Photoluminescence study of deep levels in $CuGaTe_2$ crystals

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(Received 24 March 1999; accepted for publication 27 July 1999)

A deep photoluminscence band at 0.95 eV was studied in $CuGaTe_2$ crystals. The shape of this band did not change with laser power and no *j* shift was detected. This band shifts towards higher energy with increasing temperature and its shape becomes more asymmetric. The activation energy of this band was $E_T = 0.20$ eV as measured with thermal quenching. The possible association of the 0.95 eV band with grain boundaries or dislocations is discussed. © *1999 American Institute of Physics.* [S0021-8979(99)03221-1]

In recent years much attention has been given to the I–III–VI_2-type ternary compounds having a chalcopyrite structure. Among these, $CuGaTe_2$ (CGT)—and all tellurides, in fact—have been largely ignored. Therefore, even basic parameters of CGT, such as the band-gap energy (E_g) and its temperature dependence in CGT, were not correctly measured until recently.[1] The same was true with the low-temperature photoluminescence (PL) properties of CGT crystals. The first detailed study was only recently published by Krustok *et al.*[2] In Ref. 2 most of the attention was given to the PL bands near the band-gap energy E_g. It is known that these PL bands give information about relatively ''shallow'' defect levels, but there are several indications[3] that chalcopyrite compounds contain also ''very deep'' defect levels which can be studied using PL spectroscopy. These deep PL bands, having the peak position at $E_{\max} < E_g - 0.4\,\mathrm{eV}$, were lately discovered and investigated in $CuGaSe_2$ and $CuInS_2$,[4] where they showed, curiously, very similar properties. Deep PL bands were also found in $CuInGaSe_2$ thin films.[5] In the present work we tried to detect deep PL bands in $CuGaTe_2$ crystals and study their properties.

CGT single crystals were grown by the vertical Bridgman technique. All details of the crystal growth and characterization can be found in Ref. 2. 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 ($T = 8–300\,\mathrm{K}$). The PL spectra were recorded with a computer-controlled SPM-2 grating monochromator ($f = 0.4\,\mathrm{m}$). The chopped signal was detected with an InGaAs detector, or with a photomultiplier tube with S1 characteristics for the edge emission region, using a conventional lock-in technique. The emission spectra were corrected for grating efficiency variations and for the spectral response of the detectors.

As it was shown already in Ref. 2, the typical low-temperature edge emission spectrum of CGT includes so-called E bands and the D_0 band with their phonon replicas, see Fig. 1. At lower energy we detected a new broad PL band with a peak position at 0.95 eV. The shape of this band did not change with laser power and no *j* shift was detected. Its temperature dependence is shown in Fig. 2. As can be seen, the band shifts towards higher energy with temperature and becomes more asymmetric. At higher temperatures the relative intensity of the high-energy side increases. The shift of the peak position with temperature is quite large, amounting to an increase of ~50 meV when going from $T = 15\,\mathrm{K}$ to $T = 250\,\mathrm{K}$, see Fig. 3.

In order to obtain information about the defect levels responsible for a particular PL band, the temperature dependence of the integrated intensity $\Phi(T)$ is often used. Usually, there are no problems with high-temperature measurements, but sometimes low-temperature measurements are—apparently erroneously—characterized as a thermally activated process with a well-defined activation energy. In Ref. 6, however, it was shown that low-temperature quenching

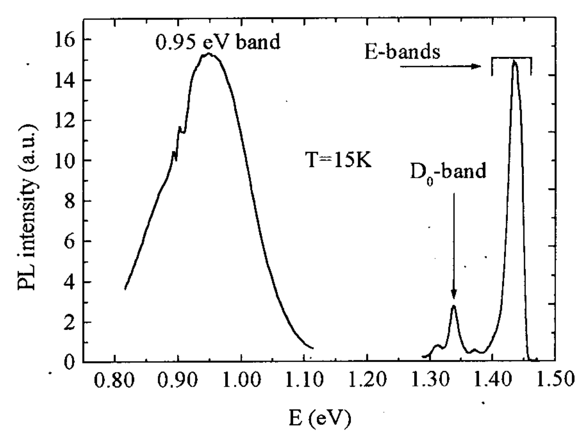

FIG. 1. Typical low-temperature PL spectrum of $CuGaTe_2$ crystal. The edge emission region and the deep region were measured with different detectors.

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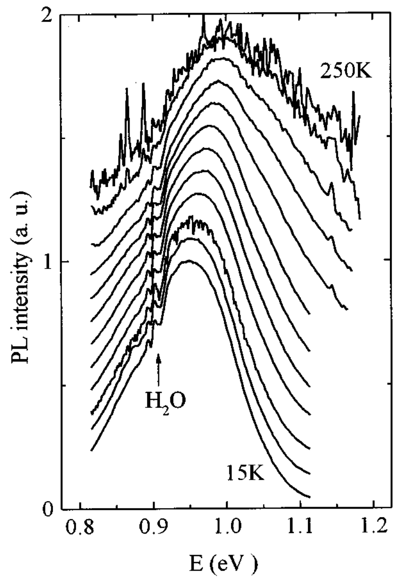

FIG. 2. Normalized PL spectra of the 0.95 eV band of the $CuGaTe_2$ crystal, shown as a function of temperature ($T = 15-250$ K). Disruptive water vapor absorption is indicated with an arrow.

may not really be a thermal activation process, instead caused by the temperature dependence of the capture cross sections of a particular recombination center. According to this theory, the temperature dependence of the integral intensity is

$$\Phi(T) = \frac{\Phi_0}{1 + c_1 T^{3/2} + c_2 T^{3/2} \exp\left(-\frac{E_T}{kT}\right)}. \tag{1}$$

In the present work, Eq. (1) was used to fit the measured temperature dependence of the 0.95 eV PL band integral intensity, see Fig. 4. The fitting parameters thus obtained are as follows: $\Phi_0 = 17.1$; $c_1 = 0.002\,\mathrm{K}^{-1.5}$; $c_2 = 219.0\,\mathrm{K}^{-1.5}$; and $E_T = 0.20 \pm 0.01$ eV. These results indicate that the 0.95 eV PL band is, indeed, associated with a relative deep defect level. The observed shift of the peak position with temperature toward higher energies proves that this PL band is not caused by electron–hole recombination including free-band states. Also, this shift cannot be explained by the simple deep donor–deep acceptor pair model as was done for the

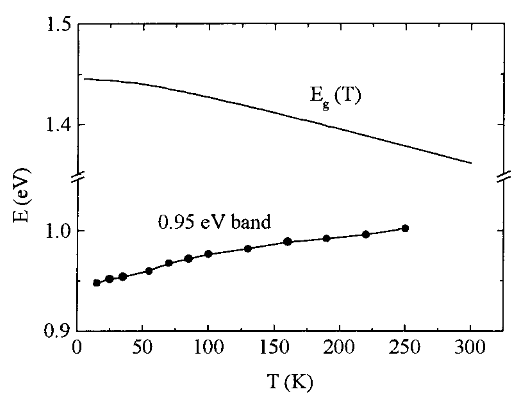

FIG. 3. Temperature dependence of the peak position of the 0.95 eV PL band and the band-gap energy E_g (Refs. 1 and 2) in $CuGaTe_2$.

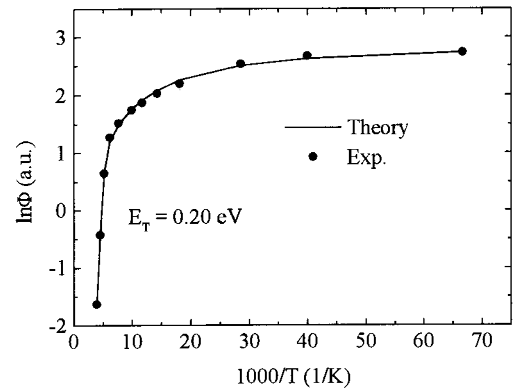

FIG. 4. Temperature dependence of integrated intensity of the 0.95 eV PL band. The continuous curve shows the result of parameter fitting to Eq. (1).

deep PL bands in $CuInS_2$ and $CuGaSe_2$.[4] Therefore, it is difficult to explain the origin of this deep PL band. However, we believe that the recombination causing the 0.95 eV band originates from the defects which are segregated near the grain boundaries or dislocations, i.e., in the places within the sample where the conduction- and valence-band edges are curved due to a space charge. It is suggested that this kind of recombination gives rise to the so-called *Z* bands in CdTe.[7,8] The spatially curved energy gap creates a situation where defect levels within the gap are also curved, spatially, and thus the defect energy level becomes a function of the distance *R* from the dislocation or a grain boundary, see Fig. 5. In this space charge region electrons and holes are also spatially separated, and the emitted photon energy, due to e–h recombination, becomes a strong function of *R*. Therefore, it is possible that at low temperature free carriers cannot move close to this region. To fill the states close to the space

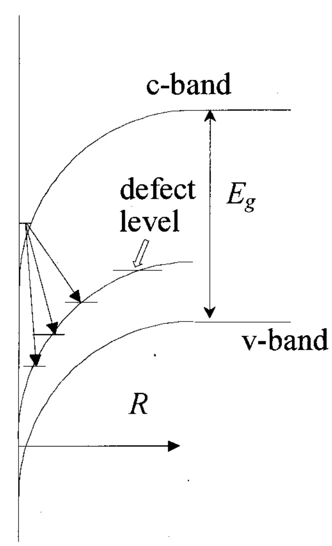

FIG. 5. Energy-band structure near a space charge region (dislocation or grain boundary) in $CuGaTe_2$.

charge region, which give an emission at higher energy, a certain thermal activation is needed. As a result of this, the shift of the peak position with temperature toward higher energies is just what would be predicted. Here, this shift was indeed detected, see Fig. 3.

There is no doubt that further studies to definitely solve the origin of this band are needed. Nevertheless, the deep levels in ternaries play a more important role than has been assumed before.

This work was supported by Estonian Science Foundation Grant No. 3714 and by EPSRC Grant No. GR/L 62757.

[1] A. Rivero, M. Quintero, Ch. Power, J. Gonzalez, R. Tovar, and J. Ruiz, J. Electron. Mater. **26**, 1428 (1997).
[2] J. Krustok, H. Collan, K. Hjelt, M. Yakushev, A. E. Hill, R. D. Tomlinson, H. Mändar, and H. Neumann, J. Appl. Phys. **83**, 7867 (1998).
[3] S. B. Zhang, S. Wei, A. Zunger, and H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).
[4] J. Krustok, J. H. Schön, H. Collan, M. Yakushev, J. Mädasson, and E. Bucher, J. Appl. Phys. **86**, 364 (1999).
[5] M. V. Yakushev, R. D. Pilkington, A. E. Hill, R. D. Tomlinson, R. W. Martin, J. Krustok, and H. W. Schock, Thin Solid Films (in press).
[6] J. Krustok, H. Collan, and K. Hjelt, J. Appl. Phys. **81**, 1442 (1997).
[7] J. Krustok, J. Mädasson, and J. Hiie, Phys. Status Solidi A **165**, 517 (1998).
[8] A. Gukasyan, A. Kvit, Y. Klevkov, and S. Oktyabrsky, Solid State Commun. **97**, 897 (1996).