Effect of Substrate Temperature on Electroluminescence of SrS: HoF_3 Thin Film*

Zhao Lijuan, Zhao Guozhu, Fan Xiwu and Li Changhua
(赵丽娟) (赵国柱) (范希武) (李长华)
Laboratory of Excited State Processes Changchun Institute of Physics Chinese Academy of Sciences, Changchun 130021, *China*

Lin Jianhua
(林建华)
State Key Laboratory of Rare Earth Materials Chemistry and Applications, Beijing University, Beijing 100871, *China*

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Abstract

The SrS: HoF_3 Electroluminescent (EL) thin films are prepared at the different substrate temperature by electron beam evaporation. The crystallinity and EL characteristics of the samples are analyzed. It is found that the main diffraction peak is (200) at the higher substrate temperature and the main diffraction peak is (111) at the lower substrate temperature. The blue emission intensity and EL brightness of the SrS: HoF_3 thin films increase with the increase of the substrate temperature. Annealing the samples can change the cyrstal phase and strengthen the blue emission of EL thin film.

Key Words: Electroluminescence, Substrate temperature, SrS: HoF_3 EL thin film.

1. Introduction

Over the past few years, intensive work has been made to achieve multi-color or full-color thin film electroluminescence (EL) devices. But the blue emission of EL thin film devices has not been reached to the applicable level up to now. The research focus has turned to the white EL thin film for realizing full-color display[1~4]. Alkaline-earth sulfide (AES) doped with rare-earth ions is a promising multi-color EL material and it can supply a variety of color emission. For example, three main emissions are just right red, green and blue in the visible light spectrum in the SrS: Ho^{3+} EL thin film. Okamoto[4] investigated the EL of the SrS: Ho^{3+} thin films and the EL brightness of the sample was 110 cd · m^{-2} on an applied voltage with 3~5 kHz frequency. Three main emission peaks located at 490 nm, 550 nm and 660 nm, respectively. It implied that the white EL display could be realized probably in the SrS: Ho^{3+} thin films. As for alkaline-earth sulfide thin

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film, in general, the substrate temperature was higher during deposition in order to obtain the good crystallinity. In addition, the improvement of crystallinity is believed to be very useful for increasing the EL brightness. However, the structural change of SrS: Ho^{3+} layers and the effect of substrate temperature on EL characteristics are not yet fully studied. In this paper, the effects of substrate temperature on EL of the SrS: HoF_3 thin films were studied. The changes of structure and element component in the SrS: HoF_3 thin films were analyzed.

2. Experimental

The schematic structure of the SrS: HoF_3 thin film EL device is shown in Fig. 1 of reference [5]. The device has a conventional double insulating layers structure consisting of ITO/ SiO_2–Ta_2O_5/ SrS: HoF_3/ SiO_2–Ta_2O_5/ Al. The insulating layers were fabricated by rf-sputtering. ITO and Al electrodes were prepared by electron beam evaporation and heat evaporation, respectively. The phosphor layer was deposited at the substrate temperature range of 220~ 580 ℃ by electron beam evaporation. The concentration of the Ho^{3+} ions in SrS host was about 1 mol%. Vacuum pressures during phosphor layer deposition were kept in the range of 3.5×10^{-2} ~ 5.0×10^{-2} Pa. Annealing was done in environment of vacuum at the substrate temperature 550 ℃ for 1 h.

EL spectra were measured by 44 W spectrometer with the excitation source of XD-7 sine-wave generator, received by R456 photomultiplier and recorded by XWT-164 recorder. The spectra were not corrected by the standard lamp. The X-ray diffraction spectra were measured by D-Max/ rA 12 kW rotated target diffraction-meter.

3. Results and Discussion

3.1. EL Characteristics

Fig. 1 shows the EL spectra of SrS: HoF_3 thin films, which is driven by sine-wave voltage with 1 kHz frequency at the different substrate temperature. The EL spectra on the substrate temperature 580 ℃, 450 ℃ and 320 ℃ are shown in Fig. 1(a), (b) and (c), respectively. Fig. 1(d) is EL spectrum of sample which was annealed at 550 ℃ in the vacuum. The 490 nm, 550 nm and 660 nm emissions bands are corresponding to the transitions $^5F_3 - {}^5I_8$ (I_b), $^5F_4$ ($^5S_2$) $- {}^5I_8$ (I_g) and $^5F_3 - {}^5I_7 + {}^5F_5 - {}^5I_8$ (I_r), respectively. The 427 nm and 595 nm emission bands are corresponding to the transition $^5G_5 - {}^5I_8$ and $^5F_1 - {}^5I_7$, respectively. The I_b/I_g and I_r/I_g intensity ratios were changed obviously with the substrate temperature. To make the situation clearer, these results were further summarized in Fig. 2. With raising the substrate temperature to the 550 nm emission, the relative intensity of 490 nm emission increases and that of 660 nm emission decreases. After the sample was annealed, the blue emission was strengthened relatively and red emission was weakened relatively. The higher the substrate temperature and annealing are beneficial for realizing the white display. The dependence of the EL brightness of the SrS: HoF_3 thin film on the applied voltage is shown in Fig. 3. The brightness of the EL thin film, when the substrate temperature is less than 220 ℃, is too low to measure B-V curve.

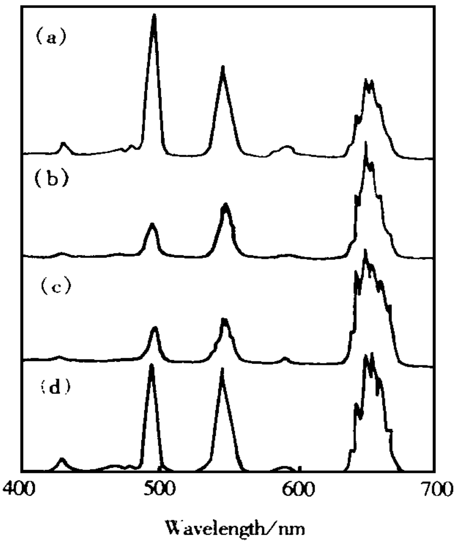

Fig. 1. EL spectra of SrS∶ HoF_3 thin films on different substrate temperature.
(a) t_s = 580 ℃; (b) t_s = 450 ℃; (c) t_s = 320 ℃; (d) t_s = 550 ℃

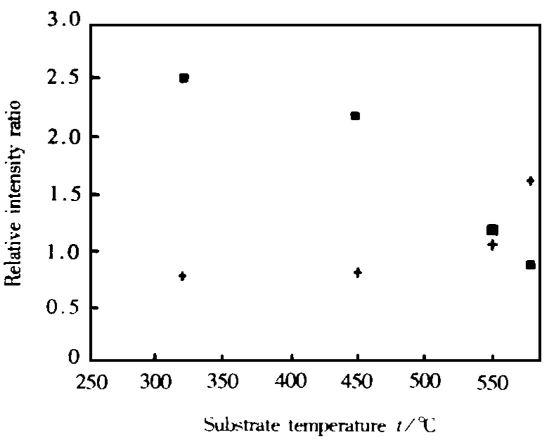

Fig. 2. I_b/I_g and I_r/I_g change with the substrate temperature.
+ I_b/I_g; ■ I_r/I_g

The higher the substrate temperature is, the higher the brightness is. The highest brightness of the SrS∶ HoF_3 thin film is 500 cd · m^{-2} (1 kHz sinewave voltage) when the thin film was prepared at the substrate temperature 580 ℃.

3. 2. *X-ray Diffraction*

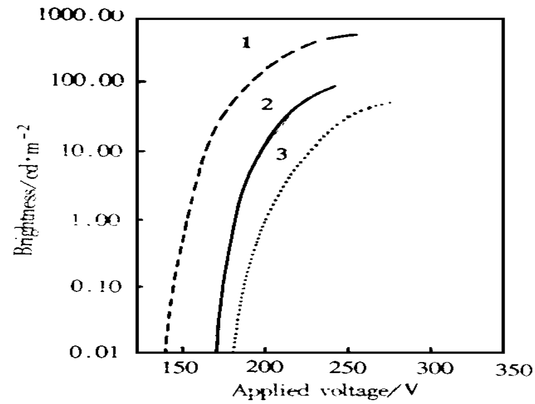

Fig. 3. Relation of brightness and applied voltage at different substrate temperature.
1 — t_s = 580 ℃; 2 — t_s = 450 ℃; 3 — t_s = 320 ℃

In order to analyze the effect of the crystallinity on the EL of the samples, the X-ray diffraction spectra of the SrS∶ HoF_3 thin films prepared at different substrate temperature were measured as shown in Fig. 4. It is found that the orientation of crystallization has been changed with the substrate temperature. At the higher substrate temperature, the higher relative intensity of the (200) diffraction peak in the thin films is obtained. But at the lower substrate temperature, the relative intensity of the (111) peak is the highest. When the sample was annealed at the substrate temperature 550 ℃, the relative intensity of the (200) and (111) peaks were changed. The crystallinity of the annealed sample was the same as the one at the higher substrate temperature. The annealing sample at the high temperature improves the crystal characteristics in the SrS ∶ HoF_3 thin films. $I_{(111)}/I_{(200)}$ relative intensity ratio is changed with substrate temperature, as shown in Fig. 5. $I_{(111)}/I_{(200)}$

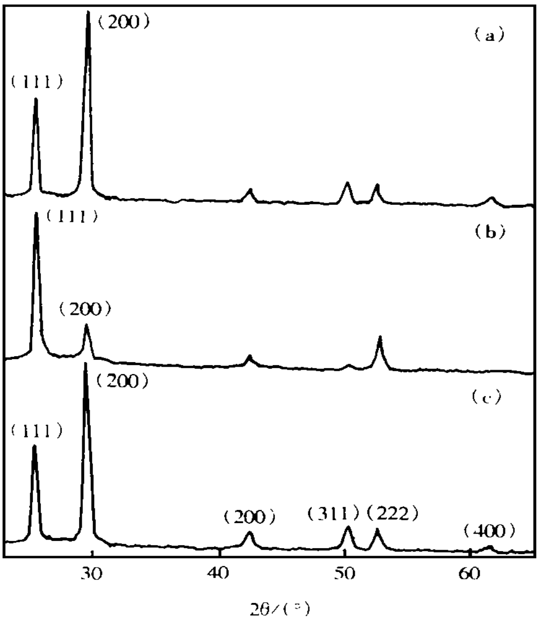

Fig. 4. X-ray diffraction spectra in SrS∶HoF_3 EL thin films on different substrate temperature.
(a) t_s = 580 ℃; (b) t_s = 450 ℃; (c) t_s = 550 ℃

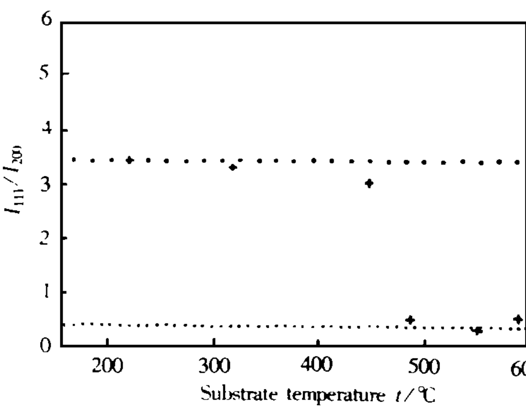

Fig. 5. $I_{(111)}/I_{(200)}$ relative intensity ratios change with the substrate temperature.
•• Sr powder; .. SrS powder; + SrS∶HoF thin film

of Sr and SrS standard powders were shown in the same figure. At lower temperature, the crystallinity of the SrS∶HoF_3 thin films approaches to the crystallinity of Sr powder. At higher temperature, it approaches to the SrS powder. It implied that the element Sr, which exists in the SrS∶HoF_3 thin films at lower substrate temperature, was excessive. In other words, the S vacancies in the EL thin film appear at lower substrate temperature.

3.3. Discussion

SrS∶HoF_3 ELTF was prepared by electron beam evaporation. When the high energy electron beam irradiated on the SrS pellet, SrS was sublimated and a part of SrS was decomposed to element Sr and S. Then they were absorbed on the surface of the substrate glass and formed the thin film. The crystallinity of the thin films were affected by the substrate temperature t_s directly. If t_s was fit for the growth of thin films, the articles of deposition on the surface of the substrate could vibrate and form regularly arrangement. It is helpful for formation of thin film with good crystallinity and stoichiometry. So the saturation brightness is higher.

At lower substrate temperature, the growth rate of the SrS∶HoF_3 thin films was faster. On one hand, SrS could not finish the arrangement regularly on the substrate. In addition, a few of elements Sr and S were not compounded to SrS at lower substrate temperature and S vacancy was formed. It resulted in disorder of the SrS∶HoF_3 thin films and had effects on the crystallinity and the stoichiometry of the thin films. The saturation brightness decreased. On the other hand, the lower substrate temperature can reduce the second evaporation during preparing the SrS∶HoF_3 thin films. It made the growth rate much faster. The thin films were thicker. The threshold voltage increased.

Annealing the samples can improve the crystallinity of the thin films. Also, it can make the Ho^{3+} ions in SrS host with well-distribution and reduce concentration quenching and cross-relax probability. The blue emission intensity is increased.

The EL mechanism of SrS: HoF_3 thin film is thought to be impact excitation and ionization luminescence. The SrS: HoF_3 thin films prepared at lower substrate temperature have the worse crystallinity and more S vacancies. The worse crystallinity increases the dispersion probability of hot electrons, prevents the hot electrons from accumulating higher energy and reduces the impact probability. The EL brightness is decreased. The emissions intensity of the shorter wavelength is weakened. The other probable reason is that the Ho^{3+} ions are not distributed well in SrS host. The cross-relax could take place and weaken the blue emission.

4. Conclusion

(1) The crystallography of SrS: HoF_3 EL thin films is decided by the substrate temperature. At higher temperature, (200) was main diffraction peak. The crystallinity belonged to SrS crystal phase. At lower temperature, the Sr content is increased obviously. It destroyed the crystallinity and the stoichiometry of the thin films.

(2) The higher the substrate temperature is, the better the crystallinity is. It is helpful for the energy accumulation of the hot electrons and exciting 4f electrons of Ho^{3+} ions to the higher energy levels. Ho^{3+} ions doping was well-distributed in SrS host and the cross-relax probability was lessened. The blue emission intensity was strengthened.

(3) The saturation brightness is increased and the threshold voltage is decreased with raising the substrate temperature. The high substrate temperature is beneficial to preparing the white ACTFEL display panels with the SrS: HoF_3 thin films.

(4) Annealing the samples can improve the crystallinity of SrS: HoF_3 EL thin films and the distribution of Ho^{3+} ions in the SrS host. In addition, the intensity of blue emission is increased, but meanwhile the intensity of red emission is decreased.

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