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# Sharp band edge photoluminescence of high-purity $\text{CuInS}_2$ single crystals

Kenji Yoshino<sup>a)</sup> and Tetsuo Ikari

Department of Electrical and Electronic Engineering, Miyazaki University,  
1-1 Gakuen Kibanadai-nishi Miyazaki 889-2192, Japan

Sho Shirakata

Department of Electrical and Electronic Engineering, Ehime University, 3 Bunkyo-cho Matsuyama,  
Ehime 790-8577, Japan

Hideto Miyake and Kazumasa Hiramatsu

Department of Electrical and Electronic Engineering, Mie University, 1515 Kamihama Tsu,  
Mie 514-8507, Japan

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Temperature-dependent photoluminescence measurements were carried out between 8 and 300 K on  $\text{CuInS}_2$  single crystals grown by a traveling heater method. Ten distinct peaks were present in the near-band edge region. Four unknown peaks, observed at 8 K, were found to be due to bound exciton emission. Moreover, the luminescence remained stable up to room temperature. © 2001 American Institute of Physics. [DOI: 10.1063/1.1345802]

Solar cell technologies using I–III–VI<sub>2</sub> chalcopyrite semiconductors have made rapid progress in recent years. In particular,  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS) based solar cells have been extensively reported in comparison to other chalcopyrite semiconductor based solar cells, primarily because of its large absorption coefficient (more than  $10^5 \text{ cm}^{-1}$  near the band gap region) and its band gap energy of between 1.0 and 1.7 eV at room temperature. Conversion efficiencies for polycrystalline CIGS based solar cells have been significantly improved over recent years and the best cell is now reported at 18.8%.<sup>1</sup> Among ternary chalcopyrite semiconductors,  $\text{CuInS}_2$  may be the most promising material for photovoltaic applications due to the band gap of 1.5 eV which perfectly matches the solar spectrum for energy conversion. However, the conversion efficiency of the  $\text{CuInS}_2$  based solar cells are so far limited to around 12%.<sup>2</sup> One reason for this relatively low efficiency is that the physical properties of  $\text{CuInS}_2$  are not accurately known because high quality single crystal growth of  $\text{CuInS}_2$  is difficult in comparison to  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$ .

In our previous articles,<sup>3,4</sup> bulk  $\text{CuInS}_2$  single crystals have been grown by a traveling heater method (THM). The samples obtained were of chalcopyrite structures, In-rich composition and *n*-type conductivity, as determined by powder x-ray diffraction, electron probe microanalysis (EPMA), and thermoprobe analysis, respectively. In addition optical properties were examined by photoluminescence (PL) measurements at 77 K.

In this letter to further characterize physical properties and radiative recombination processes we report on temperature dependent PL measurements of  $\text{CuInS}_2$  single crystals grown by THM.

Bulk  $\text{CuInS}_2$  single crystals were grown by the THM at 860–900 °C from In solutions. The samples were chemically

etched in a ~0.5% Br-methanol solution and PL measurements were carried out between 8 and 300 K with Ar<sup>+</sup> Laser (514.5 nm) using a photomultiplier tube for detection.

Typical PL spectrum at 8 K is shown in Fig. 1. Ten distinct peaks (indicated arrows) are present in the spectrum. Peak energies are listed in Table I. Binsma *et al.*'s data<sup>5</sup> at 4.2 K are also listed as a reference. Peak emission lines called FE<sub>A</sub> (free exciton  $\Gamma_6$ ), EX1, EX2, EX3, or EX4 and EX5 (EX: acceptor or donor bound excitons) are also observed in this work. However, four peaks at 1.5347, 1.5324, 1.5288, and 1.5281 eV are observed.

Excitons can form stable complexes with neutral and ionized donors or ionized acceptors. The binding energies of neutral-donor and neutral-acceptor complexes have been calculated using the Coulomb interactions and electron-phonon coupling. From these results, Binsma *et al.* estimated the exciton-neutral donor ( $E_{D1}$ ) or acceptor binding energy ( $E_{A1}$ ), using  $m_e = 0.16$  and  $m_n = 1.30$ , for  $\text{CuInS}_2$  to be

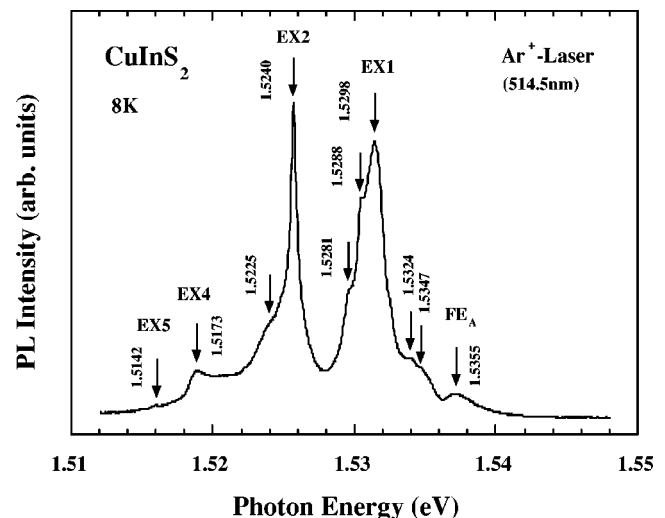


FIG. 1. Typical photoluminescence spectrum of the  $\text{CuInS}_2$  single crystal at 8 K. Ten distinct peaks are indicated by arrows.

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: yoshino@pem.miyazaki-u.ac.jp

TABLE I. Band edge emission lines observed in the In-rich CuInS<sub>2</sub> crystals. Binsma's data at 4.2 K are also listed as a reference.

$h\nu$ (eV) (this work at 8K)	Emission line (Binsma <i>et al.</i> )	$h\nu$ (eV) at 4.2 K
1.5355 eV	FE <sub>A</sub>	1.535 eV
1.5347		
1.5324		
1.5298	EX1	1.530
1.5288		
1.5281		
1.5240	EX2	1.525
1.5225	DV	1.520
1.5173	EX3	1.5185
	EX4	1.5165
1.5142	EX5	1.513

$$E_{BX} = 0.27E_{D1} + E_X, \quad (1)$$

$$E_{BX} = 0.06E_{A1} + E_X, \quad (2)$$

where,  $E_X$  is 20 meV for an exciton binding energies of CuInS<sub>2</sub>.<sup>5</sup>

Also for excitons bound to ionized donors or acceptors, calculations of the binding energies were performed both with and without photon coupling. Because no general relation can be given for the binding energy including phonon coupling, we will take the binding energies in the effective mass approximation as our starting point. The binding energy of an exciton to an ionized donor ( $E_{D2}$ ) or acceptor ( $E_{A2}$ ) is given by

$$E_{BX} = 1.044 E_{D2} + E_X, \quad (3)$$

$$E_{BX} = 1.5 E_{A2} + E_X, \quad (4)$$

and the photon energy  $h\nu$  of radiative transition of a bound exciton is represented by

$$h\nu = E_g - E_X. \quad (5)$$

Using Eqs. (1)–(5), the ionization energies of the donors or acceptors which can be calculated (Table II). All calculations have been performed for  $T = 8$  K.

The typical temperature dependent PL spectra of the CuInS<sub>2</sub> single crystal between 8 and 300 K are shown in Fig. 2. As the temperature increased from 8 to 80 K, the intensity of the EX2 peak drastically decreases and the EX1 peak becomes dominant at 80 K. One broadband is clearly present up to room temperature, this luminescence is observed at room temperature. An experimental determination of the binding energy if the peak is made possible from an analysis

TABLE II. Possible values of donor or acceptor levels as calculated from Eqs. (1)–(4).

$h\nu$ (eV) (this work at 8 K)	Neutral donor	Ionized donor	Neutral acceptor	Ionized acceptor
1.5347 eV	3 meV	20 meV	13 meV	14 meV
1.5342	11	22	53	15
1.5298 (EX1)	22	25	98	17.1
1.5288	24	25.5	112	17.8
1.5281	27	26.2	123	18.2
1.5240 (EX2)	43	30	192	21
1.5173 (EX3)	67	37	303	25
1.5142 (EX5)	79	40	355	28

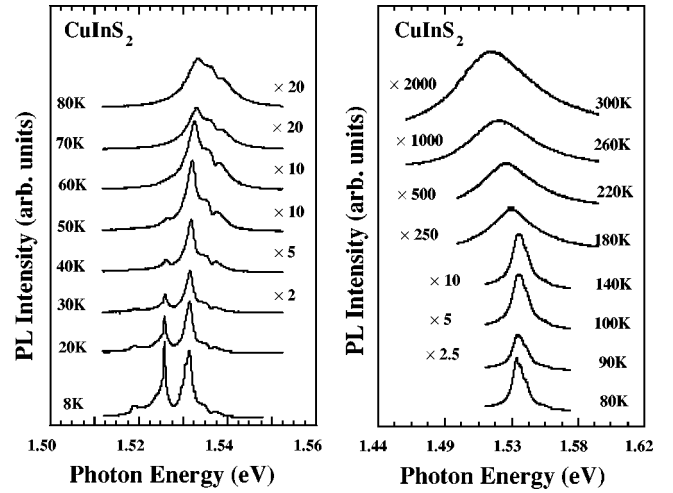


FIG. 2. Temperature dependent near band edge photoluminescence between 8 and 300 K.

of the quenching of the emission intensity with increasing temperature. In Fig. 3, the emission intensity of the peak is plotted versus a reciprocal of temperature. From  $1000/T = \text{about } 30\text{--}120 \text{ K}^{-1}$ , that is to say  $T = 8\text{--}40$  K, the PL intensity is almost unchanged indicating that the exciton, formed by the excitation light, relaxes by nonradiative recombination process. The thermal activation energy of the peak can be obtained using the PL intensity from 100 to 300 K, and is found to be 65 meV. This value is close to that the activation energy of In interstitial ( $\text{In}_i$ ).<sup>6,7</sup> The  $\text{In}_i$  defect is likely to be present in the sample as it is in line with the EPMA results which showed an excess of In.

Peak energies of, for example, FE<sub>A</sub> and EX1, seem to increase with increasing temperature from 8 to 100 K and decrease with increasing temperature from 100 to 300 K. Such an increase in band gap with increasing temperature, is, in general quite anomalous for semiconductors, has been observed previously for other chalcopyrite semiconductors.<sup>4</sup> The anomalous behavior of the energy gap can be explained on the basis of the temperature dependent  $p$ - $d$  hybridization. Shay and Wernick explained that the energy gap of the

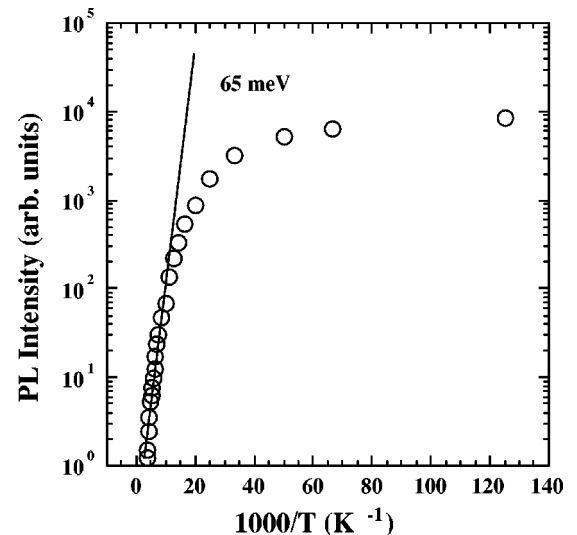


FIG. 3. Relative intensity of the EX1 peak as a function of the reciprocal temperature.

I–III–VI<sub>2</sub> chalcopyrite semiconductors is lowered with respect to the corresponding II–VI binaries by hybridization of the copper *d* levels with the chalcogen *p* levels.<sup>8</sup>

In summary, temperature dependent PL measurements were carried out between 8 and 300 K on CuInS<sub>2</sub> single crystals grown by the THM. Ten distinct peaks are present in the band edge region. Four peaks at 1.5347, 1.5324, 1.5288, and 1.5281 eV due to acceptor or donor bound excitons are observed at 8 K. Moreover, with increasing temperature, the luminescence is found to persist even at room temperature.

- <sup>1</sup>A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, and R. Noufi, *Prog. Photovoltaics* **7**, 311 (1999).
- <sup>2</sup>D. Braunger, D. Hariskos, T. Walter, and H. W. Schock, *Sol. Energy Mater. Sol. Cells* **40**, 97 (1996).
- <sup>3</sup>H. Miyake and K. Sugiyama, *Jpn. J. Appl. Phys., Suppl.* **32–3**, 156 (1998).
- <sup>4</sup>H. Miyake, M. Tsuda, and K. Sugiyama, *Inst. Phys. Conf. Ser.* **152**, 83 (1998).
- <sup>5</sup>J. J. M. Binsma, L. J. Giling, and J. Bloem, *J. Lumin.* **27**, 55 (1982).
- <sup>6</sup>J. J. M. Binsma, L. J. Giling, and J. Bloem, *J. Lumin.* **27**, 35 (1982).
- <sup>7</sup>H. Y. Ueng and H. L. Hwang, *J. Phys. Chem. Solids* **50**, 1297 (1989).
- <sup>8</sup>J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors* (Pergamon, New York, 1975).

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