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Electroluminescence from Polysilane Film Doped with Europium Complex

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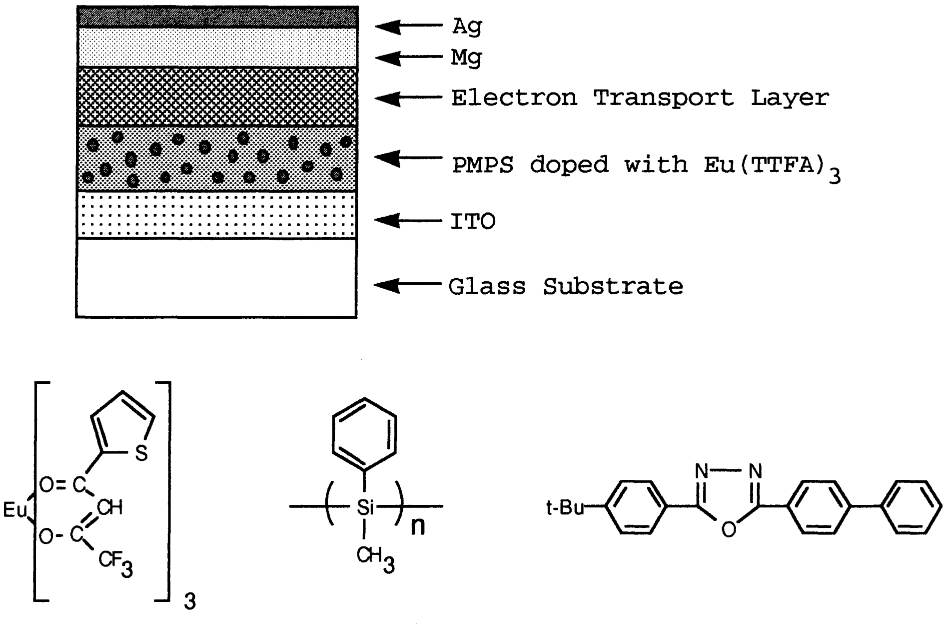
Electroluminescent devices with poly(methylphenylsilane) film doped with Eu^{3+} complexes were fabricated. The cell structure of glass substrate/indium-tin-oxide/polysilane/electron transport layer/Mg/Ag was employed. Sharp red electroluminescence of europium ion was obtained at dc bias voltage of over 12 V.

Electroluminescence (EL) in organic crystals has been investigated from fundamental as well as practical point of view.[1)] Practically, however, electroluminescence from organic single crystal is less attractive due to their high drive voltage (over 100 V). Recently Tang and VanSlyke introduced an injection type EL device with organic thin films.[2,3)] They used a hole transport layer for hole injection from electrode into the emitting organic layer. The drive voltage, in this case, is as low as a few volt, which promised the practical application of such devices. Adachi and his co-workers showed the utility of a variety of organic fluorescent dyes as emitter materials in EL devices.[4-6)] In these examples, owing to the broad nature of the luminescence spectra of organic dyes, the luminescent colors are somewhat dull and would not be best suited for actual display applications.

Our objective is to obtain bright and efficient EL devices with a narrow luminescent spectral band width, and we have already demonstrated the utility of terbium complex as a sharp green-light emitter in EL cell.[7)] In the present investigation, we report the suitability of a europium ion (Eu^{3+}) complex as a red-light emitter. This metal ion exhibits red photoluminescence with very sharp spectral bands and has been commonly used as a red phosphor in cathode ray tubes. Various Eu^{3+} complexes exhibit photoluminescence with high quantum efficiency and the properties of its complexes have been well studied in the solid state as well as in solutions.[8)] Since non-volatile Eu(thenoyltrifluoroacetonate)$_3$ (Eu(TTFA)$_3$) was employed, we developed a new cell structure. The Eu complexes were dispersed in a polymer thin film placed between indium-tin-oxide (ITO) electrode and electron transport layer as shown in Fig. 1.



Eu(TTFA)$_3$ PMPS PBD

Fig. 1. Configuration of EL cell and molecular structures of organic compounds.

The polymer employed was poly(methylphenylsilane) (PMPS) which transports holes with a high mobility of 10^{-4} cm^2/Vs at room temperature.[9)] The electron transport layer was a thin film of oxadiazole derivative (PBD) which is used as an electron transport layer in organic EL devices.[5,6)] PMPS layer (600 Å) was first spin coated by using a THF solution of PMPS and Eu onto an ITO-coated glass substrate with a sheet resistance of 10 Ω/□ (Furuuchi Chemistry Co. Ltd.), then PBD was vacuum deposited at $3x10^{-6}$ Torr to the thickness of 600 Å. Finally 100 Å of magnesium and 1500 Å of silver top electrode were successively deposited at the same vacuum pressure. The substrate was kept at room temperature and deposition rates for PBD, Mg, and Ag were 3-4 Å/s. The emitting area was 0.5x0.5 cm^2. Luminance was measured with a Minolta luminance meter LS-110 at room temperature under ambient atmosphere.

Red emission was observed from the EL cell with 20 wt% $Eu(TTFA)_3$ in the PMPS layer when operated in a continuous dc mode for a forward bias (connected ITO positive). Figure 2 shows typical luminance-current-voltage curves for an EL cell. The luminance was proportional to the injection current as well as the bias voltage. Luminescence started at 12 V and the maximum intensity of 0.3 cd/m^2 at 18 V was achieved. Although the luminescent mechanism is not fully understood, it is likely that the Eu complexes in PMPS layer are excited by the recombination energy of holes and electrons which are injected from anode and cathode, respectively. The injection of holes is made possible by employing hole transport PMPS and injection of electrons by PBD layer. PBD layer also covers pin holes which may exist in the thin polymer layer. Electron transport in PMPS layer should occur through the doped $Eu(TTFA)_3$, and the recombination takes place dominantly in the PMPS layer. Since the color of EL varied with the doping amount of $Eu(TTFA)_3$, the recombination area seems to be dependent on the Eu content which influences the electron transport property of the PMPS layer. EL color was blue in the absence of $Eu(TTFA)_3$, which may be attributed to EL from PMPS itself or a recombination of electrons and holes at a PMPS/PBD p-n junction. The details are now under investigation.

The EL intensity in this system is rather low, but the optimization of the cell structure should bring about the higher intensity. Furthermore, since the structure of the doped complex and its concentration determine the charge transport properties of the PMPS layer, the proper choice of the dopant complex and its concentration should lead to higher EL efficiency. The cell structure has an advantage of application to other emitters which may be non-volatile.

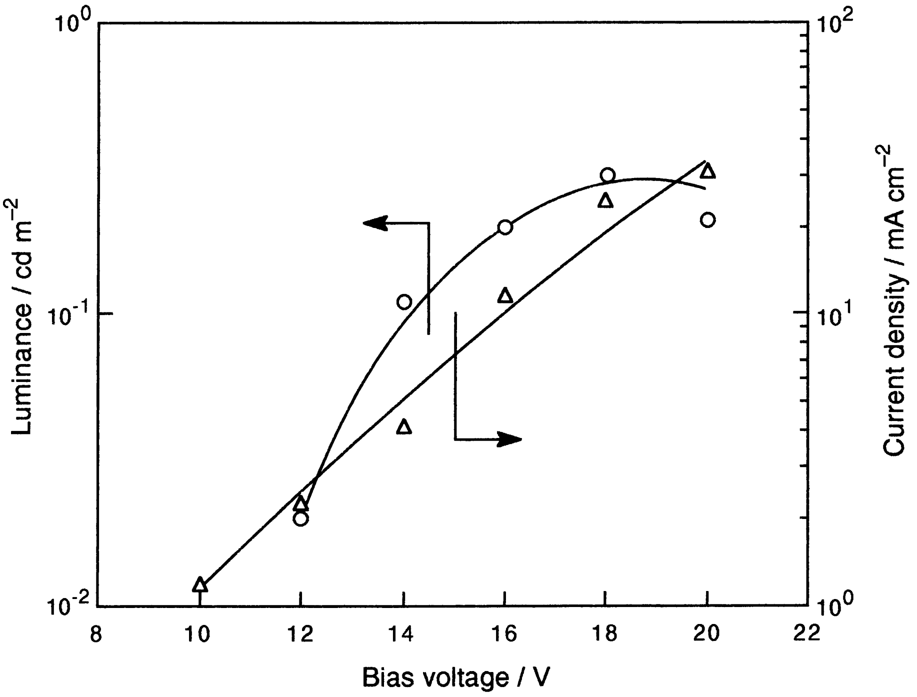


Fig. 2. Luminance-current-voltage characteristics for an ITO/PMPS/PBD/Mg/Ag cell.

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