

OPTICAL PROPERTIES AND DEFECT CHEMISTRY OF p -CuInS₂

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(Received 15 December 1983; accepted in revised form 1 March 1984)

Abstract—The absorption and photoconductivity spectra of p -CuInS₂ single crystals, grown by chemical vapour transport method, were obtained at 76 and 300 K. An acceptor level at about 150 meV, observed in as-grown and sulphur annealed samples of p -CuInS₂, has been attributed as due to copper atoms on indium sites. Also, a donor level at about 30 meV is observed, which could be identified with sulphur vacancies.

INTRODUCTION

Of the large group of ternary chalcopyrite semiconductors, CuInS₂ is of considerable interest because it has a direct energy gap of about 1.5 eV at room temperature [1], which is very near the optimum value for efficient solar energy conversion [2]. This material can also be made both n - or p -type conducting [3], which makes it a strong candidate for photovoltaic devices. Although theoretical calculation predicts an efficiency of about 30% for the CuInS₂ homojunction [4], a maximum efficiency of only 15% has been reported in literature for photocells [5]. For this reason, a detailed knowledge of the optical properties related to the defect chemistry is necessary. This is because the spectral dependence of the absorption coefficient affects the solar conversion efficiency. In spite of this importance, the information about the defect states obtained from optical studies, especially from photoconductivity measurements, are scarce. Furthermore, some controversy exists concerning the origin of intrinsic defects observed in this compound.

In this paper, the absorption and photoconductivity spectra of as-grown (S1) and annealed samples of p -CuInS₂ in vacuum (S2) and sulphur atmosphere (S3) have been studied. From the analysis of the spectra obtained at 300 K and at liquid nitrogen temperature, which is 76 K in Mérida, situated at 1600 m a.s.l., the ionization energy of defect levels has been determined and their possible origin has been suggested.

2. CRYSTAL GROWTH AND EXPERIMENTAL DETAILS

The synthesis of CuInS₂ was made by a direct high temperature reaction of the elements whose initial purity was at least 5N. This was used to grow single crystals by chemical vapour transport method using iodine as the transporting agent. The source material was sealed in an evacuated ($\sim 10^{-5}$ Torr) silica tube of 2 cm in diameter and 20 cm long with approximately 8 mg/cm³ of iodine. The tube was placed in a horizontal furnace with a temperature gradient of about 12 K/cm between the hot zone at 1110 K and the cold zone at 960 K. The time of growth was approximately 10 days. The resulting crystals had good reflecting surfaces with typical dimensions of about $10 \times 5 \times 0.5$ mm³. All these samples were p -type con-

ducting as measured by a thermal probe. X-Ray powder analysis taken at room temperature showed a chalcopyrite tetragonal structure with the lattice parameters $a = 0.556$ nm and $c = 1.119$ nm. Thermal treatments performed on the samples included annealing in vacuum and in the presence of sulphur at 773 K for 36 hr.

The crystalline samples used in this study were mechanically polished by diamond powder of variable grain size. Later they were etched in 1:1:1 solution of H₂O, HNO₃, HCl for about ten seconds and then washed with distilled water. Electrical contacts were made by evaporating gold. The contacts were ohmic within the range of interest.

For both transmittance and photoconductivity measurements, a tungsten lamp and a Hilger Watts D330 monochromator, with a diffraction grating of 600 lines/mm were employed. A slit of 1 mm guaranteed a resolution of 5 nm, which corresponds to about 10 meV in the energy range of interest. A PAR 124A lock-in amplifier was used to measure the signal. The circuits used to obtain the photoconductivity and the transmission spectra are similar to those described elsewhere [6, 7].

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Optical absorption

The absorption coefficient, α , was calculated from the transmission spectrum by means of the well-known relation:

$$I = \frac{I_0(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad (1)$$

where I , I_0 , d and R have their usual significance [8]. The reflectivity value used was 0.28 as given in [6].

The absorption spectra of three samples, that is, S1, S2, and S3 of p -CuInS₂ at 76 K, are shown in curves A, B and C respectively, in Fig. 1. The rise of α starting at about 1.48 eV in all curves can be attributed to be mainly due to the band gap. However, we were not able to determine the energy gap precisely because of the presence, especially in the samples S1 and S3, of additional absorption processes probably due to defect levels.

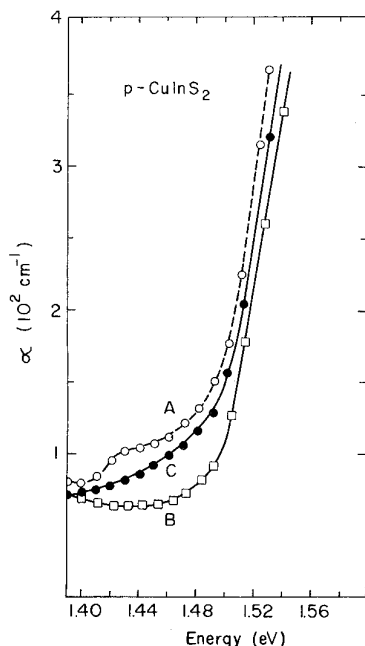


Fig. 1. Absorption spectra for p -CuInS₂ at 76 K: (A) as-grown (sample S1); (B) annealed in vacuum (sample S2); (C) annealed in sulphur atmosphere (sample S3).

The analysis of curve *A* shows that, in the energy range $1.39 \lesssim h\nu \lesssim 1.49$ eV, the absorption can be attributed as due to an acceptor-to-conduction band transition which is given by the expression [9]:

$$\alpha_{ac} = \frac{B(h\nu + E_A - E_G)^{1/2}}{h\nu[1 + (m_e^*/m_h^*)E_A](h\nu + E_A - E_G)^4} \quad (2)$$

where E_A is the acceptor ionization energy, E_G is the direct energy gap, m_e^* and m_h^* are the electron and hole effective masses, respectively, and B is a constant nearly independent of the photon energy.

The value $E_G - E_A = (1.35 \pm 0.01)$ eV is obtained by fitting the experimental points to the eqn (2).

The fundamental absorption spectrum, α_G , of the sample S1 can be found by subtracting the additional absorption coefficient, given by eqn (2), from the measured α value of the curve *A*. This is shown in Fig. 2 as a plot of $(\alpha_G h\nu)^2$ vs $h\nu$. An analysis of the curve shows that α_G can be described by the relation:

$$\alpha_G = \frac{A_G}{h\nu} (h\nu - E_G)^{1/2} \quad (3)$$

which corresponds to an allowed direct transition between parabolic bands [10].

Extrapolating the straight line portion of the plot to $\alpha_G = 0$, we find an energy gap $E_G = (1.50 \pm 0.01)$ eV at 76 K.

The acceptor ionization energy can then be calculated, and the obtained value, $E_A = (0.15 \pm 0.01)$ eV, is in very good agreement with the values 0.15 [11–13] and 0.17 eV [6], reported by other authors.

3.2 Photoconductivity

The photoconductivity spectra of p -CuInS₂ sample S1 at 300 and 76 K, are shown in curves *A*, *B* and *C*, respectively, of Fig. 3. It can be observed that the spectra at 300 K of samples S1 and S3 are very nearly identical. The photoresponse curves show three well-defined peaks in the wavelength range from 0.75 to 0.95 μ m. The main peak in all curves can be associated to the band gap of the material. The energy gaps, as determined by using the Moss criteria, which establishes that the wavelength corresponding to the band gap is that at which the photoresponse falls to half its maximum value [14], are (1.49 ± 0.01) eV at 300 K for samples S1 and S3, and (1.51 ± 0.01) eV at 76 K for the sample S3. The later energy gap value is nearly identical to the value obtained previously from absorption measurements.

A second peak is observed at 1.35 eV in all curves. This gives an average ionization energy of (0.15 ± 0.01) eV, which is in agreement with the value obtained for the acceptor level from absorption measurements.

A third peak is observed at 1.46 eV for samples S1 and S3 at 300 K, and at 1.48 eV for sample S3 at 76 K. This peak can be attributed to a shallow level with a corresponding ionization energy of about 30 meV. The fact that this level is not observed in our absorption measurements suggests that its origin could be due to a donor state. This is consistent with a donor state of about 35 meV reported in the literature [12, 13].

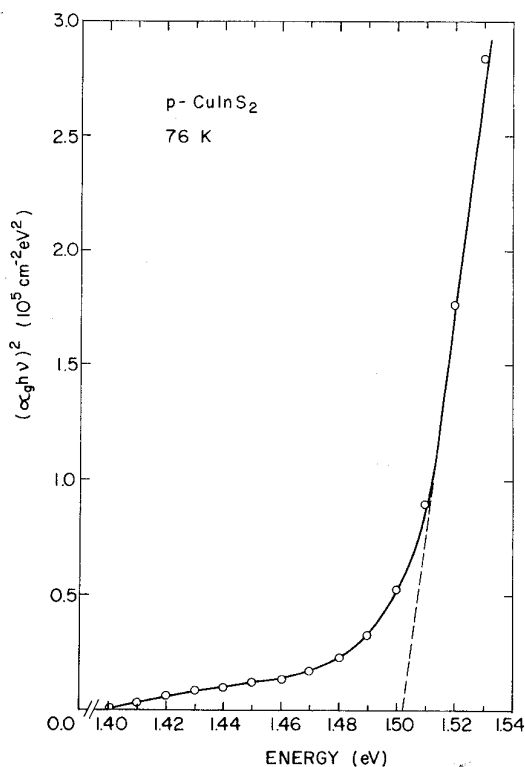


Fig. 2. Fundamental absorption spectrum for as-grown p -CuInS₂ (sample S1) at 76 K.

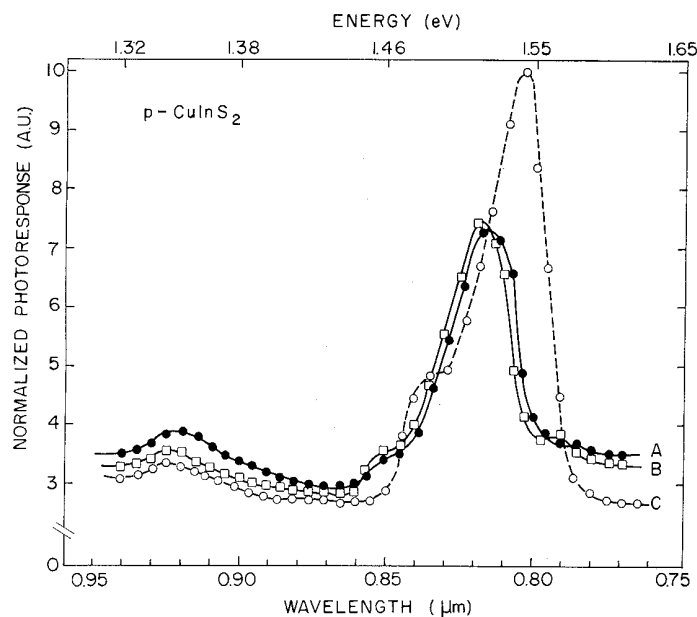


Fig. 3. Photoconductivity spectra for p -CuInS₂: (A) as-grown (sample S1) at 300 K; (B) annealed in sulphur (sample S3) at 300 K; (C) annealed in sulphur (sample S3) at 76 K.

3.3 Defect levels in CuInS₂

It is possible to speculate on the origin of the defect levels in CuInS₂. The acceptor level at about 0.15 eV identified by several authors, possibly due to V_{Cu} [11, 15], has recently been attributed by Binsma rather convincingly as due to either V_{In} or Cu_{In} [12]. Figure 1 shows that the additional absorption associated with this level tends to decrease by annealing in vacuum. This indicates that we can exclude the possibility of V_{In} , because annealing in vacuum should result in the increase of V_{In} [16]. If so, this also should increase the additional absorption below the band gap. However, such increase is not observed, which suggests that the acceptor level is due to Cu_{In} . On the other hand, this assignment is in agreement with the observed behaviour in Fig. 1, because annealing in vacuum might reduce Cu_{In} due to the migration of copper atoms to its natural sites.

The donor level at about 30 meV has been attributed to V_S or In_{Cu} [12]. The assignment of this shallow level to V_S is in agreement with the fact that a net loss of sulphur is expected by annealing in vacuum [16], which would create V_S in CuInS₂.

4. CONCLUSIONS

Absorption and photoconductivity studies show that an acceptor and a donor levels, with ionization energies of about 150 and 30 meV, dominate the optical properties of p -CuInS₂ single crystals grown by chemical vapour transport method. From the analysis of the data, it is suggested that these acceptor and donor levels could be due to copper atoms on indium sites and sulphur vacancies, respectively.

Acknowledgements—The present investigation has been carried out with financial support from “El Consejo de Desarrollo Científico y Humanístico (C.D.C.H.) de la Universidad de Los Andes”.

The authors wish to thank Professor S. M. Wasim for valuable discussion, and Tec. Freddy Sánchez for the technical assistance.

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