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ScienceDirect
Thin Solid Films 515 (2007) 6204–6207
www.elsevier.com/locate/tsf

Investigation of potential and compositional fluctuations in $CuGa_3Se_5$ crystals using photoluminescence spectroscopy

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Available online 16 January 2007

Abstract

We studied the photoluminescence (PL) properties of the ordered defect compound $CuGa_3Se_5$. Different single crystals were grown by the vertical Bridgman method and by the solid phase crystallization method. Their crystal structure and cell parameters were determined by X-ray diffraction. The PL spectra were recorded at $T=10$–300 K. Also, laser power dependences were studied. We found an asymmetric PL band at 1.76 eV. PL band shifts towards higher energies with increasing laser power. The shape and properties of this band assure the presence of potential and compositional fluctuations. The influence of both fluctuations on the PL properties of $CuGa_3Se_5$ is studied and the radiative recombination processes are explained.

PACS: 78.55.Hx; 71.55.Ht; 61.72.Ji; 78.30.A
Keywords: $CuGa_3Se_5$; Chalcopyrite crystals; Photoluminescence; Ordered defect compounds; Potential fluctuations

1. Introduction

$CuGaSe_2$ and the related I–III–VI_2 chalcopyrite compounds are of great interest due to their potential in photovoltaic and nonlinear optical applications. Another attractive property is their tolerance to large range of anion-to-cation off stoichiometry, manifested by the existence of an ordered defect compounds (ODC) with large variations in their Cu/Ga/Se ratio [1]. These ODCs, like $CuGa_3Se_5$ and $CuGa_5Se_8$, generally possess wider bandgap and the formation of ternary Cu–Ga–Se compounds with varying bandgaps enables the formation of heterojunctions used in the design of high-performance electronic and optoelectronic devices. The bandgap energy of $CuGa_3Se_5$ for bulk samples at room temperature is 1.754 eV and for thin films 1.855 eV [2].

Rincon et al. [3] have measured the PL spectrum of $CuGa_3Se_5$ that consists of one broad band $h\nu_{max}=1.63$ eV ($T=15$ K) that is proposed to result from donor–acceptor pair recombination. Guastavino et al. [4] have measured the PL spectrum of $CuGa_3Se_5$ that consists of one broad asymmetric edge emission band at $h\nu_{max}=1.6$ eV ($T=4.2$ K) and one deeper band at $h\nu_{max}\sim1.2$ eV ($T=4.2$ K). The broadness of the PL bands (150–200 meV) was interpreted also by donor–acceptor pair transitions.

At the same time, the asymmetric shape of the PL band in ternary chalcopyrites is often caused by the band tails induced by potential fluctuations due to the high concentration of intrinsic defects [5–7]. Furthermore, compositional fluctuations also affect the shape of PL bands by creating the fluctuations of the bandgap energy. In this paper, we study the photoluminescence (PL) properties of $CuGa_3Se_5$ in connection with compositional and potential fluctuations.

2. Experimental

The $CuGa_3Se_5$ crystals were grown by the solid phase crystallization (SPC) method and vertical Bridgman method.

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0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.12.068

For the SPC growth, the stoichiometric amounts of Cu (99.999% of purity), Ga (99.9999%) and Se (99.999%) (~20 g total) were placed together in quartz ampoule with an inner surface coated by carbon. Ampoule was evacuated up to 10^2 Pa and sealed. For synthesis, one-zone vertical resistance furnace was used. Ampoule with Cu, Ga, and Se was heated up to 550–600 °C and kept at this temperature for 24 h. Then, the temperature was raised with the rate of 50 K/h up to 950 °C. This temperature is about 30 °C lower than the melting point temperature of $CuGa_3Se_5$ (T_m=1359 K [8]). Ampoule was held at this temperature for 10 days before cooling. An ingot consisting of a few single crystal blocks of $CuGa_3Se_5$ was obtained.

For the Bridgman growth, crystals with given composition grown by the two-temperature method were used. The details of the growth can be found in Ref. [8].

For the structural characterization, X-ray diffraction (XRD) patterns, recorded by the Siemens D 500 diffractometer were used. The composition of the crystals was determined by energy-dispersive X-ray analysis (EDAX) performed on the Leo Supra 35 SEM. PL measurements were done using closed-cycle He cryostat (T=8–300 K) and He–Cd laser (441.6 nm) as an excitation source.

3. Results and discussion

3.1. Structural analysis

The phases and crystallographic structure of the crystals were determined by X-ray diffraction. Rietveld method was used for the derivation of crystal structure information from powder XRD data. The X-ray analysis demonstrated the single phase of the tetragonal chalcopyrite-related structure of $CuGa_3Se_5$. The Rietveld evaluation produced unit-cell parameters a=0.54874 nm, and c=1.10049 nm for $CuGa_3Se_5$ crystal grown by the SPC method and a=0.54803 nm, and c=1.09734 nm for the crystal grown by the vertical Bridgman method. These values are close to data a=0.544995(8) nm, and c=1.0946(3) nm reported in Ref. [9].

3.2. Composition analysis

The studies of the crystals' composition were done by energy-dispersive X-ray analysis (EDAX). The chemical composition was measured in several points of crystals and the presence of compositional fluctuations was detected, being larger for the $CuGa_3Se_5$ samples grown by the SPC method, see Fig. 1.

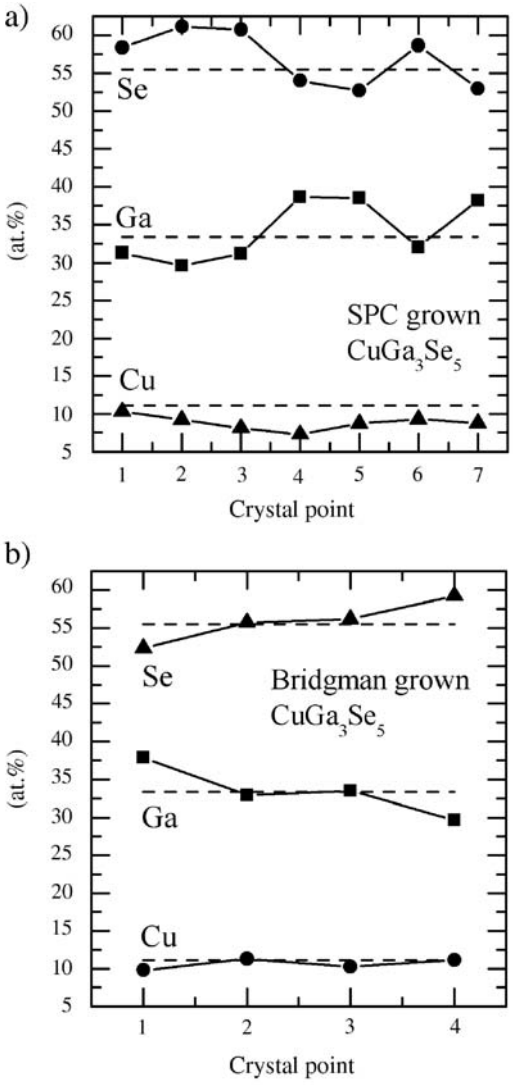

Fig. 1. Chemical composition measured in several points of $CuGa_3Se_5$ crystals grown by the SPC method (a) and by the vertical Bridgman method (b). The dashed line represents the chemical composition of $CuGa_3Se_5$ (Cu:Ga:Se=11.11:33.33:55.55 at.%).

3.3. Photoluminescence results

In heavily doped semiconductors Coulomb potential fluctuations are induced due to the random distribution of unscreened charged defects. These potential fluctuations will lead to a local perturbation of the band structure, thus broadening the defect level distribution and forming band tails [10,11]. Radiative recombination in heavily doped crystal is therefore governed by the recombination of carriers localized in spatially separated potential wells originating from Coulomb potential fluctuations. The presence of compositional fluctuations causes additional broadening of the PL bands due to the variation of the bandgap energy, see Fig. 2.

In this study, we found a broad (full width at half maximum (FWHM) ~200 meV) asymmetric PL band at 1.76 eV. It has an exponential slope on the low-energy side and steeper Gaussian incline on the high-energy side. This type of asymmetric PL bands was found in many ternaries [5–7,13]. Fig. 3 shows normalised spectra of the asymmetric PL band for SPC grown $CuGa_3Se_5$, measured from different points of the crystal. The maximum energy difference of the corresponding peak positions is ~60 meV. This difference may be taken as the approximate value of the bandgap energy fluctuations. The mean amplitude of the Coulomb potential fluctuations γ_0 is the average energetic difference between the hole energy in the Coulomb potential fluctuation minimum and maximum, see Fig. 2. The average

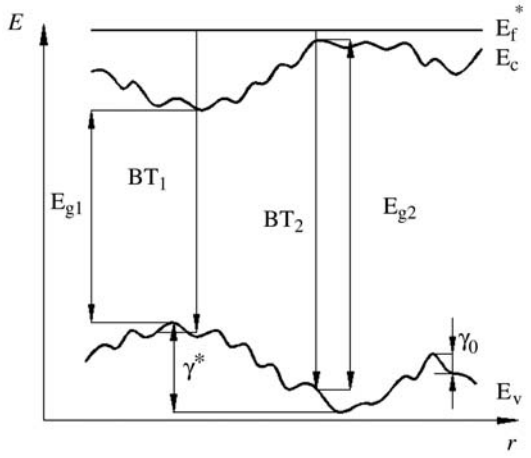

Fig. 2. BT recombination model in $CuGa_3Se_5$ in the presence of potential- and compositional fluctuations. BT_1 and BT_2 emissions originate from different parts of the crystal with different bandgap energy (E_{g1} vs E_{g2}).

amplitude of band edge fluctuations γ^* in the presence of potential and compositional fluctuations is the mean difference of the energy of holes in the valence band fluctuation minimum and maximum. The slope of the low-energy side of the PL band is determined by the density of states in the valence band and therefore depends on the amplitude of both fluctuations. Thus, the values of the mean amplitude of the band edge fluctuations γ^* can be derived form the slope of the low-energy side of the PL band [5,6,10]. The compositional fluctuations also affect the half-width of the PL band. The values of the mean amplitude of the band edge fluctuations γ^* and the FWHM of the BT-band for several chalcopyrite compounds are shown in Table 1. The average value of γ^* of the crystals investigated in this study has been determined from the exponential slope of the low-energy side of the PL band (see Fig. 2) and was about 70 meV, and 90 meV for Bridgman, and SPC grown $CuGa_3Se_5$, respectively. These rather high values of γ^* and FWHM support the idea of the coexistence of potential and compositional fluctuations in these samples.

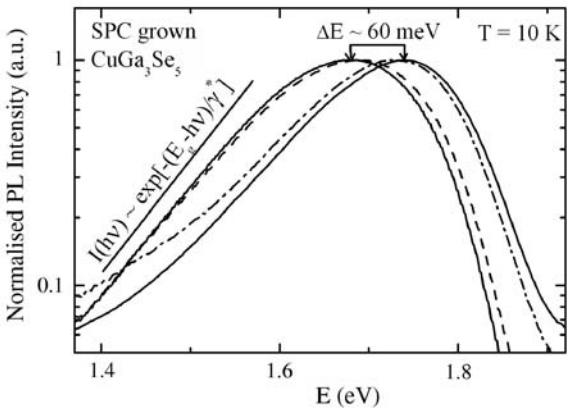

Fig. 3. Normalised spectra of the 1.76 eV PL band for SPC grown $CuGa_3Se_5$, measured from different spots of the crystal. The energy difference of the peak positions is ~60 meV. The exponential slope of the low-energy side of the BT-band gives the average depth of the band edge fluctuations γ^*.

Table 1
Values of the average amplitude of the band edge fluctuations γ^*, calculated from the low-energy slope of the PL band, and FWHM of the BT-band for several chalcopyrite compounds

Compound	γ^* (meV)	FWHM (meV)	References
$CuGaSe_2$	17.6	50	[6]
$CuIn_{0.5}Ga_{0.5}Se_2$	17.0	49	[5]
$AgGaTe_2$	4.5	16	[13]
$CuInSe_2$	24.1	51	Our data
$CuGa_3Se_5$ (Bridgman)	58.1–72.8	170–178	Present work
$CuGa_3Se_5$ (SPC)	71.4–94.5	188–220	Present work

Excitation power and temperature dependent photoluminescence measurements indicate that our spectra are dominated by the BT-type recombination that involves free electron and a hole that is localized in the valence band tail. Due to their small effective mass ($m_e^* \approx 0.08 m_e$), almost all electrons are free. Due to band edge fluctuations, at low temperatures, holes in the valence band can not be considered as free like in the undisturbed crystal with flat bands (graphical illustration and theoretical discussion of this kind of configuration are presented in Refs. [7] and [10]). Holes are localized in the valence band potential wells and form so-called pseudo-acceptor states. The activation energy of the thermal quenching of the BT-band allows us to evaluate the average depth of these pseudo-acceptor states. From Arrhenius plot of thermal quenching of the PL bands, we obtained thermal activation energies 38± 12 meV, and 53±17 meV for Bridgman, and SPC crystals, respectively. Although, the $\ln I(T)$ versus $1000/T$ dependence is very similar to the theoretical dependence for discrete energy levels [12], it is clear that in the case of BT-type recombination, the fitting is not completely valid due to continuous tail states. However, the average activation energy of pseudo-acceptor states can be estimated to be approximately 45 meV.

In Fig. 4, the temperature dependence of the peak position of the 1.76 eV PL band is shown along with the bandgap energy E_g of $CuGa_3Se_5$ [2]. The observed shift of the peak position energy

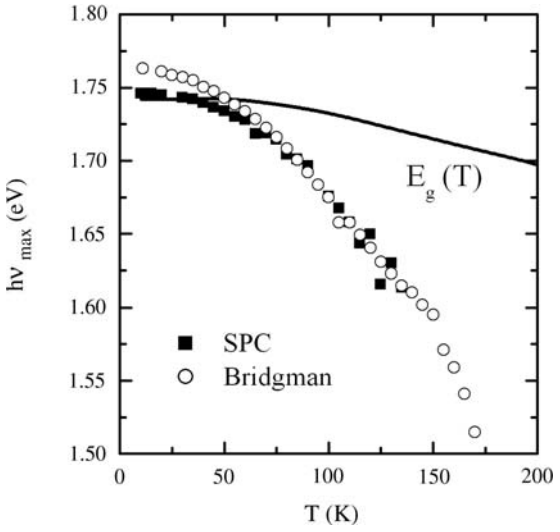

Fig. 4. Temperature dependence of the peak position of the 1.76 eV PL band and the bandgap energy E_g [2] of $CuGa_3Se_5$.

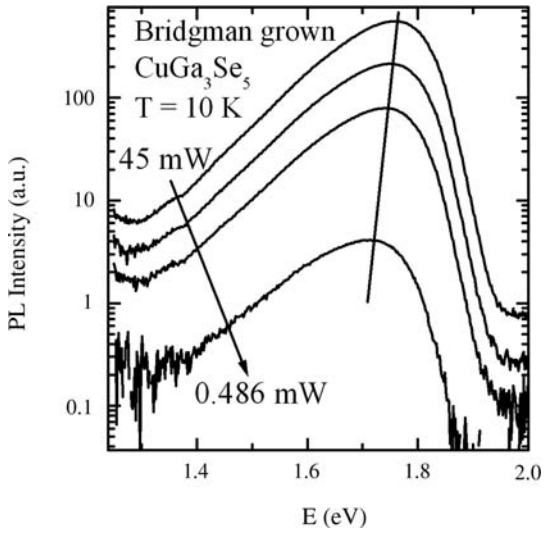

Fig. 5. The laser power dependence of PL spectrum of the $CuGa_3Se_5$ crystal grown by the vertical Bridgman method. The observed PL band shifts to higher energies with increasing excitation intensity. The magnitude of the shift is about 19 meV per decade.

exceeds the temperature dependence of the bandgap energy. This feature is predicted by the theory of heavily doped semiconductors [6,10]. According to the theory, when holes, localized in the valence band tail are freed at higher temperatures, BB-transition, that involves a free electron and a free hole, dominates the spectra. However BB-band may not appear in the presence of large compositional fluctuations, because higher thermal energy is needed to liberate holes. In our case, the thermal energy is enough to redistribute the holes between the potential wells and therefore BB-band was not detected.

The excitation power dependence of the PL peak at 1.76 eV is shown in Fig. 5. The blue shift of the BT-band with the magnitude of about 19 meV per decade was detected. This confirms that the observed emission results from BT recombination together with the bandgap fluctuations [6,10].

The detailed theoretical discussion of these results is beyond the scope of this paper and will be presented in the near future.

4. Conclusions

The photoluminescence properties of the ordered defect compound $CuGa_3Se_5$ have been studied. Broad asymmetric PL band at 1.76 eV, resulting from BT-type recombination, has been detected. The shape and the properties of this PL band were explained assuming the coexistence of compositional fluctuations and the potential fluctuations due to high concentration of charged defects. The energy-dispersive X-ray analysis confirmed the variation of composition in the samples.

Acknowledgement

This work was supported by INTAS grant nr. 03-51-6314 and by the Estonian Science Foundation grant G-6554.

References

[1] S.B. Zhang, S.H. Wei, A. Zunger, Phys. Rev. B 57 (1998) 9642.
[2] G. Marin, C. Rincon, S.M. Wasim, G. Sanchez Perez, I. Molina, J. Alloys Compd. 283 (1999) 1.
[3] C. Rincon, S.M. Wasim, G. Marin, E. Hernandez, G. Sanchez Perez, J. Galibert, J. Appl. Phys. 87 (2000) 2293.
[4] F. Guastavino, K. Zeaiter, L. Djellal, Yanuar, D. Bayaa, M. Abdelali, C. Llinares, Solid State Phenom. 67–68 (1999) 427.
[5] J. Krustok, H. Collan, M. Yakushev, K. Hjelt, Phys. Scr. T79 (1999) 179.
[6] J. Krustok, J. Raudoja, M. Yakushev, R.D. Pilkington, H. Collan, Phys. Status Solidi 173 (1999) 483.
[7] A. Jagomägi, J. Krustok, J. Raudoja, M. Grossberg, M. Danilson, M. Yakushev, Physica B 337 (2003) 369.
[8] N.S. Orlova, I.V. Bodnar, T.L. Kushner, J. Phys. Chem. Solids 64 (2003) 1895.
[9] S.M. Wasim, C. Rincon, G. Marin, R. Marquez, G. Sanchez Perez, R. Guevara, J.M. Delgado, L. Nieves, Mater. Res. Soc. Symp. Proc. 668 (2001) H1.2.1.
[10] A.P. Levanyuk, V.V. Osipov, Sov. Phys., Usp. 133 (1981) 443.
[11] B.I. Shklovskij, A.L. Efros, Electronic Properties of Doped Semiconductors, Springer, Berlin, 1984.
[12] J. Krustok, H. Collan, K. Hjelt, J. Appl. Phys. 81 (1997) 1442.
[13] J. Krustok, A. Jagomägi, M. Grossberg, J. Raudoja, M. Danilson, Solar Energy Mater. Solar Cells 90 (2006) 1973.