CuAlS$_2$:Mn Thin Film EL Devices Prepared by Electron-Beam Evaporation Method Using Phosphor Pellet

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Abstract
CuAlS$_2$:Mn phosphor thin films have been prepared by electron-beam (EB) evaporation method using CuAlS$_2$:Mn phosphor powder as EB evaporation source pellets. The films are crystallized below 500°C even without post-deposition annealing. The CuAlS$_2$:Mn electroluminescence (EL) devices have been also prepared, and show an orange luminescence with the CIE color coordinates of (x, y) = (0.59, 0.41). The threshold voltage is about 30 V, which is much lower compared to other EL phosphor materials. CuAlS$_2$:Mn is expected as orange – red EL phosphor for low-temperature process and low-driving voltage.

Keyword: inorganic EL, CuAlS$_2$:Mn, phosphor pellet, low temperature process, low threshold voltage

1. INTRODUCTION
CuAlS$_2$ has a widest band gap energy in ternary I-III-VI$_2$ chalcopyrite semiconductors, and has been investigated a light-emitting-diode (LED), and dispersive-type electroluminescence (EL) materials [1]. We have developed CuAlS$_2$:Mn Si-codoped CuAlS$_2$:Mn phosphor powder having an efficient photoluminescence (PL), and have succeeded in a selective doping of Mn$^{2+}$ centers at Cu or Al site [2]. Recently, we reported the CuAlS$_2$:Mn thin films prepared by multi-source deposition method using evaporation sources of Al$_2$S$_3$:Mn and Cu [3]. However, the films had a poor crystallinity and their PL intensity was very weak. In this study, we attempt to prepare CuAlS$_2$:Mn thin films by electron-beam (EB) evaporation method using a single source pellet made of the CuAlS$_2$:Mn phosphor powder. The crystallographic and photoluminescent (PL) characteristics of the CuAlS$_2$:Mn thin films are investigated by comparing them with those of powder samples. The electroluminescent (EL) characteristics are also investigated.

2. EXPERIMENTAL PROCEDURE
CuAlS$_2$:Mn phosphor powder used for the EB source pellet was synthesized by a conventional solid phase reaction method. Cu$_2$S, Al$_2$S$_3$, MnS, elemental S, MgS, and Si metal were used as source materials. Mg and Si were added as charge compensators for Mn$^{2+}$ centers. The Mn concentration was 5 mol%. These sources in powder were mixed in a N$_2$-filled glove box, and the mixture was fired at 1100 °C for 1 h in Ar atmosphere. The phosphor powder was pressed, and the preparation of EB source pellet was completed.

CuAlS$_2$:Mn phosphor thin film was prepared by EB evaporation method using the phosphor pellet at various substrate temperatures of 300-550°C. Thickness of phosphor film is about 500 nm.

3. RESULTS and DISCUSSION
Figure 1 shows X-ray diffraction (XRD) patterns of (a) the as-deposited thin film prepared by EB evaporation method at 500°C using the phosphor pellet, and (b) the film by multi-source deposition method and post-deposition annealing at 650°C. The diffraction pattern from inorganic crystal structure database (ICSD) of CuAlS$_2$ (No. 42124) is

Fig. 1 XRD patterns of thin films prepared (a) EB deposition using phosphor pellet (as deposited) and (b) multi-source deposition (enamel at 650°C). ICSD pattern of CuAlS$_2$ is also shown.
also shown for reference. For the film by the multi-source deposition method, only a very weak peak due to the (112) plane of CuAlS₂ is observed. By contrast, the film prepared by EB method using phosphor pellet shows stronger diffraction peaks due to the (112) and (204) planes, even without post-deposition annealing. The weak peaks observed around 45° are due to the Al-Cu alloys. The full width at half maximum (FWHM) of the (112) peak is 0.22°.

Figure 2 shows PL and PL excitation (PLE) spectra of the thin film prepared by the EB evaporation method. In Fig. 2, PL spectra of CuAlS₂:Mn powder samples, in which Mn²⁺ centers are selectively-doped at Cu site (abbreviated as [Mn]ₐ) or Al site ([Mn]ₐ), are also shown for reference [2]. The film shows a orange luminescence peaking at 605 nm. The emission band is thought to be attributed to the 3d⁴-3d⁴ internal transition from 7T₁ to 6A₁ in Mn²⁺ centers. In comparison with the PL spectra of the powder samples, Mn²⁺ in the film is considered to mainly substitute for Cu. The PLE spectrum of the film lies below 400 nm with a steep edge at approximately 360 nm, which corresponds to the band gap energy of CuAlS₂. Therefore, the PLE spectrum mainly consists of the band-to-band host excitation band.

CuAlS₂:Mn thin film EL device was prepared. The EL device has a conventional double insulating structure. An ITO transparent electrode, a 280-nm-thick ATO insulating layer, a 150-nm-thick ZnS layer, a 500-nm-thick CuAlS₂:Mn phosphor layer, a 300-nm-thick Y₂O₃ insulating layer, and an Al electrode were successively stacked on a glass substrate. Figure 3 shows the applied voltage dependences of luminance (L) and transferred charge (∆Q). The measurement was carried out using a pulse voltage with a pulse width of 50 μs at 1 kHz. Both luminance and transferred charge rise at about 30 V, and gently increase with the applied voltage. It should be noted that the threshold voltage is much low compared to other EL phosphor materials. A possible reason of such a low threshold voltage is a charge emission from the CuAlS₂:Mn phosphor layer, since we found that the film had a conductive property with resistivity of 5×10⁻² Ω cm. However, this conductivity is also considered to give rise to an electrical instability, because the EL device tends to electrically broken above 100 V. The device shows an orange luminescence with the Commission Internationale de l’Eclairage (CIE) color coordinates of (x, y) = (0.59, 0.41).

4. SUMMARY
CuAlS₂:Mn EL devices were prepared by EB evaporation method using CuAlS₂:Mn phosphor pellets. The films are crystallized below 500°C even without post-deposition annealing. The device showed an orange luminescence. Its threshold voltage was about 30 V, which is much lower compared to other EL phosphor materials. CuAlS₂:Mn is expected as orange – red EL phosphor for low-temperature process and low-driving voltage.

REFERENCES

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