Photoluminescence properties of stoichiometric CuInSe$_2$ crystals

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Abstract

We studied photoluminescence (PL) properties of stoichiometric CuInSe$_2$ (CIS) single microcrystals. Temperature and laser power dependencies of the PL spectra were measured. Two bands at 0.973 (A-band) and 0.991 eV (B-band) governed the obtained PL spectra. Measured dependencies showed very similar properties for both bands: the j-shift that was generated by altering the laser power was 2 meV per decade for both bands and thermal activation energies were 46 and 32 meV for A- and B-band, respectively. Based on these results, we assume that both bands come from the same shallow donor–shallow acceptor recombination process with different bandgap energies for CIS. The solid solution phase of CIS with K or Na is proposed as the source of distinctive bandgap.
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1. Introduction

Photoluminescence (PL) is a widely used method to study the defect structure in semiconductor materials. A large number of studies have been published also for the chalcopyrite compound CuInSe$_2$ (CIS). This material is used as a basic absorber material for the thin film solar cells despite the fact that the defect structure of CIS is still not completely understood. PL spectra of CIS crystals and thin films are very sensitive to the deviation from the ideal stoichiometry. Many researchers have measured PL of CIS as a function of the Cu/In ratio [1–4]. These studies have shown that the emission spectra for Cu- and In-rich samples are dominated by different

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types of recombination. At the same time samples with nearly stoichiometric composition or slightly In-rich show PL spectra with very distinctive pattern. They are dominated by the PL peak at about 0.99 eV [1–5]. According to the theoretical calculations [6], the shallowest single acceptor level in CIS is connected to V_{Cu} having the ionization energy around 30–40 meV. V_{Cu} is believed to be responsible for the PL emission at 0.97 eV and therefore in Ref. [5] a complex defect Cu_{In}–Cu_i was proposed for the 0.99 eV PL band. Both components of this defect pair have relatively deep levels, around 270 and 200 meV for Cu_{In} and Cu_i, respectively [6], and therefore a forming of a deep donor–deep acceptor pair is needed with relatively high coulomb interaction between components of a pair. In this case, PL properties of the 0.97 (shallow levels) and the 0.99 eV band (deep levels) must be completely different. However, most studies show that both bands show very similar properties. Moreover, the 0.99 eV band is not always present even if the proper stoichiometry of samples is maintained. All these facts indicate that more studies are needed to clarify the origin of the 0.99 eV band in CIS.

In this paper, we present a detailed analysis of the temperature and the excitation dependence of the 0.99 eV band in CIS and propose a new model for this PL band.

2. Experimental details

The samples used in this work were grown from Cu–In (50–50 at%) alloy and Se in CuSe molten phase. All used precursors were 5 N purity. The alloy and CuSe were mixed and ground in mortar, loaded into quartz ampoule and necessary Se amount was added. The ampoule with precursor materials was degassed and evacuated, then the ampoule was sealed. The duration of growth was several hours at above 700 K. After growth and "rapid" cooling, the ampoule was opened and a flux phase was removed by long-time etching in a hot KCN solution. After that crystals were post-treated in dynamic vacuum in order to heal the surface of crystals. All crystals showed p-type conductivity.

SIMS data were acquired using CAM-ECA IMS-4F ion microscope. A 10 keV Cs^+ primary ion beam was used for analysis with beam currents of 0.3 nA for mass spectra and 45 nA for depth profiling. The areas analyzed were $300 \times 300 \, \mu m^2$ for mass spectra and $170 \times 170 \, \mu m^2$ for depth profiles. The depth calibration for profiles was based on an assumed sputter rate of 4 for $CuInSe_2$ by taking into account the sputtered area, time for analysis and primary ion beam current parameters.

For PL measurements reported here, a semiconductor laser with the wavelength of 675 nm (60 mW) was used for excitation. The crystals were mounted inside a closed cycle He cryostat ($T = 8-300$ K). The PL spectra were recorded with a computer-controlled SPM-2 grating monochromator ($f = 0.4$ m). The chopped signal was detected with an InGaAs detector using the conventional lock-in technique. The emission spectra were corrected for the grating efficiency variations and for the spectral response of the detectors.

3. Results and discussion

The typical PL spectrum of our CIS crystals is dominated by a band at 0.991 eV (B-band) together with an ordinary band at 0.973 eV (A-band) followed by phonon replicas as shown in Fig. 1.

As is usual, we assume that the intensity of A and B PL bands with their phonon replicas follow a Poisson distribution

$$I(n) = I_0 e^{-S} \frac{S^n}{n!}. \tag{1}$$

Here S is the Huang–Rhys coupling parameter and I_0 is a scaling constant. We also assume that each phonon replica has a Gaussian shape. By fitting the measured spectra to Eq. (1), we can see that the S-parameter for both bands has a value $S \approx 0.25$. At the same time the energy separation between phonon replicas is very close to the LO-phonon energy in CuInSe$_2$ ($\hbar\omega_{LO} = 29$ meV [11]) and the halfwidth of these replicas is similar for both bands. All these facts indicate that there is no big difference between the recombination models for both PL bands.
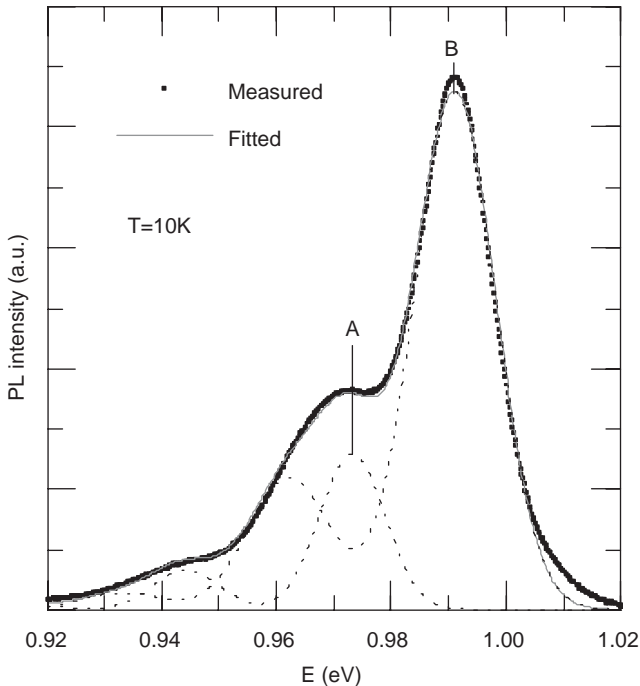

Fig. 1. Typical PL spectrum of a stoichiometric CuInSe$_2$ crystal. The measured spectrum shows 2 bands at 0.991 (B-band) and 0.973 eV (A-band). Fitting result using Eq. (1) is also shown as a dashed line.
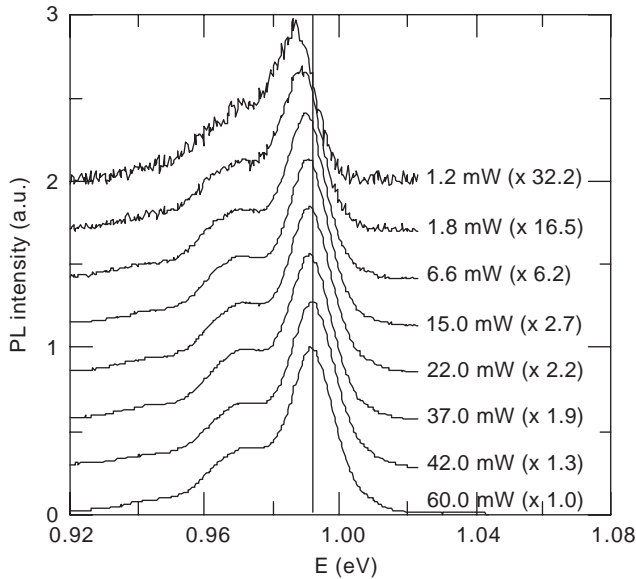
Fig. 2. Power dependence of a CIS PL signal. The peak shift with laser power is clearly seen.

PL band at 0.97 eV (A-band) is a typical PL band in Cu-rich CIS. According to Zott et al. [1] this band is most probably connected with a free-to-bound transition. At the same time other groups [3] have found evidence about donor–acceptor (DA) recombination character of this PL band.

So-called j-shift is a usual way to determine a DA recombination process. It is known that due to the different recombination probabilities of DA-pairs with different distances between components, the PL band must shift toward higher energy with increasing excitation power. This shift is called j-shift and it is typical for relatively distant DA pairs. Similar but more pronounced j-shift is also seen in In-rich samples, but it is caused by a different recombination process and explained with the potential fluctuation theory [4,7,8]. In the case of very close DA-pairs, j-shift is not seen at all [9]. Fig. 2 shows the dependence of the PL signal on the excitation power for our CIS crystal. Both bands (A and B) show a continuous j-shift of about 2 meV/decade.

Observed j-shift is typical for shallow donor–shallow acceptor recombination in $CuInSe_2$ [3].

In order to obtain information about the defect levels responsible for a particular PL band, the temperature dependence of the PL signal is often used (Fig. 3). 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. [10], however, it was shown that the low-temperature quenching may not really be a thermal activation process; instead, it is caused by a temperature dependence of the capture cross sections of a particular recombination center. According to this theory, the
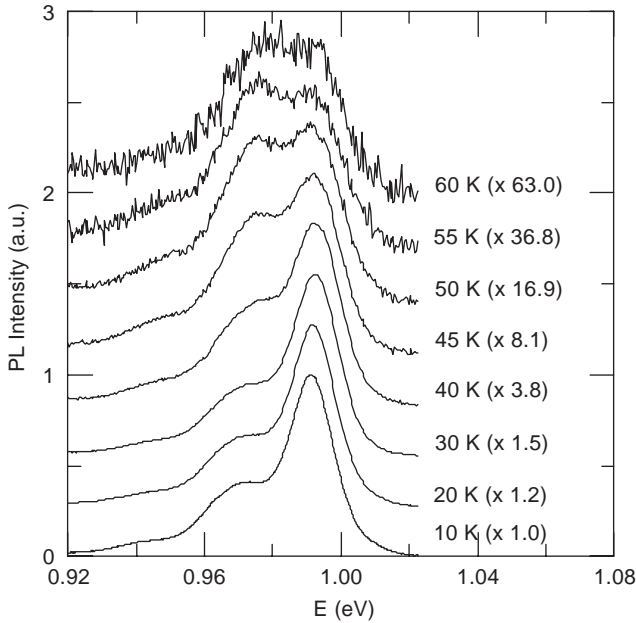
Fig. 3. Temperature dependence of the PL signal of CIS crystal.

temperature dependence of the integral intensity is

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

In the present work, Eq. (2) was used to fit the measured temperature dependence of the A- and B-band integral intensity, see Fig. 4. Again, both PL bands have very close thermal activation energies: 46 and 32 meV for A- and B-band, respectively.

All these measured dependencies indicate that both PL bands must have very similar recombination process where at least one shallow acceptor level with $E_a \approx 40$ meV is involved. According to Zhang et al. [6], the shallowest acceptor in CIS is a copper vacancy V_{Cu}. In order to explain 2 PL bands, we must assume that some kind of complex defect is responsible for the second shallow acceptor level, as it was also proposed in Ref. [5]. But then the properties of the A- and B-bands must be at least somehow different. There exist also another possibility that we have the same acceptor for both bands but different bandgap energies for host material. In earlier works there are several common properties for all samples, where the B PL band has been seen. In all cases, this PL band appears only in stoichiometric samples where Cu/In ≈ 1. Another important fact is that all samples have been prepared on a soda lime class [1–5]. The present paper is the first where the B-band is seen in a single crystal prepared without any Na source. But at the same time we have used a long-time etching in a KCN solution at relatively high temperature. SIMS analysis reveales the presence of both K and Na in our crystals after etching, see Fig. 5. The
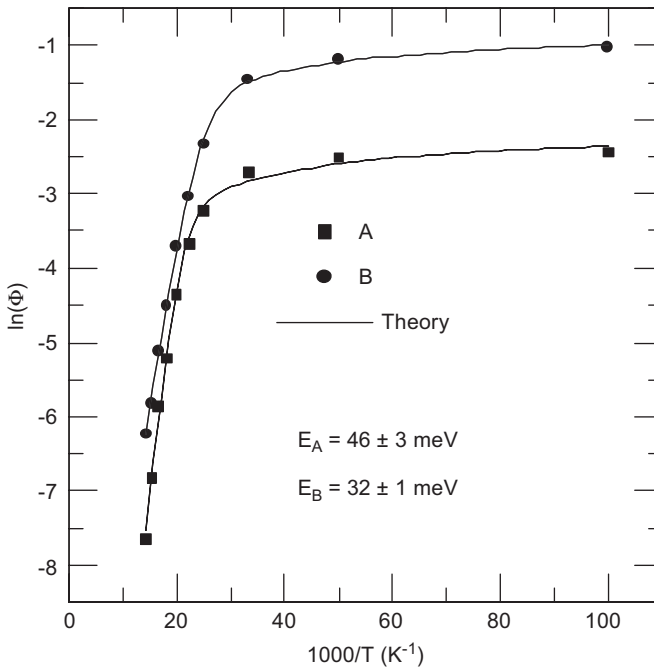
Fig. 4. PL intensity of the observed bands as a function of reciprocal temperature. The filled symbols represent data points and the fitted curves are obtained using Eq. (2).

concentration of both elements seems to be higher at the surface. It is known that K and Na have very similar properties in II–VI compounds. Very little is known about K in CIS, but lot of work has been done to understand the role of Na in CIS. It has been observed that CIS solar cells containing small amounts of Na achieve higher efficiencies compared to those without Na. The effects of Na on the electrical properties of CIS were discussed by Wei et al. [12]. It was shown that Na does not create any shallow acceptor level in CIS, but it can form a solid solution with CIS in the form of $Na_x Cu_{1-x} InSe_2$ with slightly higher bandgap energy.

It is also noted that Na (or K) incorporation into CIS increases the volume of the unit cell [13] and usually a blue shift of PL emission is seen with Na incorporation [14]. Formation of (Cu, Na)In S_2 on the surface of $CuInS_2$ was observed in Ref. [15].

In $CuGaSe_2$ the formation of a quaternary Na–Cu–Ga–Se compound was proposed which is based on the defect-chalcopyrite structure having the Cu vacancies partially filled by Na atoms [16].

Considering all these facts, we assume that there must be a solid solution phase of CIS with K or Na with slightly higher bandgap energy on the surface of our crystals. The total concentration of quaternary K(Na)–Cu–In–Se compound must be less than the detection limit of XRD, because we did not see any other phases in XRD spectra. Probably this solid solution phase is covering only the surface of crystals. PL is known to be a very sensitive technique and therefore it is not surprising that the
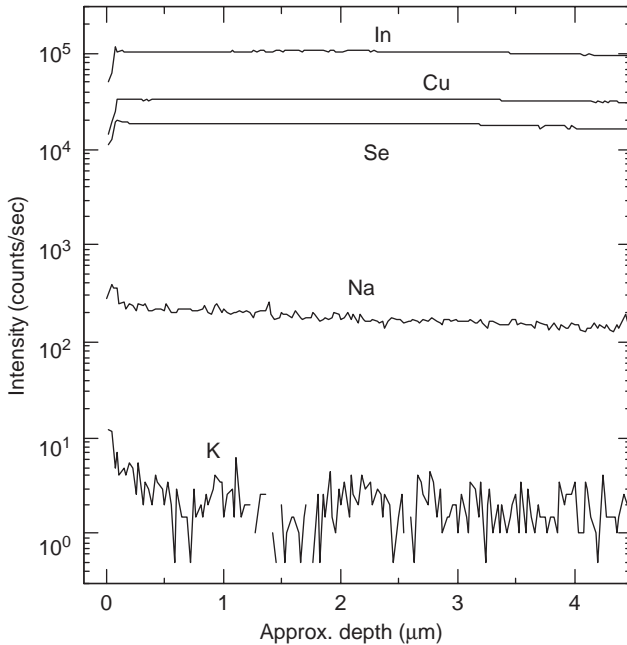
Fig. 5. SIMS depth profiles of Cu, In, Se, Na and K.

presence of quaternary K(Na)–Cu–In–Se compound can be discovered. In Cu-rich CIS, the concentration of copper vacancies is very low and therefore the formation of K(Na)–Cu–In–Se compound, where K or Na incorporates in V_{Cu}, is suppressed. As a result we do not see the B-band in Cu-rich materials. At the same time, In-rich CIS materials show totally different PL spectra without any phonon structure and with asymmetric PL band [1,4,7,8]. Therefore, the presence of the K(Na)–Cu–In–Se phase is not easy to verify by PL because the slight change of the bandgap energy is masked by other effects like potential fluctuations of charged defects.

4. Conclusion

The PL spectra of CuInSe$_2$ single microcrystals were studied. The measured spectra showed two dominating bands at 0.973 and 0.991 eV. Firstly, we determined PL spectra dependency on the excitation intensity. We found that both bands shift towards higher energies with increasing laser power. The rate of the shift was 2 meV/decade and equal for both bands. Secondly, we measured the temperature dependence of PL emission. The results were fitted and integrated intensities $\Phi(T)$ for both bands were analyzed as a function of temperature. The calculated thermal activation energies were also very similar for both bands being 46 meV for A-band and 32 meV for B-band. Thus, we have a reason to believe that both bands originate from the same type of source. We assume that both bands involve the same kind of

DA pair and the difference comes from deviant bandgap energies for CIS. Previously, the B-band has been observed in the presence of Na in CIS. Although our samples did not contain Na, etching with KCN could have doped our samples with K and Na. As known, Na and K have very similar properties in II–VI compounds. By increasing the unit cell volume, they shift the normal PL spectrum towards higher energies. According to these considerations, we propose that observed B-band is caused by a solid solution phase of CIS with K or Na in our crystals. Nevertheless, further studies are needed to establish a solid base for this statement.

Acknowledgements

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