Enhancement Properties of Organic Electroluminescence Device Using Electropolymerized Poly(3-*n*-octylthiophen) Thin Film

Tetsuya Osaka, Shin-ichi Komaba, Kenichiro Fujihana, Naoki Okamoto, and Norihiko Kaneko†
Department of Applied Chemistry, School of Science and Engineering; Kagami Memorial Laboratry for Materials Science and Technology, Waseda University, Shinjuku-ku, Tokyo 169
†*R & D Division, Casio Computer Co., Ltd., Imai 3-chome, Ome, Tokyo 198*

(Received August 9, 1995)

By using electropolymerized poly(3-n-octylthiophen) (PAT8) film as a hole transporting layer, the light-emission of an organic electroluminescence layer of poly(N-vinylcarbazole) dip-coating layer doped with 2,5-bis(1-naphthyl)-1,3,4-oxadiazole and 3-(2'-benzothiazolyl)-7-diethylaminocoumarin, was remarkably enhanced as compared with the layer without PAT8 layer. The addition of the hole transporting layer made the turn-on bias reduce and the emission intensity increase to be 600 cd m^{-2}.

For enhancement of the organic electroluminescence (EL) device, Tang *et al.*[1] reported that a double-layer construction of a hole transporting layer and an emission layer achieved a high brightness over 1000 cd m^{-2} and a low turn-on bias about 10 V. Since then, many studies on improving EL characteristics on the basis of this double-layer construction were attempted. Recently, in particular, EL devices using amine derivatives[2] or phthalocyanines as a hole transporting layer were reported to exhibit enhancements of emission efficiency and durability. By using spin-coated polyaniline film as the hole transporting layer, a flexible EL device was demonstrated by Heeger *et al.*[3] Spin-coated poly(thiophen derivative) films was applied to EL emission layers by many researchers.[4] Previously, we reported an EL device composed of single layer using electro-polymerized luminescent poly(3-substituted thiophen).[5] Yamamoto *et al.*[6] applied a vacuum-deposited polythiophen film and Saito *et al.*[7] attempted an electropolymerized poly(3-methylthiophen) film as a hole transporting layer. In this letter, we also apply an electropolymerized film to a hole transporting layer of an EL device, and try to show the possibility of EL device using this electropolymerized poly(thiophen derivative) film to use a hole transporting layer.

The poly(3-octylthiophen) (PAT8) film was electrochemically deposited on an ITO glass in acetonitrile solutions, as already reported.[5] The EL emission layer, a poly(N-vinylcarbazole) (PVCz) film dispersed with 2,5-bis(1-naphthyl)-1,3,4-oxadiazole (BND) and 3-(2'-benzothiazolyl)-7-diethylaminocoumarin (coumarin 6), was formed by a dip-coating method.[8] This emission layer is designated as PVCz layer (thickness 50~60 nm). An aluminium electrode for rectifying contact was deposited by vacuum evaporation onto the emitting layer. The emission area was 4 mmϕ or 2 mmϕ . All the measurements were carried out at room temperature in air. The film thicknesses of the dip-coated emission layer and electropolymerized PAT8 hole transporting layer were to be 50 ~60 nm and 10~80 nm, respectively. PAT8 film was relatively uniform film. The band gap of PAT8 film was 2.1 eV. Schematic structures of the EL devices were demonstrated in Figure 1. A positive bias was applied to the ITO against the Al rectifying contact.

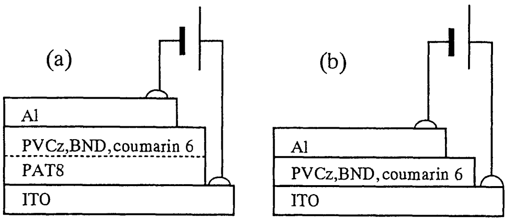

Figure 1. Device configurations of (a) double-layers of electro-polymerized layer and dip-coated layer and (b) mono-layer of dip-coated layer between cathode and anode.

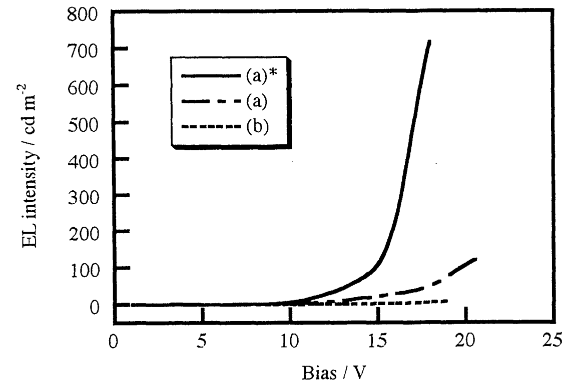

Figure 2. EL characteristics of the devices using (a) PAT8 and dip-coated emitting layers, (a)* dried PAT8 and dip-coated emitting layers and (b) dip-coated film only as active layer. The thicknesses of PAT8 and PVCz layers are 20 nm (1min deposition) and 60 nm, respectively.

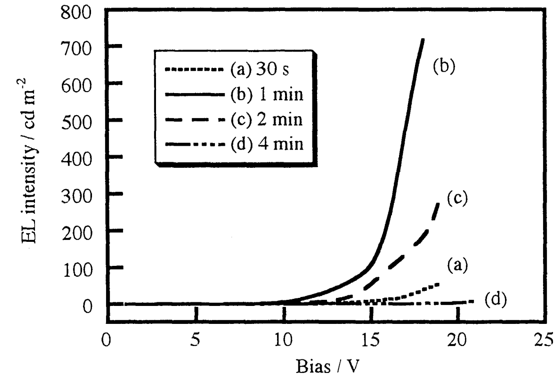

Figure 3. EL characteristics of the double-layer device using a dried PAT8 film as a function of electropolymerization periods of (a) 30 s, (b) 1 min, (c) 2 min and (d) 4 min.

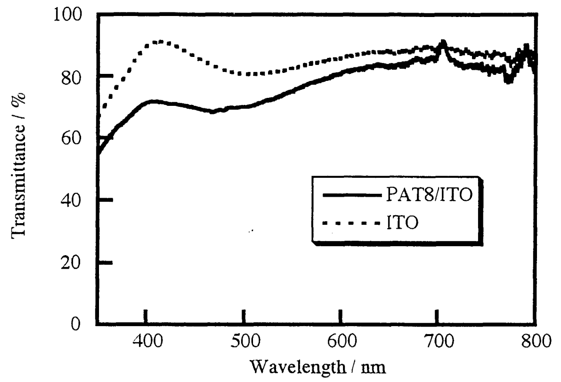

Figure 4. Transmittance spectra of electropolymerized PAT8 (dried in vacuum at 150 ℃)/ITO and ITO substrates.

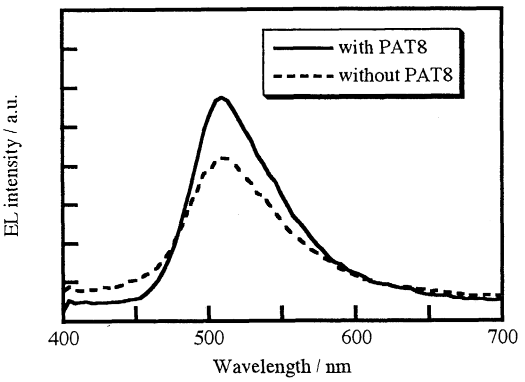

Figure 5. EL spectra of the double-layer device with a dried PAT8 film and the mono-layer without PAT8 film.

Figure 2 shows the dependence of EL intensity (L) on bias (V) of the devices of PVCz layer of 60 nm thick with or without the PAT8 layer of 20 nm thick. For the device without the PAT8, the light emission turns on at 13 V and the maximum intensity is about 10 cd m^{-2}. While, the device with the PAT8 layer demonstrates more bright emission which starts at 8 V and higher intensity of *ca.* 100 cd m^{-2}. The turn-on bias is reduced 5 V and the EL intensity is ten times by adding PAT8 layer between ITO and PVCz. Furthermore, prior to the formation of the PVCz layer, the electropolymerized PAT8 film was dried under vacuum at 150 ℃. This drying process of the PAT8 improves the EL characteristics extremely as is seen in Figure 2 (a). The light emission starts at 8 V which is lower than that of the device(b), and the intensity reaches 700 cd m^{-2} which is higher about seventy times. From now on, all the double-layer device is formed with this drying process.

The dependence of V-L curves on the charge amount of PAT8 is shown in Figure 3. The PAT8 layers were galvanostatically formed at 80 μA cm^{-2} with various deposition periods. In Figure 3, the thickness or charge amount of PAT8 layer was shown with the polymerization time. Polymerization time of 1 min (20 nm thick) gives the most excellent EL characteristics, and the thicker PAT8 layers, *i.e.*, over 1 min deposition time, make a turn-on bias increase and an emission intensity decrease. The increase of resistance of thicker PAT8 film between ITO and Al would be the cause to make the EL characteristics worse. However, too thinner PAT8 layer, as is seen in the 30 s case, also makes the EL characteristics worse as well as the layer without PAT8 layer. Thus, it seems to be necessary for a hole transporting material to have a proper thickness to act as a capacitor. The thickness of the most superior layer is formed at 1 min (20 nm).

Figure 4 shows the transmittance spectra of a PAT8 film deposited onto ITO glass and an ITO glass only. This PAT8 film was prepared by the same conditions as indicated in Figure 3(b). Figure 4 clearly indicates that the electropolymerized PAT8 is comparatively transparent in the region of visible light as compared with the electropolymerized poly(3-methylthiophen) film which Saito *et al.*[7] used as hole transporting layer.

The emission spectrum of the device of PVCz/PAT8 (see Figure 1(a)) is shown in Figure 5 and it is also the same of PVCz layer only (Figure 1(b)). The EL spectrum is similar to the PL spectrum of coumarin 6 in methanol solution. Since the PAT8 film does not affect the emission spectrum, the PAT8 layer acts as a transparent hole transporting layer, which is worked more efficectively as compared with previous reported results.[7]

In conclusion, the device of PVCz/PAT8 double-layer shows high brightness and low turn-on bias, where the PAT8 layer acts as an high effective hole transporting layer.

This work was financially supported by the Casio Science Promotion Foundation and a Grant-in Aid for Scientific Research on Priority Areas, the Ministry of Education, Science and Culture of Japan.

References

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913(1987).
2 Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, and K. Imai, *Appl. Phys. Lett.*, **65**, 807(1994).
3 G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature*, **357**, 477(1992).
4 M. Berggren, O. Inganäs, G. Gustafsson, J. Rasmusson, M. R. Andersson, T. Hjertberg, and O. Wennerström, *Nature*, **372**, 444 (1994).
5 S. Komaba, K. Fujihana, N. Kaneko, and T. Osaka, *Chem. Lett.*, **1995**, 923.
6 T. Yamamoto, T. Inoue, and T. Kanbara, *Jpn. J. Appl. Phys.*, **33**, L250 (1994).
7 S. Hayashi, H. Etoh and S. Saito, *Jpn. J. Appl. Phys.*, **25**, L773(1986).
8 Y. Mori, H. Endo and Y. Hayashi, *Ouyoubutsuri*, **61**, 1044(1991) (in Japanese).