

Photoluminescence of Se-annealed CuInSe₂ powders

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CuInSe₂ (CIS) has been the topic of much research work, especially in the area of thin film solar cell applications. It has been established that the electrical and optical properties of this compound are dominated by the presence of intrinsic defects such as vacancies, interstitials and antisite defects and their complexes. Unfortunately the position of defect levels and the identification of observed levels are still matters of controversy. This is partly due to the difficulties of preparing materials with a reproducible stoichiometry and defect chemistry.

The deviations from the ideal chemical formula of CIS can be described using two parameters, the so-called molecularity ΔX and stoichiometry ΔY parameters, which are defined as [1, 2]:

$$\Delta X = ([\text{Cu}]/[\text{In}]) - 1 \quad (1)$$

$$\Delta Y = (2[\text{Se}]/([\text{Cu} + 3[\text{In}]]) - 1 \quad (2)$$

It is obvious that the defect structure and the electrical and optical properties of CIS depend directly on the values of ΔX and ΔY . Despite the numerous investigations carried out on the properties of CIS, very little information is known about the effects of systematic compositional deviation on the properties and defect structure of CIS. One possible reason for that is that the high-temperature defect structure is often corrupted by the cooling of the material. Thus the low-temperature defect structure becomes a function of ΔX , ΔY and the cooling rate. To avoid this problem it is better to use a material that can be cooled very rapidly to freeze the high-temperature defect equilibrium. According to [3, 4], rapid cooling is possible for powder samples. Photoluminescence spectroscopy is the best method for studying the defect structure of this powder material. Up to six different photoluminescence (PL) bands have been reported in CuInSe₂ [5-8]. The majority of papers concerning the effect of compositional differences on the PL properties of CIS deal with the role of the Cu/In ratio (ΔX). It has been established that the PL spectra of CIS are extremely sensitive to the molecularity ΔX [5-7]. Less information is known about the role of stoichiometry, ΔY . In this letter we report the results of photoluminescence measurements of CIS powders, prepared under different vapour pressures of selenium, i.e. at different stoichiometries, ΔY .

CIS powder was synthesized inside highly evacuated quartz ampoules. Calculated amounts of the elements were weighed with accuracy of $2 \times 10^{-3}\%$.

The material was slowly heated to above the melting point of the compound, held at 1000 °C for 3 h, then the furnace was slowly cooled to 800 °C. After that the material was kept at 800 °C for more than 4 h to ensure homogenization then slowly cooled to room temperature. The CIS ingot was removed from the quartz ampoule and ground into powder in a porcelain mortar. X-ray analysis of this powder certified the existence of the chalcopyritic CIS phase. No other phases were observed. From the energy dispersive spectroscopy (EDS) analysis the molecularity and the stoichiometry of the starting powder were found to be $\Delta X = 0.21$ and $\Delta Y = 0.06$. The thermal probe technique was used to determine the conductivity type of the samples. The synthesized powder had p-type conductivity. The powder was then heated in an evacuated quartz ampoule in a two-zone furnace with elemental selenium at the lower temperature end. For Se-annealing, the following formula was used to calculate the total selenium vapour pressure [9]:

$$\log P_{\text{Se}_2} = 5.72236 - \frac{5486.17}{T} \quad (3)$$

where P_{Se_2} is in atm (1 atm = 1.013×10^5 Pa) and T is in K. The powder temperature was kept at 750 °C for 2 h, then the ampoules were rapidly cooled to room temperature and the powder was glued to a copper plate with a non-luminous glue. For the photoluminescence measurements, a 50 mW Ar-ion laser beam with a wavelength of 488 nm was used for excitation. The laser light was chopped at 277 Hz. The samples were mounted in a closed cycle He cryostat capable of cooling to 12 K. A computer controlled SPEX 1870 0.5 m grating monochromator with 3.2 nm spectral slit was used. The chopped signal was detected with an InGaAs detector, amplified by a low noise amplifier and a lock-in-amplifier. The emission spectra were corrected for grating efficiency variations and for the spectral response of the InGaAs detector.

Typical PL spectra of Se-annealed CIS, measured at 12 K with laser power density 6 W cm^{-2} are shown in Fig. 1. The PL spectra exhibited one asymmetrical emission band at 0.92 eV (1350 nm). The shape of this band did not depend on the partial pressure of selenium and only a slight shift of peak position was detected. According to [6], we call this band a K-band. If the laser power density was increased about 25 times (160 W cm^{-2}), a K-band shifted

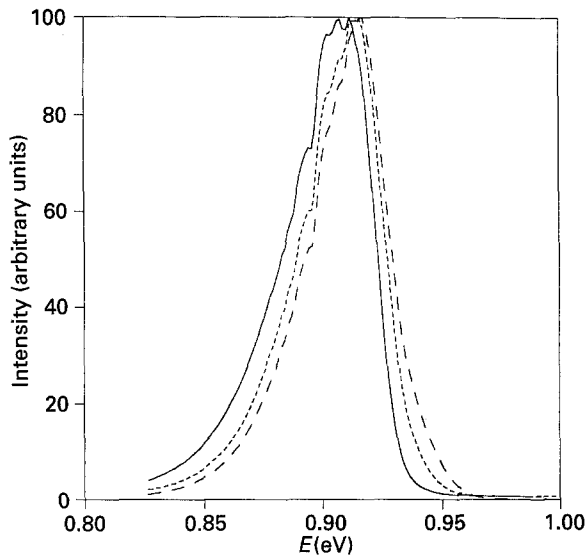


Figure 1 Normalized PL spectra of CuInSe_2 with selenium pressure: (—) 3.74×10^{-3} , (---) 3.42×10^{-2} and (-·-·-) 1.07×10^{-2} atm (1 atm = 1.013×10^5 Pa). $T = 12$ K.

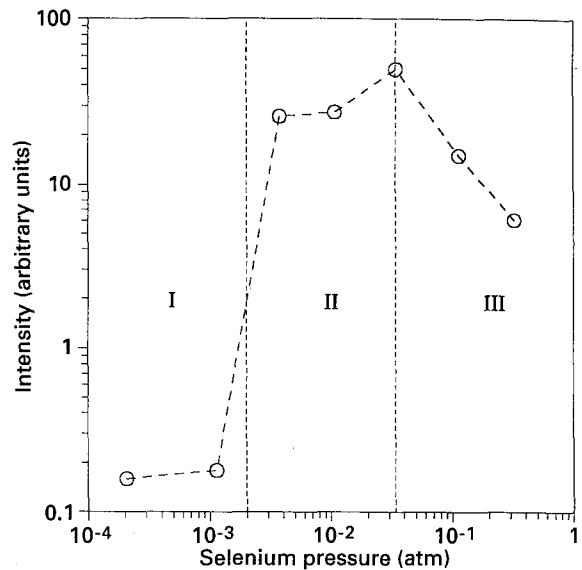


Figure 3 The intensity of the K-band as a function of the selenium pressure. (1 atm = 1.013×10^5 Pa.)

towards higher energies without any change of the shape and a new band at 0.96 eV appeared (J-band; see Fig. 2). The relatively intensive K-band in CIS PL spectrum seems to be typical of p-type materials [5–7]. The intensity of the K-band has a strong dependence upon the pressure of selenium, as can be seen from Fig. 3. The whole range of selenium vapour pressure may be divided into three regions. In the first region (low pressure region) the K-band is very weak. Also, the material prepared under minimum vapour pressure of selenium belongs to the first region. In the second region (middle pressure region) the intensity of the K-band increases abruptly and a slow increase is observed over the whole second region. At the highest selenium pressures (third region) the intensity of the K-band decreases inversely proportionally to the selenium pressure. This kind of dependence is also typical for II–VI semiconductors, where the abrupt changes in the intensity of PL bands are mostly connected with

changes of dominating charged defects and the position of the Fermi level [3, 4]. We may conclude that all three regions are characterized by different dominating charged defects, i.e. different electro-neutrality conditions.

The K-band is usually connected with donor–acceptor pairs, but there is uncertainty about the nature of these donor and acceptor defects. It is obvious that the observed j-shift can not be conclusive evidence for a donor–acceptor pair luminescence. Because of this we also measured the temperature quenching of the K-band (Fig. 4). In the case of the recombination luminescence the activation energy of thermal quenching E_T may be treated as the distance in energy of the defect level from the nearest band. The observed activation energy $E_T = 8.2 \pm 0.2$ meV indicates that there must be an extremely shallow level involved in the K-band emission. If we take $E_g = 1.050$ eV [8] and $E_T = 8$ meV, then for peak position we get

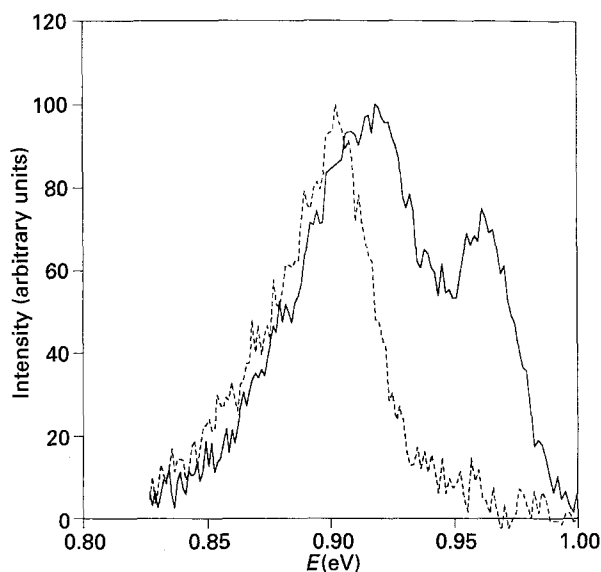


Figure 2 Normalized photoluminescence spectra of CuInSe_2 with excitation: (—) I_0 and (---) $25I_0$.

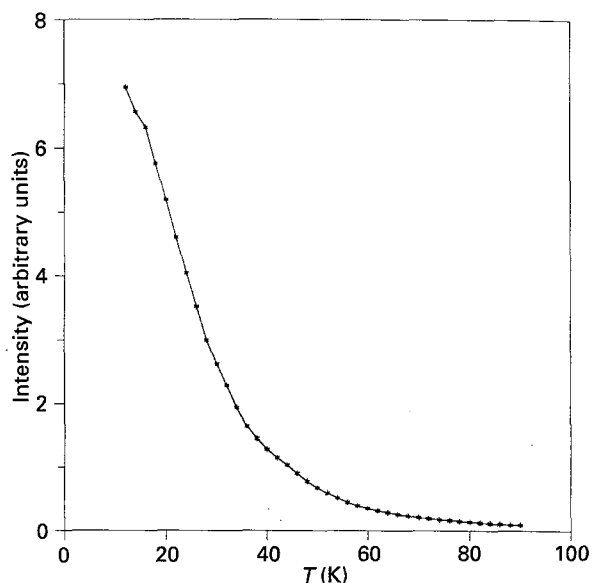


Figure 4 The intensity of the K-band as a function of the temperature. $E_T = 8.1$ meV.

$h\nu = E_g - E_T + kT = 1.043$ eV. This result is in conflict with the experimentally observed peak position $h\nu = 0.92$ eV, so we must presume that we have indeed a bound-to-bound transition. The shallow level 8 meV has also been observed in n-type CIS and it was attributed to a donor, probably In_{Cu} [10].

It is known that when the donor and acceptor defects approach one another, their energy levels begin to push apart. Because in our samples we have frozen the high-temperature ($T = 750$ °C) defect structure, the presence of donor-acceptor pairs with large distances is improbable because of the high thermal energy and only the random distribution dominates for distant pairs. In the case of close DA donor-acceptor there is always a possibility that the level of the shallowest defect is forced into the nearest band, so in our case we must presume that we are dealing with relatively deep donor and acceptor levels. Further experiments will be conducted to clarify the chemical nature of these levels.

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