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On the Shape of the Close-to-Band-Edge Photoluminescent Emission Spectrum in Compensated CuGaSe₂

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Photoluminescence (PL) properties of compensated as-grown and air-annealed CuGaSe₂ single crystals, grown by the vertical Bridgman technique, in the edge emission spectral region were studied. The intensity maximum of the broad asymmetrical PL band at $T = 8$ K was found to be at $h\nu_{\max} = 1.586$ eV. After air annealing at 673 K for 15 min the PL band shifts towards higher energies, and its intensity slightly decreases but the shape remains the same. It is shown that this typical asymmetric PL band is not associated with a certain acceptor level but originates from the band-tail recombination. The valence band tail is formed by the potential fluctuations of charged defects. The average depth of these fluctuations is determined by the Debye-Hückel correlation in the distribution of donors and acceptors. The low-temperature air-annealing reduces the concentration of charged defects, but the sample remains highly compensated.

1. Introduction

CuGaSe₂ is a promising material for several optoelectronic devices. Similarly to other ternary chalcopyrite compounds its defect structure and thus optical properties are sensitive to any deviations from the ideal stoichiometry. Therefore, it is obvious that, at times, different groups may have obtained somewhat different experimental results and that a certain confusion exists about the optoelectronic properties of CuGaSe₂. Furthermore, there seems to be an additional complication with highly compensated CuGaSe₂, namely that usually only one asymmetric photoluminescence (PL) band at $h\nu_{\max} \approx 1.6$ eV can be observed. The energy of the maximum intensity $h\nu_{\max}$ is thus about 0.1 eV below the “true” band gap energy and the emission spectrum differs considerably from the PL emission found in nearly perfect crystals. Recently, attention has been given to these unusual “below the band gap” emissions in In-rich CuIn(Ga)Se₂, see Refs. [1,2]. In those investigations it was found that the experimentally observed asymmetric PL bands can be explained by the theoretical analysis for highly compensated semiconductors assuming that potential fluctuations caused by charged defects affect directly the shape of PL bands. Several other studies have also proved that an-

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nealing of the compensated CuIn(Ga)Se_2 in air at temperatures below 673 K leads to a reduction of compensating donor states [3,4]. As a result, the average depth of the spatially fluctuating potentials decreases and in some cases so-called “flat band condition” appears. In the present paper we study these aspects in heavily compensated CuGaSe_2 crystals.

2. Experimental

An ingot of CuGaSe_2 was grown by the vertical Bridgman technique often employed for fabrication of CuInSe_2 and other chalcopyrite ternary compounds [5]. The pseudo-binary phase diagram for CuGaSe_2 , as determined by Palatnik and Belova [6], was used. At first a near stoichiometric mixture of high (99.999%) purity Cu, Ga and Se was sealed under vacuum in a quartz ampoule of 10 mm diameter. Then this mixture was prereacted at 1423 K for 2 h in a rocking furnace and solidified in horizontal position. After cooling down the ampoule was introduced into the upper (hot) zone of a two zone vertical furnace. The material was melted again and held at 1423 K for 6 h. Then temperature was reduced to 1343 K and the furnace was slowly moved upwards translating the ampoule into the lower (cold) zone with the speed of 2 cm/day through the temperature gradient. The solidified material was cooled at rate 3 K/h down to 873 K. The grown ingot contained small (with dimensions up to $5 \times 5 \times 5 \text{ mm}^3$) grains of CuGaSe_2 . The elemental composition of the resultant crystals was confirmed by energy dispersive X-ray emission (EDX) and Rutherford backscattering spectroscopy (RBS) measurements. One of the crystals was mechanically polished, first with different grade diamond pastes and finally in a vibrating bath with an $0.05 \text{ }\mu\text{m}$ alumina slurry, and then etched for 1 min in 1% Br in methanol solution. Thus, the surface prepared was analysed with RBS channelling technique along the $\langle 221 \rangle$ and $\langle 110 \rangle$ axes using a 2 MeV He^+ beam [7]. The normalised minimum yield along $\langle 221 \rangle$ axis was measured to be 3.8%. This value can be taken as an evidence of the good structural quality of the crystal lattice of our samples.

The typical resistivity of the as-grown CuGaSe_2 crystals was about $4 \times 10^4 \text{ }\Omega\text{cm}^{-1}$ at room temperature. For the PL measurements, a He–Cd laser with a wavelength of 441 nm was used for excitation. The samples were mounted inside a closed cycle He cryostat ($T = 8$ to 300 K). The PL spectra were taken with a computer-controlled SPM-2 grating monochromator ($f = 0.4 \text{ m}$). The chopped signal was detected with a photomultiplier tube with S1-characteristics using the conventional lock-in technique. The emission spectra were corrected for grating efficiency variations and for the spectral response of the detector.

3. Results and Discussion

The solid line in Fig. 1. shows a typical low temperature edge emission PL spectrum of an as-grown compensated CuGaSe_2 crystal. The intensity maximum of the asymmetrical PL band was found to be at $h\nu_{\text{max}} = 1.586 \text{ eV}$. We also detected deep emission bands D_1 , D_2 , and W at 1.146, 1.043, and 1.246 eV, respectively. The D_1 , D_2 bands, for instance, are due to a deep donor–deep acceptor (DAP) pair; in more detail the origin of these bands is discussed in Ref. [8]. As seen in Fig. 1, the main 1.586 eV PL band edge emission spectrum shows a strong decrease at the high-energy side and an almost expo-

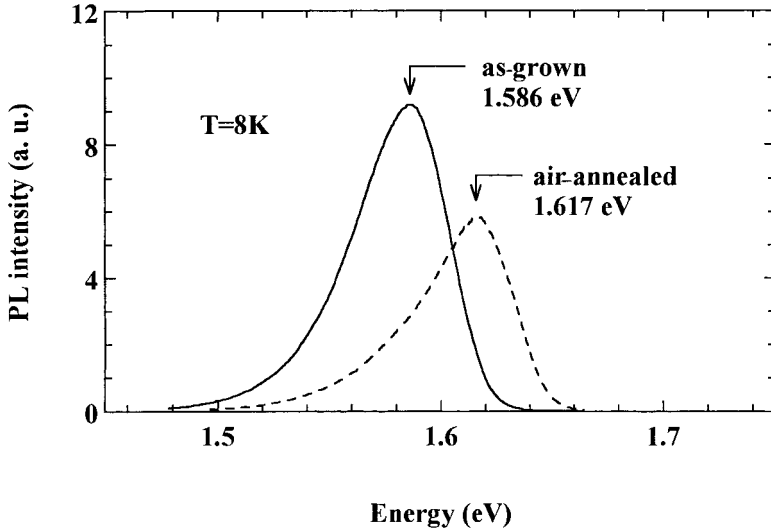


Fig. 1. Low-temperature PL spectra of compensated as-grown and air-annealed CuGaSe₂ crystals, measured in the edge emission region

nential increase at the low-energy side. After air annealing at 673 K for 15 min, the PL band shifts towards higher energies, and its intensity decreases slightly but the shape remains constant.

The temperature dependence of the peak position $h\nu_{\max}(T)$ is illustrated in Fig. 2 for both the as-grown and air-annealed samples. It is clearly visible that at low temperatures, roughly below $T < 80$ K, the peak position $h\nu_{\max}(T)$ shifts towards lower

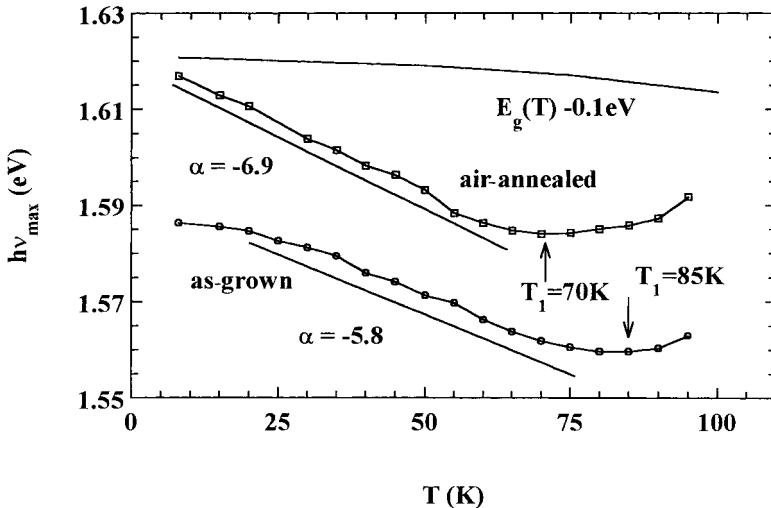


Fig. 2. Temperature dependence of the peak position of the PL spectrum in as-grown and air-annealed CuGaSe₂ crystals together with the $E_g(T)$ curve [11]. Solid lines represent linear sections and the corresponding slopes are given

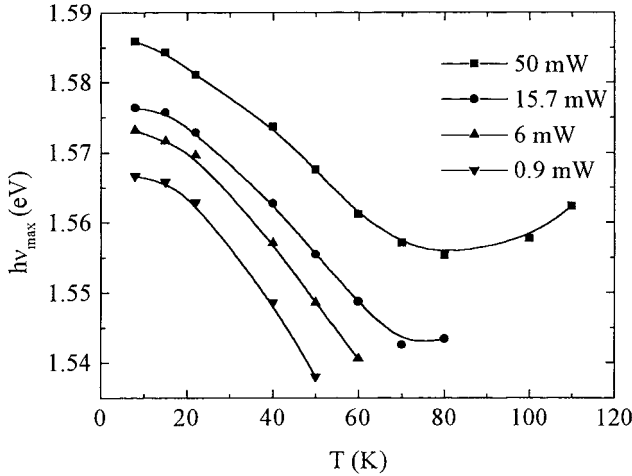


Fig. 3. Temperature dependence of the PL emission band peak position of the as-grown CuGaSe₂ crystal, measured for different excitation intensities

energies for both samples and reveals an almost linear behaviour with increasing temperature. The observed shift exceeds the temperature dependence of the true energy gap. It can also be seen from Fig. 2 that the air-annealed sample shows a strong decrease of this shift. There is a minimum value for $h\nu_{\max}(T)$ as a function of temperature for both samples. This minimum occurs at a temperature T_1 , but the T_1 value for the as-grown sample, $T_1 = 85$ K, is higher than that for the air annealed sample, $T_1 = 70$ K. The behaviour of the peak position upon temperature depends on the laser intensity as can be seen from Fig. 3, where this dependence for the as-grown sample is depicted. The analysis of the temperature quenching of the PL intensity showed that neither one of the samples follows the theoretical dependence for discrete energy levels, i.e. the Arrhenius plot of $\ln I(T)$ versus $1000/T$ had no pure linear parts. All these facts confirm that the observed emission is dominated by the so-called band to tail (BT) recombination in the compensated CuGaSe₂ samples. The theory for the BT recombination has been developed by Levanyuk and Ossipov in Refs. [9,10] cf. also Ref. [2]. It was shown in Refs. [9,10] that the edge emission in highly compensated semiconductors is essentially derived from two or even three typical emission bands of basically different character: the band to tail (BT), the tail to tail (TT) and the band to band (BB) recombinations, which are illustrated schematically in Fig. 4. The BT process usually dominates, but at low temperatures the TT band may appear, while the BB emission band becomes visible at high temperature and/or at high excitation intensities [2]. The valence band holes are mostly captured by deep conduction band states located within the fundamental energy gap due to the potential fluctuations at low temperatures. The deep conduction band states select preferentially such localized valence band holes which can be attributed to acceptor-like states rather than to ordinary valence band states. In order to find the shape of the corresponding BT-emission band it is necessary to use a density of states function and a distribution function for both electrons in the conduction band and localized holes [9],

$$I_{\text{BT}}(h\nu) \propto \iint W_{\text{BT}}(E_e, E_h) \varrho_c(E_e) f_c(E_e) \varrho_v(E_h) q_h(E_h) \delta(E_e - E_h - h\nu) dE_e dE_h, \quad (1)$$

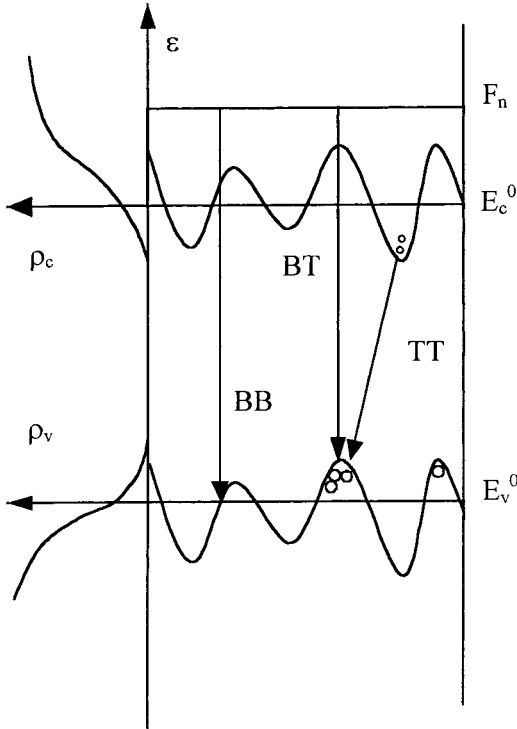


Fig. 4. Illustration of the recombination model for the compensated CuGaSe₂ crystals, used in the present work. The theoretical analysis, underlying Eqs. (1) to (9) can be found in Refs. [9,10]

where W_{BT} is a radiative recombination probability, E_e , E_h are the energies of electrons and holes, respectively, ϱ_c , ϱ_v are the densities of states of the electrons in the conduction band and of the localized holes in the valence band, respectively, f_e is the distribution function for the electrons, and q_h is the distribution function for the localized holes. The function q_h has to be calculated using kinetic equations rather than assuming that there is a quasi-equilibrium of holes with a corresponding quasi Fermi level. The latter assumption is correct, of course, in the case of free holes, i.e. for the BB emission.

The final shape of the PL spectrum depends crucially on the actual shape of the density of states function of the localized holes and, therefore, it is difficult to obtain any generally valid analytical function for the whole BT-band shape. Some predictions were made in Ref. [10] by using different functions for the density of the localized holes, ϱ_v , in the degenerated semiconductors. These assumptions may be correct also for CuGaSe₂ and related compounds because of the smallness of the effective mass of the electrons (in CuGaSe₂ it is estimated that $m_n = 0.101m_e$ [11]). The Fermi level for electrons F_n lies then within the conduction band and the electron part of the integral (1) is the same for all types of ϱ_v . According to Ref. [10] the resulting BT band at low temperatures has an asymmetrical shape and quite an abrupt decrease on the high-energy side. The shape of the low-energy side of this band is determined by the ϱ_v function while the high-energy side has much more complex nature. In most cases the density of the localized holes, ϱ_v , and the emission intensity at the low-energy side I_{LE} show the following dependences on energy at low temperatures:

$$\varrho_v(E) = \varrho_0 \exp\left(-\frac{E}{\gamma_0}\right), \tag{2}$$

$$I_{LE}(h\nu) \propto \exp\left[-\frac{E_g - h\nu}{\gamma_0}\right]. \tag{3}$$

The easiest way to treat the experimental properties of the BT band is to find its maximum energy $h\nu_{max}$ and to study its temperature and excitation intensity dependen-

cies. According to Refs. [9,10], the $h\nu_{\max}$ for BT band at low temperatures may be expressed as

$$h\nu_{\max} = E_g^0 + \mu_n - \sqrt{2}\gamma - \varepsilon_1, \quad (4)$$

with

$$\varepsilon_1 = k_B T \ln \frac{N_v}{p + n\theta}. \quad (5)$$

Here E_g^0 is the energy gap without potential fluctuations, μ_n is the Fermi energy of the electrons, γ the average amplitude of the potential fluctuations, N_v the effective density of states in the valence band, n , p are the concentrations of free electrons and holes, respectively, and θ is the ratio of electron and hole capture probabilities by the localised states.

Thus, the BT-emission band can be treated as a recombination of a free electron from the Fermi level F_n with a localized valence band state at the energy ε_1 . According to Eqs. (4) and (5) at low temperatures, $h\nu_{\max}$ decreases linearly with temperature and more rapidly than the energy gap. It can be seen from Eqs. (4) and (5), that the peak maximum energy $h\nu_{\max}$ also shifts toward higher energies with increasing concentrations of free electrons and holes, n and p , i.e. with an increasing excitation intensity. At higher temperatures, when

$$k_B T > k_B T_1 = \gamma_0 \left[\ln \frac{N_v}{p + n\theta} \right]^{-1/2} \quad (6)$$

the maximum energy, $h\nu_{\max}$, shifts toward higher energies and above a characteristic temperature, T_2 , it shows the temperature dependence of the energy gap $E_g(T)$. The BB recombination dominates at temperatures where all localized holes are thermally released.

The experimentally found parameters for both the as-grown and the air-annealed CuGaSe₂ samples are given in Table 1. It is important to note that the air-annealing decreases the carrier concentration ($p + n\theta$) in CuGaSe₂. The effect of air-annealing on CuGaSe₂ seems to have nearly the same result as the increase of the Cu/(In + Ga) ratio in CuIn(Ga)Se₂, where the decrease of the carrier concentration and the total defect concentration was determined by Dirnstorfer et al. [1]. Because the emission band shape does not change significantly due to air-annealing, we can – interestingly enough – conclude that the air-annealing does not really affect the shape of the density of states function of the localized holes ρ_v , in spite of the fact that the peak position $h\nu_{\max}$ of the corresponding PL band shifts by 30 meV. This shift may be considered as

Table 1
Relevant experimental parameters of as-grown and air-annealed CuGaSe₂ samples

parameter	as-grown sample	air-annealed sample
T_1 (K)	85	70
$\ln \frac{N_v}{p + n\theta}$	5.8	6.9
γ_0 (meV)	17.6	15.9

a reduction of the average amplitude of spatial potential fluctuations γ by the air-annealing treatment. In as-grown samples we can predict that $\gamma \geq 90$ meV. Therefore, it is not surprising that shallow acceptors are not visible in PL. Even in the air-annealed sample, where $\gamma \approx 60$ meV, shallow acceptors (typically $E_A \approx 50$ meV in CuGaSe₂ [12,13]) are still shadowed by the potential fluctuations. Apparently, an air-annealing of the compensated CuGaSe₂ samples reduces the average amplitude of the potential fluctuations, but not to the same level as the flat band condition develops.

The mean square fluctuation of the carrier energy or the average amplitude of the potential fluctuations can be calculated as [9]

$$\gamma = 2\sqrt{\pi} \frac{e^2}{\epsilon R_0} (NR_0^3)^{1/2}, \tag{7}$$

where ϵ is the dielectric constant (for CuGaSe₂, $\epsilon = 9.6$ [14,15]), N is the concentration of charged defects, and R_0 the maximum extension of the fluctuation. In case of random distribution of charged defects in compensated CuGaSe₂ p-type samples, where the carrier density is very low, the R_0 value is determined by the screening effects and is given by

$$R_0 \approx N^{1/3} p^{-2/3}, \tag{8}$$

where p being the hole density. The carrier density is about 10^{16} cm⁻³ in highly compensated ternary compounds while the charged defect concentration may be as high as $N \geq 10^{18}$ cm⁻³ [1]. Using Eqs. (7) and (8), it can be estimated that in this case $\gamma \approx 0.25$ eV. This value is clearly higher than what we find experimentally. Therefore, it is obvious that in our samples there must be a strong Debye-Hückel correlation in the distribution of donors and acceptors which reduces the extension of the potential fluctuations. The same correlation was found also in doped CdS [16]. Assuming that this

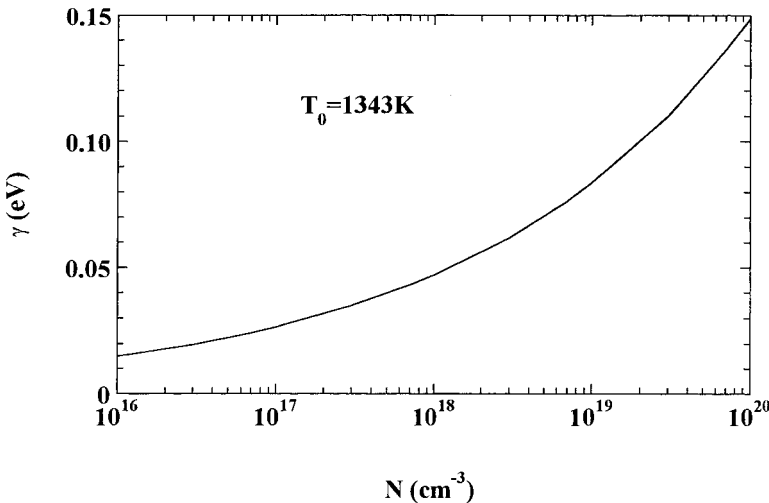


Fig. 5. Calculated values of the averaged amplitude of the spatial potential fluctuation, γ , as a function of the concentration N of charged defects. The Debye-Hückel correlation at the temperature $T_0 = 1343$ K was assumed

correlation is present, R_0 can be calculated as [9],

$$R_0 = \sqrt{\frac{\epsilon k_B T_0}{4\pi N e^2}}, \quad (9)$$

where T_0 represents the growth temperature of the crystal. It can be seen from Eq. (9), that the value of R_0 and, thus, also the value of γ is no longer determined by the carrier density but only by the total concentration N of the charged defects. The calculated values of the average amplitude, $\gamma = \gamma(N)$, at the temperature $T_0 = 1343$ K are shown in Fig. 5. We can see from Fig. 5 that the defect concentration $N = 10^{19}$ cm⁻³ is sufficient enough for producing potential fluctuations with a value of $\gamma \approx 90$ meV. It appears that the air-annealing reduces the level of potential fluctuations (to $\gamma \approx 60$ meV) indicating that in this case the charged defect concentration is decreased to $N \approx 2 \times 10^{18}$ cm⁻³.

4. Conclusion

Photoluminescence properties of compensated CuGaSe₂ single crystals in the edge emission spectral region were studied. It was shown that the typical asymmetric PL band is not associated with a certain acceptor level but originates from the band-tail recombination. The valence band tail was formed by the potential fluctuations of charged defects. The average level of these fluctuations was determined by the Debye-Hückel correlation in the distribution of donors and acceptors. The low-temperature air-annealing reduces the concentration of charged defects, but the sample remains highly compensated.

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