

Analysis of the edge emission of highly conductive CuGaTe₂

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Available online 12 January 2007

Abstract

Low temperature photoluminescence of CuGaTe₂ was studied using number of different samples. Totally 11 photoluminescence bands were detected in the edge emission region. It is shown that at least 6 bands have peak positions at higher energy than the lowest optical bandgap of CuGaTe₂. These bands were explained by using a model of resonant acceptor states (Fano-type resonances) in the valence band of CuGaTe₂. Thus, the electron from the conduction band or from the donor level recombines with holes from acceptor levels related to the different valence bands. The energetic distance between these valence bands is found to be 84 meV.

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PACS: 78.55.Hx; 71.55.Ht; 61.72.Ji; 78.30.A

Keywords: CuGaTe₂; Chalcopyrite crystals; Photoluminescence; Resonance states

1. Introduction

It is known that in chalcopyrite ternaries the deviation from ideal stoichiometry causes large concentration of intrinsic defects and so-called heavily doped material is often formed. As a result, the edge photoluminescence (PL) emission usually shows broad and asymmetric band without any clear phonon structure [1–4]. In CuGaTe₂ (CGT) very high concentration of holes is typically seen and therefore a screening of potential fluctuations by free holes occurs. It was shown that the hole gas in CGT is degenerate at hole concentrations above $5 \times 10^{18} \text{ cm}^{-3}$, therefore, due to Burstein–Moss shift, also different E_g values are measured using optical absorption [5,6]. Due to the screening of potential fluctuations the edge emission of CuGaTe₂ has more complex nature. The most exciting feature of the edge emission of this compound is that some PL bands are located at higher energy than the bandgap energy measured by optical absorption [7]. It means that the radiative recombination must take place involving states which are situated above or below the lowest bandgap. Although, the wide range of bandgap energies between 1.16 and 1.38 eV have been reported, it is generally accepted that

CGT has the lowest bandgap E_g around 1.24 eV at room temperature [8–10]. This is due to the direct allowed transitions between parabolic bands at Γ point. According to [6], the low temperature bandgap energy in CGT is 1.362 eV. At the same time, already in [7,12] several PL bands were detected with $h\nu > 1.362$ eV. In this paper we examine different samples of CGT and try to explain observed PL bands.

2. Experimental

We studied different polycrystalline and single crystal CGT samples. Details of the growth can be found in [7]. Different samples had a different stoichiometry and therefore quite different PL spectra can be seen. From the analysis of X-ray powder diffraction patterns, the single-phase nature and the chalcopyrite structure of the material were confirmed.

For the PL measurements the samples were mounted into the closed-cycle He-cryostat equipped with the temperature controller that allows to tune the temperature from 8 K to 300 K. Samples were optically excited with the 441 nm He–Cd laser line with the maximum output power of 40 mW. The spectra were recorded via the 40 cm grating computerized monochromator system and detected with the R-632 photomultiplier detector. The emission spectra were corrected according to the

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Table 1
Experimentally determined acceptors in CuGaTe₂

E _A (meV)	Method	Ref.
1	Conductivity	[11]
22	Photoluminescence	[7]
37	Conductivity	[11]
55	Photoluminescence	[12]
90	Photoluminescence	[15]
125	Conductivity	[13]
140	Photoconductivity	[14]
237	Photoluminescence	[15]
425	Conductivity	[12]
360–450	Conductivity	[11]

grating efficiency variations and the spectral response of detectors.

3. Results and discussion

CGT has the p-type conductivity and several acceptors are found to be present in this material. Most of available data about acceptors can be found in Table 1.

It is expected that shallow acceptors play certain role in the edge emission, and as they are intrinsic defects, the variation of preparation conditions leads to the different PL spectra. At the same time we can also expect the formation of complexes with donor defects. In Fig. 1 the PL spectra of different CGT samples are presented. All these spectra were carefully fitted and as a result 11 different PL bands were found. It can be seen from Fig. 1 that at least 6 PL bands have peak positions at higher energy than the lowest bandgap of CGT. Therefore, we assume that in the case of CGT resonance acceptor states are formed within the valence band. These so-called Fano-type resonances are quite common in many systems including semiconductors. Recently it was shown that resonance donor states in the conduction band of InP:Sn can show PL bands at higher energy than the bandgap of InP [16]. For another chalcopyrite compound ZnGeP₂ it was shown that deeper acceptor states show typical splitting of 60 meV according to the valence subbands and these states can be seen with PL [17]. If the energy separation between two splitted valence bands becomes

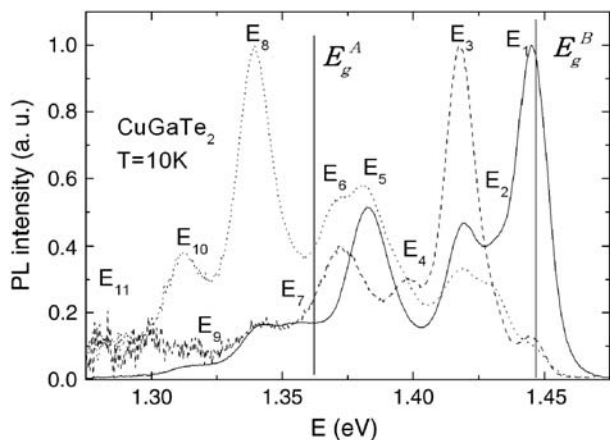


Fig. 1. PL spectra of three different samples of CuGaTe₂ measured at 10 K. The position of A and B bandgaps are also given as vertical lines.

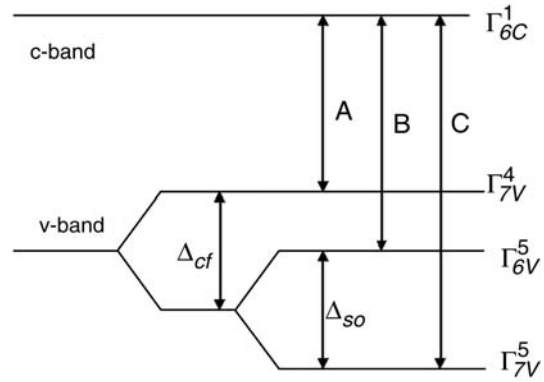


Fig. 2. Schematic band structure of chalcopyrite CuGaTe₂ showing crystal field and spin–orbit splitting of the valence band. Three different bandgaps (A, B, C) are shown.

larger than the acceptor binding energy, the acceptor level attached to lower valence band overlaps with upper valence band. A hybridization then occurs between the overlapping localized acceptor states and extended Bloch states, resulting in resonant states. These resonant acceptor states were also found in p-type Si [18], in uniaxially strained Ge:Ga [19], and in GaN:Mg [20]. In uniaxially stressed p-Ge the resonant states arise due to the splitting of light- and heavy-hole subbands at rather high value of stress, when the impurity levels shift to the upper split-off subband find themselves in the energy continuum of the lower subband [19]. In Si and Ge these resonance shallow acceptor states were discussed by Buczko and Bassani [23].

The p-like highest valence band in CGT is characterized by three split bands: Γ_{7V}^4 , Γ_{6V}^5 , and Γ_{7V}^5 [21,24]. This splitting is

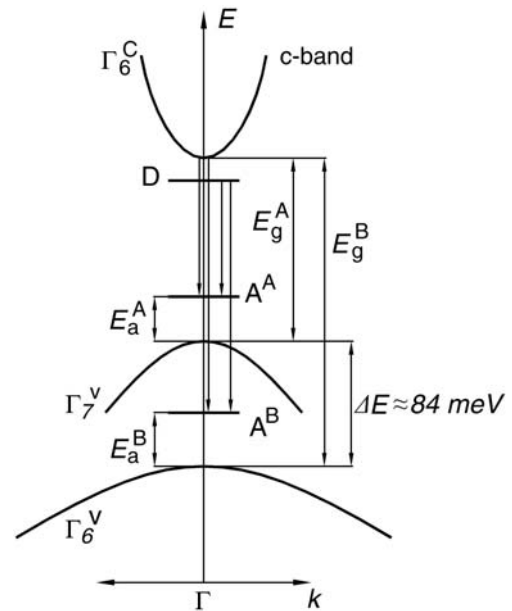


Fig. 3. A simplified figure showing the edge emission model for CuGaTe₂. With only one acceptor (A) and one donor (D) defect we expect 4 different PL bands to be present. Two of them are at higher energy than the lowest bandgap energy (E_g^A) and are related with the acceptor resonance state within the highest valence band.

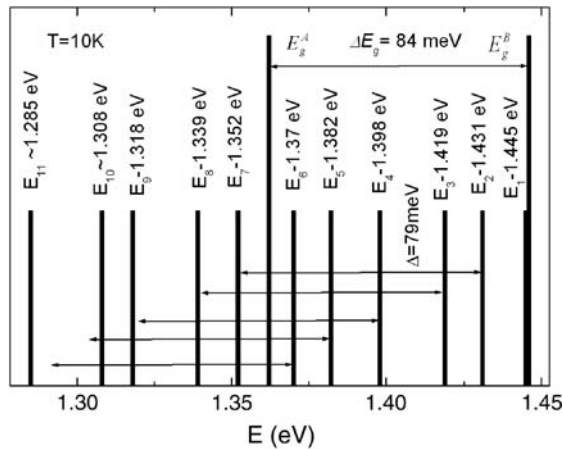


Fig. 4. The peak position of PL bands observed in different CuGaTe₂ samples at 10 K and the distance between these PL bands.

due to the combined effect of crystal field splitting and spin-orbit coupling. Due to the valence band splitting in CGT three different bandgaps can be found, see Fig. 2. They are called A, B, and C gaps, but there is a great difference between the values of these gaps measured by different groups. Also, there is very little information about bandgap energies measured at low temperatures. In [6] it was shown by optical absorption measurements that at $T=0$ K the $E_g^A=1.362$ eV and $E_g^C=2.083$ eV. Unfortunately there is no data about the low temperature value of E_g^B , but it was shown in [21] that $E_g^B - E_g^A=80$ meV at room temperature. In [7] we measured photoluminescence excitation spectra in CGT and got the value of 1.446 eV for E_g^B at $T=11.5$ K. Using bandgap values given above we obtain $E_g^B - E_g^A \approx 84$ meV for $T=0$ K. These bandgap energies were also shown in Fig. 1 as vertical lines.

In Fig. 3 the proposed recombination model is given. In most cases each shallow acceptor has two levels A^A and A^B related to Γ_7 and Γ_6 valence bands respectively. We did not detect any emission related to the lowest valence band and therefore we exclude it from our model. At the same time, we also assume that the donor defect D can also be involved at lower temperatures, and therefore, in some cases, the donor-acceptor recombination together with the conduction band-acceptor recombination can be seen. This is why some PL bands show so-called double peaks. The average distances between these double peaks are in the range of ~ 10 – 13 meV and assuming that we are dealing with distant donor-acceptor pairs, it gives us an approximate donor defect depth.

It can be seen from Fig. 4 that there is a certain correlation between the peak position of observed PL bands. Although the energetic distance between valence bands is 84 meV, the distance between PL bands from the different valence bands is only 79 meV, see Fig. 4. The reason for this difference is that the resonant acceptor levels in the lower laying valence band Γ_6 seem to be somewhat deeper than these related to the highest Γ_7 valence band. Therefore, we presume different effective mass for holes in these valence bands. Peak positions of weak E_{10} and E_{11} bands are still approximate because of their low intensity. The E_1 band seems to be different from all other PL bands and it

is probably related to the exciton or band-to-band emission. Similar so-called B-exciton is also found in CuGaSe₂ epilayers [22]. We also expect A-exciton to appear near the E_g^A , but unfortunately it was not detected. It is not excluded that E_1 can be caused by very shallow acceptor with $E_A < 10$ meV. Additional experiments are planned to clarify the nature of these resonance acceptor states in CGT and in other ternaries as well.

4. Conclusions

The low temperature edge emission of CuGaTe₂ was studied. It was shown that different samples show slightly different spectra. At the same time it was possible to detect 11 different PL bands and the peak positions of these bands in different samples seem to be the same. At least 6 PL bands had peak positions at higher energy than the lowest bandgap of CGT. The big number of discovered PL bands is explained by resonance acceptor states (Fano-type resonances) in the upper valence band of CuGaTe₂.

Acknowledgements

This work was supported by the Estonian Science Foundation Grant No. 6554. We wish to thank Dr. M. Yakushev for providing some of his single crystal samples.

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