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Electroluminescence from CaS:TmF₃ film prepared by radio frequency magnetron sputtering

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Blue electroluminescence is reported from CaS:TmF₃ thin films prepared by radio frequency magnetron sputtering method. The dependences of brightness on substrate temperature, concentration of TmF₃, and the applied voltage were investigated on alternating current thin-film electroluminescent devices. The obtained maximum brightness was above the level of ZnS:TmF₃ devices. The equivalent average energy of the excited electrons contributed to the electroluminescence in CaS:TmF₃ alternating current thin-film electroluminescent devices and was estimated at around 4.23 eV by comparing the ratio of infrared to blue peak in electroluminescent spectra with that in photoluminescent spectra excited by different photon energy. The excitation processes of electroluminescence in CaS:TmF₃ thin films were assumed to be energy transfers from the conduction band edge to Tm³⁺ centers. © 1998 American Institute of Physics.

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I. INTRODUCTION

Blue electroluminescence (EL) from Tm-ion-doped ZnS thin films has been investigated in the art literature.¹⁻⁴ However, the maximum brightness achieved for these devices was low (10–12 cd/m²),^{4,5} and the infrared emission at around 800 nm was fairly stronger than the blue emission at around 480 nm. The dominant excitation process was demonstrated to be energy transfer from host to Tm³⁺ centers in ZnS:Tm alternating current thin-film electroluminescent (ACTFEL) devices.^{3,4} It was considered that the ZnS host was unsuitable for the excitation of ¹D₂ and ¹G₄ levels of Tm³⁺ ions. Miura *et al.*⁶ tried to use several host materials having wider band gap energy than ZnS, such as Y₂O₂S, CdF₂, ZnF₂, and YF₃. Although the obtained EL brightness was lower than that in ZnS:Tm ACTFEL devices, the intensity ratio of infrared to blue emission decreased in these devices. Alkaline-earth sulfides have wider band gaps (4.41 eV for CaS and 4.30 eV for SrS) than ZnS (3.7 eV).⁷ Bright electroluminescence was obtained in CaS:Eu and SrS:Ce thin-film EL devices. The reported maximum EL brightness (15 cd/cm²) in SrS:TmF₃ thin-film EL devices was above that of ZnS:Tm ACTFEL devices (12 cd/cm²).⁸ However, electroluminescence from CaS:TmF₃ films prepared by rf sputtering method has not yet been reported to our knowledge. In this article, we report the study of EL from CaS:TmF₃ ACTFEL devices prepared by rf magnetron sputtering method. The obtained maximum brightness in this device was 30.5 cd/m² in 5 kHz driving condition.

II. EXPERIMENT

The ACTFEL device structure was shown in Fig. 1. The SiO₂/Ta₂O₅ stacked isolators were deposited by rf magne-

tron reactive sputtering in O₂+Ar atmosphere with two targets of high purity Si and Ta metal. The CaS:TmF₃ films were prepared by rf magnetron sputtering method. The targets were CaS:TmF₃ slices with circular area of 38.5 cm². The concentrations of TmF₃ were from 0.05 to 2 mol %. The CaS:TmF₃ films were deposited in conditions in which the atmosphere was 99.99% Ar gas with pressure of 1.5 Pa, the rf power was 600 W, the substrate temperatures were from 350 to 650°C, and the distance between target and substrate was 6 cm. For comparison, ZnS:TmF₃ 0.4 mol % films with thickness of around 700 nm were prepared to replace the CaS:TmF₃ film in the ACTFEL structure. The ZnS:TmF₃ films were deposited by electron-beam evaporation method at substrate temperature of 200 °C and then annealed at 600 °C for 2 h in vacuum to improve EL brightness. EL spectra were measured under 1 kHz sinusoidal wave voltage excitation by a monochromator with a photomultiplier (RCA No. 31034) connected to a recorder. The absolute EL brightness was measured by model 1980A luminometer under excitation of 5 kHz sinusoidal wave voltage. Photoluminescent (PL) spectra from CaS:TmF₃ 0.4 mol % powder were measured by the same system under excitation of 325 nm line of a 20 mW He–Cd laser. PL excitation spectra and PL emission spectra excited under different photon energy were measured by Regina Mueller-Mach in Hewlett-Packard Company using conventional method. All PL spectra were corrected according to the response of the measurement system for the EL spectrum, therefore the integrated intensity ratio of infrared to blue peaks, R_{ib} , in spectra was comparable in two systems.

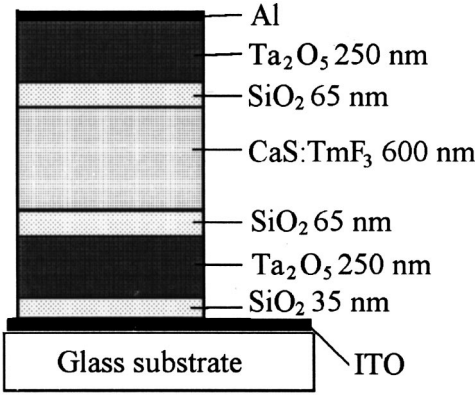


FIG. 1. Structure of CaS:TmF₃ ACTFEL device.

III. RESULTS

Figure 2 shows the EL spectra from CaS:TmF₃ 0.3 mol % and ZnS:TmF₃ 0.4 mol % ACTFEL devices. The emission spectrum of CaS:TmF₃ consists of four groups of lines peaked around 480 nm (¹G₄→³G₆), 653 nm (¹G₄→³H₄), 705 nm (³F₃→³H₆), and 804 nm (³F₄→³H₆).⁹ Figure 3 shows the integrated intensity ratio of infrared (804 nm) to blue (480 nm) peak, R_{ib}, in EL spectra versus the applied voltage. R_{ib} in EL spectra of CaS:TmF₃ is constant at around 5.5 with increasing the applied voltage within error of experiment. This value is slightly smaller than that (around 6.5) in the EL spectra of ZnS:TmF₃ 0.4 mol % ACTFEL devices. Both of the two devices show the same behavior. Figure 4 shows the brightness versus applied voltage characteristics of the best devices measured under excitation of 5 kHz sinusoidal wave voltage. The maximum brightness was 30.5 cd/m² in the best CaS:TmF₃ ACTFEL devices. This value was above that of the ZnS:TmF₃ (11 cd/m²) and SrS:Tm (15 cd/m²) ACTFEL devices.^{4,5,8}

X-ray patterns of CaS:TmF₃ films, sputtered under different substrate temperatures, are shown in Fig. 5. The films

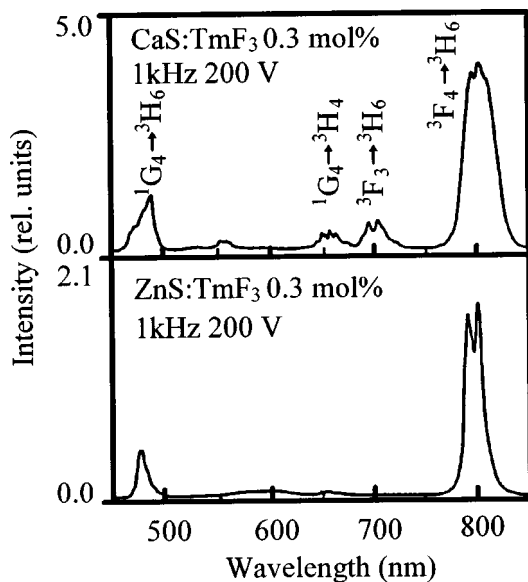


FIG. 2. EL spectrum from CaS:TmF₃ ACTFEL device.

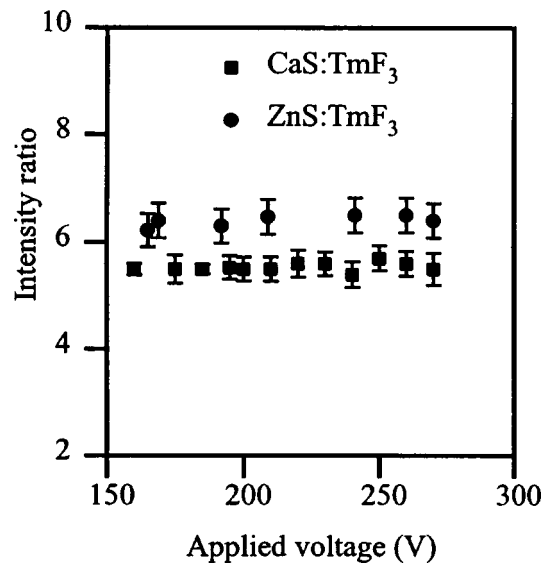


FIG. 3. EL integrated intensity ratio of the infrared to blue peak vs the applied voltage.

exhibit (200) orientation for substrate temperatures from 300 to 600 °C. It is polycrystalline at temperature up to 650 °C. The dependence of EL brightness at 60 V above the threshold voltage (V_{th}+60 V) on substrate temperature is shown in Fig. 6. The brightness increased significantly with substrate temperature from 350 to 450 °C. Above 450 °C, it cannot be effectively improved by increasing substrate temperature. Figure 7 is the dependence of the brightness on the concentrations of TmF₃ in CaS films deposited at a substrate temperature of 600 °C. The optimum concentration is at about 0.3 mol %. Above this value, concentration quenching occurs.

In order to study the possible excitation processes of EL in CaS:TmF₃ films, the PL excitation spectra of CaS:TmF₃

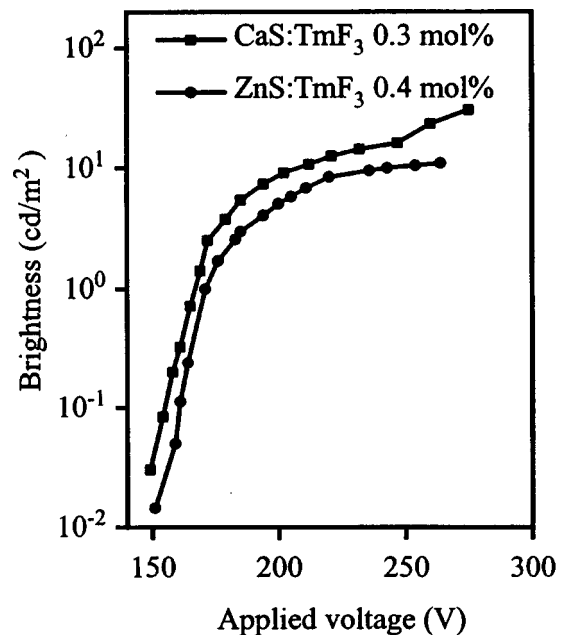


FIG. 4. Brightness-voltage characteristics of CaS:TmF₃ and ZnS:TmF₃ ACTFEL devices.

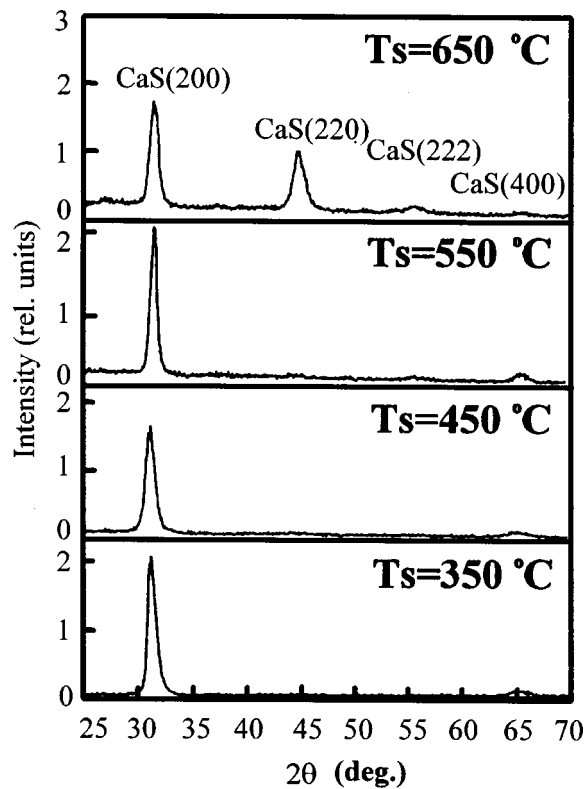


FIG. 5. X-ray diffraction patterns of the CaS:TmF₃ films deposited under different substrate temperatures.

powder were studied. The CaS:TmF₃ powder was prepared by firing CaS (99.9%) and TmF₃ (99.99%) 0.4 mol % mixture at 1000 °C in S+N₂ atmosphere for 2 h. The PL emission spectra, under excitation of 325 nm line of a He–Cd laser, was shown in Fig. 8. The positions of the emission peaks were consistent with the EL spectra. PL excitation spectra of the powder monitoring on peaks at 480, 653, 705, and 804 nm were shown in Fig. 9. The excitation bands of

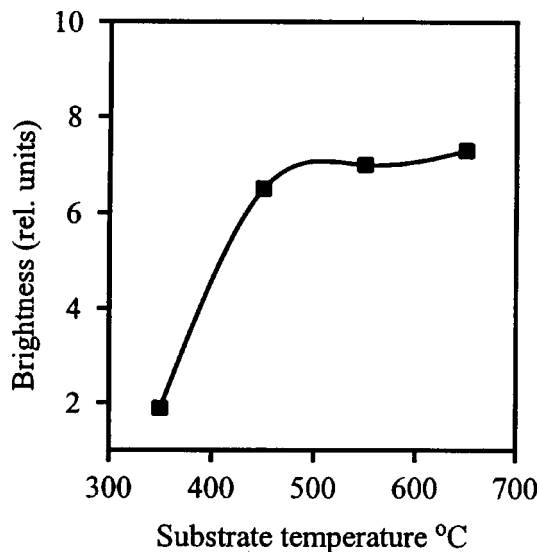


FIG. 6. Dependences of EL brightness on substrate temperatures for depositions of CaS:TmF₃ films. The brightness was measured at 60 V above the threshold voltage.

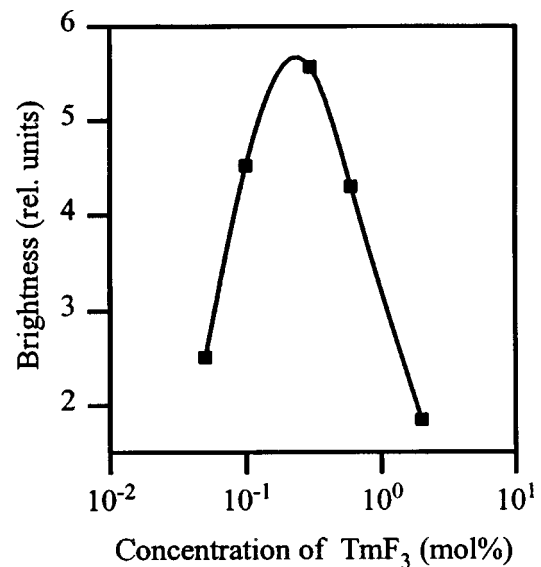


FIG. 7. Dependence of EL brightness on concentrations of TmF₃ in CaS films. The brightness was measured at 60 V above the threshold voltage.

the 480 and 653 nm emission were at around 314 nm (3.95 eV) and those of 705 and 804 nm emission were at 281 (4.41 eV) and 288 nm (4.31 eV), respectively. Figure 10 was the excitation band of 480 nm in CaS:TmF₃ powder with TmF₃ concentrations of 0.04, 0.1, and 1 mol %. It was shown that the excitation band at 314 nm increased significantly with an increase of Tm concentration.

IV. DISCUSSION

The excitation band energy (at 3.95 eV) of 480 emission band was not consistent with any possible electronic transition between two energy levels of Tm³⁺ ion and it was not affected by changing the composites of dopants (for example, doping Tm₂O₃ instead of TmF₃). Since it depends strongly on the concentration of Tm, we assume that this excitation band was probably from charge transfer state of Tm. The excitation of the PL bands at 480 and 653 nm was explained as strong energy transfer from the excitation bands

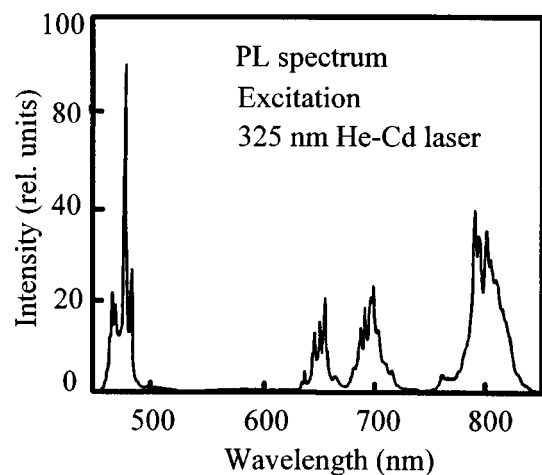


FIG. 8. PL spectra from CaS:TmF₃ 0.4 mol % PL powder under excitation of 325 nm line of a He–Cd laser.

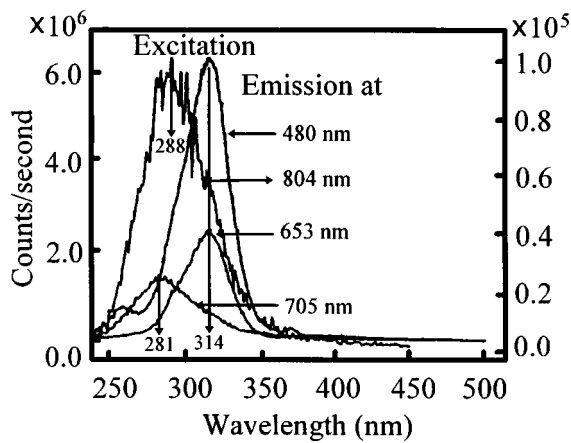


FIG. 9. PL excitation spectra from CaS:TmF₃ 0.4 mol % PL powder.

at around 3.95 eV (314 nm) to ¹G₄ level; those of the 705 and 804 nm bands were attributed to energy transfer from conduction band of CaS to ³F₄ and ³F₃ levels of Tm³⁺ ions because the excitation energies (4.41 and 4.30 eV) are close to the forbidden band gap of CaS (4.41 eV). Since the energies of PL excitation bands for the blue band (480 nm) and the infrared band (800 nm) were different, the intensity ratio *R*_{ib} in PL spectra depends strongly on the excitation photon energy as shown in Fig. 10. The change of *R*_{ib} with excitation photon energy may become a probe for the change of the excited electron energy in CaS:TmF₃ PL phosphor. On the other hand, if the excitation processes of EL were similar to that of PL, it would be used to estimate the equivalent average energy of the excited electron in EL films by comparing the intensity ratio *R*_{ib} in EL spectra with that of PL spectra excited under different photon energy. Since *R*_{ib} was around 5.5 in EL spectrum, according to the dependence of *R*_{ib} on excitation photon energy in Fig. 10, the equivalent average energy of excited electrons in CaS:TmF₃ thin films

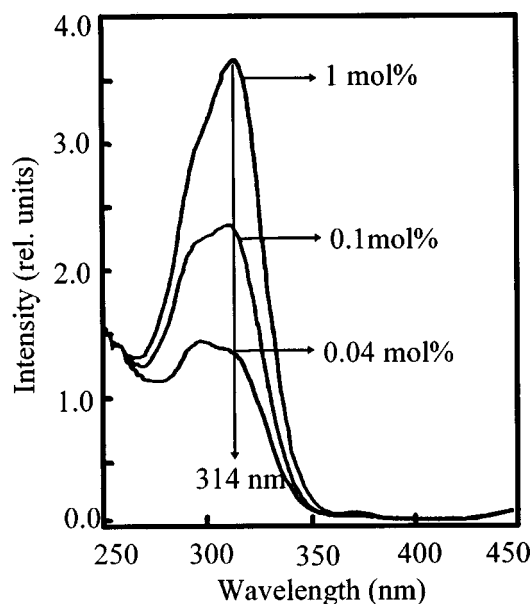


FIG. 10. PL excitation band of 480 emission peak in CaS:TmF₃ powder with different TmF₃ concentration.

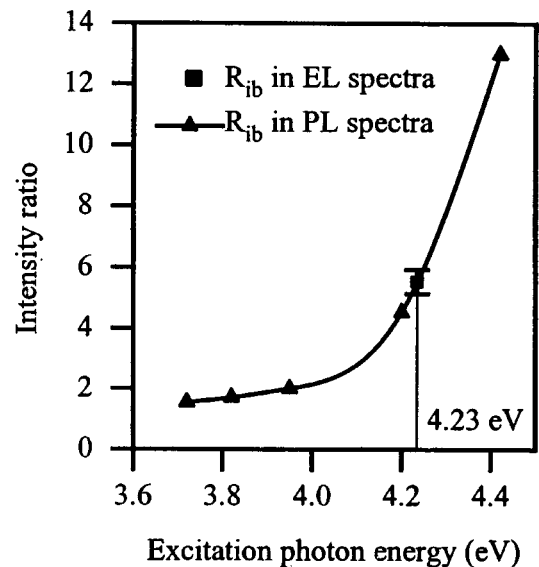


FIG. 11. PL integrated intensity ratio of the infrared to blue peak vs the excitation photon energy. The equivalent average energy of electrons in EL films was estimated at around 4.23 eV according to the *R*_{ib} in EL spectrum.

was estimated around 4.23 eV. These excited electrons probably had a much wider energy distribution than those excited by a monophoton energy in PL powder.

It is well known that there are two excitation mechanisms in rare-earth-ion doped ACTFEL devices, one is direct impact excitation of the rare-earth-ion luminescent centers by hot electrons; another is impact ionization of the host and then energy transfer from host lattice, traps, or sensitizers to luminescent centers. If the former processes were dominant in the CaS:TmF₃ EL device, the ratio *R*_{ib} of infrared to blue intensity would decrease with increasing the applied voltage, because the energy distribution of hot electrons would shift to higher energy with increasing the applied voltage. This phenomena was an evidence for the direct impact excitation in other rare-earth-doped EL devices such as ZnS:Er, in which the intensity ratio of red band to blue band decreased with increasing the applied voltage.¹⁰ If the latter process was dominant, *R*_{ib} would not depend strongly on the applied voltage because the intensity ratio of EL spectra depends mainly on the energy transfer efficiencies to the excited levels of ³F₄ and ¹G₄ and electronic transition probabilities of ³F₄→³H₆ and ¹G₄→³H₆ inside Tm³⁺ ions. Since *R*_{ib} was constant with an increase in the applied voltage in CaS:TmF₃ ACTFEL, the excitation processes were not dominated by impact excitation. The possible excitation processes may be mainly attributed to energy transfer from the conduction band edge of CaS to the Tm³⁺ centers, because the equivalent energy of the excited electrons was closer to the band gap of CaS.

V. CONCLUSION

In summary, electroluminescence from the CaS:TmF₃ film prepared by rf magnetron sputtering method was studied. The films showed a single (200) orientation in a wide substrate temperature from 300 to 600 C and the EL brightness was not significantly improved above 450 C. The opti-

mum concentration of TmF_3 was determined to be around 0.3 mol %. The maximum EL brightness was 30.5 cd/m^2 in CaS:TmF_3 ACTFEL devices. The equivalent average energy of the excited electrons contributed to the light emission in CaS:TmF_3 ACTFEL devices was estimated around 4.23 eV by comparing the integrated intensity ratio of the infrared to blue emission with that of the PL spectra excited under different excitation photon energy. The possible excitation processes of EL in CaS:TmF_3 thin films were attributed to the energy transfer from conduction band edge of CaS to the luminescent centers.

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