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Electroluminescence Color Tuning between Green and Red in MOS Devices Fabricated by Spin-coating of (Tb + Eu) Organic Compounds on Si

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Abstract

Si-based EL MOS devices, of which color can be tuned from green through yellow to red, are reported. The devices have a structure of an ITO/[(Ta+Ba)+Eu]–Si–O insulator layer/n$^+$-Si substrate fabricated by spin-coating of the mixture of organic (Tb/Ba/Eu) liquid sources. EL spectra have peaks corresponding to intrashell Tb^{3+}/Eu^{3+} (green/red) transitions, of which intensity ratio could be tuned by the Eu/Tb ratios of the liquid mixtures. The insulator layers are analyzed with TEM/XRD/XPS, and EL color tuning mechanism is discussed.

1. Introduction

Si-based light-emitting devices have an advantage of excellent process compatibility with Si metal-oxide-semiconductor (MOS) LSIs [1]. Various applications, such as intelligent displays in portable systems and optical interconnections for intra- or interchip communication, are expected. Recently, we have fabricated MOS devices with (rare-earth)-silicate-related oxides by the furnace annealing of organic compound films, which had been spin-coated on an n$^+$-Si substrate, and they showed various color EL, such as green, red, pale pink, purple and bluish white [2,3]. The simple fabrication process is preferable for a low-cost display, however, a precise and simple control method of EL color is required.

In this study, we demonstrate a simple EL color tuning method from green through yellow to red in MOS devices with spin-coated [(Tb+Ba)+Eu] organic compounds on Si with various concentration ratios of Tb and Eu. Current I_G versus voltage V_G characteristics, EL colors, and EL spectra are presented. The surface insulator layers are analyzed by cross-sectional TEM, XRD, and XPS. EL color tuning mechanism and the device structure are also discussed.

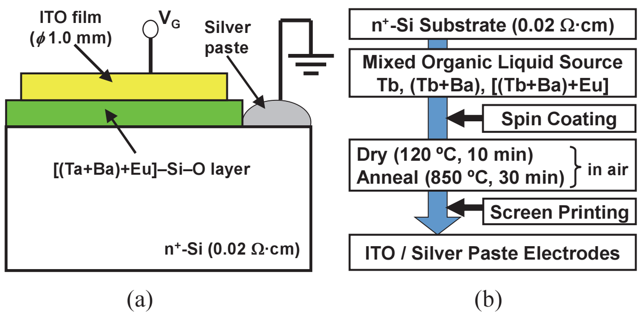


Fig. 1 (a) Schematic cross section of a MOS device and (b) fabrication process steps [2,3].

2. Device Fabrication and Experiment Procedures

Figure 1 shows a schematic cross section of a MOS device with a ITO/[(Ta+Ba)+Eu]–Si–O insulator layer/n$^+$-Si. The mixture of organic compound liquid sources of Tb, Ba, Eu was spin-coated on n$^+$-Si and furnace annealed at 850 °C for 30 min in air as shown in the process steps of [2,3].

Twelve kinds of MOS devices with various Tb/Eu mixture ratios were fabricated as given in Table I. Since #1[+Ba] with the Tb/Ba mixture solution showed much stronger green EL than #0[Tb] with the Tb liquid only, the mixture solution with the atomic ratio of (Tb:Ba=10:1) was used as the base liquid source for the devices with Eu mixtures.

The EL spectra were measured with a CCD cooled at –70 °C through a monochromator under a constant-current supply. The EL spectrum with wavelengths ranging from 290 to 1000 nm can be detected simultaneously with a resolution of 1.2 nm/pixel. The EL spectrum data were corrected with the total wavelength response curve of the system [2,3].

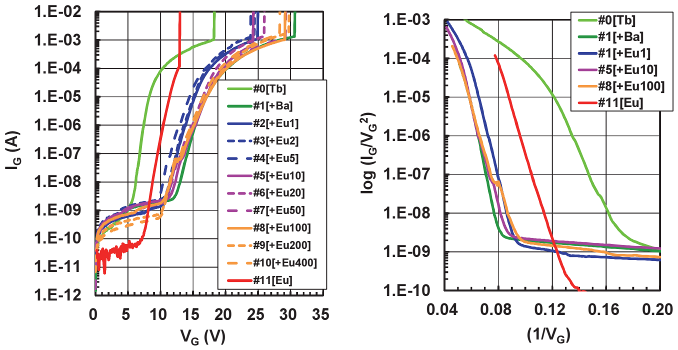
2. Results and Discussions

Figures 2(a) show I_G vs V_G characteristics of #0[Tb]-#11[Eu] devices. The rising voltages V_R, at which I_G increased steeply, increased by the addition of Ba to Tb liquid. V_R values of #2[+Eu1]-#10[+Eu400] devices were 10-12 V. Figure 2(b) shows the Fowler-Nordheim (FN) plot, of which linear relations indicates that the steep increase in I_G is due to the FN tunnel current and the hot electron injection into the insulator from the Si substrate.

Figure 3 shows composite microphotographs of the ITO electrodes and EL color images for #1[+Ba]-#10[+Eu400]. The lower semicircle of each image shows the EL, and the corresponding ITO electrode image is vertically flipped and placed on the upper side. The hue of EL colors varies from green to red with the increase of Eu ratio. The edge roughness of the ITO electrode periphery was caused by uneven transfer of the ITO ink in our screen printing process.

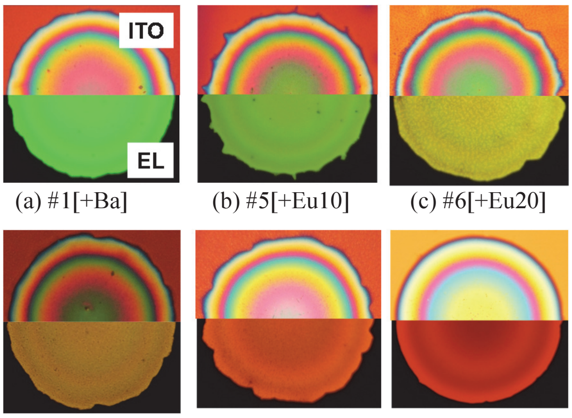
Table I. MOS EL devices fabricated with spin coated layers

Sample	Coating Liquid	Sample	Coating Liquid
#0[Tb]	Tb	#6[+Eu20]	Tb : Eu = 1000 : 20
#1[+Ba]	Tb : Ba = 10 : 1	#7[+Eu50]	Tb : Eu = 1000 : 50
#2[+Eu1]	Tb : Eu = 1000 : 1	#8[+Eu100]	Tb : Eu = 1000 : 100
#3[+Eu2]	Tb : Eu = 1000 : 2	#9[+Eu200]	Tb : Eu = 1000 : 200
#4[+Eu5]	Tb : Eu = 1000 : 5	#10[+Eu400]	Tb : Eu = 1000 : 400
#5[+Eu10]	Tb : Eu = 1000 : 10	#11[Eu]	Eu



(a) (b)

Fig. 2 (a) I_G vs V_G characteristics and (b) FN plots of #0[Tb]-#11[Eu] devices.



(a) #1[+Ba] (b) #5[+Eu10] (c) #6[+Eu20]

(d) #7[+Eu50] (e) #8[+Eu100] (f) #10[+Eu400]

Fig. 3 Composite microphotographs of the ITO electrodes and EL color images for #1, #5, #6, #7, #8, and #10.

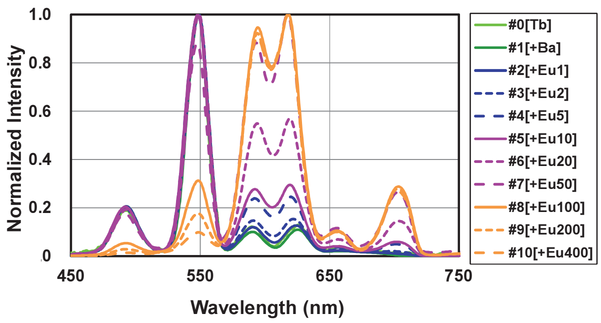


Fig. 4 (Eu/Tb) ratio dependences of normalized EL spectra for #0[Tb]-#10[+Eu400] in the wavelength ranges of 450–750 nm.

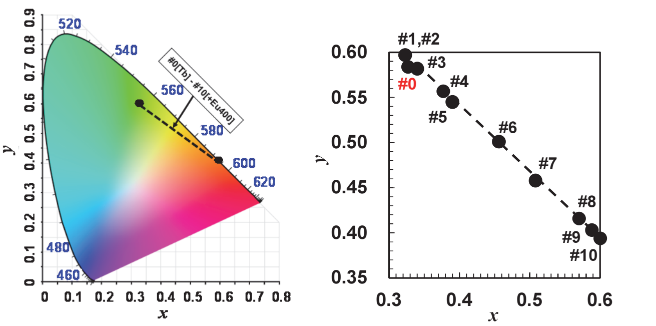
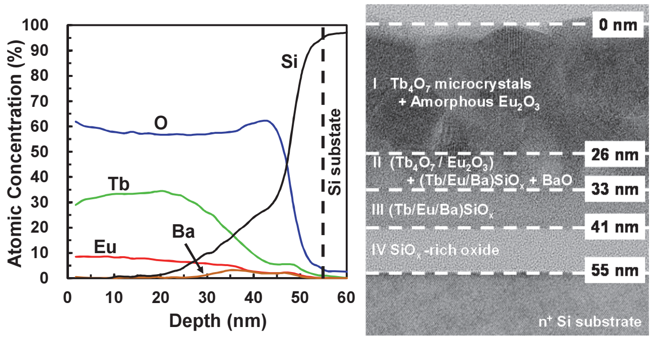


Fig. 5 (a) CIE chromaticity diagram overlaid with the chromaticity coordinates for #0[Tb]–#10[+Eu400], and (b) its enlarged diagram.



(a) (b)

Fig. 6 (a) Atomic concentration profiles of Tb, Eu, Ba, O, and Si for device #8[+Eu100] and (b) cross-sectional TEM image with a schematic structure estimated from TEM, XRD, and XPS analyses.

Figure 4 shows an Eu concentration dependences of normalized EL spectra for #0[Tb]-#10[+Eu400] measured at I_G = 200 μA. Peaks of the EL spectra correspond well to the intrashell transitions of $^5D_4$ - ^7F_J (J = 6, 5, 4 and 3) of Tb^{3+} and $^5D_0$ - ^7F_J (J = 1, 2, 3 and 4) of Eu^{3+} ions, respectively.

Fig. 5(a) gives the CIE chromaticity diagram [4] overlaid with the chromaticity coordinates of devices #0[Tb]–#10[+Eu400], which were calculated by combining each EL spectrum and the color matching functions CMFs [5]. The enlarged chromaticity coordinate for #0[Tb]-#10[+Eu400] is shown in Fig. 5(b). The emission color changed linearly from yellowish-green (0.323, 0.597) of #1[+Ba] through yellowish-orange (0.508, 0.458) of #7[+Eu50] to reddish-orange (0.600, 0.394) of #10[+Eu400].

Figure 6 shows (a) atomic concentration profiles of Tb, Eu, Ba, O, and Si for device #8[+Eu100], and (b) a cross-sectional TEM image of the insulator film (~55 nm), which is estimated to be four layer structure by taking account of XRD analysis. Layer I contains Tb_4O_7 microcrystals and amorphous Eu_2O_3. Layer II contains (Tb_4O_7 microcrystals + amorphous Eu_2O_3), (Tb/Eu/Ba)SiO_x and the bright BaO particles with around 7 nm diameter. Layer III and IV contains amorphous (Tb/Eu/Ba)SiO_x and SiO_x-rich oxide, respectively.

3. Conclusions

Si-based EL MOS devices with an ITO/[(Ta + Ba) + Eu]–Si–O insulator layer/n$^+$-Si substrate structure, of which color can be tuned from green through yellow to red, are reported. EL spectra have peaks due to intrashell Tb^{3+}/Eu^{3+} transitions corresponding to green/red color emissions, of which intensity ratio could be tuned by the Eu/Tb ratios of the liquid mixtures. TEM, XRD, and XPS analyses show the insulator structure of SiO_x-rich oxide, Tb/Eu/Ba-silicates, and Tb_4O_7/Eu_2O_3 containing oxides.

References

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[4] https://upload.wikimedia.org/wikipedia/commons/3/3b/CIE1931xy_blank.svg.
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