

Excitonic photoluminescence in CuAlS₂ powders

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Published online: 5 September 2007
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Abstract Copper aluminum disulfide (CuAlS₂) powders were synthesized in the evacuated ampoule. The luminescence properties of obtained powders were evaluated by photoluminescence (PL) at various temperatures. The visible emission peaks at 2.16 and 1.90 eV, and weak ultraviolet emission peak at 3.47 eV were obtained in the room temperature PL. The temperature dependence of the PL revealed that the ultraviolet emission at room temperature was considered to be free-exciton. Several emission peaks related to free-exciton, bound-exciton and phonons were observed in the high-resolution PL at 12 K, reflecting that the obtained powders had high crystallinity. Emission peaks at 3.459 and 3.300 eV for CuAlS₂ were observed for the first time. The former emission might be originated from the bound exciton and the latter from the donor–acceptor pair recombination.

Keywords Excitonic photoluminescence ·
Copper aluminum disulfide

1 Introduction

Recently, the data storage capacity of optical disk systems has increased rapidly. In order to develop the systems with higher capacity, it is necessary to investigate the materials exhibiting high-energy emission.

The *I–III–VI*₂ chalcopyrite compound has been attracting considerable attention as a promising new material for

optical applications because its lattice constant and energy gap change widely with a change in its elemental combination (*I* = Cu, Ag, *III* = Al, Ga, In and *VI* = S, Se, Te). Among them copper aluminum disulfide (CuAlS₂) has the widest excitonic band gap ($E_g=3.49$ eV) at room temperature [1]. In addition, the exciton binding energy of this material (70 meV) [2] is larger than other ultraviolet emitting materials such as ZnO (60 meV), ZnS (39 meV) and GaN (21 meV) [3]. It means excitons in CuAlS₂ can exist stably at room temperature (the thermal energy of room temperature is 24 meV [2]). Therefore, CuAlS₂ is expected to be a material for an ultraviolet emitter with a high emission efficiency at room temperature. However, it is not easy to induce the excitonic emission from CuAlS₂ because various types of defect caused by deviation from stoichiometric composition and/or impurities are easily formed in the crystal [4–7]. Only a few basic research of CuAlS₂, which exhibited excitonic emission, were reported [2, 5, 8].

The purpose of this report is to synthesize the CuAlS₂ powders exhibiting ultraviolet emission at room temperature. The luminescence properties of the obtained powders were evaluated by photoluminescence (PL) at various temperatures. The origins of obtained emissions were investigated by PL at 12 K.

2 Experiment

The elemental Cu (99.99%), Al (99.99%) and S (99.99%) powders with a molar ratio of Cu:Al:S=1:1:2 were mixed and pressed into pellets at 100 MPa. The obtained pellets were sealed in quartz glass ampoules (50 mm long and 6.5 mm inner diameter) at a pressure of 10^{-5} Pa. The ampoules were heated with a rate of 1.5 K/min in an

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electric furnace, maintained at 500, 600, 700, 800 and 850 °C for 300 min and then cooled to room temperature in the furnace. The photoluminescence (PL) was performed at room and low temperatures using a grating monochromator (focal length of 25 cm and spectral resolution of 1 nm) with a photomultiplier and cryostat. The high-resolution PL was performed at 12 K using a grating monochromator (focal length of 100 cm and spectral resolution of 0.16 nm) with CCD detector and cryostat. A 325 nm (photon energy of 3.82 eV) line of He–Cd laser was used as an excitation source for PL measurements.

3 Results and discussions

Figure 1 shows the room temperature PL spectra from the obtained powders heated at 500 to 850 °C. The spectra

were enlarged parallel to vertical axis in the range from 3.2 to 3.6 eV. Trail from excitation line of He–Cd laser (3.82 eV) was observed in the right end of the enlarged spectra. The powder heated at 500 °C exhibited no luminescence. The powders heated at 600 and 700 °C exhibited a visible emission peak at around 2.16 eV, and those heated at 800 and 850 °C exhibited the emission peak at 1.90 eV. Furthermore, weak ultraviolet emission peak at 3.47 eV was observed in all samples. Kudo et al. reported that the orange emission peaks at a range between 1.8 and 2.1 eV are caused by donor–acceptor (D–A) pair recombination [9]. It is thought that the emission peaks at 2.16 and 1.90 eV are related to two deep donor levels. The intensity of visible emission is a function of the concentration of the deep donor levels. Therefore, the intensity ratio of ultraviolet to visible emission might reflect a crystallinity and defect concentration [8].

In order to evaluate an origin of the weak ultraviolet emission obtained at R. T., the temperature dependence of PL was performed on the powder heated at 700 °C with the lowest defect concentration among the powders shown in Fig. 1. Figure 2 shows the PL spectra in the range between 3.1 to 3.6 eV at temperatures from 15 to 295 K. Several

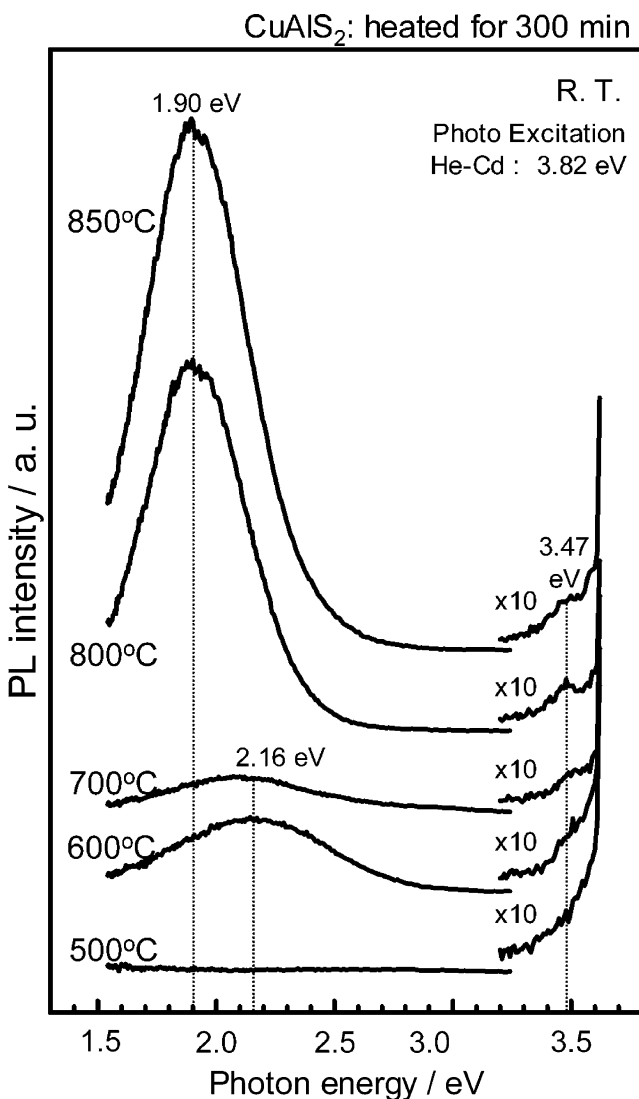


Fig. 1 Room temperature PL spectra from CuAlS_2 powders heated at 500 to 850 °C for 300 min

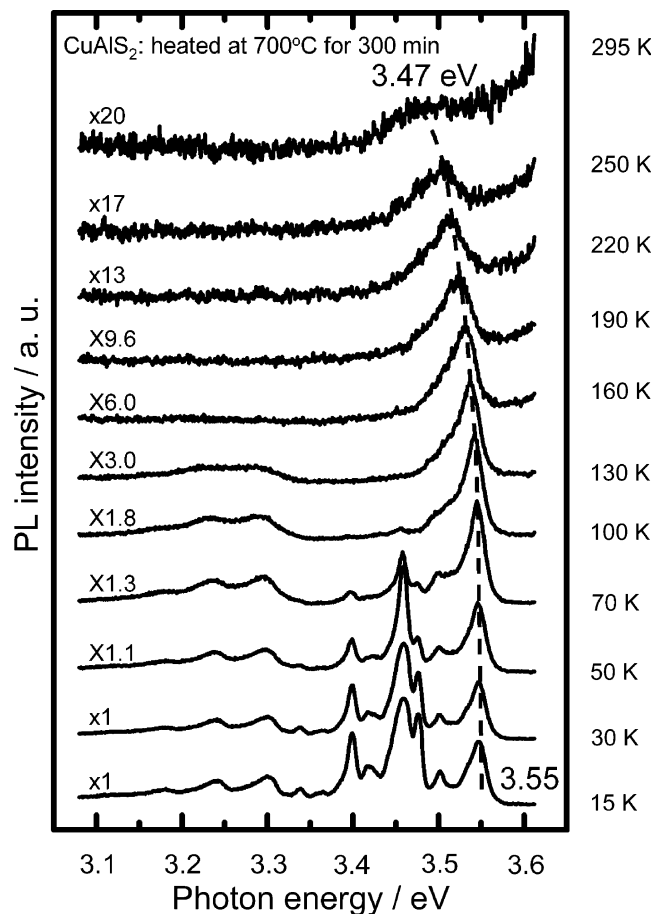


Fig. 2 Temperature dependence of PL spectra in the range from 3.1 to 3.6 eV

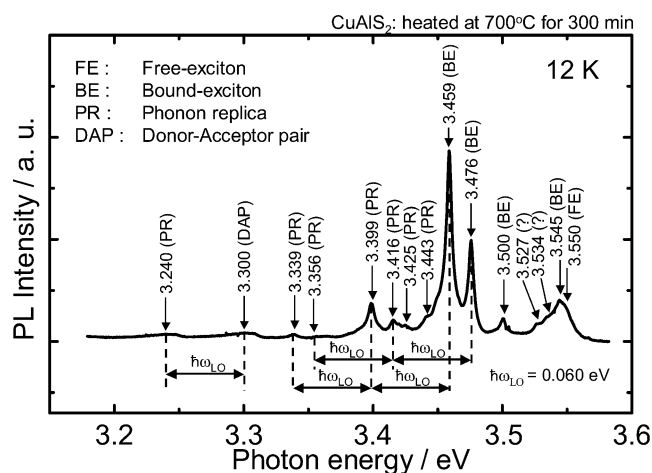


Fig. 3 High-resolution PL spectrum at 12 K

sharp emission peaks were obtained at low temperatures. The emission peak of the 3.55 eV at 15 K may be due to a free exciton which corresponds to that reported in Shirakata et al. [5]. The peak energy of a free-exciton measured at 15 K decreased with increasing temperature up to 295 K, reflecting the decrease of the energy gap. The peak energy of the emission at 295 K was 3.47 eV. It is thought that the thermal dissociation of excitons does not occur at room temperature because the exciton binding energy is approximately 70 meV which is about three times higher than the thermal energy $k_B T$ at room temperature (24 meV) [2]. Therefore, the obtained ultraviolet emissions at R. T. can be attributed to free-exciton.

Detailed PL spectrum at 12 K is shown in Fig. 3. The peak at 3.550 eV was assigned to free-exciton and the other peaks at 3.545, 3.500 and 3.476 eV were assigned to bound exciton [5]. The origin of the emission peaks at 3.534 and 3.527 eV has not been clarified yet. The emission peak at 3.459 eV which showed the highest intensity had never been reported. The origin of the emission might be attributed to bound exciton because its peak energy is lower than that of the free-exciton and its peak shape is similar to another emission of 3.476 eV assigned to bound exciton [5]. Several emission peaks in the lower energy than 3.459 eV are assigned to phonon replicas because of the energy separation of each emission peak. For example, the energy separation of each emission peak of 3.459, 3.399 and 3.339 eV is 0.060 eV which corresponds to the energy of LO-phonon observed by Raman scattering [10]. The

same relation is also observed among the emission peaks at 3.476, 3.416 and 3.356 eV. The broader emission peaks at 3.300 and 3.240 eV than excitonic emissions have not been reported yet. Based on the analogy with ZnSe, these peaks may be caused by donor–acceptor pair emission and its phonon replica [11]. The observation of various emission peaks related to excitons and phonons revealed that the obtained powder had high crystallinity.

4 Conclusion

Copper aluminum disulfide (CuAlS_2) powders were synthesized in the evacuated ampoule. From the temperature dependence of the PL, the ultraviolet emission peak at 3.47 eV at room temperature was considered to be free-exciton. Several emission peaks related to free-exciton, bound-exciton and phonons were observed in the high-resolution PL at 12 K, reflecting that the obtained powders had high crystallinity. Emission peaks at 3.459 and 3.300 eV for CuAlS_2 were observed for the first time. The former emission might be originated from the bound exciton and the latter from the donor–acceptor pair recombination.

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