Evaluation of crystallinity of SrS:Cu films for blue EL elements

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SrS:Cu films were prepared by an electron beam deposition method to improve the emission properties of blue EL elements. SrS:Cu pellets were used as an evaporant of SrS:Cu films. The correlation between pellet-sintering condition and crystallinity of SrS:Cu films was investigated. As a result, it was found that the 2-hour pellet-sintering under 600°C was best to prepare superior SrS:Cu films. It was also found that the crystallinity of SrS:Cu films were greatly improved after 2-min rapid thermal annealing (RTA) process under 450°C.

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

1. Introduction

Flat-panel displays with thin, light-weight, and high resolution have been desired in the area of multi-media . Up to now, displays of cathode ray tube (CRT) and liquid crystal display (LCD) have been widely spread all over the world. Recently, many scientists have been actively devoted to the research of flat panel displays, for example, plasma display panel (PDP) and electroluminescence display (ELD).

The inorganic electroluminescence (EL) display devices have many good points, 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 a conventional resistive heating method because of its high melting point. So, an electron beam (EB) deposition method was introduced to prepare these films. The Cu_2S was used as a copper emission center which evolves blue emission. Recently much attention has been focused on a new material $(BaAl_2S_4:Eu)$ for blue emission.[14]

Thermal annealing was proceeded in our early study.[13] 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 thr high temperature annealing process. The EL elements have been damaged after a long-time annealing under 600°C. It could be overcome with compensating sulfur or applying a rapid thermal annealing (RTA) process proposed in this paper.

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

The purpose of this work is to investigate an optimum sintering condition of SrS:Cu pellets. The effects of sintering and annealing conditions on film properties were also investigated.

2. Experiment

Figure 1 shows an annealing apparatus used for sintering of SrS:Cu pellets. These pellets involve 0.5 mol% Cu_2S as a blue-emission center. The powders of SrS and Cu_2S were mixed and pressed to be pellets. They were embedded in active carbon in a quartz boat. They were sintered from 1 to 3 hours under the temperature from 600 to 900°C. The sintering temperature was measured by using a K thermocouple.
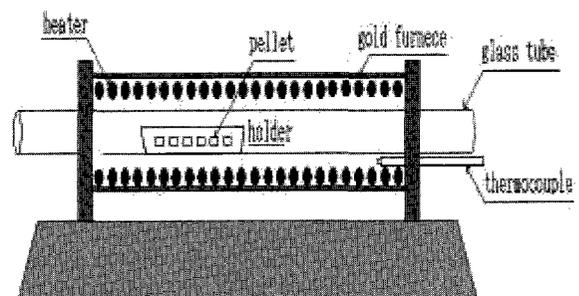
Fig. 1 Annealing apparatus used for sintering of SrS:Cu pellets

Figure 2 shows an electron beam deposition apparatus. This apparatus has three deposition sources (hearthes). The double insulating layer EL elements could be fabricated without breaking vacuum.

SrS:Cu films were deposited on slide-glass substrates under accelerating voltage of 4kV, filament current of 10 mA for 10 min and followed by 20 mA for 25 min. The substrate temperature and vacuum pressure during deposition were 300°C and 1×10^{-5}Torr, respectively.

Deposited films were introduced to a RTA apparatus. Figures 3(a) and 3(b) show a RTA apparatus and an annealing pattern, respectively. The annealing temperature and time were 450 °C and 2 min, respectively. The annealing of films were proceeded under Ar flow rate of 100 cc/min.
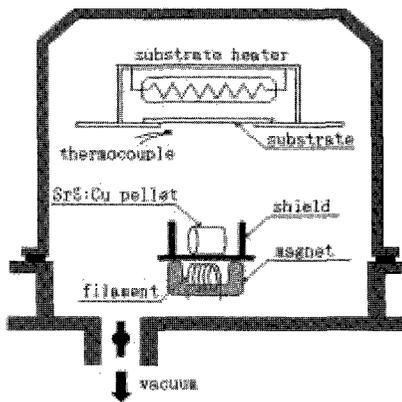
Fig. 2 Electron beam deposition apparatus.
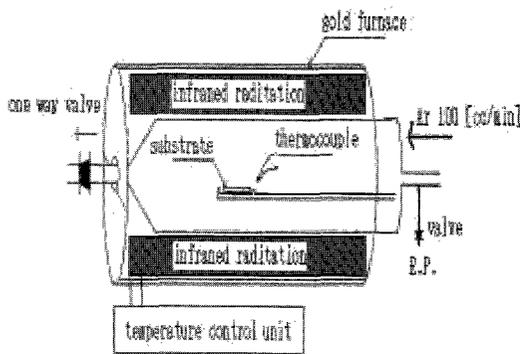
Fig. 3(a) Rapid thermal annealing (RTA) apparatus
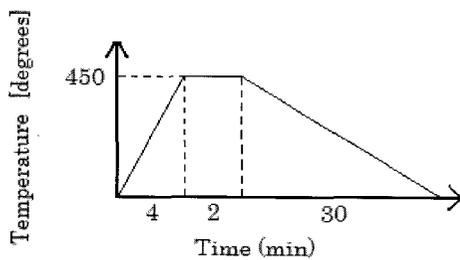
Fig. 3(b) An annealing pattern

The effect of annealing temperature on the crystallinity of films was evaluated by using photoluminessence (PL) and X-ray diffraction (XRD) measurements. Only the result of XRD data was introduced in this paper.

3. Results and discussion

The sintering time dependence of XRD peak intensity of sintered SrS:Cu pellets is shown in Fig. 4(a), 4(b) and 4(c). The sintering temperature and time were 600 ~800℃ and 1~3 hours, respectively.
The sintering time dependence of the (200) XRD intensity is shown in Fig. 4(d).
The SrS:Cu films were deposited by using these sintered pellets.
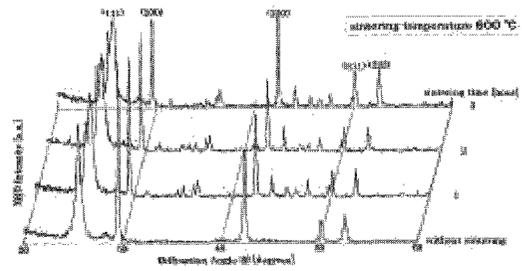
Fig. 4(a) Pellet-sintering time dependence of XRD peak intensity of SrS:Cu pellets under the sintering temperature of 600℃. The indexed and other peaks denote SrS and Cu_2S crystallites, respectively.
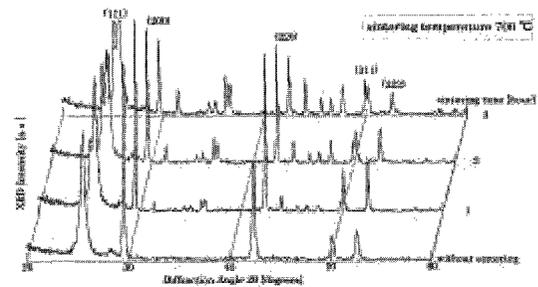
Fig. 4(b) Pellet-sintering time dependence of XRD peak intensity of SrS:Cu pellets under the sintering temperature of 700℃.
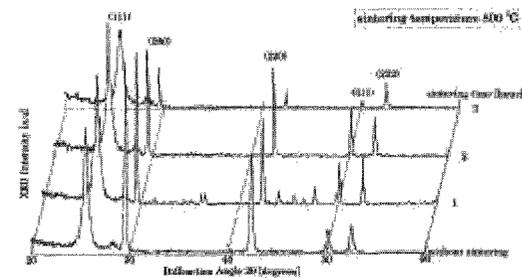
Fig. 4(c) Pellet-sintering time dependence of XRD peak intensity of SrS:Cu pellets under the sintering temperature of 800℃.
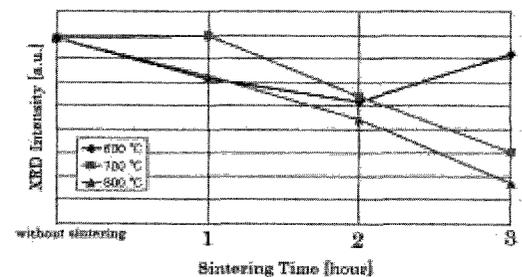
Fig. 4(d) Pellet-sintering time dependence of the (200) XRD peak intensity of SrS:Cu pellets
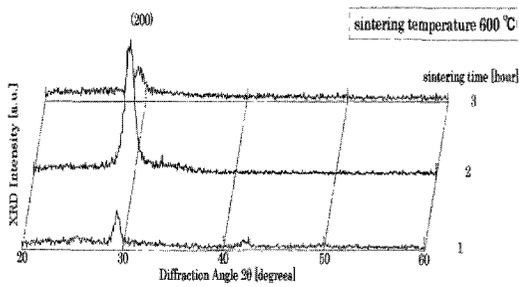
Fig. 5(a) Pellet-sintering time dependence of XRD peak intensity of as–deposited SrS:Cu films under the sintering temperature of 600°C.
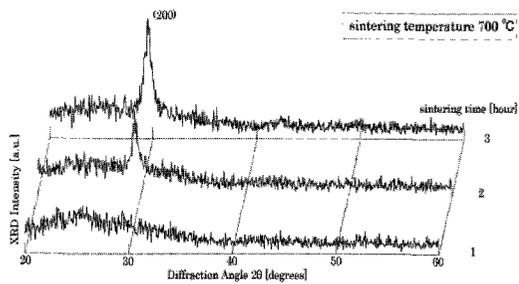
Fig. 5(b) Pellet-sintering time dependence of XRD peak intensity of as–deposited SrS:Cu films under the sintering temperature of 700°C.
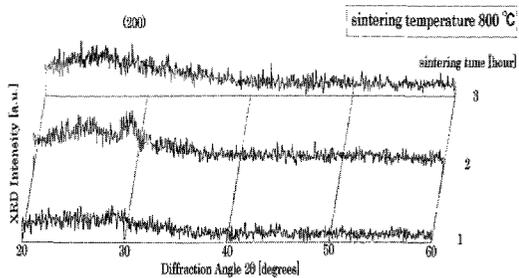
Fig. 5(c) Pellet-sintering time dependence of XRD peak intensity of as–deposited SrS:Cu films under the sintering temperature of 800°C.
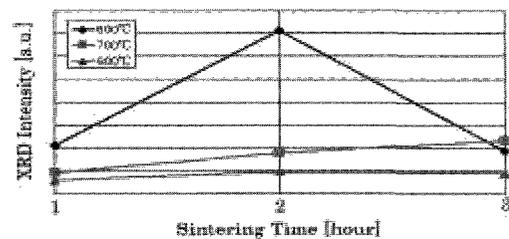
Fig. 5(d) Pellet-sintering time dependence of the (200) XRD intensity of as–deposited SrS:Cu films under the sintering temperature from 600 to 800°C.

The pellet-sintering time dependence of XRD peak intensity of as-deposited SrS:Cu films is shown in Fig. 5(a), 5(b) and 5(c). The sintering time dependence of the (200) XRD intensity is also shown in Fig. 5(d). A RTA process was applied to the films as shown in Figs. 5(a), 5(b) and 5(c). The annealing temperature and time were 450°C and 2 min, respectively. The RTA process was proceeded under the Ar flow rate of 100cc/min. The XRD data are shown as shown in Figs. 6(a), 6(b) and 6(c). The pellet-sintering time dependence of the (200) XRD peak intensity is shown in Fig. 6(d).
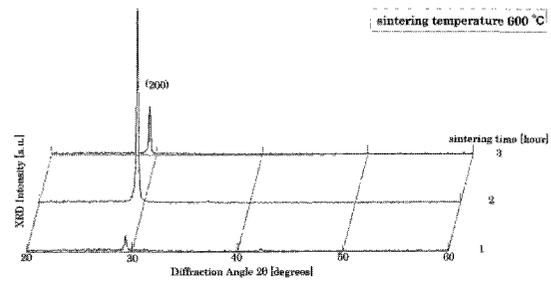
Fig. 6(a) Pellet-sintering time dependence of XRD peak intensity of annealed (RTA) SrS:Cu films under the sintering temperature of 600 °C . The annealing temperature and time were 450 °C and 2 min, respectively.
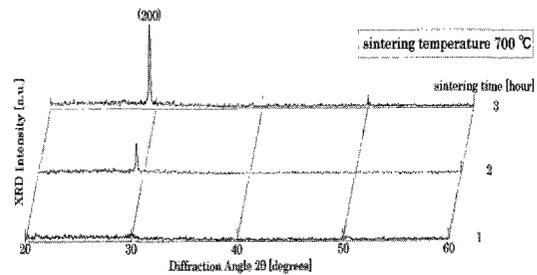
Fig. 6(b) Pellet-sintering time dependence of XRD peak intensity of annealed (RTA) SrS:Cu films under the sintering temperature of 700 °C . The annealing temperature and time were 450 °C and 2 min, respectively.
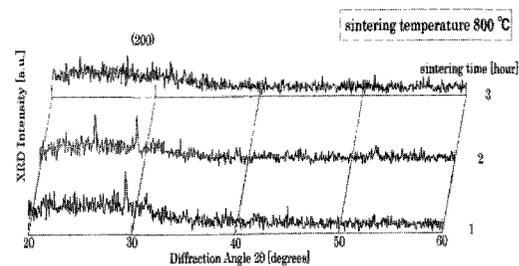
Fig. 6(c) Pellet-sintering time dependence of XRD peak intensity of annealed (RTA) SrS:Cu films under the sintering temperature of 800 °C . The annealing temperature and time were 450 °C and 2 min, respectively.
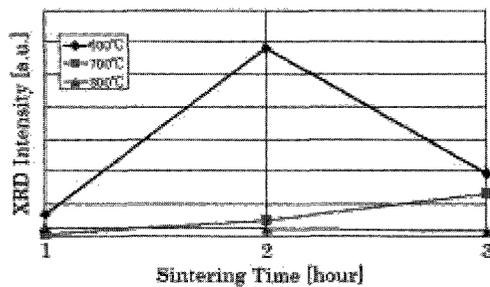
Fig. 6(d) Pellet-sintering time dependence of the (200) XRD intensity of annealed (RTA) SrS:Cu films under the sintering temperature from 600 to 800℃. The annealing temperature and time were 450 ℃ and 2 min, respectively.

It was found that color of pellets were changed from pink to black after sintering process. There was a tendency that the concentration of black color was increased as increasing the sintering temperature.

There are many XRD peaks in the pellets as shown in Fig. 4(a), 4(b) and 4(c). The indexed peaks of (111), (200), (220), (311) and (222) were attributed to SrS crystallites. Other peaks not indexed were also attributed to Cu_2S crystallites. This means that both Cu_2S and SrS crystallites coexist in these pellets.

During the pellet-sintering process, Cu_2S crystallites are decomposed and Cu^+ ions are doped in SrS crystallites. So, the chemical formula could be written as SrS:Cu in the case. Weak XRD peaks except for these peaks were disappeared for the pellets having sintering temperature of 800℃ for 2 and 3 hour-sintering time as shown in Fig. 4(c). This means that SrS:Cu crystallites were deteriorated after 2 and 3 hour-sintering time under 800 ℃. It was found that the intensity of (200) XRD peak had a maximum value under the sintering condition of 700℃ and 1 hour. It was also found that the intensity of (200) XRD peaks was decreased after sintering processes under more than 2 hours at 700℃ or at 800℃. At the sintering temperature of 600℃, there was a tendency that the intensity of (200) XRD peak was increased as increasing sintering time.

In the case of SrS:Cu films prepared by sintered pellets, only the (200) XRD peak related to SrS crystallites was observed. There were no peaks related to Cu_2S crystallites.

In the case of pellets sintered under 600℃, 2 hours, the deposited films have maximum (200) XRD peak. But, in the case of pellets sintered under 800℃, there were little XRD peaks. These films were not crystallized. It means that they are varied to amorphous structure during the sintering process.

After RTA process, the XRD peaks were increased providing that the films had peaks before the annealing process. The full width at half maximum (FWHM) of the XRD peaks was also decreased after the RTA process. So the crystallinity was improved during this annealing process. In the case of pellets sintered under 600℃, 2hours, the annealed films have maximum (200) XRD peak.

It was found that the optimum pellet-sintering temperature and time were 600 ℃ and 2 hours, respectively.

4. Conclusion

The SrS:Cu films were prepared by using an electron beam deposition method. The relation between sintering condition of pellets for evaporant and the crystallinity of deposited films were investigated. As a result, it was found that the optimum condition of pellet-sintering temperature and time were 600 ℃ and 2 hours, respectively.

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