

Preparation of SrS:Cu Films for Blue EL Elements by Thermal Evaporation of Compound SrS

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SrS:Cu films were prepared to improve blue chromaticity in the EL elements. The compound SrS was used as an evaporant and was evaporated by using a carbon heater. It was found that the PL peaks shifted to lower wavelength as the Cu content increased. There was no variation of the PL peaks as the substrate temperature varied. The PL peaks were shifted to higher wavelength after annealing process. The EL spectra varied for the materials of insulating layers.

Key words: electroluminescent elements, SrS:Cu, blue emission, vacuum deposition

I. INTRODUCTION

EL Display device has many characteristics, for example, all solid state, self emitting, high speed response time, and wide view angle.¹ This is one of the candidate devices for flat display panels of large size. The biggest problem to overcome is the deficiency of blue emission strength.

The SrS films have been prepared by various methods to improve chromaticity as well as emission intensity.²⁻³ It is difficult to prepare SrS films with high stoichiometry because of its high melting point. High quality films are easily obtained by using compounds as evaporants especially in the II-VI compound materials. So we have been trying to prepare SrS films by using the compound SrS as a source material.⁵ The Cu₂S was used as an copper emission center.

The purpose of our work has been to build blue EL elements having pure chromaticity as well as strong blue emission. In this paper, we show some of the emission properties of SrS:Cu films.

II. EXPERIMENT

Figure 1(a) shows the deposition apparatus. The SrS powder was held in a pyrolytic boron nitride (p-BN) crucible and was resistively heated by a carbon heater. The carbon heater and the p-BN crucible were specially made by Toyo Tanso Co. and Shin-Etsu Chemical Co. Ltd., respectively. The electrodes and thermal shield plates for the carbon heater were made of molybdenum (Mo) sheet. It was possible for the crucible to reach a temperature higher than 1200 °C, as shown in Fig.1 (b).

The Cu₂S powder was involved in the SrS powder as a blue emission center. The dependences of Cu₂S content, substrate temperature (T_{sub}) and annealing temperature (T_{anneal}) on the film properties were examined in this study. The temperature of 300, 400 and 500 °C was used as T_{sub} and T_{anneal} .

The PL spectra were measured by using a deuterium lamp, which excites the electrons in the luminescent centers. It contains a filter, which cuts off the visible radiation.

The EL properties were also evaluated for various insulating materials. In this case, the emission layers were prepared by an electron-beam deposition method.

In order to obtain crystallographic information, X-ray Diffraction (XRD) measurements were carried out on a RIGAKU Rotaflex 12kW system with a CN2173D6 goniometer. The film thickness was measured optically by a Hitachi 340 spectrophotometer and mechanically by a DEKTAK-II surface profiler.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the variation of PL data with T_{sub} . The Cu₂S concentration was fixed at 0.5 mol %. There is a peak near 450 nm in the case of 500 and 300 °C. On the other hand, there is a peak near 540 nm in the case of 400 °C. It seems there is no dependence of T_{sub} on the PL spectrum.

Figure 2(b) shows the variation of PL data with Cu₂S concentration. The T_{sub} was fixed at 500 °C. There is a peak near 450 nm when the concentration is between 0.3 and 1.0 mol %. They have blue-green emission colors. On the other hand, there is a peak near 530 nm in the case of 0.1 mol %, which has an orange emission color. It is found that higher dose of Cu₂S results in shorter emission wavelength. The reason could be explained as follows: There are two peaks in the emission spectrum of SrS:Cu.^{7,8} They are denoted as H and L bands, respectively. The luminescence of the H band (460 nm) is originating from the paired or aggregated copper centers. The luminescence of the L band (520 nm) is originating from the off-center Cu⁺ ions. Yamashita^{9,10} examined PL spectrum of SrS:Cu powder samples. He deduced that these H and L bands come from Cu⁺ monomer and dimer centers, respectively. The exact explanation has not been done yet.

Figure 2(c) shows the variation of PL spectrum of SrS:Cu films after annealing process. The film suffered successive 30 min. annealing after deposition process. The concentration of Cu₂S and anneal

temperature were 0.5 mol % and 500 °C, respectively. It is found that the L band peak evolved after annealing process. This phenomenon could be explained that S atoms are easily re-evaporated during the annealing process and then Cu⁺ ions land in these vacancy sites.

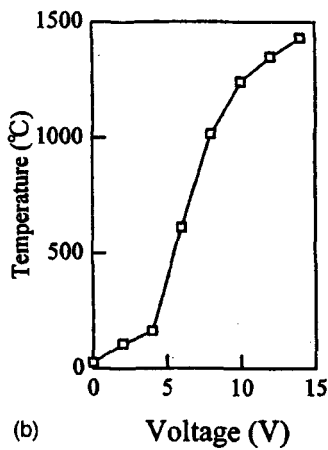
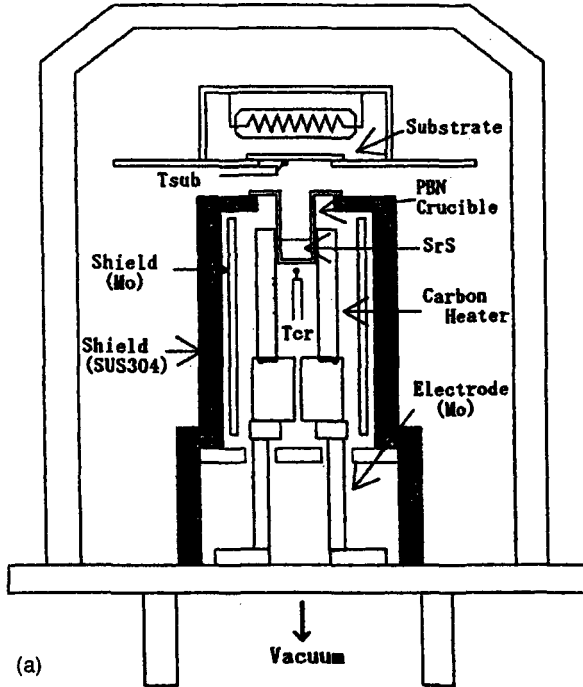
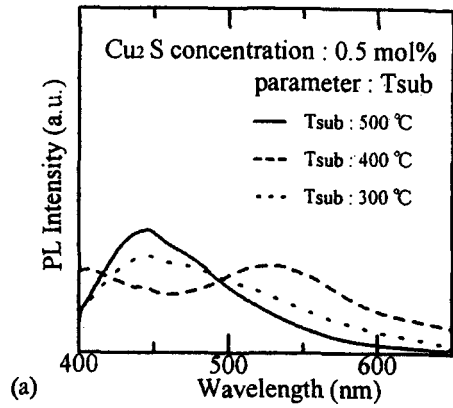
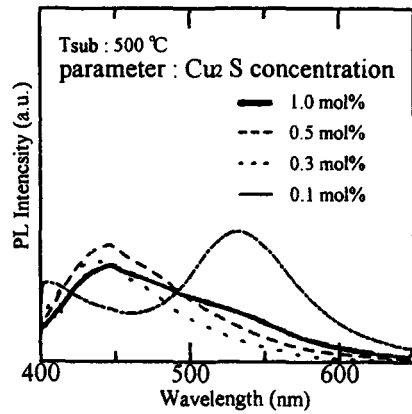


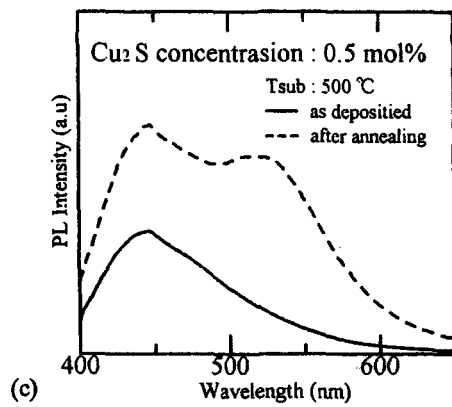
Fig. 1(a) Deposition apparatus. (b) Maximum attainable temperature of the crucible in the deposition apparatus, for various applied voltages.



(a)



(b)



(c)

Fig. 2 (a) PL spectra of SrS:Cu films with substrate temperature (T_{sub}). (b) PL spectra of SrS:Cu films with Cu_2S concentration. (c) PL spectra of SrS:Cu films before and after the annealing process.

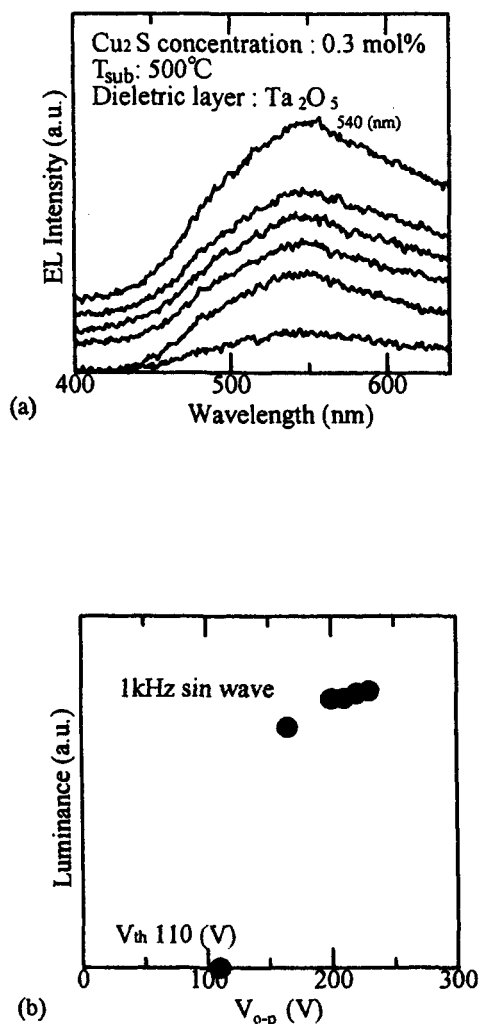


Fig. 3 (a) EL spectra for SrS:Cu films prepared with 0.3 mol % Cu_2S concentration at T_{sub} of 500 °C. (b) EL data for SrS:Cu films prepared with 0.3 mol % Cu_2S concentration at T_{sub} of 500 °C and. The V_{0-p} means the peak voltage measured from the zero voltage line.

Figure 3(a) shows EL spectra of SrS:Cu films prepared with 0.5 mol % Cu_2S concentration at T_{sub} of 500 °C. The EL phosphor was sandwiched between double insulating Ta_2O_5 layers.^{1,5} The SrS:Cu and Ta_2O_5 layers were 1 and 0.5 μm thick, respectively. The first layer was deposited on an ITO coated alumino-silicate glass substrate (Hoya NA-40). A 1kHz ac voltage was applied to the EL device. No annealing process was applied in this case. These data were obtained by varying the applied voltage. These EL elements have white-blue emission color, which was recognized by naked eye. They have EL peaks at the wavelength of 540 nm.

Figure 3(b) shows a luminescence variation with applied voltage. The threshold voltage was 110 V. In the case of SiO_2 insulating layer, the EL peak was obtained at 480 nm. The threshold voltage was 180 V. This EL element has white-blue emission color. In the case of Y_2O_3 insulating layer, the EL peak was obtained at 520 nm. The threshold voltage was 150 V. This EL element has white-blue emission color. This EL showed point emission. It is due to the roughness of the Y_2O_3 layers.

The EL emission characteristics depend on the properties of insulating layers as well as that of phosphor material. The performance of insulating layer depends on the thickness as well as the material of insulating layer. So, it is difficult to compare the properties of various insulating layers. The optimization of insulating layers will be the subject of a future study. The sulfur compensation is also one of the problems to be overcome. The improvement of EL characteristics will be conducted through investigating the correlation between structure of EL elements and EL emission mechanism.^{9,10}

IV. CONCLUSION

The variation of PL spectra of SrS:Cu in the T_{sub} and Cu_2S concentration was investigated. It was found that higher dose of Cu_2S moves the PL emission peak to shorter wavelength. It seems to be due to the deficiency of sulfur atoms in the SrS:Cu films, especially after annealing process.

In the case of EL elements, there are many problems, for example, low emission and high threshold voltages. We are hopeful of success because the white-blue color was recognized by naked eye.

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