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Rapid Thermal Annealing of SrS:Cu Films for Blue EL Elements

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SrS:Cu films were prepared for the blue EL elements. Compound SrS was evaporated by using an electron beam deposition. A rapid thermal annealing was applied to the deposited films. An optimum annealing condition was investigated as varying the parameter of temperature and time. The crystal properties were greatly improved at the annealing condition of 800℃ and 2 minutes. The PL properties were also improved after this annealing process.

Key words: Electroluminescent elements, SrS:Cu, Blue emission, Vacuum deposition

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 strength.

The SrS films have been prepared by various methods to improve blue chromaticity as well as emission intensity.[2-10] It is difficult to evaporate compound SrS by resistive heating method because of its high melting point. So these films were prepared by an electron beam deposition. The Cu_2S was used as a copper emission center which evolves blue emission color.

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 studiy.[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. EL elements have been damaged after annealing of 700℃. It could be overcome with compensating sulfur or applying a rapid thermal annealing process.

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

2. Experiment

Cu_2S was used as a blue emission enter. The effects of doping ratio of Cu_2S, substrate temperature (Tsub), annealing time and annealing temperature on the crystal properties were evaluated by photoluminessence (PL) and X-ray diffraction (XRD) measurement.

Rapid thermal annealing was proceeded in the Ar atmosphere in order to prevent reevaporation of sulfur component in SrS matrix. At first, the Ar flow rate was fixed at 100 cc/min for 10 minutes. The temperature of quartz tube (Gold harness) is raised with a sample sitting out of the quartz tube until the annealing temperature is attained. After that, a sample is moved into the quartz tube and an annealing process is started. Annealing was executed in the state of EL elements. They have double insulating layer sturacture.

Figure 1 shows a deposition apparatus. The EL elements were prepared, and PL luminescence spectrum was measured. Y_2O_3 was used for an insulating layer. The film thickness of a SrS:Cu and an insulating layer was 0.8 and 0.4 μ m, respectively.

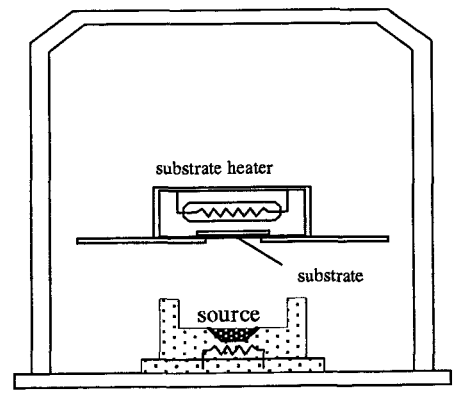

Fig. 1 deposition apparatus.

3. Results and discussion

3.1. Optimization of deposition condition

3.1.1 Optimization of substrate temperature in SrS thin film

An optimum temperature of Tsub was examined to

prepare SrS films. The concentration of luminescence center was fixed at 0.5mol%, and glass substrates were used. Fig. 2(a) shows that the XRD peak of (200) were appeared. It means that they have good crystal properties. In this result, the best crystal properties were obtained at Tsub of 400℃.

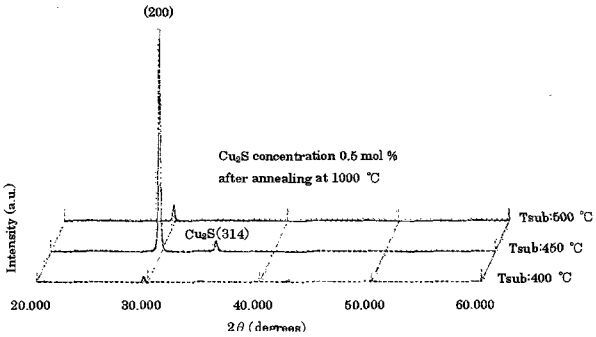

Fig. 2(a) XRD peak of (200)

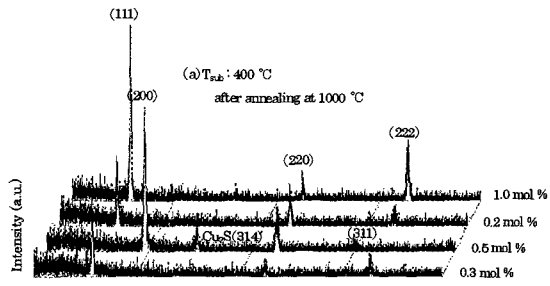

Figure 2(b) XRD spectrum of SrS:Cu films.

3.1.2. Optimization of concentration of emitting center

Figure 2(b) shows the XRD spectrum of SrS:Cu films. The parameter is the concentration of emitting center. The Tsub and annealing temperatures are 400 and 1000℃, respectively.

Good crystal properties were obtained at the concentration of 0.5mol%. A strong peak of (111) was observed. But, no (200) peak was observed.

Crystal properties were increased as increasing the concentration of Cu_2S from 0.3 to 1.0 mol%. It is seemed that sulfur atoms in Cu_2S could compersate sulfur vacancies in the SrS matrix.

3.2 Effect of rapid thermal annealing on crystal properties

XRD studies were proceeded to investigate the crystal properties of Y_2O_3/SrS:Cu/ Y_2O_3 films. The emission coefficient and PL spectrum depend on crystal properties and concentraition of emission centers. They also depend on the distribution of emission centers. The emission properties were evaluated by the PL spectra of Y_2O_3/SrS:Cu/ Y_2O_3 films.

The annealing temperature was varied from 400 to 800℃.

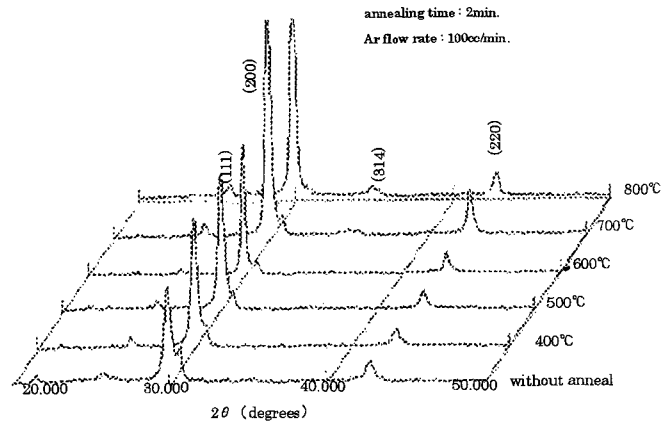

Fig. 3 (a) XRD peaks in the case of annealing time of 2 minutes.

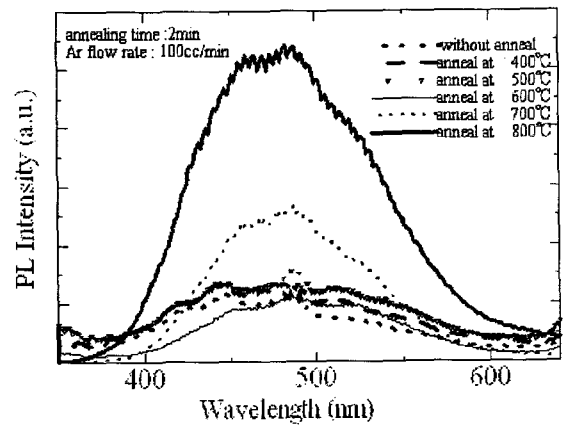

Fig. 3 (b) PL properties in the case of annealing time of 2 minutes.

3.2.1 2 minutes annealing time

Figure 3(a) shows the results of annealing time of 2 minutes. The (200) XRD peaks were increased as increasing the annealing temperature. The SrS:Cu films were strongly oriented to (200) plane. It was seemed that crystal properties of SrS:Cu films were improved after this annealing process.

Figure 3(b) shows the PL properties. The PL peaks were drastically increased under the temperature of 700 and 800℃. An as grown film gained 3 times of peak strength after 800 ℃ annealing. The peak wavelength was not varied after annealing. It means that Cu emission centers move into SrS matrix in a same manner with varying the annealing temperatures.

3.2.2 5 minutes annealing time

The annealing temperature was varied from 400 to 800℃. The annealing time was fixed at 5 minutes.

Figure 4(a) shows that the maximum XRD peak was obtained under the annealing temperature of 700℃.

Figure 4(b) shows the result of PL measurements. It was shown that the maximum PL peak was obtained under the annealing temperature of 700℃. The PL peak was decreased as increasing the annealing temperature to 800℃. It means that 5 minutes annealing time is too long in the case of 800℃ annealing condition. Sulfur atoms in the SrS matrix are easy to reevaporate at such a long annealing time. It is seemed that the SrS:Cu emission layer deteriorates through this process.

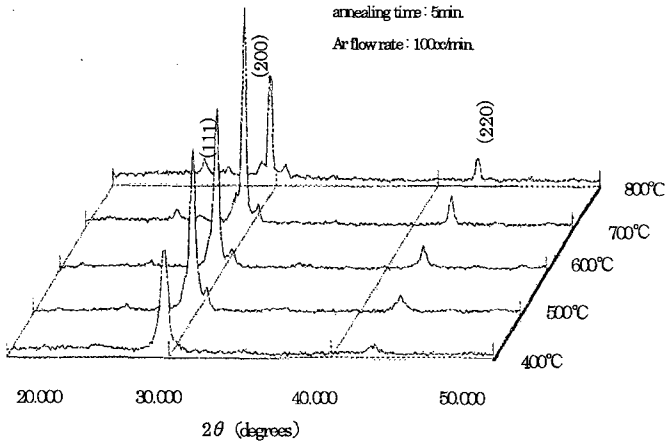

Fig. 4 (a) XRD peaks in the case of annealing time of 5 minutes.

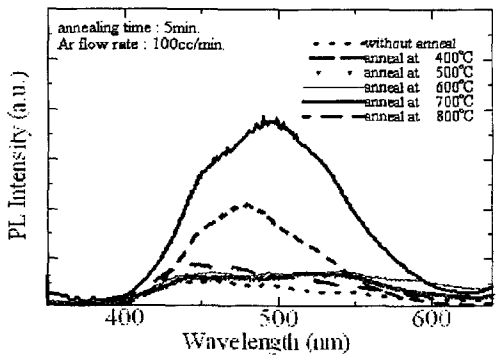

Fig. 4 (b) PL properties in the case of annealing time of 5 minutes..

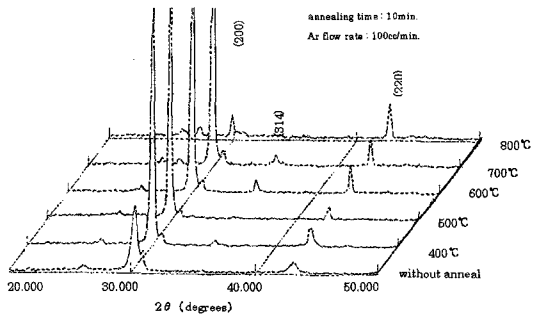

Fig. 5 (a) XRD peaks in the case of annealing time of

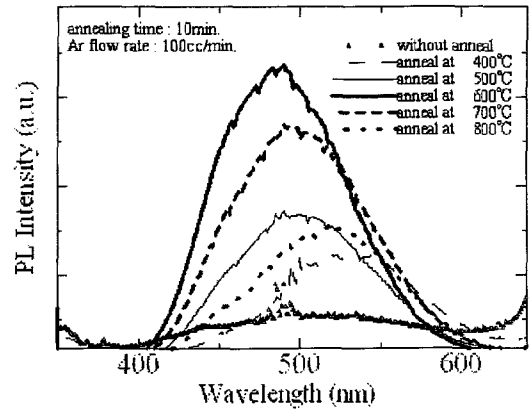

Fig. 5 (b) PL properties in the case of annealing time of 10 minutes..

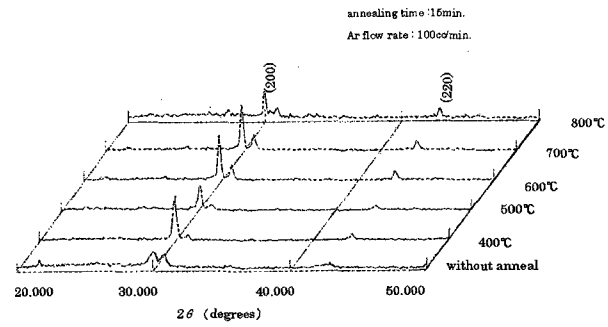

Fig. 6 (a) XRD peaks in the case of annealing time of 15 minutes.

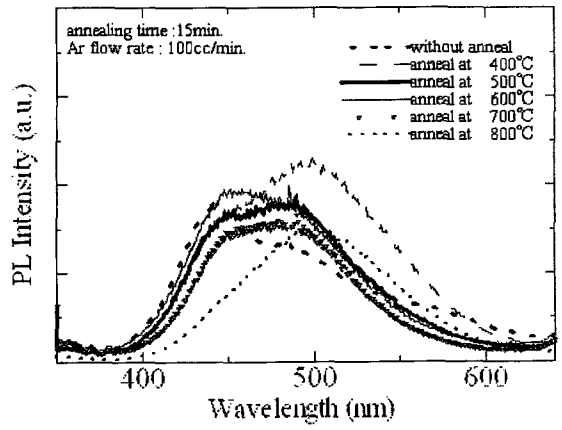

Fig. 6 (b) PL properties in the case of annealing time of 15 minutes..

3.2.3 10 minutes annealing time

The annealing temperature was varied from 400 to 800℃. The annealing time was fixed at 10 minutes.

Figure 5(a) shows the XRD results. It was found that the annealing at 700℃ gave a maximum XRD peak.

Figure 5(b) shows the PL results. A sample annealed at 600℃ had a maximum PL intensity. The glass substrates were softened after 10 minutes annealing time at 800℃.

3.2.4 15 minutes annealing time

The annealing temperature was varied from 400

to 800℃. The annealing time was fixed at 10 minutes.

Figure 6(a) shows the XRD results. The crystal properties were slightly improved after annealing process. There was no difference between the samples with varying the annealing temperature. The glass substrates were softened after 15 minutes annealing time at 800℃. It is not appropriate to anneal such a long time at 800℃.

Figure 6(b) shows the PL results. There was no difference between the samples with varying the annealing temperature. It was found that the PL peaks slightly shift to shorter wavelength as increasing the annealing temperature. It suggests that the Cu emission centers move into SrS matrix in a different way as varying the annealing temperature.

3.3 Dependence of PL and XRD spectrum on annealing time

Figure 7(a)-(b) shows the dependence of PL peak intensities of 460 and 520 nm on annealing time.[5,6] Figure 7(c) also shows the dependence of (200) XRD peaks on annealing time.[5,6]

It was found that the optimum annealing temperature and annealing time were 800℃ and 2 minutes, respectively.

The PL peaks of 460 and 520 nm were obtained in a shorter time as increasing the annealing temperature.

The long annealing time, for example 10 minutes, at 800℃ softened glass substrate during the annealing process. The crystal properties could be deteriorated under this condition. It is due to reevaporation of sulfur atoms from SrS matrix.

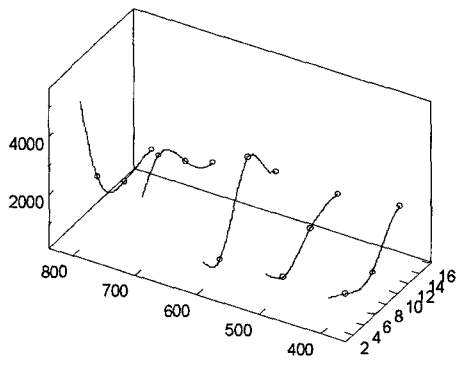

Fig. 7 (a) PL peak intensities of 460 nm on annealing time.

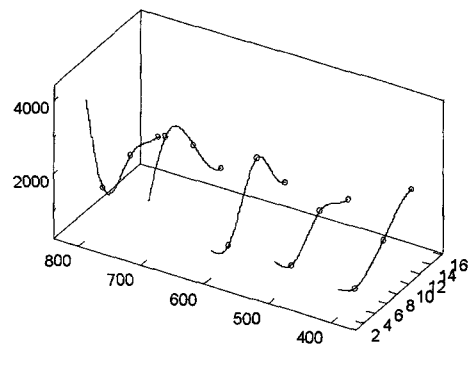

Fig. 7 (b) PL peak intensities of 520 nm on annealing time.

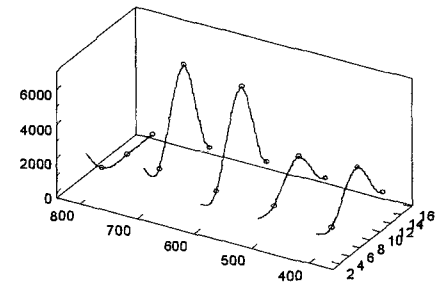

Fig. 7 (c) XRD peak intensities on annealing time.

4. Conclusion

After the optimization of evaporation conditions, high quarity SrS:Cu films could be prepared at the Tsub of 400℃ and the Cu_2S concentration of emission centers of 0.5 mol%.

It was found that crystal properties of SrS:Cu were drastically improved after the annealing process. The optimum annealing conditions of temperature and time were 800℃ and 2 minutes, respectively.

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