Organic electroluminescent device having a hole conductor as an emitting layer

Adachi, Chihaya
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University

Tsutsui, Tetsuo
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University

Saito, Shogo
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University

https://hdl.handle.net/2324/19439

出版情報：Applied Physics Letters. 55 (19), pp.1489-1491, 1989-10-09. American Institute of Physics
バージョン：

Organic electroluminescent device having a hole conductor as an emitting layer

Chihaya Adachi, Tetsuo Tsutsui, and Shogo Saito
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816, Japan

(Received 8 May 1989; accepted for publication 31 July 1989)

We have succeeded in fabricating a novel thin-film electroluminescent device with a luminescent hole transport layer as an emitter. The cell structure is composed of an indium-tin-oxide substrate, a luminescent hole transport layer (emitter), an electron transport layer, and a MgAg electrode. The most essential feature of our device owes for adoption of an oxadiazole derivative as an electron transport layer. The emission intensity of 1000 cd/m^2 was achieved at a current of 100 mA/cm^2.

Recently it has been reported that organic electroluminescent (EL) devices composed of multilayer structures of organic thin films have high brightness and operate at low drive voltages.[1-3] Excellent performance of the EL cells originates from the insertion of a hole transport layer and/or an electron transport layer between the electrode and the emitting layer. Particularly the insertion of a hole transport layer of aromatic diamine which possessed high hole mobility between an electrode and an organic emitting layer was crucial for improving the emission efficiency, as shown by Tang and VanSlyke.[1] In previous reports, we proposed a novel thin-film EL cell with a three-layer structure [indium-tin-oxide (ITO) substrate/hole transport layer/emitting layer/electron transport layer/MgAg electrode] based on the idea that the insertion of an electron transport layer is also important for achieving high brightness if one tries to use a variety of emitter materials.[2,3] Thus, we showed that the introduction of the hole and electron transport layers made possible an enhancement in efficiency of hole and electron injections.[4]

From our studies on two- and three-layer EL cells, we have concluded that the carrier transport layer has three major functions. First, the transport layer assists effective carrier injection from the electrode into the emitting layer accompanied by a lowering of drive voltage. Second, it blocks the carriers which pass through the emitter layer and thus controls the recombination process.[1] Finally, it helps prevent the quenching of molecular excitons created by the recombination of holes and electrons at the boundary between an emitter and an electrode.[5] All of these effects are expected to result in high emission efficiency, although we cannot specify which is the most dominant at this stage.

From the view point of material selection, an appropriate combination of carrier transport materials and emitter materials is necessary. As all the emitter materials in previous studies possessed an electron transporting tendency, the insertion of a hole transport layer was effective for achieving high brightness, as shown in the diamine/emitter system.[1] On the other hand, if appropriate electron transport materials are available, hole transport materials with intense luminescence, in principle, can play the role of an emitter. This type of EL cell, however, has been impracticable owing to a lack of outstanding electron transport materials.

In this letter we report a novel thin-film EL device with a luminescent hole transport layer as an emitter. The cell is composed of ITO/luminescent hole transport layer (emitter)/electron transport layer/MgAg. In other words, a hole transport layer and an emitter layer in the three-layer structure was combined into a single layer. The most essential feature of this device is the adoption of the oxadiazole derivative as an electron transport layer. The recombination of electron-hole pairs occurs primarily inside the hole transport emitting layer, resulting in emission which is characteristic of the luminescent hole transport layer. The success of this type of EL cell spreads the choice of emitter materials over a variety of organic hole conductors.

Figure 1 shows the structure of the EL device and the molecular structure of the materials used in this study. The

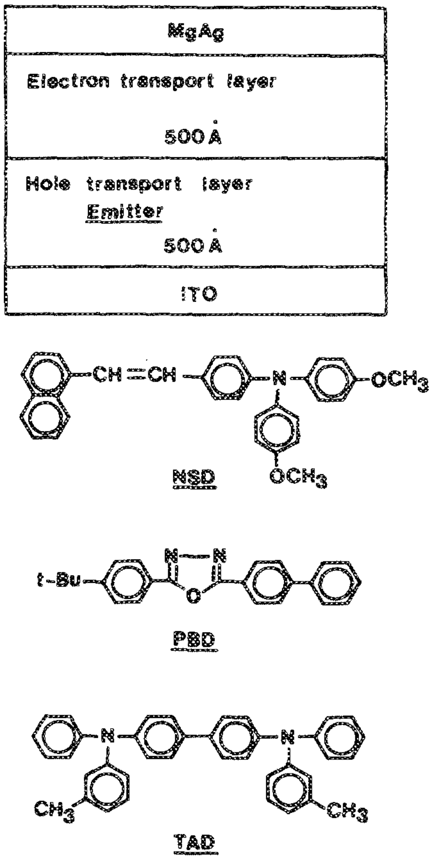

FIG. 1. Structure of the EL device and the molecular structures of materials used in this study.

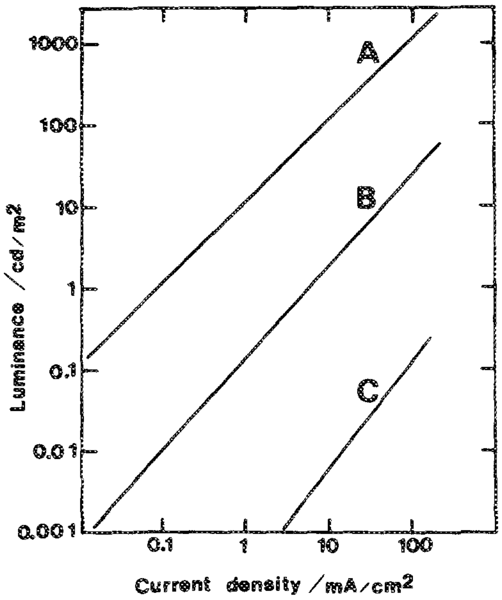

FIG. 2. Luminance-current characteristics in three EL cells. (A) ITO/NSD/PBD/MgAg, (B) ITO/TAD/NSD/MgAg, and (C) ITO/NSD/MgAg.

EL cells were fabricated by vacuum deposition at a pressure of 6.0×10^{-7} Torr at room temperature. First, a luminescent hole transport material, a triphenylamine derivative (NSD)[6] which possesses intense green fluorescence in its solid state, was deposited onto a precleaned ITO-coated glass substrate.[7] Second, an electron transport material, a oxadiazole derivative (PBD),[8] was deposited. Lastly, a MgAg alloy was deposited by codeposition from two separate sources on the PBD layer. The deposition rate for the organic layers was about 2–4 Å/s. The emitting area in the cells was 0.2×0.2 cm^2. Both of the deposited films were semitransparent and showed no birefringence when viewed under a cross-polarized microscope. In addition, they appeared to be almost pinhole-free dense films. All measurements of EL characteristics were carried out in a vacuum of 10^{-3} Torr or in a nitrogen ambient. Luminance in units of cd/m^2 was measured by a luminance meter (TOPCON BM-8, measuring field 2°).

The EL cell (ITO/NSD/PBD/MgAg) behaved like a diode at a high bias field ($\sim10^6$ V/cm). A so-called rectification effect was observed in the device where the forward bias voltage corresponded to positive on the ITO electrode. The observed large current is attributable to carrier injection from the electrodes into the organic layers at the high bias field.[9] In other words, both the NSD and the PBD layers become sufficiently conductive at the injection mode. A steady current of more than 100 mA/cm^2 was observed at a dc voltage of 16 V. The EL emission could be detected only for a forward bias and the threshold voltage for emission was as low as 4.0 V.

To understand the role of the PBD layer, three types of EL cells were tested: (A) ITO/NSD(500 Å)/PBD(500 Å)/MgAg, (B) ITO/TAD(500 Å)/NSD(500 Å)/MgAg, and (C) ITO/NSD(500 Å)/MgAg. Here, TAD means the hole transporting diamine derivative shown in Fig. 1.[10] Figure 2 shows the luminance-current characteristics of three cells. Evidently, the emission efficiency of the EL cell with inserted PBD layer (A) was 10^4 times larger than the EL cell composed of a NSD single layer (C). On the other hand, the emission efficiency in the TAD-inserted EL cell (B) was only about 10^2 times larger than that of the EL cell without the TAD layer (C). This result verifies that the insertion of the PBD layer is responsible for a tremendous increase in emission efficiency of this emitter. In the case of the NSD single layer (C), the recombination and the emission sites must be located near the cathode since NSD, which contains a triphenylamine unit possesses a hole transporting ability.[10] Thus, the insertion of the appropriate electron transport layer PBD resulted in a high emission efficiency because of the three reasons mentioned before. It should be emphasized again that the EL emission from luminescent hole conductors became really feasible by selection of the appropriate electron transport materials.

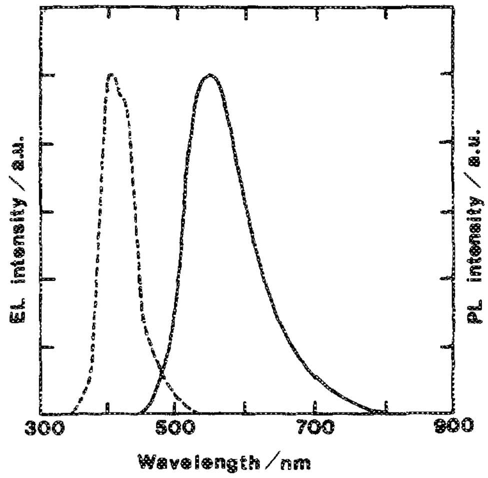

FIG. 3. Photoluminescence and EL spectra. Solid line: EL spectrum in (ITO/NSD/PBD/MgAg) cell. Broken line: PL spectrum in vacuum-deposited PBD film.

In the two-layer cell (A), the luminance was linearly proportional to the injection current in the current range from 10^{-3} to 100 mA/cm^2. Evidently, a current-dependent mechanism is operative in this EL cell. In addition, this dependence suggested that the prompt EL process was dominant rather than a delayed EL process.[11] An emission intensity of ~1000 cd/m^2 was achieved at a current of 100 mA/cm^2 and a voltage of 16 V. In this case, the luminous efficiency is 0.2 lm/W and this value corresponds to one of the highest emission efficiencies of the EL devices yet reported.

The emission spectrum also demonstrated the role of the PBD layer. The emission spectrum of the EL device is shown in Fig. 3. The peak of EL emission was at 520 nm and the color was green. This emission spectrum corresponds exactly to the photoluminescence (PL) spectrum of the NSD thin film. Moreover, no emission from PBD whose evaporated film shows a PL peak at 390 nm was observed. Therefore, EL emission in this cell is ascribed to luminescence from the singlet excited state which is produced by the recombination of holes and electrons in the emitter layer. This result indicates that the injection of holes from the NSD layer into the

PBD layer is forbidden, although the injection of electrons from the PBD layer into the NSD layer is possible. Consequently, the PBD layer has been proven to fulfill the function of a so-called electron transporting layer in this EL cell. It is noteworthy that the PBD layer has a large exciton energy in comparison with that of the NSD layer, as is assumed from their PL spectra. The excitons created in the NSD layer are expected to be blocked by the PBD layer; if the exciton energy of the electron transport layer is smaller than that of NSD layer, the transfer of excitons into the electron transporting layer easily occurs and a number of excitons which contribute to the radiative decay are decreased.

In conclusion, we have succeeded in obtaining a bright organic electroluminescent device having a luminescent hole transporting layer as an emitter. Excellent performance of the EL cells was attributed to the PBD layer which operated as an excellent electron conductor in our system. Our result demonstrates that one now apply a large variety of luminescent materials for an emitter regardless of their carrier transporting tendencies, if one takes account of inserting properly selected hole and/or electron transporting layers.

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).

[2] C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, Jpn. J. Appl. Phys. **27**, L269 (1988).

[3] C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, Jpn. J. Appl. Phys. **27**, L713 (1988).

[4] C. Adachi, S. Tokito, M. Morikawa, T. Tsutsui, and S. Saito, Proceedings of the 4th International Workshop on Electroluminescence, October 11–14, 1988, Tottori, Japan (Springer, to be published).

[5] K. C. Kao and W. Hwang, *Electrical Transport in Solids* (Pergamon, New York, 1981), p. 486.

[6] This compound was kindly donated by RICOH Co. Ltd., Shizuoka, Japan.

[7] ITO was purchased from Hoya Co. Ltd., Tokyo, Japan. The thickness of the ITO layer is 1000 Å and sheet resistance is ~20 Ω/□.

[8] This compound was purchased from Dojindo Laboratories Co. Ltd., Kumamoto, Japan.

[9] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Oxford University, New York, 1982), p. 273.

[10] M. Abkowitz and D. M. Pai, Philos. Mag. B **53**, 193 (1987).

[11] W. Hwang and K. Kao, J. Chem. Phys. **60**, 3845 (1974).