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Photoluminescence Properties of Ge-Implanted $CuGaSe_2$ Crystals

J. KRUSTOK[1]) (a), J. RAUDOJA (a), and J. H. SCHÖN[2]) (b)

(a) Tallinn Technical University, Ehitajate tee 5, Tallinn 19086, Estonia

(b) Faculty of Physics, University of Konstanz, P.O. Box X916, D-78457 Konstanz, Germany

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Photoluminescence (PL) properties of Ge-doped $CuGaSe_2$ single crystals were studied in the temperature range between 8 and 300 K. The doping was done using the ion implantation technique. As-grown crystals exhibit two PL bands at 1.68 and 0.96 eV. The Ge doping gives rise to two additional deep PL bands at 1.28 and 0.73 eV. Based on the temperature quenching of these PL bands we show that the 1.68 and the 0.73 eV PL bands are probably both related to the V_{Cu} acceptor. We suppose that the (V_{Cu}–Ge_{Cu}) complex where the Ge donor defect has a double charge is responsible for the 0.73 eV band. The 0.96 and 1.28 eV bands are explained as close donor–acceptor pairs where the acceptor defect is V_{Ga}. We assume that the single charged Ge_{Cu} donor defect paired with the V_{Ga} is connected with the 1.28 eV PL band while an unknown intrinsic donor paired with the V_{Ga} is responsible for the 0.96 eV band.

1. Introduction

It is known that $Cu(InGa)Se_2$ thin film solar cells have a high potential to become a leading member of the future solar cells market. Therefore, it is not surprising that the defect physics of these materials has attained a considerable attention in recent years. Although there are great similarities between the defect structures of $CuInSe_2$ and $CuGaSe_2$ [1, 2], many differences also exist. One of them is the difficulty of preparing n-type conduction in $CuGaSe_2$, whereas $CuInSe_2$ can easily be converted from p-to n-type and reverse by annealing in vacuum or Se pressure [3, 4]. To overcome this difficulty extrinsic donor doping was investigated, which, however, resulted only in strong electrical compensation [5 to 7]. Finally, n-type conductivity was achieved in $CuGaSe_2$ using ion implantation of Ge followed by annealing in the presence of Zn [8].

Ge implantation creates several donor defects like Ge_{Cu} or Ge_{Ga}, which tend to form complexes with native acceptors leading to self-compensation. Due to the relative depth of the Ge donor levels these complexes are expected to exhibit a photoluminescence (PL) emission in a "deep" spectral region, i.e. far below the band gap energy. As it was shown already in [8], Ge-doped $CuGaSe_2$ has at least one additional PL peak at $h\nu =$ 1.28 eV. Deep PL bands were studied recently in undoped $CuInS_2$ and $CuGaSe_2$ [9, 10], where some of these deep PL bands can be explained as an electron–hole recombina-

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[1]) e-mail:krustok@cc.ttu.ee

[2]) Present address: Bell Laboratories, Lucent Technologies, 600 Mountain Ave., Murray Hill, NJ 07974, USA

tion within donor–acceptor (DA) pairs involving deep donor and deep acceptor levels. In the present paper, we study PL properties of Ge-implanted $CuGaSe_2$ more carefully in order to follow the formation of Ge-related defect complexes.

2. Experimental

$CuGaSe_2$ single crystals were grown from a stoichiometric mixture of the elements by chemical vapour transport at temperatures between 780 and 830 °C using iodine as a transport agent. In order to decrease the acceptor concentration, the as-grown samples were annealed in the presence of Cu (500 °C/120 h) which reduces the room temperature hole concentration to approximately 10^{15} cm^{-3}. These electrically compensated crystals were used for ion implantation of Ge at an acceleration voltage of 200 kV and a dose 5×10^{15} cm^{-2}. Rapid thermal annealing at 400 °C in vacuum was used in order to heal the implantation damage. All implanted and annealed samples exhibited p-type conductivity. However, it has been demonstrated that annealing at 400 °C in the presence of Zn results in type conversion [8].

A He–Cd laser at a wavelength of 441 nm was used as the excitation source for steady-state PL measurements at temperatures ranging from 8 to 300 K. The 30 mW laser beam was focused onto the sample with a spot diameter of about 100 μm and the luminescent light was analyzed with a 0.4 m monochromator and detected by either a PbS detector, InGaAs detector or a photomultiplier tube with S1-characteristics. All samples were etched prior to measurement in a solution of bromine in methanol in order to ensure good and comparable surface properties.

3. Results and Discussion

As-grown $CuGaSe_2$ crystals exhibit two PL bands, which are shown in Fig. 1. The 1.68 eV band with its phonon structure is assumed to be a free-to-bound transition via V_{Cu} defects (see for example [8]). The same band is also present in Ge-doped $CuGaSe_2$ samples. The second band found in as-grown crystals has a peak position at approximately $h\nu = 0.96$ eV. It is worth mentioning that this band has been observed at slightly lower energies compared with D1 and D2 bands found previously in $CuGaSe_2$ crystals [7, 9, 10]. Therefore, it cannot be related to the DA pairs including an interstitial donor defect as it was done for D1 and D2 bands in [9, 10]. The 0.96 eV band does not disappear after Ge implantation. Since the band is present in as-grown samples, it is obvious that it originates from intrinsic defects. Ge implantation gives rise to two additional deep PL bands with peak positions at $h\nu = 1.28$ and 0.73 eV (see Fig. 1). All these PL bands did not show any shift with increasing laser power. Therefore, we conclude that they are not related to distant DA pairs or to the band-to-tail recombination usually seen in compensated ternary compounds [11, 12]. They seem to be related to the radiative recombination involving very close DA pairs.

Temperature quenching experiments indicated that the 1.68 and the 0.73 eV bands behave in a very similar way (see Fig. 2). The rapid quenching process for both bands starts at 50 K. They practically disappeared at temperatures above 70 K. In order to extract thermal activation energies of the quenching we used an equation proposed in [13]

$$I(T) = \frac{I_0}{1 + \varphi_1 T^{3/2} + \varphi_2 T^{3/2} \exp\left(-E_T/kT\right)}\,, \tag{1}$$

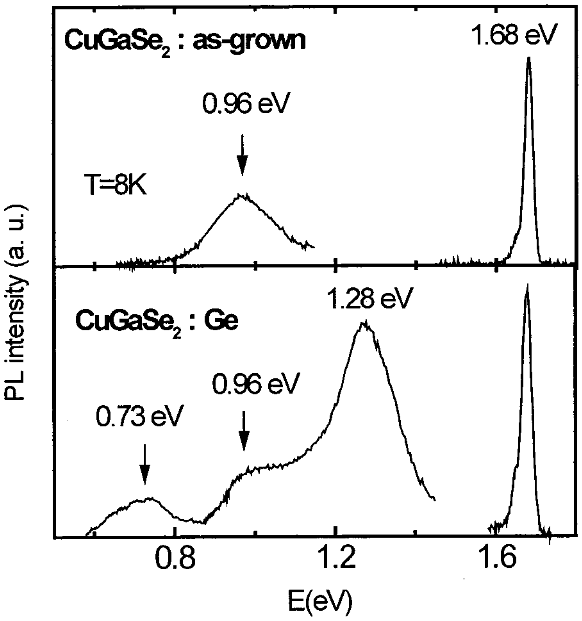

Fig. 1. Photoluminescence spectra of an as-grown and an Ge ion-implanted CuGaSe$_2$ samples at $T = 8$ K

where φ_1, φ_2, I_0 and E_T are fitting parameters. As was shown in [13], this equation includes the temperature dependence of the capture cross-sections of both the donor and the acceptor defects and therefore it should give a more correct fit especially in the low-temperature region. The activation energies E_T for the various PL bands are summarized in Table 1 and the fitting results are also given in Fig. 2 as continuous lines.

The 1.68 eV band has a thermal quenching activation energy of $E_T = 49$ meV. This value is consistent with the value obtained from the difference of the energy of the band gap ($E_g = 1.73$ eV [6]) and the peak position of this band: $E_A = 50$ meV. Although the 0.73 eV band exhibits a quite similar quenching behaviour as the 1.68 eV band, its activation energy is even smaller than that for the 1.68 eV band.

The other two PL bands, the 1.28 eV band and the 0.96 eV band,

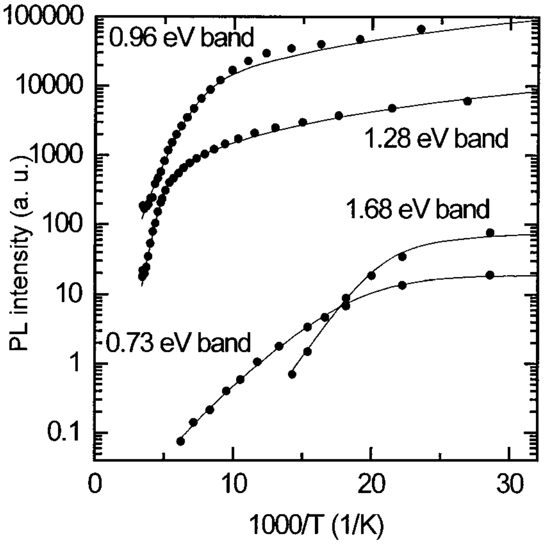

Fig. 2. Temperature dependence of the integrated intensities of the PL bands in CuGaSe$_2$:Ge. Continuous curves show the result of parameter fitting to Eq. (1). Activation energies are given in Table 1

Table 1
Thermal quenching activation energies of PL bands in $CuGaSe_2$:Ge

PL band	1.68 eV	1.28 eV	0.96 eV	0.73 eV
E_T (meV)	49 ± 5	167 ± 2	75 ± 7	27 ± 10

also revealed very similar thermal quenching although their activation energies are quite different (see Fig. 2 and Table 1). Both bands quenched at temperatures very close to room temperature. We assume that the similarity of the thermal quenching is related to the same acceptor defect involved in both emissions. In this case the 1.68 eV band and the 0.73 eV band are both related to the V_{Cu} defect, where in the 0.73 eV PL band the V_{Cu} forms a DA pair with a Ge donor. Considering the relative depth of this PL band the donor defect should be very deep. It is generally known, that pairing with deep donors shifts the acceptor level (V_{Cu}) closer to the valence band edge, leading to a decrease of the activation energy. The same model also holds for the 1.28 and 0.96 eV PL bands, where the most probable acceptor defect is V_{Ga}. According to the theoretical calculations, the isolated V_{Ga} level in $CuGaSe_2$ is expected to be at $E_A = 190$ meV [2]. Due to the pairing with donor defects this level is shifting closer to the valence band edge. This shift is larger for closer DA pairs. Hence, it is obvious that the 0.96 eV band is caused by DA pairs, which are closer than those for the 1.28 eV band. It has already been stated, that the donor defect involved in the 0.96 eV band has an intrinsic origin, but at this point it remains unknown.

Ge doping creates two different types of donor defects: Ge_{Cu} and Ge_{Ga}. As it was supposed in [8] the $Ge_{Cu}^{\bullet}$ donor level is slightly deeper than the $Ge_{Ga}^{\bullet}$ level. Consequently, we assume that the Ge_{Cu} donor is responsible for the 1.28 eV band. At the same time, the 0.73 eV band must be related to an even deeper Ge donor level. Therefore, we also have to consider the Ge_{Cu} donor with double charge: $Ge_{Cu}^{\bullet\bullet}$. The presence of donor levels with double charge is possible, if the Fermi level is quite low. Our results show that after annealing in Zn atmosphere, when the crystal is converted to n-type [8], the 0.73 eV band indeed vanishes, but the other PL bands are still present.

Based on the afore-mentioned facts we present a defect model for the Ge-implanted $CuGaSe_2$ crystals (see Fig. 3).

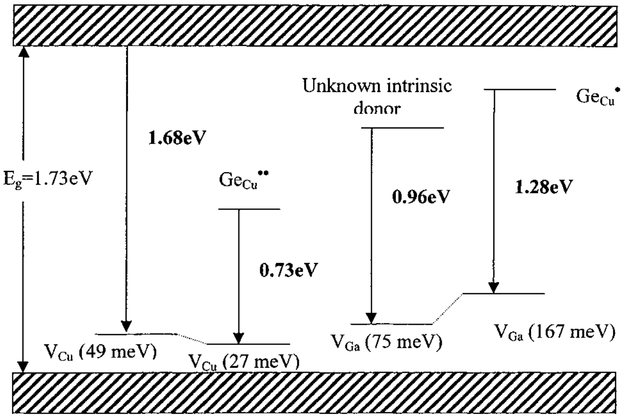

Fig. 3. The proposed defect model for the Ge-implanted $CuGaSe_2$

It is worth mentioning that the intensity of the 1.28 eV band is strongly reduced in the n-type samples compared to vacuum-annealed p-type $CuGaSe_2$ [8]. We assume that the formation of close DA pairs of an intrinsic acceptor and an extrinsic (Ge) donor is related to the amount of self-compensation in this material. In order to obtain type conversion it is necessary to minimize the effects of self-compensation. The presented results reveal that the change of annealing conditions after the implantation step has a significant influence on the formation of defect pairs. Annealing in the presence of Zn seems to reduce the spontaneous formation of Cu vacancies. Hence, doping becomes more effective. Furthermore, we believe that the type of the formed Ge donor changes. Vacuum annealing leads to mostly Ge_{Cu} defects, whereas Ge_{Ga} defects dominate in Zn annealed samples [8]. However, in order to gain a complete understanding of self-compensation in $CuGaSe_2$ further studies are needed.

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