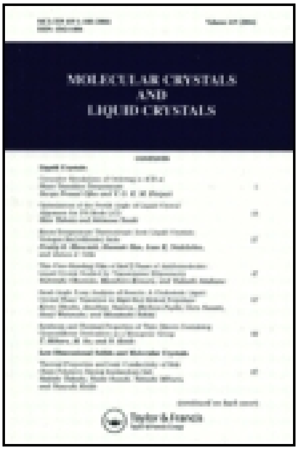

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Hiroyuki Suzuki [a] & Satoshi Hoshino [a]

[a] NTT Basic Research Laboratories, Atsugi, Kanagawa, 243-01, Japan

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Electron Injection Process in Light-Emitting Diodes Made from Polysilanes as Manifested by Incorporation of Electron Injection Layers

HIROYUKI SUZUKI and SATOSHI HOSHINO
NTT Basic Research Laboratories, Atsugi, Kanagawa, 243-01, Japan

The electron injection process was investigated for poly(methylphenylsilane) (PMPS) in two-layer light-emitting diodes (TL-LEDs) composed of a PMPS film and a vacuum-deposited film of oxadiazole molecules (OXDs). The latter acts as an electron injection layer. The basic characteristics of the TL-LEDs were markedly better than those of single-layer LEDs. The magnitude of the accompanying red-shift in the EL spectrum coincides with the energy difference between the conduction band and/or the one-dimensional exciton level of PMPS, and the conduction band of an OXD layer. This study has revealed that electron injection in PMPS is an energy selective process occurring via surface defect levels which exist below the conduction band of the OXD layer in terms of energy, and that the electron-hole recombination takes place in the PMPS layer near the interface with the OXD layer.

Keywords: organic LEDs; polysilanes; electron injection; oxadiazoles

INTRODUCTION

Polysilanes (PSs) are *quasi* one-dimensional (1-D) materials with delocalized σ-conjugated electrons along the polymer backbone chain.[1] In contrast to π-conjugated polymers, Ps exhibit sharp strong absorption and luminescence, usually in the near-ultraviolet (NUV) region. Recently near-ultraviolet electroluminescence (NUV-EL) was observed from such typical PSs as poly(methylphenylsilane) (PMPS)[2-5] and dialkyl PSs.[6] This NUV-EL is a novel tool for studying their electronic properties and presents the possibility of employing them in a solid-state NUV light source. Previous studies have clarified basic aspects of the EL process in PSs[3-6]. One of the essential features of their EL is that it is emitted near the interface between the polymer and the electron injecting electrode (EIE) because of their strong unipolar (hole conductive) nature[3-6]. An effective way of greatly improving the EL efficiency is therefore to increase the supply of electrons into PSs. However, the electron injection process in PSs has yet to be described in detail. In this work, we studied the electron injection process in PMPS for two-layer LEDs (TL-LEDs) with an electron injection layer made from a vacuum-deposited thin-film of oxadiazole molecules (OXDs).

EXPERIMENTAL

The structure of the TL-LEDs we used is shown in Fig. 1. The methods used for fabricating the PMPS layers (90 nm thick) and Al electrodes have been reported elsewhere[3]. An electron injection layer made from a thin OXD film (70 nm thick) was vacuum deposited on the PMPS layer. We used two kinds of OXD, BBD and BND (Fig. 1), which were chosen from five OXDs based on their electronic structure and on the optical quality of the thin-films.

RESULTS AND DISCUSSION

<u>TL-LEDs with a BBD Layer</u>

The I-V-EL intensity curve of a TL-LED with a BBD layer (TL-LED/BBD) at

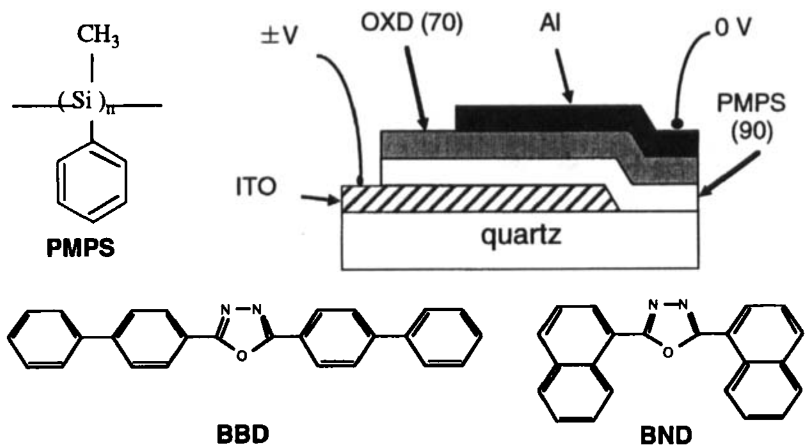

FIGURE 1 The structure of TL-LEDs and the materials used.

R.T. (Fig. 2(a)) indicates noticeable improvements in its basic characteristics; the turn-on electric-field strength ($5x10^5$ V/cm) is half that for single-layer PMPS-based LEDs (SL-LEDs), and the total EL intensity double that for SL-LEDs. These are ascribable to the combined effects of improvements in electron injection and carrier confinement, and separation of the emissive layer from the EIE. As with SL-LEDs, the EL spectrum of a TL-LED/BBD is composed only of a broad emission in the visible region, and is different from the PL spectrum of either PMPS or BBD (Fig. 2(b)). Note that a red-shift and a decrease in intensity at wavelengths longer than 550 nm were observed in the EL spectrum of the TL-LED/BBD in comparison with that of the SL-LED.

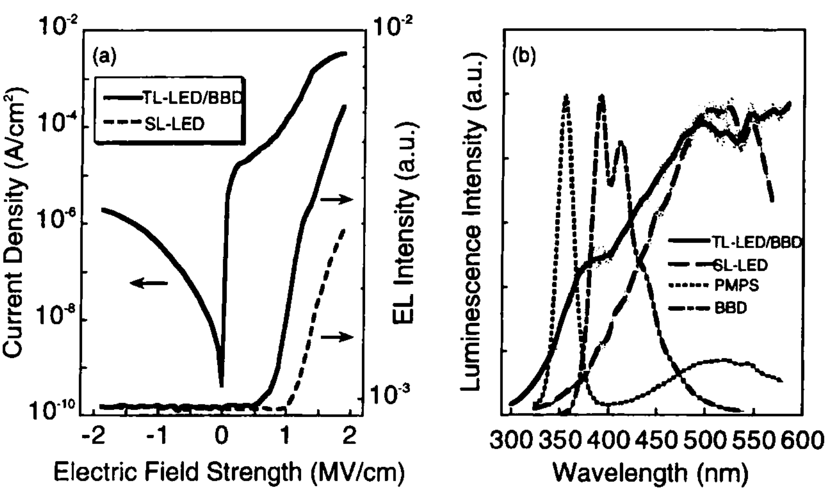

FIGURE 2 The I-V-EL intensity curve (a) and the EL spectrum (b) of a TL-LED/BBD at R.T.

The temperature dependence of the EL characteristics (Fig. 3(a)) shows that a temperature decrease causes an increase in the total EL intensity (by three orders of magnitude between R.T. and 140 K) and in the EL turn-on voltage (8 V at R.T. and 13 V below 230 K). The NUV-EL from PMPS also becomes detectable at temperatures below 230 K (Fig. 3(b)), although the EL spectrum of the TL-LED/BBD is mainly composed of a broad VIS-EL. The temperature dependence of the PL spectra for a BBD film confirms that the EL of the TL-LED/BBD originates from the PMPS layer.

TL-LEDs with a BND Layer

A TL-LED with a BND layer (TL-LED/BND) exhibits similar temperature dependent EL characteristics to a TL-LED/BBD. The EL spectrum at 100 K is also composed of NUV-EL and VIS-EL (Fig. 4). We confirmed that the EL was emitted from the PMPS layer by measuring the temperature dependence of the PL spectra for a BND film.

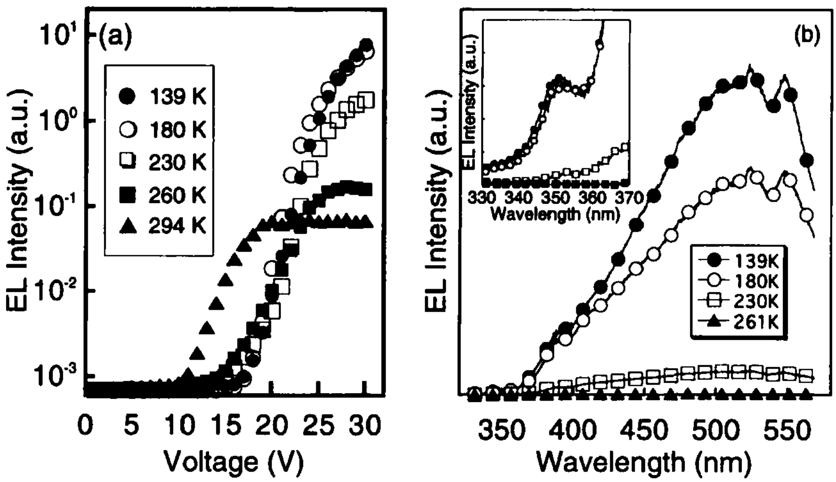

FIGURE 3 The temperature dependence of the V-EL curve (a) and the EL spectrum (b) for a TL-LED/BBD.

The Electron Injection Process

The electron injection process in PMPS is discussed based on a schematic energy diagram of the TL-LED (Fig. 5). The fact that the EL is only observed from the PMPS layer indicates that the electron-hole recombination takes place in the PMPS layer since the band gap is larger for PMPS than for the OXDs we used, and so the excitation energy transfer from the OXDs to PMPS is negligible. We thus conclude that the EL is emitted from the PMPS layer near the PMPS-Al interface because PMPS is strongly unipolar. The EL spectrum exhibits a red-shift when an OXD layer is introduced into the PMPS-LEDs (Fig. 2(b)), and the magnitude of this spectral shift coincides with the energy difference between the conduction band and/or the 1-D exciton level of PMPS, and the conduction band of the OXD layer (Fig. 4). This observation

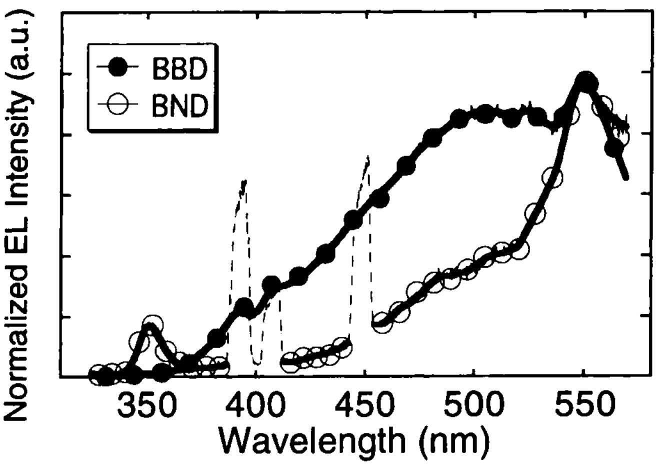

FIGURE 4 The dependence of the EL spectrum on the OXD layer for the TE-LED at 100 K. The narrow emissions shown in broken lines are sparks.

suggests that the electron injection is an energy selective process occurring via surface defect levels which exist below the conduction band of the OXD layer in terms of energy, and thus the probability of these electrons having energy enough to generate *quasi* 1-D excitons becomes smaller than for the SL-LEDs. This is why the VIS-EL in the TL-LEDs shifts to the red, and the intensity of the NUV-EL with respect to the VIS-EL is smaller in the TL-LEDs. The decrease in the VIS-EL intensity at wavelengths longer than 550 nm is additional evidence that the defect levels, responsible for the VIS-EL, have two different origins -those generated during the EIE fabrication[3] and those existing prior to the EIE fabrication- because the PMPS layer cannot be damaged during EIE fabrication by the incorporation of the OXD layer.

CONCLUSION

The electron injection process in PMPS was clarified by utilizing the EL from TL-LEDs with an OXD layer as a monitor. Noticeable improvements were observed in basic device characteristics of the TL-LEDs as compared with those of SL-LEDs. The present study confirms that the electron injection in PMPS is energy selective occurring via surface defect levels, and that the EL of PMPS originates from the electron-hole recombination which takes place in the polymer near the interface with the OXD layer. The incorporation of an electron injecting layer with a wider band gap than PSs is essential to improve the basic EL characteristics of PS-based LEDs.

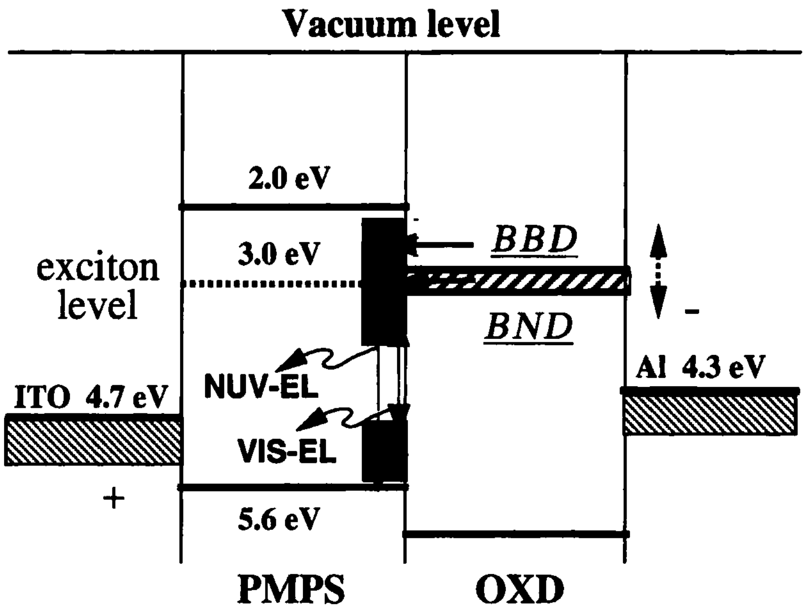

FIGURE 5 A schematic energy diagram of the TL-LED with an OXD layer.

References

[1.] R. D. Miller and J. Michl, Chem. Rev. **89**, 1359 (1989).
[2.] A. Fujii, K. Yoshimoto, M. Yoshida, Y. Ohmori and K. Yoshino, Jpn. J. Appl. Phys. **34**, L1365 (1996).
[3.] H. Suzuki, Adv. Mater., **8**, 657 (1996).
[4.] H. Suzuki, J. Lumin., **72-74**, 1005 (1997).
[5.] H. Suzuki, Mol. Cryst. Liq. Cryst., **294**, 127 (1997).
[6.] S. Hoshino, H. Suzuki, M. Fujiki, M. Morita, and N. Matsumoto, Synth. Met., in print.