Low temperature time resolved photoluminescence in ordered and disordered Cu_2ZnSnS_4 single crystals

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ABSTRACT

In this work we performed time-resolved micro-photoluminescence (TRPL) studies of Cu_2ZnSnS_4 (CZTS) single crystals grown in molten KI salt. The order/disorder degree of CZTS was varied by the thermal post treatment temperature. Photoluminescence spectra measured at T=8 K showed an asymmetric band with a peak position of 1.33 eV and 1.27 eV for partially ordered and disordered structures, respectively. Thermal activation energies were found to be $E_{T (PO)}$ =65 ± 9 meV for partially ordered and $E_{T (PD)}$ =27 ± 4 meV for partially disordered. These low activation energy values indicating to the defect cluster recombination model for both partially ordered and disordered structures. TRPL was measured for both crystals and their decay curves were fitted with a stretched exponential function, in order to describe the charge carriers' recombination dynamics at low temperature.

1. Introduction

The quaternary compound Cu_2ZnSnS_4 (CZTS) is a promising non-toxic absorber material for solar cells made from earth abundant elements. In 2013, an IBM group reported 12.6% efficiency of a $Cu_2ZnSn(S, Se)_4$ solar cell by hydrazine-based solution processing [1]. However, the record efficiency of similar $CuInGaSe_2$ based solar cells has reached up to 22.6% [2]. One of the main limiting factors of kesterite CZTS cells is believed to be high concentration of point defects and/or defect clusters. Several theoretical calculations have shown extremely low formation energies of different defect clusters in CZTS [3,4]. These defect clusters will either produce deep recombination centers for electron hole pairs or cause trapping of charge carriers. Both mechanisms are detrimental to solar cell parameters and should be avoided. Additionally, high concentration of intrinsic defects in CZTS leads to the formation of spatial potential fluctuations and to a local perturbation of the band structure [5]. Moreover, many groups have shown that CZTS is subjected to disorder in the Cu and Zn containing lattice planes of the kesterite structure by Cu-Zn exchanges [5,6]. The impact of Cu/Zn disorder on the properties of CZTS is an intensely discussed field and there are still unresolved problems such as differences in the recombination mechanisms and carrier dynamics

in the ordered and disordered CZTS. According to ref [7]. the long-range order parameter S is used to describe the degree of ordering of crystals, as calculated in Vineyard's theory of order–disorder kinetics [8]. The long-range order parameter S was introduced by Rey et al. [9] and it is in the range from 0 to 1, with 0 corresponding to complete disorder and 1 corresponding to perfect ordering. S decreases with increasing annealing temperature, and drops to zero at a critical temperature, T_C. The order–disorder transition occurs at this critical temperature. The ordering of kesterite absorbers improves after post-annealing below T_C, but deteriorates after post-annealing above T_C. The presence of disordered structure in kesterites was first discovered by Schorr et al. [6] using neutron diffraction data. The parameter S in this work was controlled by a different cooling rate. Later the coexistence of ordered and disordered kesterite phases was proved using photoluminescence (PL) and Raman scattering measurements in high-quality polycrystalline CZTS [10]. It was confirmed by near-resonant Raman scattering measurements, where the low temperature (T_C =533 K) transition between ordered and disordered CZTS was discovered [11]. According to this study, the ordered CZTS is only possible below this temperature, although finite amount of disorder is expected to be present for T > 0 K. It is also known that the bandgap energy for disordered CZTS is about 100 meV lower than for the

ordered CZTS [12] resulting in different position of PL bands. Moreover, recent PL studies showed that the radiative recombination could be different in ordered and disordered structures [13]. In case of extensive cation sublattice disorder, the concentration of different defect clusters is relatively high and radiative recombination involving these clusters that induce local band gap decrease dominates at cryogenics temperatures. At temperatures below the order-to-disorder transition temperature 533 K, the concentration of defect clusters can be reduced. As a result, radiative recombination involving deep acceptor defect with ionization energy of about 200 meV is dominating in the PL spectra of ordered CZTS [13]. Both recombination channels, the one related to bandgap energy fluctuations caused by the defect clusters and the other related to deep acceptor defects are usually detrimental for solar cells. While the bandgap widening in ordered CZTS usually leads to higher open-circuit voltage it also decreases short-circuit current and therefore it is not so easy to detect an improvement of solar cell efficiency with increasing ordering. Recently, it was however shown that in CZTSe the ordering resulted in an increase in the collection of photo-generated carriers, resulting in a higher current density and a significant improvement in device efficiency [9]. At the same time, the improvement seems to be related not only to ordering but also to the nature of defects acting as recombination centers [14]. It is shown that defect clusters have very high recombination rate and the deep acceptor in ordered CZTS is active even at room temperature [15]. Therefore, more studies are needed to understand the recombination mechanisms in both ordered and disordered CZTS. The recombination kinetics could be one possible research topic for further studies. So far, there are not so many studies about recombination kinetics in kesterites. Phuong et al. [16] studied CZTS single crystals using temperature dependent TRPL. They used three exponential functions to fit the PL time decays and found mean lifetime of minority charge carriers in a microsecond scale in the temperature range from 10 K to 100 K. The thermal activation energy calculated from the PL thermal quenching was 112 meV. They explained this relatively long recombination time at low temperature with localization of the photocarriers to the band tails. In this work, we performed low temperature TRPL study to partially ordered and partially disordered crystals and report the influence of the ordering state of CZTS on the low temperature recombination kinetics.

2. Experimental details

The investigated Cu_2ZnSnS_4 crystalline powder was synthesized under Cu-poor and Zn-rich conditions from high purity (5N) elemental Cu, Sn, S and binary ZnS precursors in molten KI salt as flux material in sealed quartz ampoules at 740 °C. The synthesized material contains Cu_2ZnSnS_4 crystals with elemental concentration ratios of Cu/(Zn + Sn) =0.88 and Zn/Sn =1.1 as determined by energy dispersive X-ray (EDX) analysis. The powder was divided into portions and annealed for 1 h in the two temperature zone tube furnace at 740 °C in sulfur atmosphere of $1.33 \cdot 10^5$ Pa (10^3 Torr) pressure. After annealing, the ampoules were naturally cooled in furnace to 350 °C (partially disordered state) and 200 °C (partially ordered state), the sample above the critical temperature of order-to-disorder transition in CZTS (T_C =533 K (260 °C) [11]) resulted in partial disordering and the sample below the critical temperature resulted in partial ordering of the crystal lattice. Then, the ampoules were quenched down to RT in air with a rate of 75 °C/min and 50 °C/min, respectively. After the heat treatment monocrystals (50–60 μm) were covered with 30 nm layer of CdS using chemical bath deposition, in order to avoid surface contamination.

Time-resolved micro-photoluminescence (TRPL) experiments were carried out at cryogenic temperature (5 K) in a helium-flow cryostat. Carrier injection in the single crystal CZTS is provided by a 200-fs pulsed Ti: sapphire laser, with a repetition rate of 240 kHz. This laser beam, tuned at 650 nm, is focused down to a 1.5-μm-diameter spot on the sample with a microscope objective (N.A. =0.75), which also
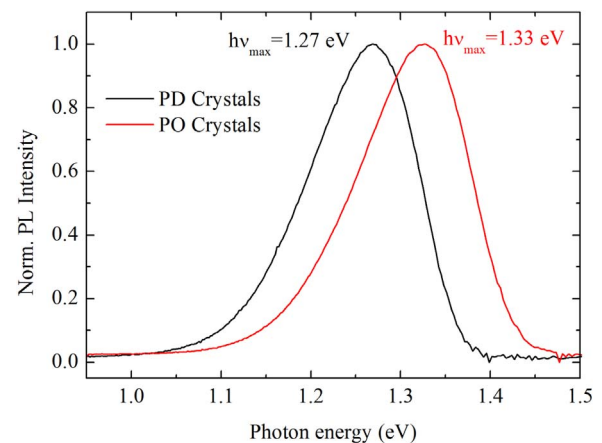
Fig. 1. Normalized low temperature (T=8 K) steady state PL spectra of PO and PD CZTS crystals.

collects the luminescence signal. The luminescence of the single crystals is then spectrally filtered by a 310 mm focal length monochromator and detected by a silicon avalanche photodiode. The instrument response of the setup, measured with the excitation laser, presents 300-ps FWHM associated with the time jitter of the avalanche photodiode.

The energy density per pulse was around $7.1 \cdot 10^{-4}$ J/cm2 (energy of pulse was 12.5 pJ).

For steady state PL measurements, the samples were mounted in the closed-cycle He cryostat and cooled down to 8 K. The 441 nm He-Cd laser line with maximum output 80 mW was used for PL excitation, the spectra were recorded via the 400-mm focal length grating monochromator system and detected with the InGaAs detector.

3. Results and discussion

The low temperature photoluminescence spectra of partially ordered (PO) and partially disordered (PD) CZTS monocrystals are presented in Fig. 1. The PD CZTS has a PL band maximum at 1.27 eV and PO showed peak at 1.33 eV. Both PL bands have asymmetric shape that is typical for semiconductors with high defect concentration causing spatial potential fluctuations in the material [13]. The potential fluctuations lead to local perturbation of the band structure, thus broadening the defect level distribution and forming band tails. The density of the band tail states usually has an exponential shape resulting in an exponential tail of the low-energy side of the PL band [17]. At low temperatures band-to-tail (BT), band- to-impurity (BI) and/or band-to-band (BB) recombination usually dominate the PL spectra of such highly defective materials [10,13]. In the case of the BT recombination free electrons recombine with the holes localised in the valence band tail. The BI recombination involves deeper acceptor defects that do not overlap with the valence band tail and the corresponding density of the states can be usually described with the Gaussian distribution. The average depth of the spatial potential fluctuations γ can be determined from the slope of the low-energy side of the PL band [18]. In our study it was found to be 38 meV and 44 meV for PO and PD kesterite, respectively.

From the previous work [5] it is known that for ordered or disordered kesterite structure the cooling rate in the critical temperature range should be very slow or very fast, respectively. The highest PL peak energy in the most ordered CZTS was found to be around 1.38 eV while the lowest in most disordered CZTS was around 1.22 eV. In the present study we have PL peak energies at 1.27 eV and at 1.33 eV for PD and PO crystals, respectively, see Fig. 1. These values indicate the presence of partially ordered and disordered structures.

The temperature dependencies of PL bands can be seen on Fig. 2. Both the PO and PD crystals revealed a redshift around 25 meV as
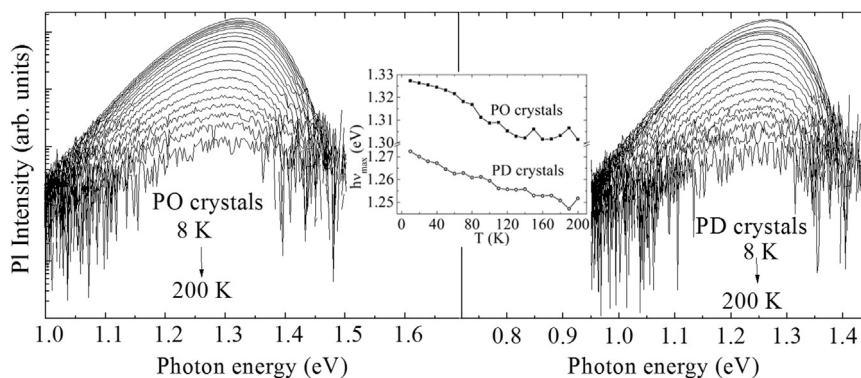
Fig. 2. Temperature dependence of photoluminescence for partially ordered and partially disordered crystals, inset graph shows PL band peak positions $h\upsilon_{max}$ in dependence from the temperature.

temperature increases from 8 K to 200 K, the shift is related to the bandgap shift with temperature and the redistribution of the holes between the potentials wells that have different depth. In comparison to the temperature dependence of the bandgap energy of CZTS reported in [19] the shift of the PL bands (see inset Fig. 2.) are following more or less the shift of the bandgap energy.

Thermal activation energies were determined from the Arrhenius plots (Fig. 3) using theoretical expression proposed in Ref [20].:

$$I(T) = \frac{I_o}{1 + \alpha_1 T^{\frac{3}{2}} + \alpha_1 T^{\frac{3}{2}} \quad \exp \ (-E_T/kT)} \tag{1}$$

where, I is integrated intensity, α_1 and α_2 are the process rate parameters and E_T is the thermal activation energy. Thermal activation energies $E_{T\ PO} = 65 \pm 9$ meV and $E_{T\ PD} = 27 \pm 4$ meV for the PO and PD crystals with PL bands at 1.33 eV and 1.27 eV, respectively, were found. These quite low activation energies are in the range of the average depth of the potential fluctuations indicating that the recombination involves shallow defects. On the other hand, the PL bands are located quite far from the bandgap energy of CZTS indicating to deep defects. We have shown in our previous study [13] that PL bands with such properties result from the recombination related to defect clusters that lead to the narrowing of the bandgap energy. This results in the bandgap energy fluctuations and in this case the density of states function for holes has some kind of maximum.

These quite low activation energies in the range of the average depth of the potential fluctuations together with the separation between the PL bands from the bandgap energy of CZTS indicate that the recombination does not involve very deep acceptor levels typical for ordered CZTS and are probably related to defect clusters and the
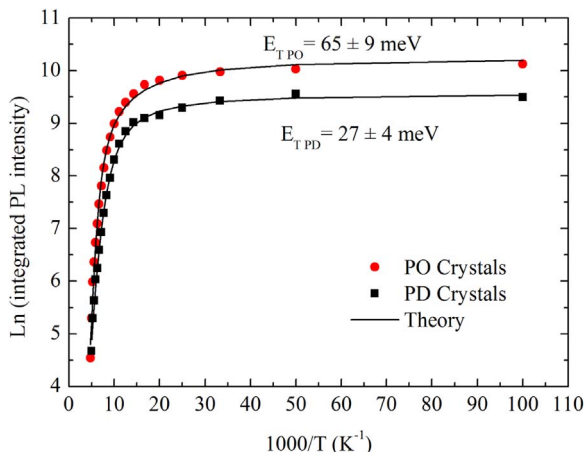
density of states function for holes has some kind of maximum. In our previous studies [5,13] we discovered that the main low temperature recombination mechanism in disordered CZTS is related to the defect cluster $(2Cu_{Zn}^{-}+Sn_{Zn}^{2+})$, that also induces a significant local band gap decrease of 0.35 eV creating spatial bandgap fluctuations in the material. Additionally, these defect clusters will cause a strong charge carriers trapping for both electrons and holes. The thermal activation energy of this type of recombination was found to be around 100 meV, the exact value depending on the degree of disordering and on the nature of defect clusters [5,12]. Disordering in CZTS is usually related to high concentration of antisite defects Cu_{Zn} and Zn_{Cu} that have the lowest formation energy of forming a defect cluster in the whole compositional range [3,4]. $[Zn_{Cu}+Cu_{Zn}]$ defect clusters induce a local bandgap energy decrease of about 0.1 eV [13]. Different PL peak positions and thermal activation energies for PO and PD CZTS suggest also to the change of the nature of these defect clusters.

The recombination kinetics of partially ordered and disordered CZTS was studied using time resolved photoluminescence decays, see Fig. 4. The photoluminescence decays did not show the classical exponential behavior and fitting with exponential function did not give good result, even fitting with triple exponential function. The best fit was obtained by fitting the photoluminescence decays with so called stretched exponential function describing highly defective materials [21]:

$$I = I_0 \exp\left[-\left(\frac{t}{\tau}\right)^n\right] \tag{2}$$

Here, I_O is the initial luminescence intensity following the excitation, τ is the luminescence decay time and n power factor in the range of $0 \leq n$
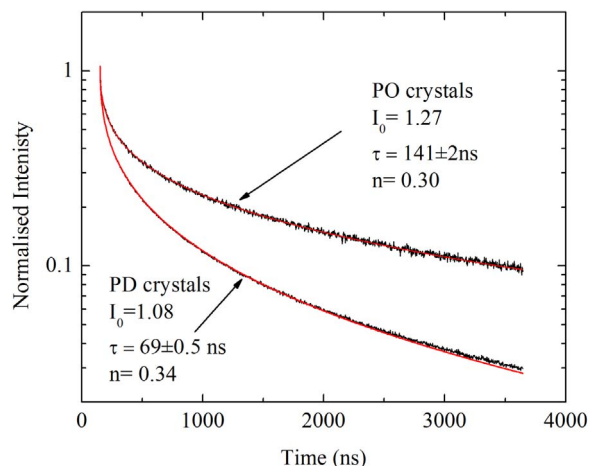

Fig. 3. Arrhenius plot derived from the temperature dependencies of the PL spectra of PO and PD CZTS crystals. Solid lines present the fitting of the experimental data with the theoretical expression (1).

Fig. 4. Normalized TRPL decays of PO and PD crystals at 5 K, PL decays were measured at PL peak maxima. Solid lines are results of fitting with stretched exponent function (2).

≤ 1, that is associated with the density of trap states and trap release rates [21]. Obviously, for the limiting case of $n = 1$ we get the "normal" exponential decay with the characteristic lifetime τ. We have used this model for both CZTS samples and decay times were found to be $\tau = 69 \pm 0.5$ ns and $\tau = 141 \pm 2$ ns and power factor 0.34 and 0.30, for PD and PO crystals, respectively, see Fig. 4. PO crystals show almost 2 times longer decay time than PD crystals and this is definitely related to different recombination in partially ordered sample, also it is sure that non radiative recombination is playing significant role in the differences of PL and TRPL results of PD and PO crystals. The recombinations are probably related to different type of recombination clusters as was also seen in PL. So we can conclude from the obtained TRPL characteristic lifetime values that this partially ordered CZTS crystal has properties more suitable for better solar cells. Low and almost equal values of parameter n for both samples indicate that the retrapping processes of charge carriers are very significant in both structures as can be expected due to the high concentration of defect clusters in both samples. The current study showed remarkable difference in the recombination kinetics of CZTS with different degree of ordering. More detailed studies to identify the recombination mechanism and minority carrier lifetimes in ordered and disordered CZTS are in progress.

4. Conclusion

Low temperature TRPL study was performed to the CZTS single crystals with different concentration of Cu/Zn antisite defects in the crystal structure and resulting changed degree of ordering. For partially ordered kesterite the recombination decay time was two times higher compared with partially disordered material, $\tau = 141 \pm 2$ ns and $\tau = 69 \pm 0.5$ ns, respectively, due to recombination mechanisms related to different defect clusters. At the same time a significant retrapping of charge carriers is present in both structures.

Acknowledgement

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