Jpn. J. Appl. Phys. Vol. 31 (1992) pp. L 1071–L 1074
Part 2, No. 8A, 1 August 1992

1992–13

Photoluminescence Studies in $CuAlS_2$ Crystals

Sho SHIRAKATA, Igor AKSENOV[1,*], Katsuaki SATO[1] and Shigehiro ISOMURA

Faculty of Engineering, Ehime University, Matsuyama, Ehime 790
[1]*Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184*

(Received April 24, 1992; accepted for publication May 29, 1992)

Photoluminescence (PL) measurements have been carried out at low temperature (77 and 10 K) on $CuAlS_2$ crystals grown by the chemical vapor transport method. Seven sharp PL lines have been observed near the band edge. Based on the photoreflectance measurements, the PL line at 3.550 eV has been assigned to a free exciton emission. The lines at 3.540, 3.532, 3.500 and 3.475 eV are tentatively assigned to the bound excitons, and they are discussed in terms of the crystal composition and the annealing conditions. This study also refers to the PL lines and peaks at about 2.9 eV.

KEYWORDS: single crystals of $CuAlS_2$, chalcopyrite semiconductor, photoluminescence, exciton luminescence

$CuAlS_2$ ternary compound is the widest band-gap member of I-III-VI_2-type chalcopyrite compounds which is expected to be a promising material for blue-light-emitting device realization, since it has a wide direct band gap,[1)] a rather low melting point,[2)] and emits strong purple luminescence.[3)]

However, very few luminescence results in $CuAlS_2$ have been reported so far,[3-6)] most of them being concerned with the purple peak (410 nm) and broad orange band (590 nm). In general, $CuAlS_2$ crystals grown by the chemical vapor transport (CVT) method show a dominant broad orange luminescence band, with other emissions being very weak. No exciton emission has been detected since the cathodoluminescence study by Aksenov *et al.*,[6)] in which the free exciton emission at 353 nm and free-to-bound emissions at 370, 374 and 383.5 nm were observed. Intensities of these emissions have been reported to be 10^{-2} times weaker than that of the orange emission. At the present time, no clear observation of exciton emission has been reported.

In the present study, low-temperature photoluminescence (PL) investigations have been carried out on the CVT-grown $CuAlS_2$ single crystals. Several exciton lines have been observed in addition to the PL peaks around 2.9 eV and the broad PL band at 2.2 eV. Free exciton emission has been identified on the basis of the photoreflectance (PR) measurement results. The PL peaks observed are discussed in terms of the crystal composition and annealing conditions.

The $CuAlS_2$ single crystals were grown by the CVT method in a closed system with iodine as a transport agent, the crystal growth conditions being similar to the previously reported ones.[7)]

The PL was excited by a cw He–Cd laser (325 nm, 10 mW), analyzed by a grating monochromator (focal length of 50 cm), and detected by a Hamamatsu R-636 photomultiplier. Sometimes, the signal-to-noise ratio was improved by averaging the record of several PL runs using a computer data acquisition system. The PL measurements were carried out at the temperature of 77 and 10 K.

Figure 1 shows two typical PL spectra of undoped $CuAlS_2$ crystals grown from stoichiometric $CuAlS_2$ powder under the same growth condition (source and growth temperatures were 800 and 650°C, respectively, and iodine charge was 5 mg/cm^3). Most of the crystals exhibited a strong orange PL band peaked at 2.1 eV and weak peaks at 2.9 and 3.55 eV, as can be seen in the upper part of Fig. 1. A part of the crystals exhibited very in-

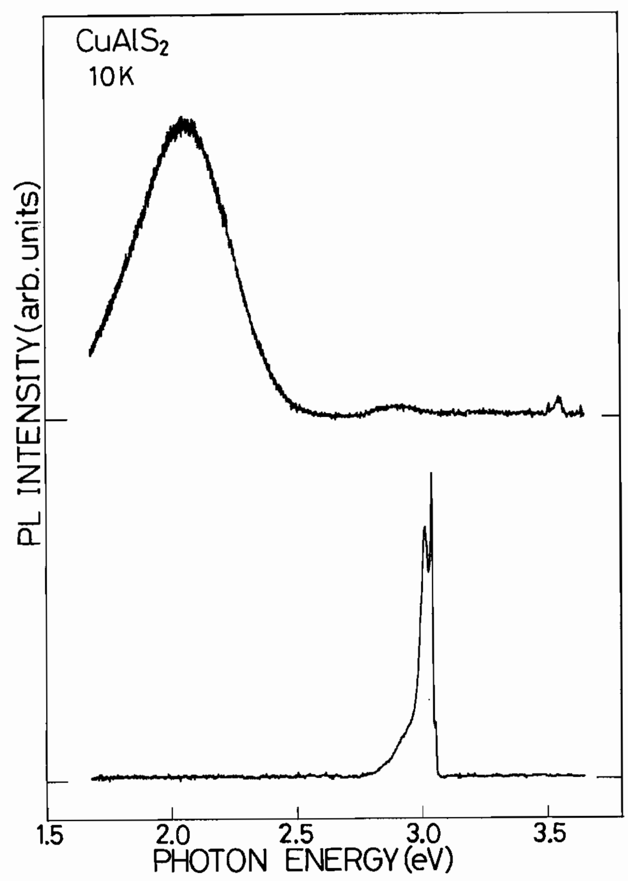

Fig. 1. PL spectra of $CuAlS_2$ crystals grown from the stoichiometric starting materials (10 K).

*On leave from Institute of Physics of Solid and Semiconductors, Academy of Science of Buelorussia, Minsk, Buelorussia.

tense purple emission, as can be seen in the lower part of Fig. 1, in which several sharp PL lines and somewhat broader peaks are observed between 2.9 and 3.1 eV.

The detailed PL spectra (10 and 77 K) in the energy region between 3.45 and 3.65 are shown in Fig. 2 for the crystal whose PL is shown by the upper curve in Fig. 1. We can see seven sharp PL lines near the band edge, the lines being labelled I_1-I_7. Lines denoted by the star are spontaneous emission lines of the He–Cd laser which was used as the photoexcitation source. The PL lines were distinguished from the laser lines by the polarized PL measurements, the lines polarized parallel to the optic axis (*c*-axis) of the crystal being considered as emission from the crystal. The results on the sharp near-band-gap PL lines are summarized in Table I, these lines being assigned to the exciton emissions in view of their spectral positions and small half-width. No noticeable change of the spectral positions and relative intensities of the exciton lines has been observed with the temperature changing from 10 to 77 K.

In order to find out which of the I_1-I_7 lines is caused by free exciton emission, photoreflectance (PR) measurements have been performed at 77 K. The PR spectrum is shown in Fig. 2 together with the PL spectra of the same crystal. It can be seen in the upper part of Fig. 2 that the PR spectrum shows very sharp structure, indicating the free exciton signal. The free exciton energy of 3.550 eV obtained by the analysis of the PR spectrum by the three-point method[8] is in good agreement with the energy of the PL line I_3. Therefore, line I_3 is considered to be the free exciton emission. Lines I_4-I_7 in the low-energy side of the free exciton emission are considered to be bound exciton emissions. At the present stage, we cannot definitely determine the origin of the two weak lines I_1 and I_2, the spectral position of which corresponds to higher energy as compared with that of the free exciton emission. These two lines may be caused by emissions involving excited states of excitons.

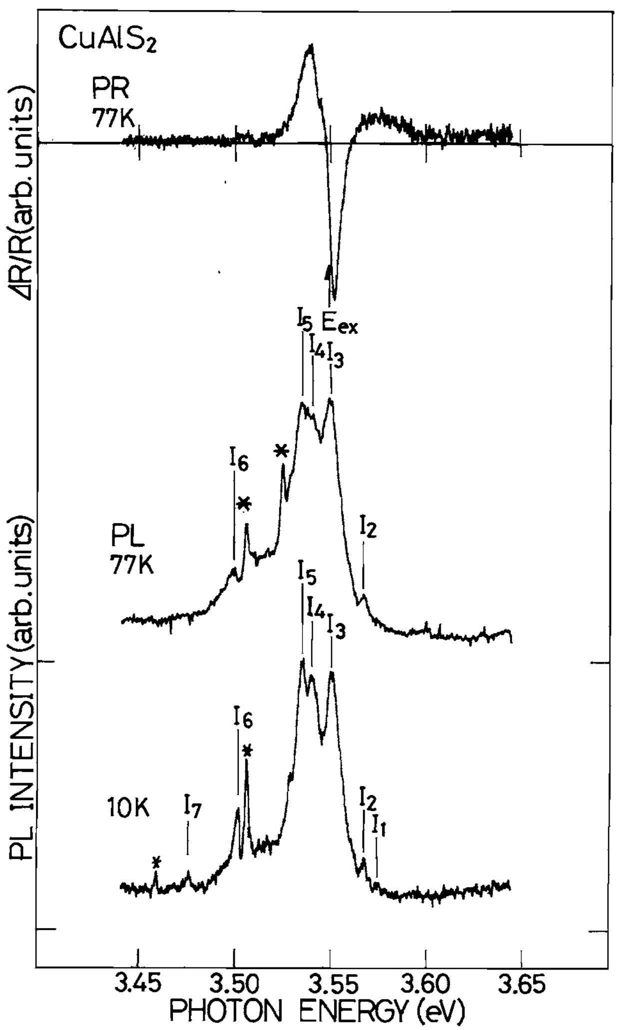

Fig. 2. Exciton emissions of stoichiometric $CuAlS_2$ crystal (10 and 77 K) together with the PR spectrum (upper curve) taken at 77 K.

Table I. Peak energies and assignment of the exciton PL lines in $CuAlS_2$ crystals. The crystals under consideration are as-grown ones of stoichiometric (stoichio.), $Cu_{0.97}Al_{1.03}S_2$ (Al-rich) and $Cu_{1.03}Al_{0.97}S_2$ (Cu-rich) compositions as well as crystals annealed in sulfur (in S) and in vacuum (in vac.). Strong lines are indicated by (++), weak lines by (+) and missing lines by (−).

line	energy (eV)	crystals					assignment
		as-grown			annealed		
		stoichio.	Al-rich	Cu-rich	in S	in vac.	
I_1	3.576	+	−	+	−	−	?
I_2	3.567	+	broad	+	+	+	?
I_3	3.550	++	−	++	++	++	free exciton
I_4	3.540	++	−	++	+	++	bound exciton
I_5	3.532	++	broad	++	+	++	bound exciton
I_6	3.500	+	−	−	++	−	bound exciton
I_7	3.475	+	−	−	++	−	bound exciton

Figure 3 shows the detailed PL spectra between 2.8 and 3.1 eV in the $CuAlS_2$ exhibiting purple luminescence, where the spectra taken from two different positions of the same crystal are shown. It can be seen in Fig. 3 that the purple emission consists of four sharp lines at 3.053, 3.049, 3.042 and 3.040 eV (lines 1–4 in Fig. 3). Two broader peaks can also be seen at 3.01 and 2.93 eV, their relative intensities changing depending on the position within one crystal. The peaks at 3.01 and 3.93 eV are considered to be the donor-acceptor pair (D-A pair) emissions similar to the previously reported peaks at 3.02[3-6] and 2.95 eV,[5] respectively.

The resemblance of the PL spectra shown in Fig. 3 to those of $CuGaS_2$ is striking in that the sharp PL lines are superimposed on the D-A pair emission.[9-11] In $CuGaS_2$, sharp PL lines have predominantly been observed in Cu-rich crystals in the spectral region of 2.4 eV where the Ga-rich crystals show strong D-A pair emission.[9,10] Based on the analogy with $CuGaS_2$, the D-A pair peaks at 2.93 and 3.12 eV are deduced to be caused by the defects characteristic of Al-rich crystals, whereas the sharp PL lines (3.053, 3.049, 3.042 and 3.040 eV) are considered to originate from the defects characteristic of Cu-rich ones. It should be noted that in the $CuAlS_2$ crystal, which exhibits intense purple emission, no exciton emissions has been observed. At the same time, the crystal with purple emission exhibits a very strong and broadened electron spin resonance (ESR) signal of the Fe^{3+} impurity ions that play a significant role in the process of elec-

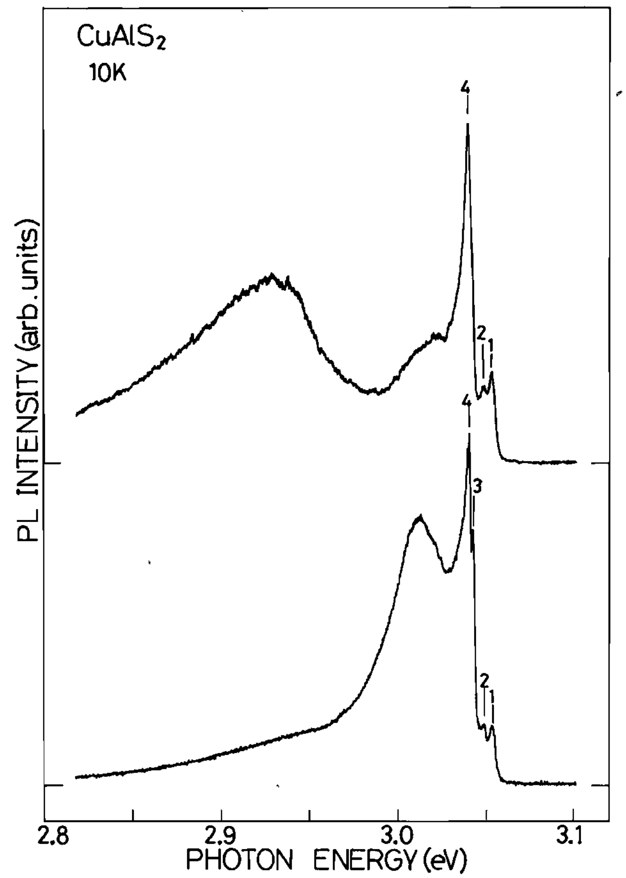

Fig. 3. PL spectra of $CuAlS_2$ exhibiting purple luminescence taken from different positions on one crystal (10 K). Energies of lines numbered 1–4 are 3.053, 3.049, 3.042 and 3.040 eV, respectively.

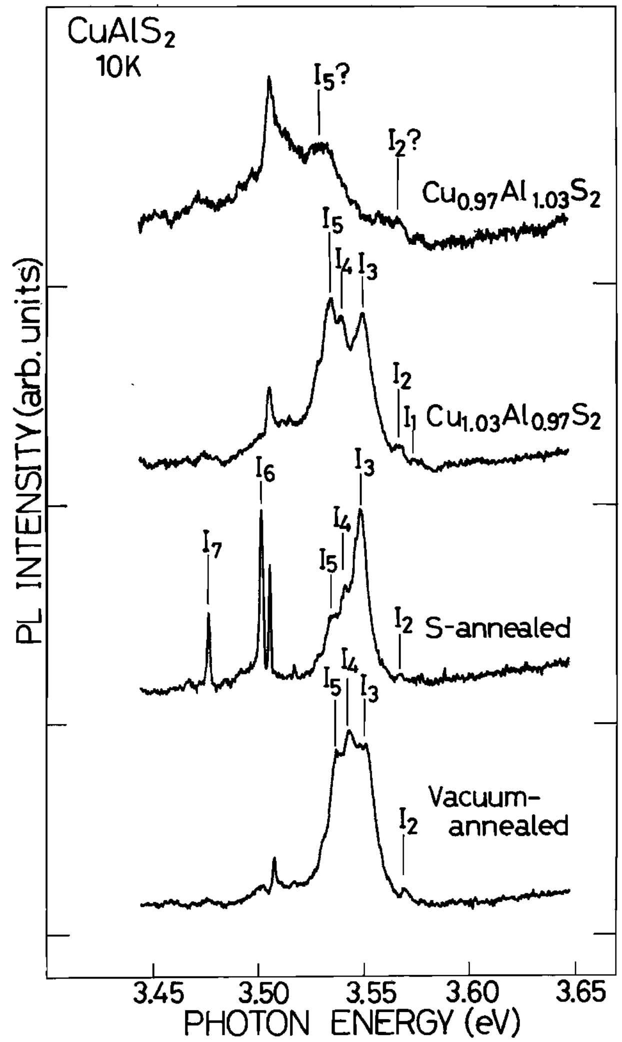

Fig. 4. Exciton emissions at 10 K in several crystals grown from nonstoichimetric starting materials and annealed crystals. The compositions of the starting materials are indicated.

trical charge compensation in the crystal lattice. Therefore, the large concentration of electrically active defects, which makes the ESR spectrum broad, may lead to the dissociation of excitons and the enhancement of D-A pair emissions. The relationship between PL and ESR will be discussed in detail in a later paper.

The bound exciton lines have been examined for $CuAlS_2$ crystals grown from nonstoichiometric polycrystalline powder and for those annealed under different conditions. The PL spectra of these crystals in the spectral region between 3.45 and 3.65 eV are summarized in Fig. 4. The crystals grown from the Al-rich ($Cu_{0.97}Al_{1.03}S_2$) polycrystalline powder exhibit a dominant orange broad band and very weak exciton emissions. The intensity of the orange band is about one order stronger than that in the stoichiometric crystal. These results are in good agreement with the PL spectra observed in Ga-rich $Cu_{0.88}Ga_{1.04}S_2$, which are dominated by a strong broad red emission band with no exciton emission.[12] It should be noted that the intensities of broad exciton peaks I_2 and I_5 (Fig. 4) are two orders weaker than the intensities of the exciton lines observed in the stoichiometric crystals. The small intensities and the large half-width of exciton peaks indicate the poor crystal quality of the Al-rich crystal.

The PL spectra of the crystals grown from Cu-rich ($Cu_{1.03}Al_{0.97}S_2$) starting material are similar to those in the stoichiometric crystal: lines I_6 and I_7 are absent in the spectra (Fig. 4).

Crystals annealed in sulphur vapor at 700°C (S-vapor pressure of about 2 atm) for 60 h exhibited an increase in the intensities of the exciton emissions and a decrease in the intensity of the orange band. The intensities of the bound exciton lines I_6 and I_7 increase in this case, while those of lines I_4 and I_5 decrease.

Annealing in vacuum (700°C, 60 h) leads to the increase of relative intensities of the bound exciton lines I_4 and I_5, and the elimination of lines I_6 and I_7.

These results indicate that the bound exciton lines tend to be affected by the crystal stoichiometry (the results are summarized in Table I). Based on this tendency, there is a possibility that lines I_4 and I_5 are related to the sulfur vacancy, whereas lines I_6 and I_7 are related to the cation vacancies or sulfur interstitials.

In summary, PL measurements have been carried out on $CuAlS_2$ crystals at low temperature. Exciton lines have been resolved for the first time. The free exciton line has been determined to be the line at 3.550 eV based on the photoreflectance spectrum. Four bound exciton lines are discussed in terms of the annealing conditions. Furthermore, several new sharp PL lines at 3.053, 3.049, 3.042 and 3.040 eV, as well as the D-A pair emissions at 3.01 and 2.93 eV, have been observed.

References

1) J. L. Shay and J. H. Wernick: *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications* (Pergamon Press, New York, 1975).
2) I. A. Aksenov, L. A. Makovetskaya, G. P. Popelnyuk and I. P. Shilorich: Phys. Status Solidi a **105** (1988) K97.
3) N. Yamamoto: *Proc. 4th. Int. Conf. Ternary and Multinary Compounds, Tokyo, 1980,* Jpn. J. Appl. Phys. **19** (1980) Suppl. 19-3, p. 95.
4) P. Bridenbaugh and B. Tell: Mater. Res. Bull. **10** (1975) 1127.
5) S. Iida, Y. Oguro, H. Honda and S. Suzuki: *Proc. 5th. Int. Conf. Ternary and Multinary Compounds, Cagliari, 1982,* Il Nuovo Cimento **2D** (1983) 1933.
6) I. A. Aksenov, I. R. Gulakov, V. I. Lipnitskii, A. I. Lukomskii and L. A. Makovetskaya: Phys. Status Solidi a **115** (1989) K113.
7) I. Aksenov, Y. Kudo and K. Sato: Jpn. J. Appl. Phys. **31** (1992) L145.
8) D. E. Aspnes: Surf. Sci. **37** (1973) 418.
9) T. Miyazaki, S. Shirakata and S. Isomura: Jpn. J. Appl. Phys. **30** (1991) L1850.
10) S. Shirakata and S. Isomura: J. Appl. Phys. **68** (1990) 291.
11) S. Shirakata and S. Isomura: Jpn. J. Appl. Phys. **30** (1991) 1666.
12) S. Shirakata, K. Murakami and S. Isomura: Jpn. J. Appl. Phys. **28** (1989) 1728.