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TEMPERATURE DEPENDENCE OF DECAY PROPERTIES OF BOUND EXCITON EMISSIONS IN $CuInS_2$ Crystals

YOSHIHIKO OHTA, KAZUHITO NISHI, TAKASHI ONISHI AND KAZUKI WAKITA

Department of Physics and Electronics, Graduate School of Engineering,
Osaka Prefecture University,
Gakuen-cho 1-1, Sakai, Osaka 599-8531, Japan
e-mail: wakita@pe.osakafu-u.ac.jp
Phone: +81-72-252-1161(Ext.2275);Fax: +81-72-254-9908

Temperature dependence of decay properties of bound exciton emissions is investigated for $CuInS_2$ crystals. Decay curves of the bound excitons at 1.525 and 1.520 eV display a single exponential behavior over the temperatures 10-40 K, while the bound excitons at 1.530 eV decay in double exponential way in the temperature range 10-30 K. A thermal release process of the observed bound excitons is discussed in terms of the obtained activation energy. The capture center cross-section for free exciton is also estimated.

1. INTRODUCTION

On account of its optimum band-gap energy of 1.5 eV [1] the ternary semiconductor $CuInS_2$ has a potential to provide a higher conversion efficiency of the $CuInS_2$ based solar cells, by comparison with the currently achieved value of 12.5 % [2]. Until now a number of research works on $CuInS_2$-thin films have been performed but the progress toward a desirable increase of the conversion efficiency has not been achieved yet. This is partly due to the lack of the comprehensive information on the defect-related properties of $CuInS_2$. In particular, photoluminescence (PL) of bound excitons, which has to be examined in the first place in the case of the defects in the high quality $CuInS_2$ crystals used for solar cell application, has not been studied enough and the analyses of the origin of the defects associated with the bound excitons have not been sufficient [3-8].

Time-resolved PL is a powerful method for studying relaxation of the excited states, particularly the bound excitons. Recently, we have measured time-resolved PL of $CuInS_2$ at 10 K and discussed the radiative lifetime and charge state of the defect-centers associated with the bound excitons [9].

In this paper we report the results of our more comprehensive studies in the temperature range extended to higher temperatures. We have managed to obtain more information about bound excitons in $CuInS_2$ bulk-crystals. In particular, we have determined the capture center cross-section associated with two different bound excitons.

2. EXPERIMENTAL DETAILS

In this work the samples of $CuInS_2$ bulk single-crystals grown by traveling heater method (THM) were used. The surface of the samples was polished mechanically in two steps. We used alumina powder with particle size of 1.0 μm, first, and 0.1 μm-alumina powder, then, to remove the damaged layer caused by previous rough polishing. The samples were mounted in a cryostat and kept at a temperature between 10 and 40 K. Excitation was provided by a pulsed mode-locked titanium sapphire laser with 82 MHz-repetition rate and 2 ps-pulse width. A typical diameter of the laser spot on the samples was 1 mm, and the average power density of the excitation was 0.4 W/cm^2. The time-resolved PL spectra were measured using a streak camera coupled to a 25-cm polychromator. More details on experimental set-up and measurement conditions can be found elsewhere [10].

3. RESULTS AND DISCUSSION

Fig. 1 shows a time-integrated PL spectrum at 10 K, with three sharp peaks of bound excitons (E_{x1} at 1.531 eV, E_{x2} at 1.525 eV and E_{x3} at 1.520 eV) and a weak shoulder in the higher energy side (A free exciton, E_A at 1.535 eV)

of the near-band-edge region of $CuInS_2$. The temperature dependence of peak intensity of bound excitons, E_{x1}, E_{x2}, and E_{x3} is shown in Fig. 2. The solid lines represent the results of simulation using conventional methods [11]. Obtained values of the activation energy are 7.7, 11, and 16 meV for E_{x1}, E_{x2}, and E_{x3} bound excitons, respectively. These values are practically the same as the energy differences between the levels of free and bound excitons in $CuInS_2$, *i.e.* 5, 10, and 15 meV, respectively. Such a coincidence indicates that observed bound excitons are not released thermally from one to another, higher energy bound exciton state, but directly to free exciton state.

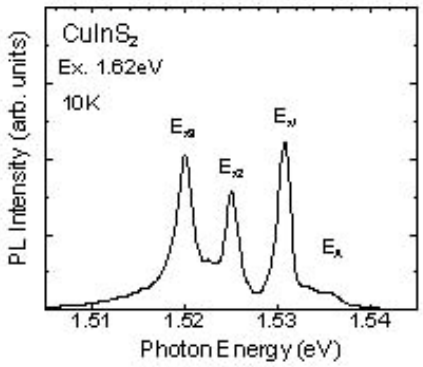

Fig. 1. Time-integrated PL spectrum at 10 K in the band-edge region.

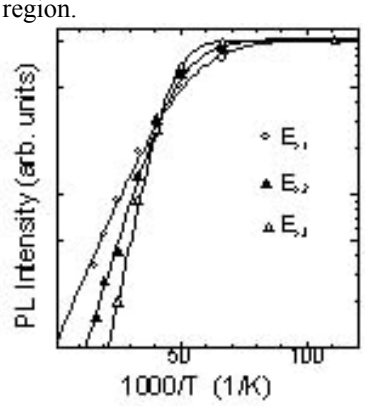

Fig. 2. Temperature dependence of PL peak intensity for E_{x1}, E_{x2}, and E_{x3}. The solid lines represent simulation results.

Decay curves of the three bound excitons, E_{x1}, E_{x2}, and E_{x3}, at 10, 20, 30, and 40 K are shown in Fig. 3. The E_{x2} and E_{x3} curves show clearly a single-exponential decay, while the E_{x1} curve is double-exponential at least for the temperatures between 10 and 30 K. As temperature increases, the decay-time constant of each bound exciton becomes larger. At low temperatures (10 K) the decay-time constant of E_{x2}, and E_{x3} is 2.1 ns and 3.5 ns, respectively. At the same time the respective values of this constant for fast and slow components of E_{x1} bound exciton are 120 and 500 ps for a good fit to the experimental data. It is very likely that at low temperatures the obtained time constants for E_{x2}, and E_{x3}, and slow component of E_{x1} represent nothing else but relevant radiative lifetimes since no excitation power dependence of the obtained time-constants was observed [9].

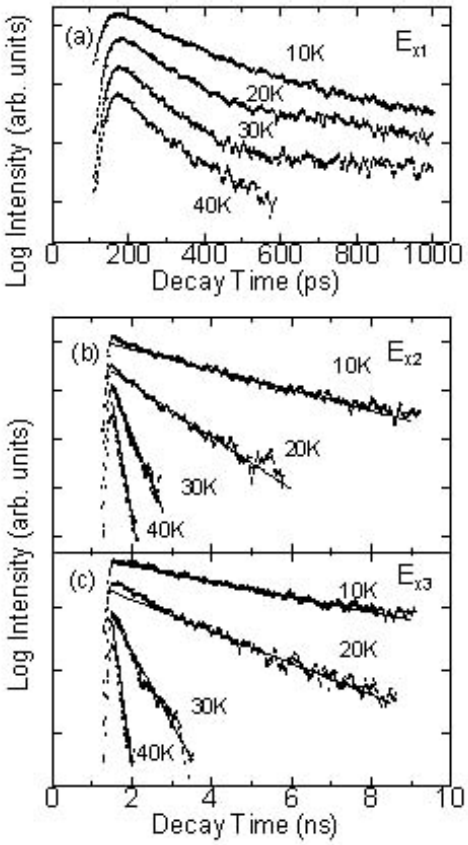

Fig. 3. Decay curves of three bound excitons at various temperatures, 10, 20, 30, and 50 K; (a) E_{x1}, (b) E_{x2} and (c) E_{x3}.

Here we focus on single exponential decay of E_{x2} and E_{x3} bound excitons. Fig. 4 shows the temperature dependence of the decay-time constant for E_{x2} and E_{x3}. As already explained above, we can assume that each bound exciton defect center captures a free exciton, with thermal release of the latter from the capture-center back to free exciton state. Also, the density of bound excitons is assumed to be small in comparison with the density of capture centers, so that several 100 ps past the excitation [9], *i.e.* when the free exciton emission is almost decayed, a bound exciton decay-time, τ_{Bi} (i = 2 or 3), can be written as [12]

$$\tau_{Bi} = 1/(\gamma_{Bir} + \gamma_{Binr} + w_{BiF}), \qquad (1)$$

where γ_{Bir} and γ_{Binr} are respectively the rates of radiative and nonradiative recombination of bound-exciton, w_{BiF} is the rate of its thermal dissociation, given by [12,13]

$$w_{BiF} = \frac{4\sqrt{6}\pi^{3/2} m (k_B T)^2}{h^3} \sigma_i \exp(-E_{Bi}/k_B T), \qquad (2)$$

where σ_i is a capture center cross-section for the free exciton, E_{Bi} is an energy difference between free and bound exciton states, m is the free exciton effective mass, k_B is the Boltzmann constant, h is Planck's constant, and T is the absolute temperature. Fitting eqs. (1) and (2) to the experimental temperature-dependent decay-time

constants and obtaining σ_i has been performed after neglecting γ_{Binr} in eq. (1). The values of σ_2 and σ_3 (or squared exciton radiuses) have been found to be 2.6 x 10^{-12} $cm^2$and 2.4 x 10^{-11} cm^2, respectively.

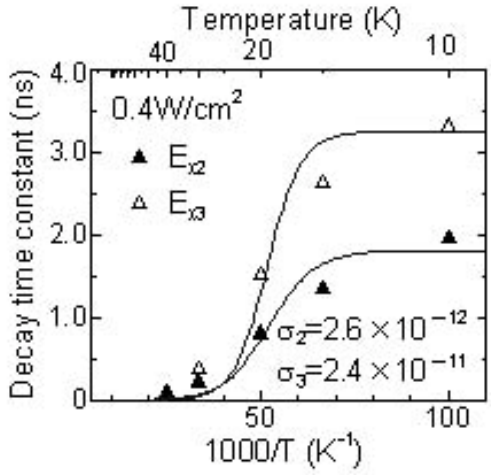

Fig. 4. Temperature dependence of the decay-time constant for E_{x2} and E_{x3}. The solid lines are the results of fitting by eqs. (1) and (2).

4. CONCLUSIONS

The temperature dependence of time-resolved PL of the bound excitons, E_{x1}, E_{x2}, and E_{x3} in $CuInS_2$ has been examined with a result of the determination of their activation energy and thermal dissociation mechanism. A detailed analysis to the decay curves of E_{x2}, and E_{x3} bound excitons in the temperature range 10 to 40 K has also been given, capture center cross-sections have been estimated.

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