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Analysis of the edge emission of highly conductive $CuGaTe_2$

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Abstract

Low temperature photoluminescence of $CuGaTe_2$ 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 $CuGaTe_2$. These bands were explained by using a model of resonant acceptor states (Fano-type resonances) in the valence band of $CuGaTe_2$. 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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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 $CuGaTe_2$ (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 5×10^{18} 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 $CuGaTe_2$ 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 $CuGaTe_2$

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 $ZnGeP_2$ 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

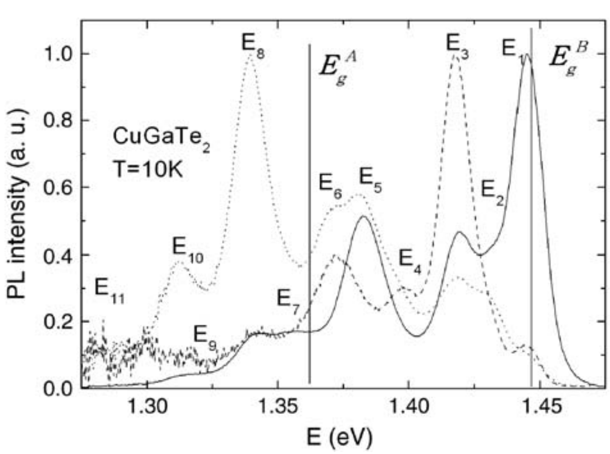

Fig. 1. PL spectra of three different samples of $CuGaTe_2$ measured at 10 K. The position of A and B bandgaps are also given as vertical lines.

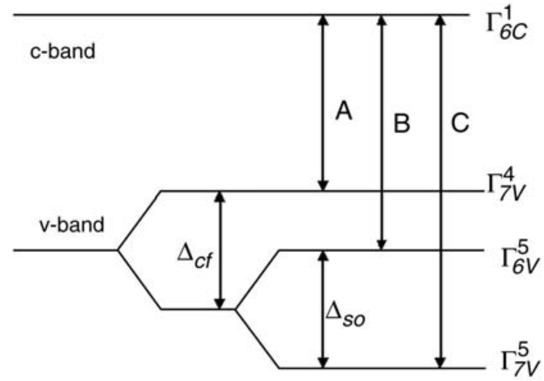

Fig. 2. Schematic band structure of chalcopyrite $CuGaTe_2$ showing crystal field and spin–orbit splitting of the valence band. Three different bandgaps (A, B, C) are shown.

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 unaxially 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^4_{7V}, Γ^5_{6V}, and Γ^5_{7V} [21,24]. This splitting is

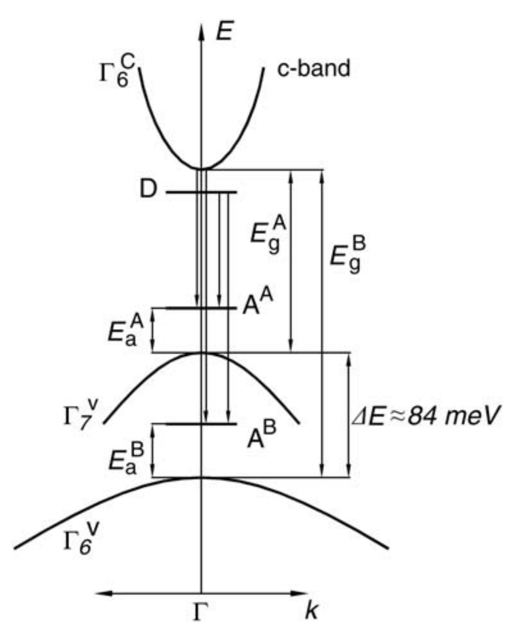

Fig. 3. A simplified figure showing the edge emission model for $CuGaTe_2$. With only one acceptor (A) and one donor (D) defect we expect 4 different PL bands to be present. Two of them are at higher energy than the lowest bandgap energy (E^A_g) and are related with the acceptor resonance state within the highest valence band.