Color electroluminescence from ZnS thin films multi-doped with rare-earth ions.

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The electroluminescence (EL) cell is made from thin films formed by the co-evaporation of ZnS and rare-earth metals. The radiation from this cell is caused by electron transitions between the levels of rare-earth ions. In this study we determine the relationship between the concentration of the rare-earth ions and the luminous spectral intensity in the EL cell and the applied voltage. The luminescence center of rare-earth ions in ZnS is localized center. If the ZnS is activated by two different rare-earth ions then the resultant emission color is the sum of two individual emission colors. Thus the emission color can be changed, as desired by controlling the concentrations of rare-earth ions. On the other hand it is observed that the spectrum of an EL cell containing several kinds of rare-earth ions changes when the applied voltage changes.

1. Introduction

At the beginning of the present studies, it was observed that the Electroluminescence (EL) cell using a ZnS phosphor provides a plane light source. However there are problems related to brightness and operating life time, which are not easy to solve but which nevertheless limit its application as a general illuminating light source. On the other hand there has been recent progress in optical information processing techniques along with other developments in the field of optoelectronics. Now the main components presently used in panel display devices are light-emitting diodes and liquid crystals, but there has also been considerable progress in the development of the thin-film EL for practical use.

In 1968, D. Kahng and his colleague predicted that the thin film EL will be produced using the combination of ZnS phosphor as the host and rare-earth atoms as the activators, both evaporated at the same time. Since this report the EL has again become a subject of deep interest to the researcher seeking a solid-state lamp and studies have been made of the factors affecting brightness, luminance mechanism and life time. It is known that ZnS as host does not influence the emission color with various rare-earth atoms as activator. An attempt was therefore made to change the emission color by multi-doping with rare-earth ions and by changing

the applied voltage. This report examines the structure of the EL cell and its electrical and optical characteristics as well as the relation between the emission spectrum and applied voltage.

2. Structure and Fabrication method of the EL cell

Fig. 1 shows the structure of the EL cell which is fabricated as follows.

The substrate, consisting of a conductive glass, is first washed in detergent and then with pure water and acetone, for 15 minutes each, in an ultrasonic tank. This process must be carried out carefully since it has a strong influence on the contact

1. Metal Electrode (Al)
2. Insulating Layer (SiO_2)
3. Active Layer (ZnS:LnF_3)
4. Transparent Electrode (SnO_2)
5. Glass Substrate

Fig. 1 Structure of the EL cell

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strength of the luminous layer.

High-purity ZnS powder is placed in an unglazed crucible and rare-earth fluoride in a platinum one. They are heated under vacuum to remove all trapped gas. Evaporation then takes place onto the substrate. The substrate temperature during evaporation is maintained at 340 C but is subsequently raised to 450 C for 30 minutes, in a nitrogen atmosphere, to improve the stability of the thin film. It is then covered with an insulating layer of SiO about 2,000 Å in thickness. Finally the back electrode of aluminum is placed on the SiO.

3. Experiment

The EL cell is excited by voltage pulses of 200 μsec duration at a repetition rate of 270 Hz.

In the current-voltage curve of Fig. 2 the voltage is shown as being positive when the voltage on the aluminum electrode is negative. The characteristic is similar to that of a rectifier and the current increases more rapidly when the voltage exceeds a certain value, called the threshold voltage. With reverse bias the luminous intensity is low but when the forward bias exceeds the threshold voltage the

Fig. 2 Current—Voltage characteristic

Fig. 3 Luminous intensity—Voltage characteristic (1)

Fig. 4 Luminous intensity—Voltage Characteristic (2)

luminous intensity increases rapidly, as shown in Fig. 3. When the applied voltage is increased still further the luminous intensity becomes saturated, as indicated in Fig. 4. This figure gives the variation of luminous intensity with voltage which may be expressed by the following formula:

$$B = B_0 \exp(-CV^{-1/2})$$

where B ; luminous intensity

V ; applied voltage

B_0, C ; constant

In order to study the relation between the luminous intensity and the concentration of rare-earth ions, EL cells have been made in which the doping level of the rare-earth atoms has been changed from 1 atom % to 4 atom %.

Fig. 5 shows this relationship for ZnS; TbF₃ for

Fig. 5 Relationship between the luminous intensity and concentration of Tb ion with applied voltage as parameter

several values of applied voltage. From this graph it may be concluded that the highest brightness is obtained with 2 atom % of Tb concentration. With a concentration of less than 2 atom %, the luminous intensity is weak because the concentration of luminescence centers is low.

Then even if enough energy is supplied to excited all the luminescence center the emitted intensity is poor because of this small number.

On the other hand, when the concentration exceeds 2 atom %, the luminous intensity is weak due to concentration quenching. This occurs when the numbers of luminescence center is too large so that the mean-free path for impact electrons (hot electrons) becomes shorter and the collision probability of electrons with luminescence center is lower.

Fig. 6 Relationship between the luminous intensity and electric field with Tb ion concentration as parameter

Fig. 6 shows the relation between the luminous intensity and the electric field with Tb ion concentration as parameter. The result from this graph agrees well with that from the earlier graph of Fig. 5, that is the highest luminous efficacy is obtain at 2 atom %.

In Fig. 5 and Fig. 6 the vertical axis shows the luminous intensity in arbitrary units but 10^3 unit is approximately equal to 3.0 cd/m^2 .

Fig. 7 and Fig. 8 show the same graphs for the Sm ion. The result shows that the most suitable concentration of Sm ions is 3 atom %.

Fig. 9 and Fig. 10 show the same graphs for the Tm ion. In this case the most suitable concentration of Tm ions is 2 atom %.

Figs. 11, 12 and 13 show respectively the emission spectra of TbF_3 , SmF_3 , TmF_3 doped into ZnS.

Fig. 7 Relationship between the luminous intensity and concentration of Sm ion with applied voltage as parameter

Fig. 8 Relationship between the luminous intensity and electric field as parameter of Sm ion's concentration

These figures indicate that the luminous intensity of the peak wavelength is about 100. According to these graphs, each spectral line corresponds to the following transitions (see Transition Table).

Figs. 14, 15 and 16 show typical spectra obtained by the blending of two kinds of rare-earth fluoride. (for example TbF_3 and SmF_3 , SmF_3 and TmF_3 , TbF_3 and TmF_3).

Fig. 9 Relationship between the luminous intensity and concentration of Tm ion as parameter of applied voltage

Fig. 10 Relationship between the luminous intensity and electric field as parameter of Tm ion's concentration

Fig. 11 Emission spectrum on ZnS; TbF₃

Fig. 12 Emission Spectrum of ZnS; SmF₃

Fig. 13 Emission spectrum of ZnS; TmF₃

Transition Table

Material	Peak Wavelength	Transition Levels	Luminous Intensity Ratio
Tb ³⁺	4875	⁵ D ₄ — ⁷ F ₆	29
"	5450	⁵ D ₄ — ⁷ F ₅	100
"	5840	⁵ D ₄ — ⁷ F ₄	13
"	1190	⁵ D ₄ — ⁷ F ₃	6
Sm ³⁺	5650	⁴ G _{5/2} — ⁶ H _{5/2}	8
"	6050	⁴ G _{5/2} — ⁶ H _{7/2}	28
"	6500	⁴ G _{5/2} — ⁶ H _{9/2}	100
Tm ³⁺	4800	¹ G ₄ — ³ H ₆	100
"	6600	¹ G ₄ — ³ H ₄	63

Fig. 14 Emission Spectrum of ZnS; TbF₃, SmF₃

It should be noticed that the spectrum changes with the blended ratio as may be seen by the difference between the solid lines and dotted lines. It must be emphasized that the mechanism of these EL cells involves radiative transitions from localized states, so there is little interaction between one doped ion and another. Thus a desired spectrum can be obtained by summing two individual spectra with suitable mixture ratio.

Fig. 15 Emission Spectrum of ZnS; SmF₃, TmF₃

Fig. 19 Emission spectrum of ZnS; SmF₃, TmF₃ at different applied voltages (2)

Fig. 16 Emission spectrum of ZnS; TbF₃, TmF₃

Fig. 17 Emission spectrum of ZnS; ZbF₃, SmF₃ at different applied voltage

Fig. 18 Emission spectrum of ZnS; SmF₃, TmF₃ at different applied voltages (1)

Fig. 20 Relationship between the relative luminous intensities at each of the peak wavelengths and applied voltage of ZnS; TbF₃, SmF₃

Fig. 21 Relationship between the relative luminous intensities at each of the peak wavelengths and applied voltage of ZnS; SmF₃, TmF₃ (1)

Figs. 17 to 19 show the change of the relative emission spectra with applied voltage.

Figs. 20 to 23 show the dependence on applied voltage of the relative luminous intensities at each of the peak wavelengths of two rare-earth ions from ZnS; SmF₃ TbF₃ and ZnS; SmF₃, TmF₃ and

Fig. 22 Relationship between the relative luminous intensities at each of the peak wavelengths and applied voltage of ZnS; SmF₃, TmF₃ (2)

Fig. 23 Relationship between the relative luminous intensities at each of the peak wavelengths and applied voltage of ZnS; TbF₃, TmF₃

ZnS; TbF₃, TmF₃ cells. This dependence can be expressed by the following formula in the case of the ZnS; TbF₃, SmF₃ EL cell.

$$I(\text{Tb})/I(\text{Sm}) = A \exp(-bV^{1/2}) \quad ***$$

where $I(\text{Tb})$; luminous intensity of TbF₃ at 5450 Å
 $I(\text{Sm})$; luminous intensity of SmF₃ at 5500 Å
 A, b ; constant

The color coordinates of the emission from both individual and blended cells are plotted in the CIE chromaticity diagram in Fig. 24. The color shift resulting from a change in applied voltage is also shown. This shift is attributed to the change of the hot electron distribution in the ZnS films to higher energies with increasing voltage.

Fig. 24 The color coordinates of the emission from individual and blended cells

4. Conclusion

The emission color of the blended EL cell may be changed by altering the blending ratio. Thus any emission color can be obtained by optimizing the blending ratio and by cascading cells. Using the latter technique even a white output is possible. The emission color of EL cells also changes an irregular way with applied voltage.

Acknowledgements

The authors wish to thank Professor Gambling of Southampton University. This work was supported in part by Scientific Research Grant-In-Aid (Special Project Research "Optical Guided-Wave Electronics") from the Ministry of Education, Science and Culture, Japan.

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Appendix

$$\log I(\text{Sm}) = -C_{\text{Sm}}V^{1/2} + \log B_{\text{Sm}}$$

$$\log I(\text{Tb}) = -C_{\text{Tb}}V^{1/2} + \log B_{\text{Tb}}$$

$$C_{\text{Sm}}, C_{\text{Tb}}, B_{\text{Sm}}, B_{\text{Tb}}; \text{Constant}$$

$$\log [I(\text{Tb})/I(\text{Sm})] = (C_{\text{Sm}} - C_{\text{Tb}})CV^{-1/2} + \log (B_{\text{Tb}}/B_{\text{Sm}})$$

Received 11 May, 1979; Revision Received 18 June, 1979