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Photoluminescence and the tetragonal distortion in $CuInS_2$

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Abstract

Low temperature photoluminescence (PL) measurement of a deep–donor–deep–acceptor (DD–DA) pair recombination emission of close DA pairs in $CuInS_2$ at $h\nu = 0.62$ eV reveals two well resolved lattice vibrational modes, of energy $\hbar\omega_1 = 40.5$ meV and $\hbar\omega_2 = 8$ meV. Furthermore, the recombination emission has an additional fine structure of $\Delta E = 2$ meV. It appears that the 2 meV fine structure can be interpreted as being due to a small difference in the DA separation between two otherwise equivalent interstitial donor sites. This is due to the tetragonal lattice distortion in the $CuInS_2$ structure. The measured full width at half maximum, inclusive of instrumental resolution, of these two zero-phonon-emission lines was approximately 0.6 meV at $T = 8$ K.

Keywords: Luminescence; Donor-acceptor pairs; CuInS2; Zero-phonon lines; Phonons

1. Introduction

It is known that the $CuInS_2$ chalcopyrite lattice may be considered as a 'distorted double zincblende lattice', with the lattice parameter $c > 2a$. As a result of this, some point-to-point distances within the lattice, as compared with the corresponding zincblende structure, now appear as slightly differing doublets. If the crystal contains donor-acceptor pairs (DAPs) then these slightly different DAP separations are expected to lead to distinctly different emission line positions also. This may not be easy to observe experimentally, since close donor-acceptor pairs often give rise, as a rule, to very wide photoluminescence (PL) bands, but with an increasing distance between the donor and acceptor defects the average electron-phonon coupling decreases and at some critical distance it is possible to find narrow zero-phonon lines (ZPLs).

In [1] the systematic experimental study of some deep PL bands in $CuInS_2$ and $CuGaSe_2$ was performed. It was found that in $CuInS_2$ the so-called D1 and D2 PL bands, having a peak positions at $h\nu = 0.954$ and 0.864 eV respectively, are caused by the recombination within a deep–donor–deep–acceptor (DD–DA) complex. The underlying model was that the D1 and D2 bands are formed via a DAP recombination between pairs of the closest neighbours, and between pairs of the next-closest neighbours, respectively. Later even deeper PL bands were found in many ternaries, corresponding, in the same model, to the next larger distances between the deep-donor and the deep-acceptor [2]. Moreover, in the same way as in GaP or ZnSe, we should also observe zero-phonon lines (ZPL) corresponding to the distant pair PL. Due to the fact that in our case both defects in the DAP are deep centres, there is practically no overlap of the electron and hole wave functions for too distant pairs. Therefore, it is unlikely to see any PL lines for DAPs above some critical distance. In GaP the first ZPL lines were observed starting from distances $r \approx 7$–8 Å. [3] In ZnSe this distance was even bigger, $r \approx 13$–14 Å [4]. In both of these 'classical' materials at least one component of DAP was a relatively shallow defect and therefore, the DAP ZPLs had an observable intensity up to distances of $r \approx 30$–40 Å. In polycrystalline $CuInS_2$ we observed

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a weak PL emission corresponding to the DAP distances $r \approx 4.5$ Å [2]. Here we report about the fine structure of this emission in $CuInS_2$.

2. Experimental

The polycrystalline $CuInS_2$ material was synthesized from a stoichiometric mixture of the constituent elements (5 N-purity). The ampoule, sealed with the starting materials was heated up to 1360 K in a tunnel furnace and held for 3 h After that, the temperature was lowered to 1110 K and held for 12 h, followed by a cooling of the furnace to room temperature. Small pieces with a size approximately 2 mm were broken off the ingot for annealing and/or photoluminescence studies. The Cu annealing was arranged in small evacuated quartz ampoules containing some $CuInS_2$ pieces and a 5 N-purity Cu piece. The annealing time was 12 h and the annealing temperatures were 670 or 770 K. Finally a slow cooling to 470 K at a rate of 2–3 K/h was performed.

For the PL measurements reported here, a He-Cd laser with a wavelength of 441 nm was used for excitation. The samples were mounted inside a closed cycle He cryostat ($T = 8$–300 K). The PL spectra were recorded with a computer controlled SPM-2 grating monochromator ($f = 0.4$ m). The chopped signal was detected with an InGaAs or PbS detector using the conventional lock-in technique. The emission spectra were corrected for the grating efficiency variations and for the spectral response of the detectors.

3. Results and discussion

Our previous results show that in the case of very close DA pairs it is possible to calculate the approximate energy difference ΔE_{mn} between two DA pair emissions with the DA pair separations of r_m and of r_n, respectively [1,2], simply as:

$$\Delta E_{mn} = \frac{e^2}{\varepsilon}\left(\frac{1}{r_m} - \frac{1}{r_n}\right) \quad (1)$$

Here ε is the dielectric constant. In [1] we used Eq. (1) to calculate all possible energy separations ΔE for donor-acceptor pairs and compared them with the experimentally measured deep PL band positions in $CuInS_2$ and $CuGaSe_2$. This showed that the observed deep PL bands must be related to such DA pairs where one of the components (probably the donor) is located at an interstitial position. It is worth noting that there are two types of interstitial positions in the chalcopyrite lattice (i_1 and i_2). Taking the unit cell corners to be defined by the cations (i.e. at each corner a Cu ion), these interstitial positions have the coordinates (1/2; 1/2; 1/4) and (3/4; 3/4; 3/8), respectively. According to this model we calculated all possible distances between interstitial donor and acceptor at In or Cu sites and corresponding peak positions of PL bands, see Table 1. As the basis of our calculation we used the experimentally determined D1 band position 0.954 eV [1,2] and the dielectric constant value $\varepsilon = 8.67$. This value lies between optical and static values of ε in $CuInS_2$ (6.3–7.8 and 10.2, respectively [5,6]).

As it can be seen from Table 1, the most interesting PL bands (or pairs) are D4 and D5. Both DA pairs appear to have a donor defect at the interstitial position i_2 [2]. In $CuInS_2$ $a = 0.5523$ nm and $c = 1.1123$ nm [7], i.e. $c > 2a$. For $c = 2a$ r_4 and r_5 would be equal, but the fact that $c > 2a$ causes a small difference between r_4 and r_5 as well as between r_2 and r_3, see Table 1. It was impossible to detect any fine structure for the D2 and D3 PL bands, because they were too wide. But our first measurements [2] showed that there is a certain possibility to observe fine structure for D4 and D5 PL bands. With improved experimental conditions we recorded a PL spectrum which is shown in Fig. 1a. This spectrum was measured using a PbS detector. It can be seen from Fig. 1a that the spectrum definitely has quite a pronounced phonon replica structure with two distinctly observable phonon energies, $\hbar\omega_1 = 40.5$ meV

Table 1
Calculated distances between interstitial donors and acceptors (at In or Cu sites) in the chalcopyrite $CuInS_2$ lattice and the corresponding PL bands peak positions

PL-band	DA distance, (Å)	Calculated PL band position, (eV)	Experimentally measured peak positions, (eV)
D1	2.3971	0.954	0.954
D2	2.7615	0.8626 }	0.864
D3	2.7808	0.8584	–
D4	4.5823	0.6236	0.6237
D5	4.6056	0.6218	0.6216
D6	4.7942	0.6076	–
D7	6.0208	0.5370	–

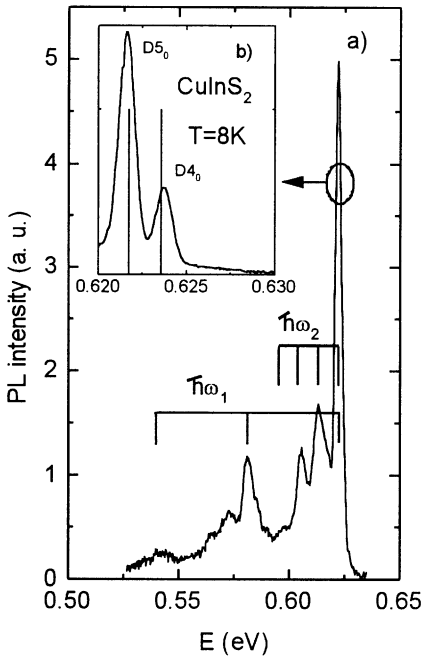

Fig. 1. Deep photoluminescence spectrum of the $CuInS_2$ sample (a). The D4 and D5 zero phonon lines are well resolved, as shown in the insert (b).

(327 cm^{-1}) and $\hbar\omega_2 = 8$ meV (65 cm^{-1}), respectively. These phonon energies are very close to the E_4 (315 cm^{-1}) and E_1 (60 cm^{-1}) phonon modes found by the resonant Raman scattering in $CuInS_2$ crystals [8]. With the measurement set-up using the PbS detector, the spectral resolution was not sufficient to distinguish between the ZPLs of the D4 and D5 PL bands. However, with the more sensitive InGaAs detector we clearly resolved the zero-phonon peaks for the D4 and D5 bands, see Fig. 1b. The energy separation between them was approximately 2 meV and the measured full width at half maximum, inclusive of instrumental resolution, of the two zero-phonon-emission lines was approximately 0.6 meV. The calculated, theoretical positions for the D4 and D5 zero-phonon lines are shown in Fig. 1b as vertical lines. Within the same model, the next DA pair with a distance r_6 should have a PL emission peak D6 at $h\nu = 0.608$ eV. We could not detect this band and therefore, it is obvious that the electron and hole wave functions, being very localized and of specific shape, do not overlap practically at all for distances $r = 4.79$ Å and 6.02 Å.

To conclude, the ZPLs of Fig. 1b are found to result from recombination within deep–donor–deep–acceptor complexes, where the donor defect is probably an interstitial copper-Cu_i. Our calculation shows that these ZPLs correspond to the separations of 4.5823 Å and 4.6056 Å, respectively, between the donor and the acceptor defects cf. (Table 1). The narrowness of these ZPLs may give various possibilities to use several spectroscopic methods in order to study the defect structure of $CuInS_2$.

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References

[1] J. Krustok, J.H. Schön, H. Collan, M. Yakushev, J. Mädasson, E. Bucher, J. Appl. Phys. 86 (1999) 364.
[2] J. Krustok, J. Raudoja, J.-H. Schön, M. Yakushev, H. Collan, Thin Solid Films 361-362 (2000) 406.
[3] P.J. Dean, C.H. Henry, C.J. Frosch, Phys. Rev. 168 (1968) 812.
[4] J.L. Merz, K. Nassau, J.W. Shiever, Phys. Rev. B 8 (1973) 1444.
[5] P.W. Li, R.A. Anderson, R.H. Plovnick, J. Phys. Chem. Solids 40 (1979) 333.
[6] J.JM. Binsma, L.J. Giling, J. Bloem, J. Luminescence 27 (1982) 55.
[7] H.W. Spiess, U. Haeberlen, G. Brandt, A. Räuber, J. Schneider, phys. stat. sol. (b) 62 (1974) 183.
[8] K. Wakita, H. Hirooka, S. Yasuda, F. Fujita, N. Yamamoto, J. Appl. Phys. 83 (1998) 443.