

Improvement of crystal properties of SrS:Cu films for blue EL elements using rapid thermal annealing

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Blue EL (electroluminescence) elements with double insulating layer structure have been prepared with an electron beam deposition. A blue emission is evolved from the SrS:Cu layer. A rapid thermal annealing process was applied to the EL elements to improve the crystal and emission properties. The XRD (X-ray diffraction) and PL (photoluminescence) data were greatly improved through this process. It was found that an optimum annealing condition was 2 min annealing time under the temperature at 450°C.

Key words: Blue EL (electroluminescence) elements, SrS:Cu, Electron beam deposition, Rapid thermal annealing

1. Introduction

The inorganic electroluminescence (EL) display devices have many characteristics, for example, high durability, wide view angle, high speed response time, and self emitting.¹ They are one of the candidate devices for flat display panels which could be used in the wide temperature range. The biggest problem to overcome is the deficiency of blue emission intensity.

The SrS films have been prepared by various methods to improve blue chromaticity as well as emission intensity.²⁻¹³ It is difficult to evaporate compound SrS by conventional resistive heating method because of its high melting point. So these films were prepared by an electron beam deposition. The Cu₂S was used as a copper emission center which evolves blue emission color. Recently much attention has been focused on a new material for blue emission.¹⁶

The purpose of this work is to investigate the relationship between a rapid thermal annealing condition and film properties.

Thermal annealing was proceeded in our early study.¹¹ The deposited films were succeedingly annealed without breaking vacuum. It takes long time to increase and decrease the annealing temperature. It is easy for sulfur to reevaporate from SrS matrix during high temperature annealing process. The EL elements have been damaged after annealing of 700°C. It could be overcome with compensating sulfur or applying a rapid thermal annealing process proposed in this paper.

In this study, a rapid thermal annealing process was applied to the EL elements. It was intended to improve the crystal properties of SrS:Cu films.

2. Experiment

Figure 1 shows a deposition apparatus. The EL elements could be prepared without breaking vacuum.

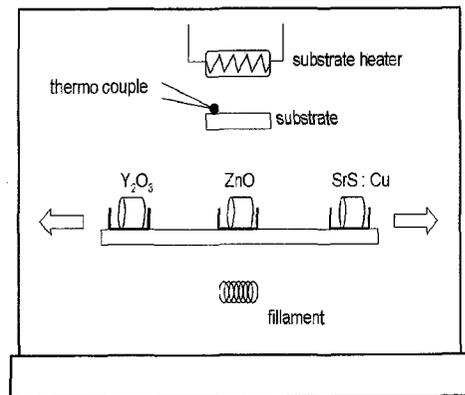


Fig. 1 Deposition apparatus.

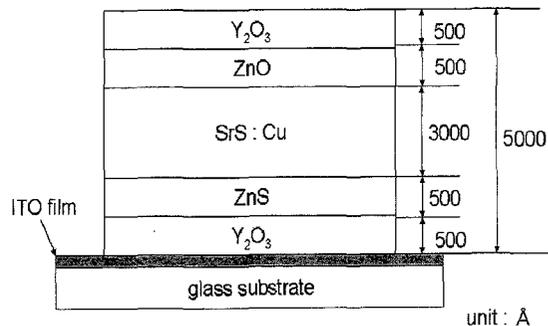


Fig. 2 Structure of double insulating layer type EL element.

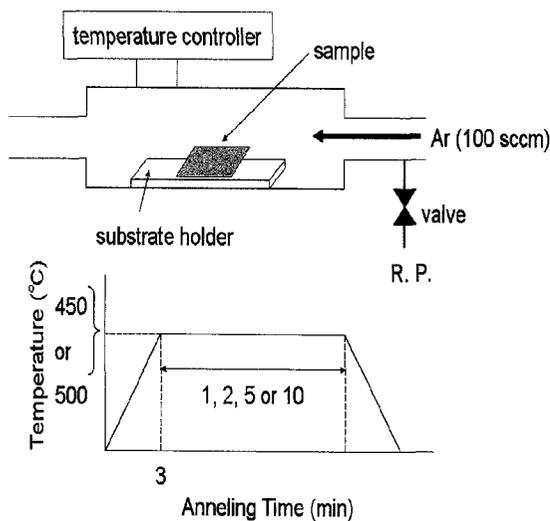


Fig. 3 Rapid thermal annealing apparatus

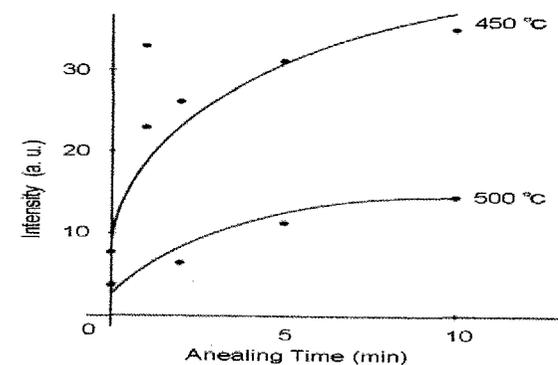
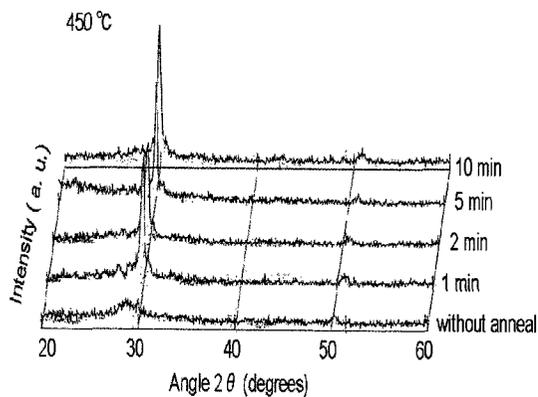


Fig. 4(a) and (b) Annealing time dependence of XRD peak intensity at the annealing temperature of 450 and 500°C.

The EL elements have double insulating layer structure as shown in Fig. 2. The blue light is emitted from the SrS:Cu emitting layer. The Cu_2S was used as a blue emission center. The SrS is a deliquescence substance and is easy to make an alloy with Y_2O_3 insulating layer. So the ZnS layers were inserted between the SrS:Cu emission layer and the Y_2O_3 insulating layers. They could inhibit the Y_2O_3 diffusion into the SrS:Cu layer. They also inhibit immersion of water vapor into the SrS:Cu layer. The film thickness of a SrS:Cu, ZnS and Y_2O_3 layers were 3000, 500 and 500 Å, respectively.

A rapid thermal annealing was proceeded in the Ar atmosphere in order to prevent reevaporation of sulfur component in the SrS matrix. The Ar flow rate was fixed at 100 cc/min during annealing process. The annealing pattern was programmed and automatically controlled as shown in Fig. 3. The annealing process was proceeded on the EL elements.

The effects of doping ratio of Cu_2S , substrate temperature (T_{sub}), annealing time and annealing temperature on the crystal properties were evaluated by photoluminescence (PL) and X-ray diffraction (XRD) measurement.

3. Results and discussion

The annealing time dependence of XRD peak intensity at the annealing temperature of 450 and 500°C is shown in Fig. 4(a). The peak intensity was increased as increasing the annealing time. A similar results were obtained at the annealing temperature of 500°C. The XRD intensity has a peak at the annealing time of 1 min as shown in Fig. 4(b). It is seemed to be due to the undulation of annealing temperature before getting at the settled value. The annealing temperature was increased over the settled temperature in a short time because of a transient phenomenon. This is so called overshoot.

Figures 5(a) and (b) show the variation of PL characteristics between without anneal and with anneal at 450°C at 2 min, respectively.

The notation of high energy (H) and low energy (L) bands means the 460 and 520 nm emissions which suggest the PL emission from Cu emission center.^{5,6} There are peaks which are sifted from the H and L bands as shown in Fig. 5 (a) and (b). They are explained as follows. The green shift of the PL spectrum could be caused by the impurity incorporation and defects⁷ during the film growth, increasing paired-Cu⁺ ions⁸ and increasing Cu_2S concentration.¹⁵ The increase of H and L band-peaks shows the effectiveness of the annealing process.

Figures 6(a) and (b) show the annealing time dependence of PL emission intensity of blue and green component, respectively. The annealing temperature was 450 and 500°C. Figure 6 (a) shows that the PL intensity of blue component has a maximum at 2 min annealing time and it does not depend on the annealing temperature. The emission intensity was about the same even increasing the annealing time from 5 to 10 min. Figure 6 (b) shows that the PL intensity of green component has a maximum at 2 min annealing time. The emission intensity was gradually increased as increasing the annealing time from 5 to 10 min. Similar data were

obtained as varying the annealing temperature. The emission intensity of blue and green components at annealing temperature of 500°C was stronger than that at 450°C.

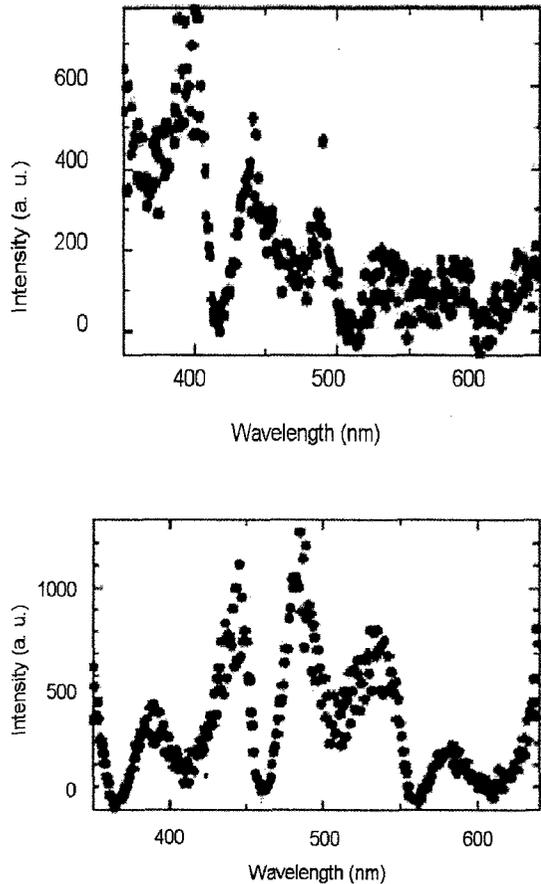


Fig. 5(a) and (b) Variation of PL characteristics between without anneal and with anneal at 450°C at 2 min, respectively.

It is seemed that the emission property depends on how the Cu^+ emission centers are dispersed in the SrS matrix.^{6,14} The L band may be attributed to the emission from an isolated Cu^+ ion replacing the host Sr^{2+} ion but at an off-center site, and it undergoes a red shift caused by aggregated Cu centers.⁶ The H band is evolved to be due to the Cu^+ ion at different site symmetry. However the exact location of this site remains an open question.^{6,9} Some scientists think that aggregated Cu^+ ions decrease the H band peak.^{6,11,15} If the dispersion of Cu^+ ions in the SrS matrix could be manipulated, the emission property could be controlled.

No EL data could be acquired because of low emission intensity. Blue light could be recognized by naked eyes. The reason why we could not get the EL data is as follows. The dielectric breakdown was occurred at about 20 V in applied voltage. The insulating layer thickness is too thin (500 Å) to apply more than 20 V. This problem could be overcome with increasing the insulating layer thickness.

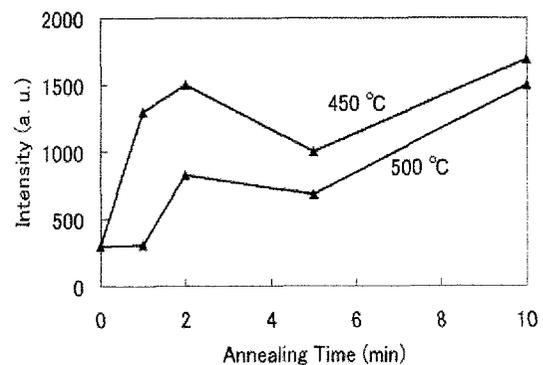
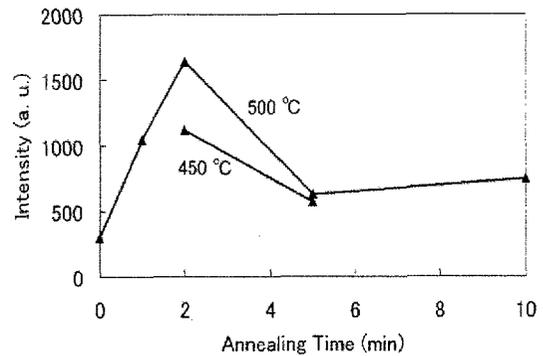


Fig. 6(a) and (b) Annealing time dependence of PL emission intensity of blue (a) and green (b) component (constituent). The annealing temperature was 450 and 500°C.

4. Conclusion

The SrS:Cu EL elements were prepared under the condition of substrate temperature of 350°C and Cu_2S concentration of 0.5 mol%.

The crystal properties of emission layer were increased with a rapid thermal annealing process. The variation of crystal properties were evaluated with XRD and PL characteristics.

Superior crystal properties were obtained under the condition of annealing temperature of 450°C and annealing time of 2 min.

The PL peaks of H (460 nm) and L (520 nm) band were recognized. It was suggested that these peaks were evolved from the Cu emission center.

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