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A study on the characteristics of SrS:Cu TFEL devices prepared by hot wall deposition

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Abstract : SrS:Cu, Cl thin films have been grown by the hot wall technique with S furnace placed on the outside of the growth chamber in order to investigate the crystallographic and optical characteristics. The films have a good crystallinity independent of CuCl wall temperature and PL characteristics showed a peak assigned by the transition form $3d^9 4s^1$ (^3Eg) to $3d^{10}$ ($^1A_{1g}$) of Cu^+ center. It has also been found that, from the PLE spectra, Cu^+ luminescent centers are doped in the host materials. The EL emission from SrS:Cu-based device showed a greenish-blue but shifted to short wavelength compared to SrS:Ce-based EL. The device was obtained the maximum luminance of 110cd/m^2 and the maximum luminous efficiency of 0.1 lm/W at V_{40}.

Key words : Strontium compounds, Copper, Phosphors, Electroluminescence

1. Introduction

Thin film electroluminescent (TFEL) devices are of commercial and scientific importance because of their application in flat panel displays. Recently, yellowish-orange ZnS:Mn based EL display panels are being applied to the dashboard panel of automobiles[1],[2]. Nowadays, one of the main targets is the development of a high-quality multicolor EL display. As red and green emitting EL displays have reached the required brightness values, the research is currently focused on the development of an efficient blue emitting EL device. As for the blue emitting TFEL devices, although SrS, $CaGa_2S_4$ and $SrGa_2S_4$ doped with rare earth or transition metal ions have been extensively studied for the highly promising phosphors[3],[4], these phosphor TFEL devices have not been put to practical use due to an insufficient luminance or a poor chromaticity of blue color. It was reported that Cu-doped SrS has improved chromaticity of blue color compared to conventional Ce-doped SrS[5],[6]. Furthermore, a two-component electroluminescent phosphor, SrS:Cu,Ag revealed that the emission characteristics of SrS:Cu,Ag are identical to SrS:Ag,

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whereas the excitation spectra resemble SrS:Cu[7]. However, these studies were mainly focused on the optical characteristics of Cu or Ag luminescent center but not on the TFEL emission characteristics.

In this paper, SrS:Cu,Cl thin films have been grown by hot wall technique and their crystallographic and optical characteristics have been systematically investigated. And SrS:Cu-based TFEL devices fabricated by hot wall deposition have been also investigated.

2. Experiments

The devices have been a conventional double insulating structure, as shown in Fig. 1. The devices were prepared by sequential depositions of each layer on a non-alkali glass substrate. An indium-tin-oxide(ITO) transparent electrode, the Si_3N_4 first insulating layer and the Si_3N_4 second insulating layer were deposited by rf-sputtering, and an Al rear electrode was thermally prepared. The 1.0μm-thick SrS:Cu phosphor layer was deposited by hot wall method with 4 evaporation walls. The substrate is fixed on the turn table which is rotated by well-controlled stepping motor. The phosphor layer was grown at the substrate temperature of 600℃ and vacuum pressure of 2.0×10^{-2}Pa with sulfur(S) which is supplied from a S furnace placed on the outside of the growth chamber. The metal Sr and CuCl were used for evaporation sources and Sr wall temperature was kept at 600℃, and CuCl wall temperature was varied from 200℃ to 260℃. S furnace was heated at 230℃ and S wall at which S is supplied was heated 550℃. The staying time of substrate at each wall is 2, 5 and 1sec at Sr, S and CuCl wall, respectively. And the substrate stays only one time on the CuCl wall by 3 rotations.

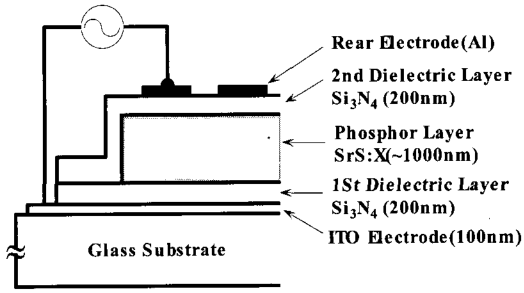

Fig. 1 The schematic structure of the TFEL devices.

The crystallographic characteristics of the thin films have been analyzed by x-ray diffraction(XRD). Cu-K (λ=1.5405Å) radiation and an acceleration voltage of 30kV were employed for the measurement and 2θ spectra from 20° to 60° were recorded. The optical characteristics of the phosphor layers have been analyzed by photoluminescence(PL) and the PL excitation (PLE) spectra using a conventional measurement system. A deuterium lamp(D_2) of 150W was used as an excitation light source. The spectra were measured at room temperature of 300K. The luminance-applied voltage(*L-V*) and luminous efficiency-applied voltage (*η*-V) characteristics were measured using a conventional method. The device was driven with 1 kHz pulse.

3. Results and discussion

3.1 Crystallographic characteristics

Fig. 2 shows XRD patterns of SrS:Cu, Cl thin films grown at the CuCl wall temperature of 200, 220, 240 and 260℃. Although the peak intensity for each sample is slightly different, the whole features of the XRD patterns are nearly the same independent of CuCl wall temperature, i.e., the XRD patterns indicate a strongly preferential orientation in the [200] direction, implying that the films have a rocksalt structure. The diffraction angle, $2\theta_{(200)}$, is about 29.6° for all samples. The patterns are similar to that of SrS powder[8].

Full widths at half maximum (FWHM) at (200) peak, $\Delta 2\theta_{(200)}$, become greater from 0.16° to 0.21 with increasing the CuCl wall temperature, implying that the crystallinity becomes poor with increasing the Cu concentration. However, considering the FWHM of 0.18° for SrS powder, it implies that the films have a good crystallinity.

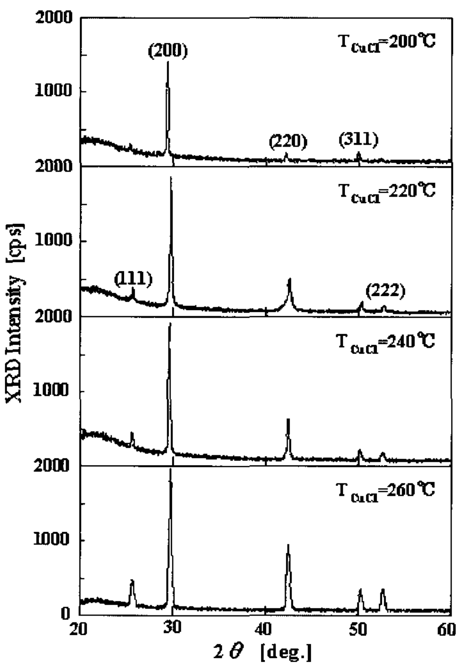

Fig. 2 X-ray diffraction patterns of SrS:Cu thin films grown at several CuCl wall temperatures.

3.2 Optical characteristics

Fig. 3 shows the PL emission spectra of SrS:Cu, Cl thin films grown at the CuCl wall temperature of 200, 220, 240 and 260℃. For measurement, the films were excited by a monochromatic light of 310nm from a D_2 lamp. As shown in Fig. 3, PL intensity is increased with increasing the CuCl wall temperature and the whole features of PL spectra were found to be nearly the same independent of CuCl wall temperature. That is, the PL spectra have an emission peak of about 470nm. It is considered that the peak is assigned by the transition from $3d^9 4s^1$ (^3Eg) to $3d^{10}$ ($^1A_{1g}$) of Cu^+ center. Although it is known that the emission wavelength is shifted to longer wavelength with increasing the Cu concentration, the shift is not nearly found in the experiment.

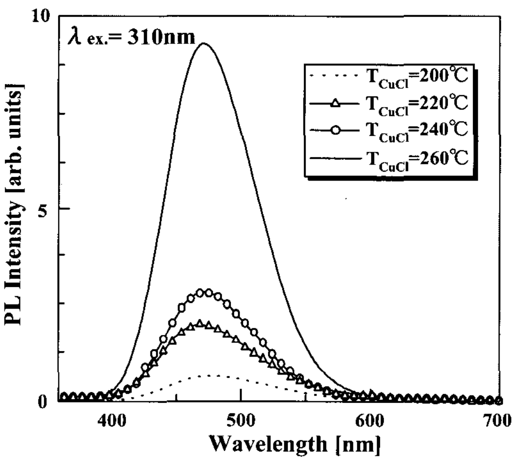

Fig. 3 PL emission spectra of SrS:Cu thin films grown at several CuCl wall temperatures.

Fig. 4 shows the PL excitation spectra of SrS:Cu, Cl thin films grown at the CuCl wall temperature of 200, 220, 240 and 260℃. It is measured at the monitoring wavelength of 463nm. As shown in Fig. 4, the whole features of PLE spectra are almost the same independent of CuCl wall temperature. That is, the excitation spectra exhibited a strong broad excitation band at 200-350nm, in which the peak at around 260nm is due to the band to band excitation in the SrS host materials, and the peaks at around 285nm and 310nm are considered to be assigned to the excitation bands corresponding to the $3d^{10}$ ($^1A_{1g}$) to - $3d^9 4s^1$ ($^1T_{2g}$) and the $3d^{10}$ ($^1A_{1g}$) - $d^9 4s^1$ (^1Eg) transitions of the Cu^+ in a cubic crystal field, respectively, implying that Cu^+ luminescent centers are doped in the host materials.

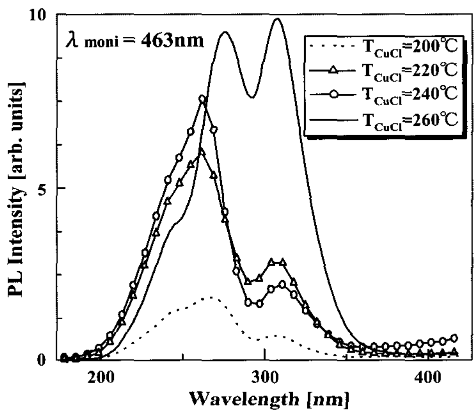

Fig. 4 PL excitation spectra of SrS:Cu thin films grown at several CuCl wall temperatures.

2.3 Electroluminescence

Electroluminescent device shown in Fig. 1 was prepared by using the hot wall deposition technique. The Cu luminescent centers were doped by using CuCl hot wall cell heated at 240℃. Fig. 5 shows electroluminescence spectrum of SrS:Cu thin films grown at CuCl wall temperature of 240℃. The decice showed a broad greenish-blue EL emission peaking at around 474nm and 510nm, which are shorter wavelength than 490nm and 540nm of SrS:Ce[9].

The luminance-applied voltage (L-V) and luminous efficiency-applied voltage (η-V) characteristics of SrS:Cu thin film EL device grown at CuCl wall temperature of 240℃ are shown in Fig. 6. The luminance rises steeply at 210V and the maximum luminance of 110cd/m^2 is obtained, which was low compared to the reported luminance of L_{max}=1100cd/m^2 [10]. The luminous efficiency is obtained 0.1lm/W at V_{40}.

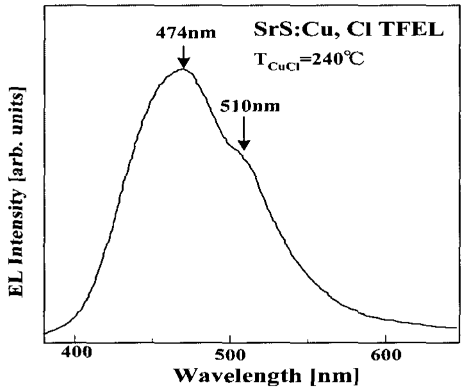

Fig. 5 Electroluminescence spectrum of SrS:Cu thin films grown at CuCl wall temperature of 240℃.

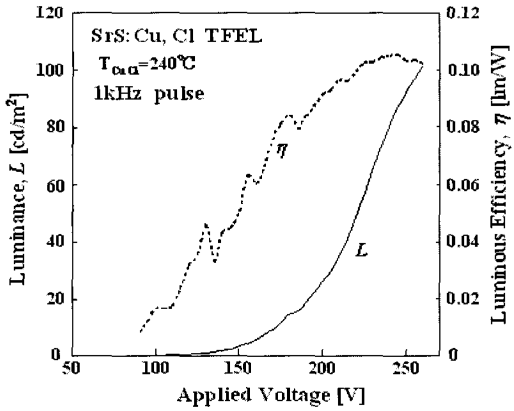

Fig. 6 Luminance-applied voltage (L-V) and luminous efficiency-applied voltage (η-V) characteristics for SrS:Cu thin film EL device.

4. Summary

SrS:Cu, Cl thin films have been grown by the hot wall technique with S furnace placed on the outside of the growth chamber in order to investigate the crystallographic and optical characteristics. The films had a good crystallinity independent of CuCl wall temperature and PL characteristics showed a peak assigned by the transition form $3d^9 4s^1$ (^3Eg) to $3d^{10}$ ($^1A_{1g}$) of Cu^+ center. It has also been found that, from the PLE spectra, Cu^+ luminescent centers are doped in the host materials.

EL emission from SrS:Cu-based EL device showed a greenish-blue EL emission peaking at around 474nm and 510nm. The device was obtained the maximum luminance of 110cd/m^2 under 1 kHz drive and the maximum luminous efficiency of 0.1lm/W at V_{40}. To improve the luminance level and luminous efficiency, the growth conditions such as substrate temperature, Cu concentration and film thickness have to be optimized.

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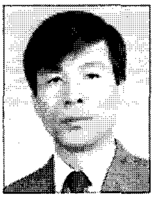

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