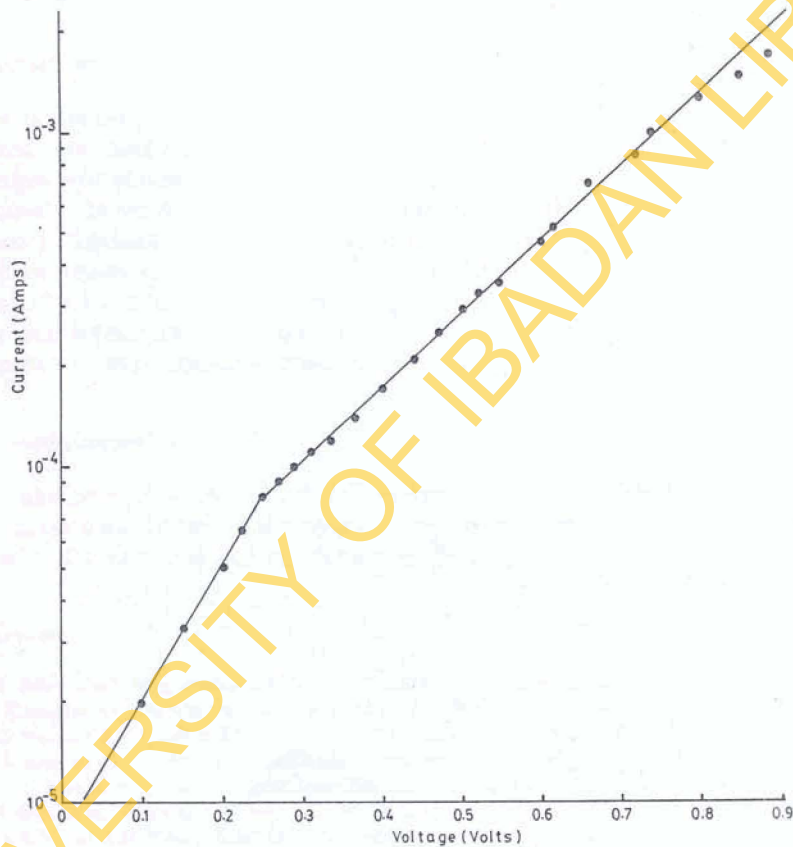

Fig. 4. Dark I–V characteristics of the In–Cu$_2$SnS$_3$ Schottky barrier cells.

The saturation current, J_s, was extrapolated to be 8.0×10^{-6} A/cm^2. This was employed to calculate the barrier height ϕ from the relation [8]

$$J_s = AR \frac{m^*}{m_0} T^2 \exp\left(-\frac{\phi}{kT}\right),$$

where A is the rectifying area, R is the Richardson constant and $m^* \simeq 0.1 m_0$ [8]. ϕ was obtained to be 0.73 eV at 300 K.

For typical rectifying areas of 0.22 cm^2, the cells are observed to be characterised by an open circuit voltage of 0.17 V, a short circuit current of 0.3 mA and a fill factor of 0.48, giving an efficiency of about 0.11%. This low efficiency is believed to derive from the poor ohmic contact at the collector junction, and the low quality barrier layer at the top contact. Though somewhat limited in its overall behaviour, the Cu_2SnS_3 Schottky barrier cell has shown good stability. No degradation has been observed for the devices tested, even after being heated to about 373 K under room temperature environmental condition for periods of over 24 h. These are encouraging observations especially if the cell output can be significantly increased.

4. Conclusions

Our investigation of the absorption properties of stoichiometric thin films of Cu_2SnS_3 show that the films are characterised by both indirect and direct absorption edges well placed in the visible region of the spectrum at 1.510 and 1.770 eV respectively. There is a shift in these edges to lower photon energies with copper deficiency. Schottky type diodes fabricated from stoichiometric films show promising photovoltaic characteristics, with open circuit voltage of 0.17 V, a short circuit current of 0.3 mA and a fill factor of 0.48, for a rectifying area of 0.22 cm^2, thus giving an efficiency of 0.11%. We hope that improved efficiency may be obtainable with improved deposition and contacting methods.

Acknowledgements

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