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TEMPERATURE-RESOLVED PHOTOLUMINESCENCE STUDIES OF $CuInSe_2$

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Photoluminescence (PL) studies of $CuInSe_2$ powders, as function of temperature, have been performed. At low temperatures the k-band, centered at $h\nu_{max} \approx 0.92$ eV dominates the PL intensity. Increasing the temperature leads to rapid quenching of the intensity k-band and thus the j-band with $h\nu_{max} \approx 0.95$ eV appears. The calculated activation energies of temperature quenching for j-band lie near 20 meV value and seems to have a tendency to increase with an increasing of selenium vapour pressure. The phonon-broadening analysis of the j-band indicates, that the radiative recombination is accompanied by the emission of 3.4 phonons with mean energy of 10.23 meV. The j-band is concluded to be associated with donor-acceptor recombination from donor level $E_D = 60$ meV to acceptor level $E_A = 20$ meV.

Keywords: A. semiconductors, C. point defects, D. electron–phonon interactions, E. luminescence.

$CuInSe_2$ (CIS) is widely used in producing low-cost and high efficiency $CdS/CuInSe_2$ heterojunction solar cells. However, the general state of understanding of CIS and CIS-based solar cells is not sufficient at present. An improvement of this understanding can be achieved by continued research into both the basic properties of CIS and the relationship of CIS properties to device performance. It is obvious that most of the CIS optoelectronic properties are governed by point defects in the crystal lattice. Achieving good control over the defect formation seems to be a possible way to improve CIS properties. Unfortunately there is no sufficient information about point defects and their formation processes in CIS. Additional research in this area may well be a necessary step to the final improvement of CIS-based solar cells.

The photoluminescence (PL) spectroscopy is one of the most effective and simple methods to examine defects in semiconductors. A review and interpretation of PL data acquired by a number of groups on both single-crystal and polycrystalline CIS can be found in [1–3]. Our analysis of those data indicates that in many cases the interpretation of PL spectra was affected by the presence of strong absorption lines of water vapour. Therefore major attention is needed to process correctly the PL spectra. It is generally accepted that the PL spectra of CIS have a strong dependence upon the composition of the material. In indium-rich and nearly stoichiometric materials the low-temperature PL spectrum of CIS consists of two bands: the j-band at 0.95 eV and the k-band at 0.92 eV, while in Cu-rich materials the i-band at 0.98 eV dominates [1–6]. The origin of these bands is still abstruse and further studies will be needed to elucidate the physical mechanism of recombination. In this paper we report the results of temperature resolved PL measurements of In- and Se-rich CIS powders.

The CIS powder was synthesised inside highly evacuated quartz ampoules. Calculated amounts of elements were weighed with an accuracy of 2×10^{-3}%. The material was slowly heated to above the melting point of the compound. A temperature of 1000°C was held for 3 h, then the furnace was slowly

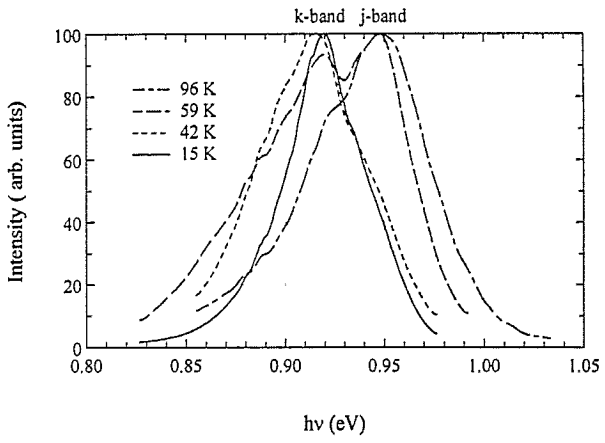

Fig. 1. Normalized PL spectra of $CuInSe_2$ powder sample ($P_{Se_2} = 0.34$ atm) at different temperatures.

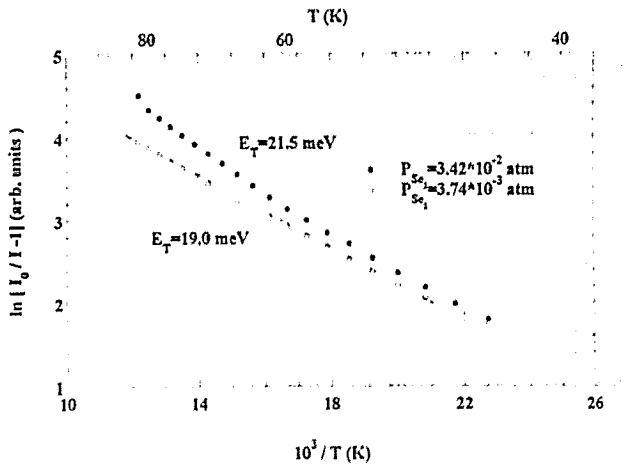

Fig. 2. Temperature quenching of the PL intensity of the j-band of two CIS powder samples, and linear fits for equation (1).

cooled to 800°C. After that the material was kept at 800°C more than 4 h to ensure the homogenization of the samples and then slowly cooled to room temperature. The CIS ingot was removed from the quartz ampoule and ground into powder in a porcelain mortar. The X-ray analysis of this powder ascertained the existence of the chalcopyritic CIS phase. No other phases were observed. The powder was then heated in an evacuated quartz ampoule in a two-zone furnace with elemental selenium at the lower temperature end. In this way small compositional changes in the material could be effected by changes in the selenium vapour pressure inside the heat treatment ampoule [7]. The powder temperature was kept at 750°C for 2 h. Then the ampoule was rapidly cooled to room temperature and the powder was glued to a copper plate with a non-luminous glue. In the PL 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 down to 12 K. A computer controlled SPEX 1870 0.5 m grating monochromator with a spectral slit of 3.2 nm 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, for water vapour absorption and for the spectral sensitivity of the InGaAs detector.

As an illustration, Fig. 1 shows normalized PL spectra of a CIS powder sample measured at four different temperatures from $T = 15$ K to $T = 96$ K. At low temperature the k-band centered at $h\nu_{max} \approx 0.92$ V dominates. An increase of T leads to a rapid quenching of the k-band emission intensity and thus the j-band with $h\nu_{max} \approx 0.95$ eV becomes visible. The activation energy of this quenching $E_T = 8.2 \pm 0.2$ meV determined earlier [7] indicates that there must be an extremely shallow level involved in the k-band emission. This shallow level has been observed on n-type CIS only and attributed to a donor, probably In_{Cu} [4, 8]. In this work we investigated and analysed the quenching of the j-band.

As it can be seen from Fig. 2, the j-band intensity decreases with temperature according to Mott's formula

$$I(T) = I_0/[1 + \alpha \exp(-E_T/kT)], \quad (1)$$

where I_0 is the PL intensity without quenching ($T \to 0$), α is a constant and E_T is the activation energy. For the external quenching mechanism the E_T is a thermal energy of hole or electron ionization from a centre level to the nearest energy band. The fitted activation energy for the j-band is approximately $E_T = 20$ meV and seems to have a tendency to increase with increasing selenium vapour pressure, see Fig. 2. This activation energy approximately coincides with the shallowest observed acceptor level at $E_a = 12$–30 meV, assigned to V_{Cu} [8]. The identification of these levels is not yet final and several candidates for them have been proposed.

Analysis of the PL spectra reveals that a phonon-broadening of PL bands also takes place when temperature increases. The traditional method of analysis of electron–phonon interaction in case of PL bands with relatively large halfwidths and without phonon structure is to compare the experimentally measured temperature dependence of the luminescence band half-width $W(T)$ with the theoretical one, expressed as [9]

$$W(T) = W(0)^*[\coth(\hbar\omega_e/2kT)]^{1/2}, \quad (2)$$

where

$$W(0) = 2(2\ln 2)^{1/2} S^{1/2} \hbar\omega_e. \quad (3)$$

is the half-width at 0 K, $\hbar\omega_e$ is the interacting "effective" phonon energy in the excited state of the luminescence centre, and S is the average number of phonons emitted per transition. Although equation (2) is an approximation, especially the use of only one single "effective" phonon instead of entire phonon spectrum, it often fits experimental data quite well in many semiconductor compounds [9, 11–13]. Also, there is some ambiguity in using equation (2) in case of asymmetrical PL bands because, according to the theory [9], equation (2) is strictly valid only for a symmetrical Gaussian line shape. Both the k- and the j-band spectra for our samples have a Gaussian high energy side and an exponential low energy tail. This kind of shape is possible if the phonon broadening is accompanied by another effect, mainly affecting the low energy side of the PL bands. Taking into account the peak position of the j-band and the magnitude of the observed thermal quenching energy E_T it is reasonable to assume that the j-band is associated with donor–acceptor pair recombination. In this case the spectrum shape should include effects of both the phonon broadening and of the donor–acceptor pairs. According to theory [9, 14] the Gaussian high-energy side of the PL band indicates that the phonon broadening is stronger than the pair distribution effect. In this case the half-width determined by analysing the high-energy side of the PL band instead of the "true" half-width can be used in phonon-broadening analysis.

In order to find a half-width and a peak-position of the j-band we used a method, suggested by Treptow [10]. In this method the PL spectra are first converted to

$$I'(h\nu) = \frac{\partial[\ln I(h\nu)]}{\partial h\nu}. \tag{4}$$

If the original spectrum $I(h\nu)$ has a Gaussian shape, then $I'(h\nu)$ will be a straight line. The half-width W and the position of the maximum of the band $h\nu_{\max}$ can be determined from the slope of this straight line and from the intersection with the $h\nu$-axis, respectively. It is obvious that this method tends to give a half-width W, which is smaller than the "true" half-width of this asymmetrical PL band. The results thus obtained are shown as open circles in Fig. 3. It can be seen that the temperature dependence of the half-width of the j-band is well represented by equation (2) with $W(0) = 44.44$ meV, $\hbar\omega_e = 10.23$ meV and $S = 3.4$. It is also of interest to observe (cf. Fig. 3) that the measured temperature dependence $h\nu_{\max}(T)$ is given by the expression

$$h\nu_{\max}(T) = 0.8878 + W(T), \tag{5}$$

i.e. it has the same origin as $W(T)$. This affirms once again that the conduction or valence band states are

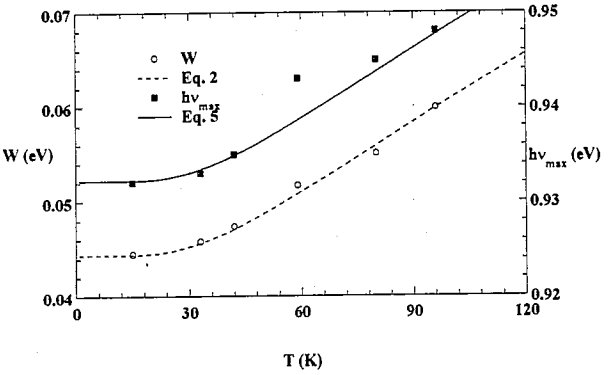

Fig. 3. Experimentally determined temperature dependencies of the j-band half-width $W(T)$, fitted with equation (2) (broken line), and of the j-band peak position $h\nu_{\max}(T)$, fitted with equation (5) (continuous line), respectively.

not involved in the j-band emission. One can estimate the Stokes shift $2S\hbar\omega = 69.6$ meV and the zero-phonon transition energy $h\nu_0 = h\nu_{\max} + S\hbar\omega = 0.967$ eV at 15 K, assuming that the phonon energies in the ground state and in the excited state are equal. These results indicate, that the excited state of the j-centre lies in the forbidden gap and is probably connected with the donor level of a DA pair. The depth of this donor level will be $E_D \approx E_g - h\nu_{\max} - E_T = 1.03 - 0.95 - 0.02 = 0.06$ eV. The donor level $E_D = 60$ meV is well known in CIS and has been attributed to V_{Se} [4]. The "effective" phonon energy $\hbar\omega_e = 10.23$ meV observed here corresponds to $\nu = 82.5\,\text{cm}^{-1}$. According to Neumann [15] the low-energy phonon modes (near $82\,\text{cm}^{-1}$) in CIS are connected with B_2 [3] mode with $\nu_{LO} \approx 70\,\text{cm}^{-1}$ and with an E^5 mode. The latest Raman studies [16] have shown, that the phonon mode at $\nu = 76\,\text{cm}^{-1}$ corresponds to the lowest energy B_1 mode. In [17] the low-temperature Raman mode at $\nu = 78\,\text{cm}^{-1}$ was found and it was also connected with an E^5 mode.

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