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Photoluminescence of Cd-Doped CuAlS₂

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The observation of the intense yellow-green photoluminescence band peaked at 565 nm from CuAlS₂ crystals, grown by the chemical vapour transport technique and subsequently doped with Cd, is reported. The emission is interpreted as originating from donor-acceptor pair recombination, involving deep levels, formed by the Cd-introduced defects.

KEYWORDS: CuAlS₂:Cd, photoluminescence, donor-acceptor pair recombination

CuAlS₂ semiconductor is the widest band gap member of the A¹B³C₂-type ternaries, which crystallizes in a chalcopyrite structure and is expected to be a promising material for blue LED realization.¹⁾

Undoped crystals of the CuAlS₂ compound exhibit p-type of conductivity with high resistivity values of 10⁴-10⁸ Ω·cm,²⁾ and the typical photoluminescence (PL) spectrum of undoped crystals at 70 K consists of a series of sharp lines in the ultraviolet spectral region due to the free and bound exciton recombination, and a purple P-emission peaked at 410 nm, as well as a broad orange O-emission peaked at 610-630 nm, originating from the DA-pair recombination.³⁾

In the present study we report the observation of a bright green emission from the CuAlS₂ crystals, doped with Cd.

The single crystals were grown by the iodine vapour transport technique from the polycrystalline CuAlS₂ compound, prepared by the direct melting of the constituent elements in a BN crucible.⁴⁾ The resulting crystals were then annealed in evacuated and sealed quartz ampoules in the presence of Cd, Cd metal in amount of 50 mg being placed in one end of the ampoule, and the CuAlS₂ crystals being placed into the other end of the ampoule. Thermal treatments were carried out for 50, 80 and 120 h at 700°C and 900°C. After the annealings, the samples were etched in hot HNO₃ just long enough (~1 min) to dissolve the red blotches that had been found to develop on the surfaces of the annealed samples due to an alloying of Cd with CuAlS₂, rinsed in methanol, and mirror-polished using the lapping films. No noticeable change in the electrical properties of the Cd-doped crystals as compared with those of the undoped ones was observed, the Cd-doped samples exhibiting p-type conductivity with high resistivity values.

The typical PL spectra of Cd-doped samples, taken under He-Cd laser (325 nm, 12 mW) excitation, are shown in Fig. 1. Annealing of the crystals in the presence of Cd at 700°C does not result in any significant change in the PL properties of the crystals, the resulting PL spectrum being essentially the same as that for the as-grown crystals (Fig. 1, dashed curve).

However, the spectra of the samples annealed at 900°C for 50 h exhibit a G-shoulder at 565 nm, superposed on the high-energy edge of the orange emission (Fig. 1, dot-dashed curve). This shoulder rises in inten-

sity with the increase in the annealing time and turns to dominate the spectrum of the samples annealed for 120 h (Fig. 1, solid curve), the emission in this case being intense yellow-green. In addition to the dominant G-emission the spectra of the crystals annealed for 120 h also exhibit the P-emission and the shoulder at 625 nm (O-band), as well as a weak B-emission at 450 nm, the spectral position of which is close to that of the intense B-emission, observed in Zn-doped crystals.⁵⁾

The intensity of the G-emission decreases after step-by-step progressive polishing off the crystal surface in 20 μm steps, the G-emission at the depth of 20 μm being ~5 times stronger than that at the depth of 200 μm. This phenomenon can be explained by the heavier Cd concentration at the surface of the sample as compared with that in the bulk; this inhomogeneity of the Cd concentration is believed to be caused by the slow diffusion rate of Cd due to its large atomic size (1.49 Å).

Using of a Xe-lamp as an excitation source results in

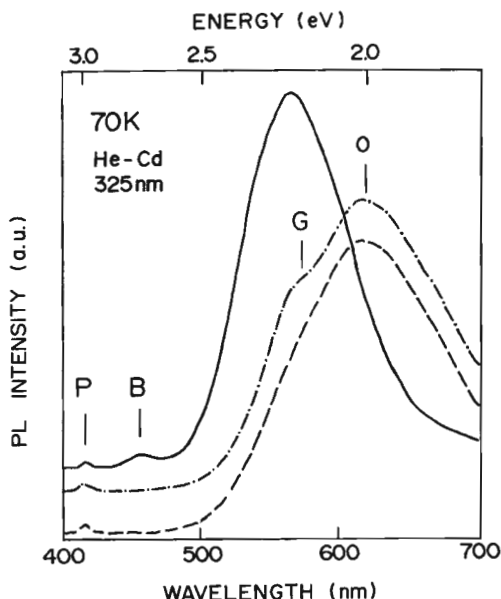


Fig. 1. PL spectra of CuAlS₂ crystals, annealed in the presence of Cd at 900°C for 50 h (---) and 120 h (—). The spectrum of undoped crystal (----) is also shown.

essentially the same PL spectra as were observed under He-Cd laser excitation. The PL-excitation (PLE) spectra for the G-emission are shown in Fig. 2, and consist of two peaks, the spectral position of the higher-energy A-peak, located at 3.72 eV, having been found to be almost the same for different samples under investigation, whereas the position of the lower-energy B-peak changes from sample to sample in the range of 3.2 ± 0.15 eV. Since essentially the same PLE spectra have been observed for a blue emission in Zn-doped CuAlS_2 ,⁶⁾ we tentatively attribute both A- and B-peaks of the PLE spectra to the direct band-to-band absorption of the host crystal. The B-peak has been assigned to the transitions from the highest valence sub-band of Γ_7 -symmetry to the conduction band, the low-energy shift of this peak from the band gap energy of 3.55 eV, as well as the dependence of the spectral position of the B-peak on the sample having been attributed to the band-tail absorption caused by the high concentration of the crystal defects, this concentration being dependent on the sample. The A-peak has been assigned to the transitions from the lower valence sub-band of Γ_6 -symmetry to the conduction band since the spectral position of this peak agrees well with the results of photoconductivity studies.⁷⁾

The time-resolved spectra for the G-emission, measured under XeCl excimer laser excitation (308 nm, 20 ns pulse), show a red shift of the peak of the G-emission as time proceeds. Therefore, the G-emission has been attributed to the DA-pair recombination.

The temperature dependence of the intensity of the G-emission, shown in Fig. 3, reveals two linear portions, which are believed to correspond to activation energies of $0.2 (\pm 0.02)$ eV and $1.08 (\pm 0.05)$ eV of the two energy levels, involved in the G-emission. The sum of the observed activation energies (1.28 eV) agrees well with the energy separation between the spectral positions of the free exciton emission (3.55 eV)³⁾ and the peak of the G-emission (2.19 eV), which confirms

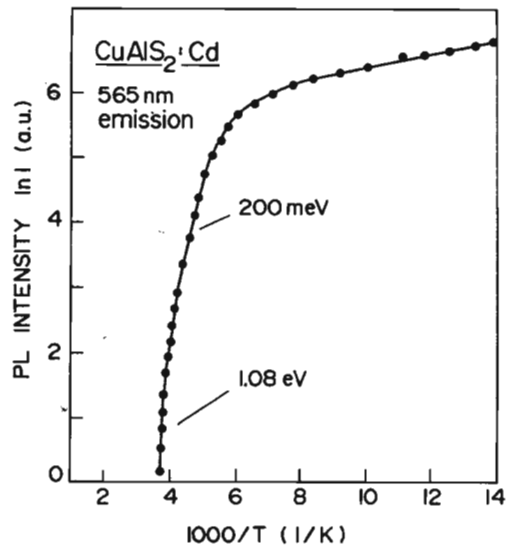


Fig. 3. Temperature dependence of intensity of the G-emission.

the nature of the G-emission as originating from the DA-pair recombination.

Taking into account that the Cd-diffusion carried out with S added to the ampoule does not result in the G-emission (no changes in the PL spectra have been observed in the case of (Cd+S)-annealing as compared with that of the as-grown crystals), we tentatively attribute the energy level with the activation energy 0.2 eV to sulphur vacancies (donor-like), this assignment being in accordance with the results of PL studies in the as-grown CuAlS_2 .⁸⁾ The deep acceptor level (1.08 eV) is believed to originate from some Cd-introduced defect, the exact nature of which is yet unknown.

In conclusion, we have shown in this paper that the Cd-doped CuAlS_2 crystals emit a strong yellow-green PL peaked at 565 nm, caused by the DA-pair recombination, involving deep Cd-introduced energy level with the activation energy of 1.08 eV.

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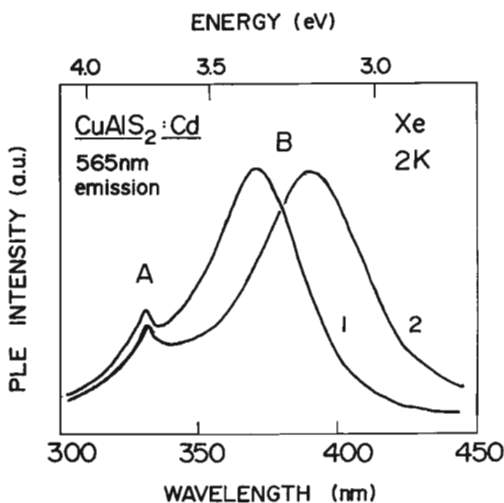


Fig. 2. PLE spectra for the G-emission for two samples (1 and 2).

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