Electroluminescence Spectrum of Manganese-Doped $CuAlS_2$

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1. INTRODUCTION

The authors have been working with optical studies on a number of chalcopyrite-type crystals doped with transition elements and have clarified electronic energy levels introduced by such impurities[1]. In the previous studies[2], we observed a red photoluminescence(PL) band in a single crystal of $CuAlS_2$:Mn and assigned the luminescence to the ligand-field transition from the lowest excited state $^4T_1$ to the ground state $^6A_1$ in the $3d^5$ manifold of Mn^{2+} ion, just like the orange luminescence in ZnS:Mn. It was also found that the similar luminescence can be excited by the electron beam, as well as by the electric field.

Recently, we carried out studies of the time-resolved PL spectra on this material to clarify the mechanism of luminescence. We also measured the electroluminescence(EL) spectrum in a simple MIM diode using single crystals of $CuAlS_2$:Mn. This paper describes the results of these optical studies.

2. EXPERIMENTAL

2.1 Sample Preparation

Single crystals of $CuAlS_2$ doped with 5 mol% Mn were grown by the chemical transport technique. The obtained crystals were needle-like with a typical dimension of 5 mm x 1 mm x 0.5 mm. These crystals were analyzed by X-rays. The major surface of the crystal was determined as {112} plane of the chalcopyrite structure.

Samples for EL measurements were prepared as follows: Crystals were polished with lapping films and etched slightly by the HNO_3 solution. Thin aluminum film was evaporated on one side of the crystal as an electrode. The sample was pasted to a copper plate by a Ga-In soldering alloy.

2.2 Photoluminescence Spectrum Measurements

A CW-PL spectrum was measured at room temperature using the 488nm line of an Ar^+ ion laser as an excitation source. The emitted light was dispersed by a JASCO CT-25C monochromator and detected by a photomultiplier with the S-20 response. A lock-in detection system was used.

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The PL-decay characteristics and the time-resolved PL spectra were measured using a nitrogen laser(for 10ns-30μs) and a Xe flash lamp (for 10μs-10ms) as light sources. Boxcar integrator was employed to average the photo-signal. Measurements and data-processing were performed with the help of a microprocessor-controlled data acquisition system.

2.3 Electroluminescence Spectrum Measurements

An ac. voltage with a frequency 5 kHz from an audio-frequency oscillator was boosted to 150-300 Vrms by a transformer and was applied between the copper plate and the aluminum electrode at room temperature. The spectroscopic measurements were performed using the same system as described in the previous section.

3. EXPERIMENTAL RESULTS

3.1 Photoluminescence Spectrum

Figure 1 illustrates a PL spectrum observed in a single crystal of $CuAlS_2$:Mn at room temperature. The spectrum is broad with a peak at 1.96 eV and a small shoulder at 1.9 eV. This spectrum agrees completely with that measured with an excitation by a 356 nm line of a high pressure Hg-lamp excitation reported earlier[2].

Time-resolved spectra measured with a nitrogen laser are given in Fig. 2 for several delay times (from 20 to3000 ns) after excitation. The spectrum has been corrected for the spectral dependence of the measuring system. The spectral shape is essentially the same as the CW-PL spectrum. The peak energy showed a negligible shift throughout the measured time interval.

A semi-logarithmic plot of the decay curve of the PL peak at 1.96 eV measured with a nitrogen laser and a Xe flash lamp is illustrated in Fig. 3, from which the recombination lifetime was estimated: As seen in the figure the curve consists of three exponential decay curves with time constants of 54 μs, 111 μs and 152 μs.

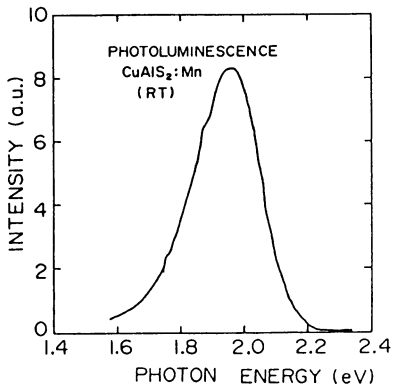

Fig.1 Photoluminescence spectrum of $CuAlS_2$:Mn measured at room temperature using an Ar^+ ion laser as an excitation source.

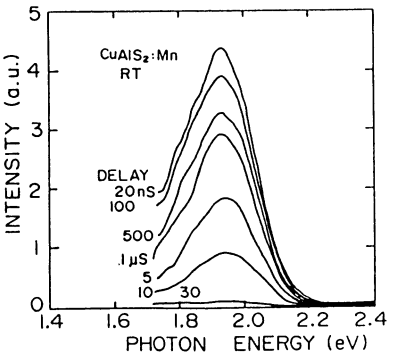

Fig. 2 Time-resolved PL spectra in a single crystal of $CuAlS_2$:Mn measured at room temperature with a nitrogen laser excitation.