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PHOTOLUMINESCENCE SPECTRA OF $CuInS_2$ CRYSTALS IN LOW ENERGY REGION

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Deep levels in bulk single-crystals of $CuInS_2$ were investigated by PL technique. Three broad peaks at 0.83, 0.99, and 1.24 eV, found in the low energy region of PL spectra were observed and attributed to the recombination between deep donors and acceptors. These deep levels are likely to be caused by the crystallinity disturbances rather than deviation from the stoichiometric composition.

1. INTRODUCTION

The ternary semiconductor $CuInS_2$ is considered to be one of the most promising materials for fabrication of thin-film solar cells, because of its optimum band gap of 1.5 eV and large absorption coefficient above the bandgap energy. However, the conversion efficiency of $CuInS_2$-based solar cells is still to a level of 12.5% [1]. And, possible improvements of this efficiency need clear understanding of the defect-related properties of this compound.

Photoluminescence (PL) is a very sensitive method for detection of the emissions related to defects and a number of PL studies have been performed so far on $CuInS_2$, with a purpose of defect investigation [2-7]. However, few of them have dealt with deep PL levels in this material [8]. The reason for this is that meaningful results can be obtained only on the samples with high degree of crystallinity and low impurity concentrations, which are not readily available.

Recently, we have grown high quality bulk single-crystals of $CuInS_2$ and have examined their excitonic properties [9-14]. In this work we address deep PL levels in bulk single-crystals of $CuInS_2$, including discussion about the origin of the defects associated with the observed emissions.

2. EXPERIMENTAL DETAILS

The samples used for PL measurements were bulk single crystals grown by traveling heater method (THM) [9] and Bridgman method (BG) [15]. The surfaces of THM-samples were mechanically polished using alumina powder (particle size 0.1 μm). The samples were attached to the cold finger of a closed-cycle helium cryostat (JANIS CCS-100) and maintained at a temperature between 10 and 160 K. Photoluminescence was excited using a Ti:sapphire laser (Spectra Physics 3950/3960) with a wavelength of 760 nm, and was detected using a photomultiplier (HAMAMATSU R316-02) and a cooled photodiode (HAMAMATSU G6126).

3. RESULTS AND DISCUSSION

Figure 1 shows a typical PL spectrum in the band-edge region at 10 K for a THM-crystal. The spectrum displays three sharp peaks (E_A at 1.535 eV, E_{x1} at 1.530 eV and E_{x2} at 1.525 eV) and a weak shoulder (DV at 1.520 eV). Referring to the reported PL spectra, [3,7,9,10] the observed emissions are assigned to A free exciton

(E_A), two bound excitons (E_{x1} and E_{x2}) and a donor-to-valence band transition (DV), respectively. The presence of the observed sharp excitonic emissions is generally recognized to be the evidence of very high quality of our $CuInS_2$ samples. The similar excitonic spectra in the band-edge region are also observed on our BG-crystals.

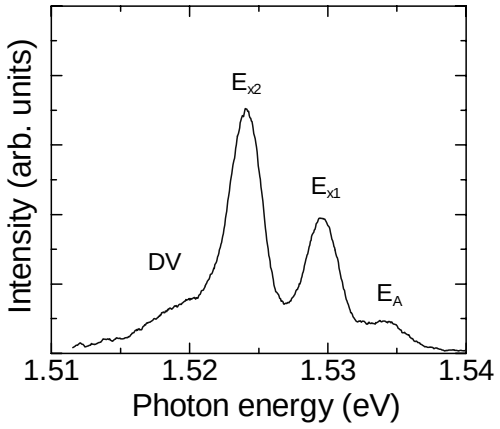

Fig. 1. Typical PL spectrum in the band-edge region at 10K of THM-$CuInS_2$ crystals.

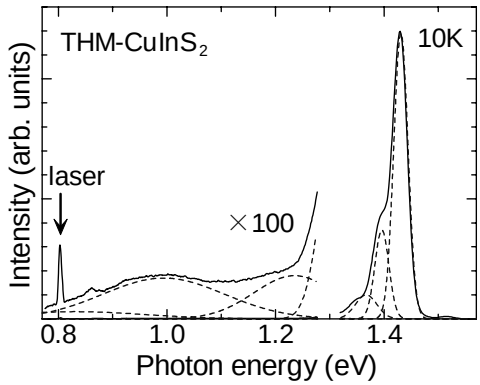

Fig. 2. PL spectrum in the low energy region at 10 K of THM-$CuInS_2$ crystals. The spectrum was resolved into eight Gaussians.

At lower photon energies the PL spectra were rather complex, as demonstrated by Fig. 2 showing a PL spectrum obtained for the range 0.77-1.5 eV for THM-grown $CuInS_2$. The spectrum was resolved into eight Gaussians for all PL spectra obtained at temperatures between 10 and 160 K. The three PL peaks centered at 1.37, 1.40 and 1.43 eV were already reported and interpreted previously [2,4,6] as due to donor-acceptor pair transitions. Our examination of the excitation power dependence of the peak energy for each emission confirmed the previous assignment of the peaks. A new peak centered at 1.31 eV displayed a similar temperature dependence to the above peaks of donor-acceptor pair transition.

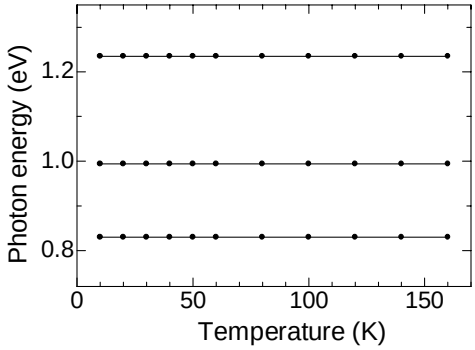

Fig. 3. Relationship between each resolved peak energy in the PL spectra in the low energy region on THM-$CuInS_2$ crystals versus temperature.

On the other hand, we found three broad peaks at 1.24, 0.99, and 0.83 eV in the low energy region, whose energies did not change with increasing temperature between 10 and 160 K, as demonstrated by Fig. 3. Such results indicate that the transitions causing these deep PL emissions do not involve shallow states as well as band states because the band gap of the $CuInS_2$ crystals changes drastically with temperature [3].

For last three peaks, we have obtained the activation energy E_a from the temperature dependence of the emission intensity I , by using the conventional equation [16]

$$I = \frac{A}{1 + C \cdot \exp(E_a / k_B T)}$$

where T is the absolute temperature, k_B is the Boltzmann constant, and A and C are constants. The peaks at 1.24, 0.99, and 0.83 eV have activation energies of 47, 16, and 16 meV, respectively. The obtained values of activation energy are rather small and apparently correspond to the energy difference between two different localized states rather than defect states and band states.

Figure 4 shows the excitation intensity dependence of the normalized PL spectra in the low energy region for THM-$CuInS_2$ crystals. The resolved peak energies obtained from Fig. 4 are plotted as a function of excitation intensity in Fig. 5. As seen from Fig.5, the positions of the peaks at 1.24, 0.99, and 0.83 eV are constant and independent of excitation intensity. It is well-known that the electron (or hole) wave functions of deep donor (or acceptor) states are strongly localized. That is, the nearest neighboring donors and acceptors can recombine in a donor-acceptor pair transition without shift of peak energy with excitation intensity. Therefore the observed deep band emissions are very likely to be caused by the recombination of the deep donor and deep acceptor pairs.

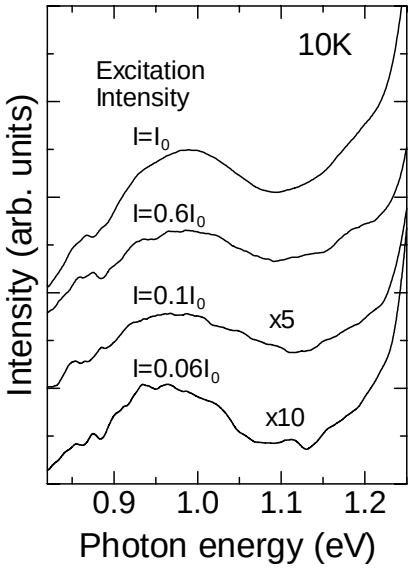

Fig. 4. Excitation intensity dependence of the normalized PL spectra in the low energy region for THM-$CuInS_2$ crystals.

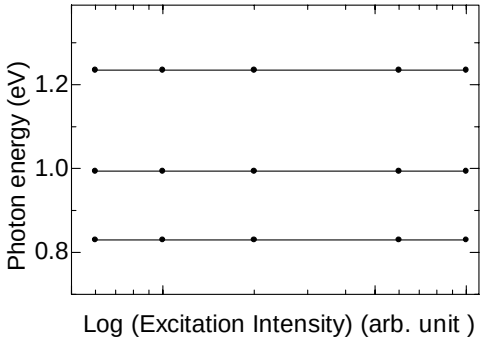

Fig. 5. Resolved peak energy obtained from Fig. 4, plotted as a function of excitation intensity.

In order to clarify the origin of the defects associated with the above deep PL bands, we measured the PL spectra of BM-grown $CuInS_2$ samples with different composition ratios. These samples are denoted hereafter as Samples (a) and (b) and composition ratios measured on these samples by EDX (energy dispersive x-ray spectrometry) are given in Table I.

From Table I, we can conclude that Sample (a) is Cu-poor and S-rich, while Sample (b) is more soichiometric by comparison. On the other hand, the part of the ingot from which Sample (a) was obtained appeared as a relatively large single crystal, whereas that for Sample (b) just as a small crystalline inclusion. Therefore, Sample (a) is considered to have higher crystallinity than Sample (b).

Table I. Composition ratio of Samples (a) and (b) on BG-crystals.

	Composition ratio		
Sample	Cu (at%)	In (at%)	S (at%)
(a)	20	25	55
(b)	24	24	52

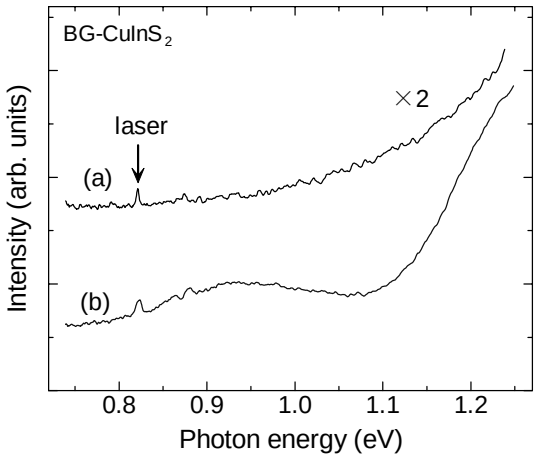

Fig. 6. PL spectra in the low energy region at 10 K on samples (a) and (b) of BM-$CuInS_2$ crystals.

Figure 6 shows the PL spectra of Samples (a) and (b) in the low energy region. Although Sample (b) displays similar peaks at 1.24, 0.99, and 0.80 eV to the THM-crystals, Sample (a) shows only a tail emission. Therefore, the deep emissions are most likely to be associated with the defects emerging in the course of the crystallization process, such as dislocations and relatively large vacancies which are considered as crystallinity disturbances rather than a result of deviation from stoichiometry. For THM-crystals, these defects are considered to be created by a separation of the large $CuInS_2$ clusters from indium solvent during crystal growth.

5. CONCLUSIONS

We have examined deep PL levels in THM- and BG-$CuInS_2$ crystals by PL technique. Three broad peaks at 0.83, 0.99, and 1.24 eV have been observed in the low energy region. The observed deep emissions seem to be caused by the recombination of the deep donors and deep acceptors. It is proposed that the deep defect levels involved in the observed radiative recombination are due to crystallinity disturbances rather than deviation from stoichiometry.

[1]. J. Klaer, J. Bruns, R. Henninger, K. Siemer, R. Klenk, K. Ellmer, D. Bräunig, Semicond. Sci. Technol. 13 (1998) 1456-1458.
[2]. J. J. M. Binsma, L. J. Giling, J. Bloem, J. Lumin. 27 (1982) 35-54.
[3]. J. J. M. Binsma, L. J. Giling, J. Bloem, J. Lumin. 27 (1982) 55-72.
[4]. H. Y. Ueng, H. L. Hwang, J. Phys. Chem. Solids 50 (1989) 1297-1305.
[5]. G. Masse, J. Appl. Phys. 68 (1990) 2206-2210.
[6]. H. Matsushita, T. Mihira, T. Takizawa, Jpn. J. Appl. Phys. 40 (2001) 4789-4793.
[7]. K. Yoshino, T. Ikai, S. Shirakata, H. Miyake, K. Hiramatsu, Appl. Phys. Lett. 78 (2001) 742-744.
[8]. J. Krustok, J. H. Schön, H. Collan, M. Yakushev, J. Mädasson, E. Bucher, J. Appl. Phys. 86 (1999) 364-369.
[9]. K. Wakita, H. Hirooka, S. Yasuda, F. Fujita, N. Yamamoto, J. Appl. Phys. 83 (1998) 443-447.
[10]. K. Wakita, F. Fujita, N. Yamamoto, J. Appl. Phys. 90 (2001) 1292-1296.
[11]. K. Wakita, G. Hu, N. Nakayama, D. Shoji, Jpn. J. Appl. Phys. 41 (2002) 3356-3357.
[12]. K. Wakita, K. Nishi, Y. Ohta, N. Nakayama, Appl. Phys. Lett. 80 (2002) 3316-3318.
[13]. K. Wakita, M. Matsuo, G. Hu, M. Iwai, N. Yamamoto, Thin Solid Films 431-432 (2003) 184-185.
[14]. K. Wakita, K. Nishi, Y. Ohta, T. Onishi, Appl. Phys. Lett. 85 (2004) 3083-3085.
[15]. N. Sato, Y. Miyoshi, K. Wakita, K. Mochizuki, Ext. Abst. 51th Spring Meeting of the Japan Society of Applied Physics, Hachioji, March 31a-P21-13.
[16]. J. I. Pankove, Optical Processes in Semiconductors, Dover Publications., New York, (1971) p. 166.