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Radiative recombination in $Cu_2ZnSnSe_4$ monograins studied by photoluminescence spectroscopy

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ABSTRACT

In this study we investigated the optical properties of $Cu_2ZnSnSe_4$ monograin powders that were synthesized from binary compounds in the liquid phase of flux material (KI) in evacuated quartz ampoules. The monograin powder had p-type conductivity. Radiative recombination processes in $Cu_2ZnSnSe_4$ monograins were studied using photoluminescence spectroscopy. The detected low-temperature ($T=10$ K) photoluminescence band at 0.946 eV results from band-to-impurity recombination in $Cu_2ZnSnSe_4$. The ionization energy of the corresponding acceptor defect was found to be 69±4 meV. Additional photoluminescence bands detected at 0.765 eV, 0.810 eV and 0.860 eV are proposed to result from Cu_2SnSe_3 phase whose presence in the as-grown monograins was detected by Raman spectroscopy and SEM analysis. Considering photoluminescence results, it is proposed that the optical bandgap energy of $Cu_2ZnSnSe_4$ is around 1.02 eV at 10 K.

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1. Introduction

Lately, quaternary semiconductors $Cu_2ZnSnSe_4$, Cu_2ZnSnS_4, $Cu_2CdSnSe_4$ have attracted lot of attention as possible absorber materials for solar cells. These materials have optimal direct bandgap for solar energy conversion and high absorption coefficient ($>10^4$ cm^{-1}) [1]. They are believed to be suitable alternatives for $CuInSe_2$ absorbers that contain expensive In.

There are some difficulties in determining the bandgap energy of $Cu_2ZnSnSe_4$ (CZTSe) due to the formation of secondary phases in low temperature growth. Matsushita et al. [2] have determined the bandgap value of 1.44 eV for CZTSe from optical absorption measurements. Yasuda et al. [3] obtained bandgap energy of 1.40 eV for CZTSe. On the other hand, Raulot et al. [4] have performed *ab initio* calculation of electronic structure of CZTSe and found bandgap around 0.8 eV. In our previous paper [5], it was proposed based on the quantum efficiency curves of the CZTSe monograin layer solar cells that CZTSe has lower bandgap energy than proposed by the authors mentioned above. According to the additional quantum efficiency and photoluminescence measurements, the bandgap energy of CZTSe is expected to be in the vicinity of 1 eV.

Only a little information about the defect structure of $Cu_2ZnSnSe_4$ can be found in the literature. Raulot et al. [4] have studied the defect formation energies of CZTSe. The lowest formation energy was found for V_{Cu} that can be considered as dominating defect in CZTSe. We have previously published photoluminescence (PL) spectrum of CZTSe that consisted of one PL band at 0.85 eV [5], however the detailed analysis was not made. In this paper, we study the defect structure of $Cu_2ZnSnSe_4$ using photoluminescence spectroscopy.

2. Experimental

The $Cu_2ZnSnSe_4$ monograins were synthesized from CuSe, ZnSe and SnSe precursors in molten KI at 720 °C. More details about the synthesis can be found in Ref. [5]. The obtained material consisted of around 100 µm grain size powder crystals with tetragonal shape and rounded grain edges. The chemical composition of monograin powders was determined by the energy dispersive X-ray spectroscopy (EDS). The monograins had p-type conductivity. In order to increase the quality of the monograins, vacuum annealing was performed to the crystals. Comparison of the PL properties of the two as-grown (samples a and b with different compositions) and annealed CZTSe (sample b*) monograins is discussed (see the compositional details of the samples in Table 1).

The room temperature Raman spectra were recorded by using a Horiba's LabRam HR high resolution spectrometer equipped with a multichannel CCD detection system in the backscattering configuration. In micro-Raman measurements, the incident laser light with the wavelength of 532 nm can be focused on the sample within a spot of 10 µm in diameter. For PL measurements, the samples were mounted in the closed-cycle He cryostat and cooled down to 10 K. The 441 nm He–Cd laser line was used for PL excitation.

3. Results and discussion

The room-temperature Raman spectra of two as-grown CZTSe monograin powders and an annealed monograin powder are presented in

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Table 1
Summary of the results obtained from the PL analysis of CZTSe monograins

PL band position	Recombination mechanism	Thermal activation energy (meV)	Origin	Sample
0.946 eV	BI	69±4	CZTSe	Annealed CZTSe [Zn]/[Sn]=0.96, sample b*
0.860 eV	BB	–	Cu_2SnSe_3	as-grown CZTSe [Zn]/[Sn] = 1.03, sample a
0.810 eV	BI	44±5	Cu_2SnSe_3	as-grown CZTSe [Zn]/[Sn] = 0.96, sample b
0.765 eV	DAP	26±6	Cu_2SnSe_3	as-grown CZTSe [Zn]/[Sn] = 1.03, sample a

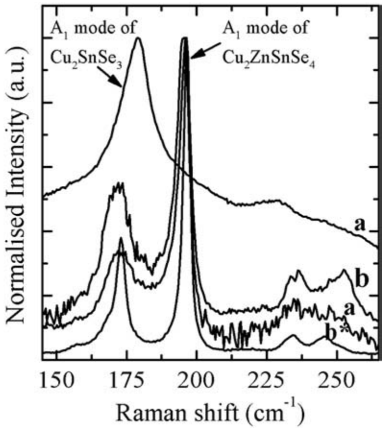

Fig. 1. Normalised Raman spectra of the surface of the CZTSe monograins: a, b — as-grown CZTSe and b* — CZTSe after annealing. Two spectra taken from different points of the crystal surface of sample a are presented. As can be seen, the presence of ternary Cu_2SnSe_3 phase was detected on the surface of as-grown CZTSe monograins (Raman mode at 180 cm^{-1}). This phase disappears after vacuum annealing.

Fig. 1. In the spectra of as-grown CZTSe (Raman modes at 167 cm^{-1}, 173 cm^{-1}, 196 cm^{-1}, 231 cm^{-1}, and 245 cm^{-1}) the presence of additional Cu_2SnSe_3 phase was detected (Raman peak at 180 cm^{-1}). The frequencies of the A_1 Raman modes of Cu_2SnSe_3 and CZTSe are 180 cm^{-1} and 196 cm^{-1}, respectively [5]. After vacuum annealing the presence of the Cu_2SnSe_3 phase (peak at 180 cm^{-1}) could no longer be detected.

Fig. 2. presents SEM micrograph of the as-grown CZTSe monograin surface. The presence of secondary phase on the surface is clearly seen. The secondary phases being observed in CZTSe in other studies include CuSe, ZnSe and Cu_2SnSe_3 [6]. Magorian-Friedlmeier et al. [7] studied the formation of $Cu_2ZnSnSe_4$ by evaporation of reactants from elemental and binary sources with varying metallic ratios. It was found that only in the case of Zn deficiency a ternary compound Cu_2SnSe_3, has been formed. No other ternary compounds were found. It was also found in Ref. [8] that for a synthesis process in which the metallic elements are well intermixed in the ratio [Cu]:[Zn]:[Sn]=2:1:1 the compound Cu_2SnSe_3 might form in addition to $Cu_2ZnSnSe_4$ since [Cu]:[Sn]=2:1.

The low-temperature (T=10 K) photoluminescence spectra of the as-grown and annealed CZTSe monograins together with the spectra of Cu_2SnSe_3 crystals are presented in Fig. 3 and corresponding data are summarised in Table 1. The PL spectrum of one of the as-grown CZTSe monograins (a in Fig. 3) consists of three Gaussian shaped PL bands at 0.765 eV, 0.86 eV and 0.95 eV. The other as-grown CZTSe spectrum (b in Fig. 3) consists of one PL band at 0.81 eV and in the spectra of annealed CZTSe (b* in Fig. 3) one PL band at 0.946 eV was detected. Temperature and excitation power dependencies were used to identify the origin of the PL emission of CZTSe monograins.

From the laser power dependencies of the PL spectra a blueshift with the magnitude of about 14 meV per decade was detected for the PL bands at 0.765 eV, 0.810 eV and 0.946 eV while the PL band at 0.86 eV shows no shift with excitation power. The blueshift of the PL bands can be taken as an evidence of donor–acceptor pair (DAP) recombination. However, the slightly asymmetrical shape of the PL bands and rather large blueshift with increasing laser power indicate the presence of Coulomb potential fluctuations in the material [9,10]. These fluctuations are small in sample a that shows PL bands with Gaussian shape. These potential fluctuations will lead to a local perturbation of the band structure, thus broadening the defect level distribution and forming band tails. These fluctuations are often detected in multinary compounds [9–11]. In a p-type material and in case of small effective mass of electrons, the radiative recombination can therefore mainly arise from four different channels: band-to-tail recombination (BT), that comprises a free electron and a hole that is localised in the valence band tail; band-to-band recombination (BB), that involves a free electron and a free hole, band-to-impurity (BI) recombination that involves an acceptor state that is deep enough not to overlap with the valence band tail, and donor–acceptor pair recombination that involves an acceptor and a donor state that are deep enough not to overlap with the corresponding band tails. The average depth of the fluctuations in samples b and b* was determined from the shape of the low-energy side of the PL bands (see details in Ref. [9]) and was found to be around 25 meV.

In order to determine the thermal activation energies of the recombination processes in CZTSe the temperature dependencies of the PL spectra were measured. The temperature dependence of the PL spectrum of annealed CZTSe monograin powder is presented in Fig. 4. The thermal activation energies were determined from the Arrhenius plot (Fig. 5.). Since for the PL bands at 0.765 eV, 0.810 eV and 0.946 eV we found linear ln$I(T)$ versus 1000/T dependence at high temperatures, that is common to BI-transition [9], we used theoretical expression for discrete energy levels proposed in Ref. [12] to fit the experimental data:

$$\Phi(T)=\frac{\Phi_0}{1+\alpha_1 T^{3/2}+\alpha_2 T^{3/2}\exp(-E_T/kT)}, \tag{1}$$

where Φ is integrated intensity, α_1 and α_2 are the process rate parameters and E_T is the thermal activation energy. Thermal activation energies 26±6 meV, 44±5 meV and 69±4 meV were obtained for the PL bands at 0.765 eV, 0.810 eV and 0.946 eV, respectively. The Arrhenius plot of the PL band at 0.860 eV did not show linear dependence at high temperatures, so the thermal activation energy for this recombination process could not be found. This band vanishes very slowly with temperature, being detectable even at room-temperature. It also shifts towards higher energies with increasing temperature with the magnitude of 5 meV per 100 K. The laser power and temperature dependencies of the PL band at 0.860 eV indicate that this emission results from band-to-band (BB) recombination. Therefore, the bandgap energy of the corresponding phase in as-grown CZTSe sample must be around 0.86 eV at T=10 K. We attribute the bandgap energy of 0.86 eV to the secondary Cu_2SnSe_3 phase detected by Raman spectroscopy in as-grown monograins. This conclusion is explained in more detail below.

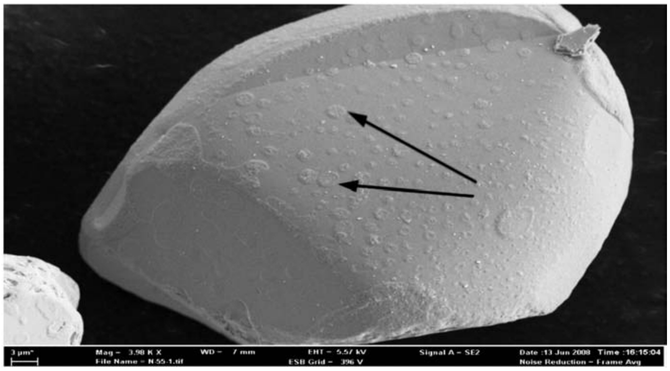

Fig. 2. SEM micrograph of a CZTSe monograin. The presence of Cu_2SnSe_3 phase forming small islands on the crystal surface (two of them are indicated by arrows) is clearly seen.

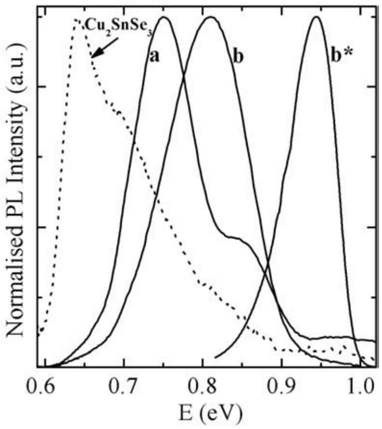

Fig. 3. Comparison of the normalised low-temperature PL spectra of as-grown CZTSe (a, b) and annealed CZTSe (b*) monograins. The as-grown CZTSe monograin spectra (a) consists of three PL bands at 0.765 eV, 0.86 eV and 0.95 eV. The other as-grown CZTSe spectra (b) and the spectra of annealed CZTSe monograins (b*) consist of one PL band at 0.81 eV and 0.946 eV, respectively. PL spectra of Cu_2SnSe_3 crystals are shown for comparison with dotted line.

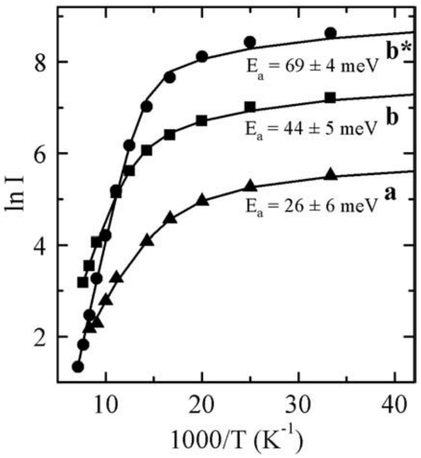

Fig. 5. Arrhenius plot derived from the temperature dependencies of the PL spectra of CZTSe monograins. Thermal activation energies 26±6 meV, 44±5 meV and 69±4 meV were obtained for the PL bands at 0.765 eV, 0.810 eV and 0.946 eV, respectively. Eq. (1) was used for fitting the experimental data.

The PL emission at 0.765 eV shows very fast quenching with temperature, the thermal activation energy being $E_T=26\pm6$ meV. Considering also the blueshift with increasing laser power, we attribute this emission to donor–acceptor pair recombination. This low activation energy is probably the ionization energy of a donor defect that should be lower defect in a p-type material. We cannot distinguish the vanishing of the free-to-bound emission in this sample, what should follow the ionization of a donor defect, therefore we cannot estimate the ionization energy of a corresponding acceptor. However, in the absence of remarkable potential fluctuations in sample a, it can be estimated considering that the energy of the emitted photon in a DAP transition is given by:

$$h\nu = E_g - E_A - E_D + e^2/(4\pi\varepsilon_0\varepsilon R), \tag{2}$$

where E_g is the bandgap energy, E_A and E_D are the acceptor and donor binding energies, respectively, and the last member is Coulomb energy. Taking into account that the BB band allows us to estimate the bandgap energy of Cu_2SnSe_3 phase, that was found to be around 0.86 eV, we obtain the acceptor activation energy of around 70 meV. From the thermal quenching of the PL band at 0.810 eV, that was obtained from another as-grown monograin powder (sample b), we obtained activation energy of 44±5 meV. This emission results from BI-recombination and may involve the same acceptor defect forming the donor–acceptor pair. The small difference in activation energies is due to the rough guess of the bandgap energy.

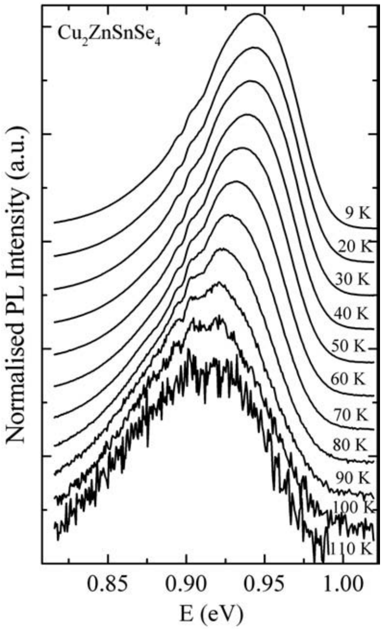

Fig. 4. Temperature dependence of the PL spectra of annealed CZTSe monograins (sample b*), measured in the temperature range of 9 K to 110 K.

Analysing the high energy PL band at 0.946 eV that dominates the spectra of annealed CZTSe monograin powder (sample b*) and is also present in the spectra of one of the as-grown powders, we find that this emission results from the BI-recombination and involves an acceptor defect with ionization energy of $E_T=69\pm4$ meV. The results of the analysis of this PL band are inconsistent with the results obtained from the analysis of the other PL bands detected in these monograins. Considering the presence of the secondary phase of Cu_2SnSe_3 in the as-grown CZTSe monograins, we propose that the lower energy PL bands at 0.765 eV, 0.810 eV and 0.860 eV to this additional phase that according to literature has a bandgap energy of 0.843 eV at room temperature [13]. This has to be investigated in more detail in further studies. For comparison we grew separately Cu_2SnSe_3 crystals and their PL spectrum is presented in Fig. 3 with dotted line. As can be seen from Fig. 3, the lower energy bands detected in CZTSe monograins lie in the same spectral region. Vacuum annealing seems to remove the additional phase and the emission at 0.946 eV can be attributed to CZTSe. The results of the PL analysis of CZTSe monograins are summarised in Table 1.

The theory of heavily doped semiconductors [9] proves that at low temperatures the BI-bands' maximum is located at $h\nu_{max}=E_g-I_a$, where I_a is the defect ionization energy. In case of BI transition, the effect of fluctuations to the bandgap energy is not remarkable. The resulting bandgap energy of CZTSe is found to be around 1.02 eV at $T=10$ K. The obtained approximate bandgap energy of CZTSe is lower than the one reported in the literature as was mentioned in the introduction. However, it is reported that Cu_2ZnSnS_4 has bandgap energy of around 1.5 eV [14]. Our studies of $Cu_2ZnSn(Se_{x-1}S_x)_4$ solid solutions (to be published) indicate that the bandgap energy is decreasing with Se concentration and allow us to consider the obtained bandgap energy of $Cu_2ZnSnSe_4$ to be correct. Also the results of quantum efficiency measurements made for solar cells made from these CZTSe monograin powders confirm this result [5].

4. Conclusions

The photoluminescence properties of as-grown and vacuum annealed $Cu_2ZnSnSe_4$ monograin powders were studied. PL bands at 0.765 eV, 0.810 eV and 0.860 eV found in as-grown monograins were proposed to arise from the additional phase Cu_2SnSe_3 whose presence in the monograins was detected by Raman spectroscopy and SEM/EDS analysis. After vacuum annealing of the CZTSe powder, pure CZTSe was obtained and the resulting PL emission at 0.946 eV was attributed to an acceptor defect with ionization energy of $E_T = 69 \pm 4$ meV. According to the PL results, it is proposed that the bandgap energy of CZTSe at $T = 10$ K is around 1.02 eV.

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