Full-Color Light-Emitting Devices Based on π- and σ-Conjugated Polymer Materials

Reiji Hattori, Takeshi Sugano, Tsuyoshi Fujiki**, Yi He, Jerzy Kanicki*

Department of Electrical Engineering and Computer Science,
Center for Display Technology and Manufacturing, University of Michigan, Ann Arbor, MI

* Department of Electrical Engineering, Faculty of Engineering, Osaka University, Osaka, Japan

** Advanced Technology Center, Osaka Gas Co., Ltd., Kyoto, Japan

Abstract

Two kinds of full-color light-emitting devices have been fabricated using π- and σ-conjugated polymers. One device is based on poly(bithiazole)'s, which have emission peaks ranging throughout visible region. The other device has a novel architecture in which ultraviolet-light emitted by electroluminescent diode, based on an evaporated poly(dimethylsilane) layer, is converted by phosphors into visible light emission. The luminance of 0.2 cd/m^2 is obtained for a green light emitting device (injected current density of 0.8 mA/cm^2 and external quantum efficiency is calculated to be 0.0054%).

Introduction

Organic light-emitting diode (OLED) is one of the most promising candidates for the next generation of flat panel display (FPD). Recently, a small and monochrome display using OLED has been demonstrated and manufactured in a small quantity [1]. However, to replace the liquid crystal display (LCD) we must resolve the problems associated with full-color, large-area and high-resolution. Therefore, new materials and new schemes for full-color OLED display are needed.

Recently, we have reported that poly(bithiazole)'s, which have emission peaks ranging throughout the visible spectrum [2], can be a good candidate for OLED emitter. These materials are a new class of π-conjugated polymer that has thermal decomposition temperature above 300^{o}C, and they are very stable in the air at room temperature.

On the other hand, polysilane is also an attractive material for OLED because of the high hole-mobility and high quantum efficiency [3]. The σ-bonding of Si-backbone is delocalized, so that the polysilane is called "σ-conjugated" polymer in contrast to "π-conjugated" polymer mentioned above. Recently, several papers about electroluminescent (EL) diode using polysilane as an active layer have been reported [4,5,6]. These EL diodes are characterized by an ultraviolet (UV) light-emission originating from the σ–σ* transition in silicon backbone. However, at room temperature, this peak disappears, because of the Si-Si bond-breaking or the phase-transition. We have succeeded in preparing an room temperature organic EL diode emitting UV-light (350 nm) using the poly(dimethylsilane) (PDMS) evaporated film [7]. In this case the room temperature light emission is possible, because PDMS molecules have a rigid conformation and a high crystallinity.

In this paper, we focus on two kinds of polymer materials, poly(bithiazole) and poly(dimetylsilane) that can be used in fabrication of OLED. They are π- and σ-conjugated polymers, respectively.

Poly(bithiazole)'s

Figure 1 shows the EL spectra of poly(bithiazole)'s at room temperature under ambient conditions. The emission peak can be located from blue to red region of the spectrum. These polymers have a high thermal decomposition temperature and are very stable in the air at the room temperature. However, the lifetime of these OLEDs is not very long at present time, because of the electrode instabilities in the air.

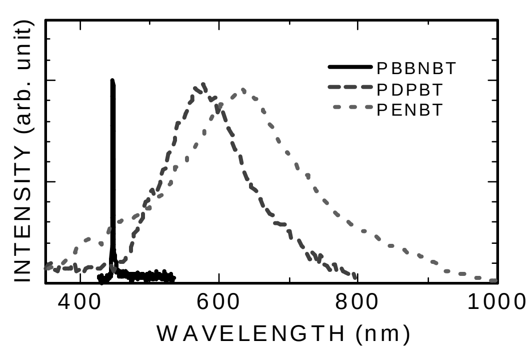


Fig. 1 EL spectra of poly(bithiazole)'s.

ISSN0098-0966X/98/2901-$1.00 + .00 (c) 1998 SID

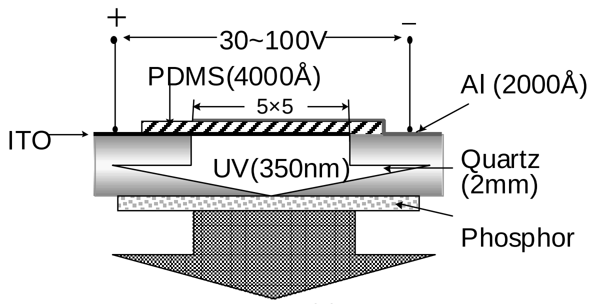


Fig. 2 Possible structure of full-color display pixel using PDMS-EL diode configuration.

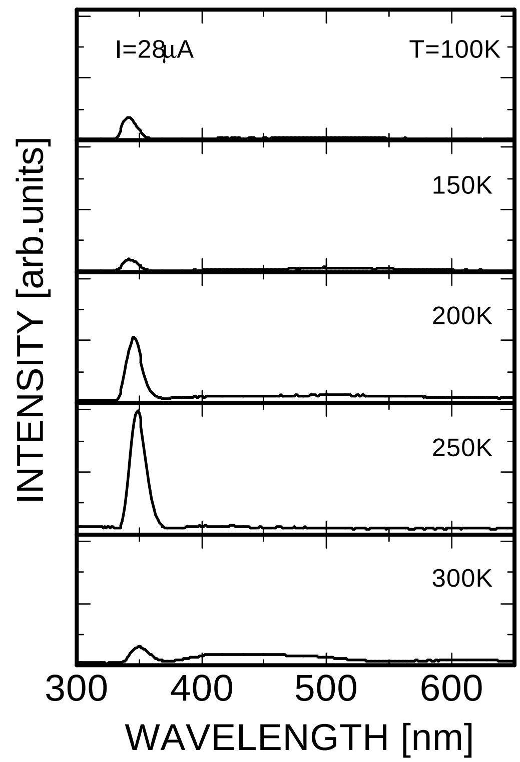


Fig.3 Temperature dependence of the PDMS-EL spectrum.

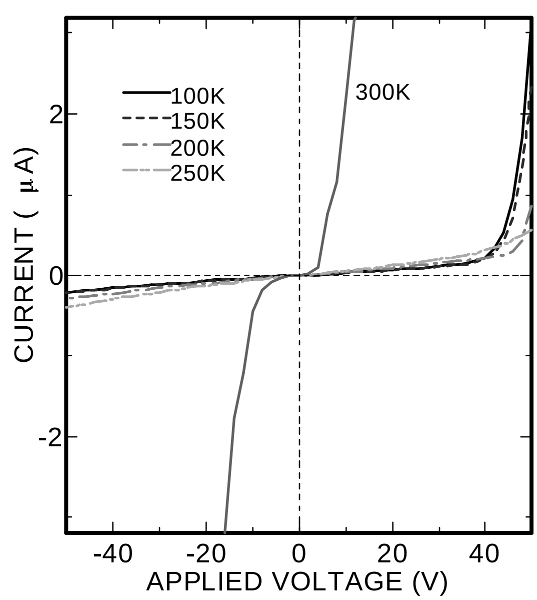


Fig.4 Current-voltage characteristics of the PDMS EL diode at various temperatures.

Poly(dimethylsilane)

The full-color light-emitting devices using PDMS evaporated film have a tandem structure composed of an EL diode (Al/PDMS/ITO) to emit UV-light (~350 nm) and of an phosphor layer to convert the emitted light to RGB light in Fig. 2. The phosphors used are Y_2O_2S:Eu, ZnS:CuAl and ZnS:AgAl for red (R), green (G) and blue (B) light-emissions, respectively. These phosphors have an excitation band corresponding to the light emission of PDMS-EL diode. The full-color display can be fabricated by arranging these devices in the matrix configuration similar to color filters in AM-LCDs. Note that this structure does not need any additional processes to define the polymer layer for a full-color display. To fabricate a high-resolution display the glass substrate should be very thin, because of the light diffusion that occurs through the glass substrate. However, usage of a very thin substrate may be difficult. Another solution is to use different device structures in which the phosphor layer is inserted between ITO and glass or ITO is deposited on the top of PDMS layer.

In the present stage the PDMS layer 4000 Å thick was deposited over the ITO coated quartz substrate by evaporation of the powder source at about 300^{o}C under a vacuum of less than 1.0×10^{-6} Torr. An Al top electrode 2000 Å thick was then evaporated in another evaporator, and the electrode area was 5 mm × 5 mm.

Figure 3 shows the temperature dependence of PDMS-EL spectra. These spectra were measured in helium environment under constant current condition. The EL spectra have a peak around 350 nm and a negligible emission in the visible region that increases at 300K. The EL peak position corresponds to peak position of photoluminescence (PL) spectrum; this peak sifts from 342 to 350 nm as temperature increases. The

ISSN0098-0966X/98/2901-$1.00 + .00 (c) 1998 SID

EL peak intensity increases and decreases with temperature below and above 250K, respectively. At room temperature the emission of UV-light decreases very rapidly, but an acceptable level of the UV-light emission is obtained for about one hour. The origin of the enhancement of UV-emission at lower temperatures is not clear. Most likely it is due to the disappearance of the nonradiative current path; initially a large current was observed when the bias was applied, but its value decreased rapidly with the time.

Figure 4 shows the temperature dependence of the current-voltage characteristics. It can be observed that the rectification behavior of the diode disappears at 300K. The leakage current and the threshold voltage increase with temperature. The device peculiar behavior observed at 300K is due to the device degradation. The threshold voltage depends on the PDMS thickness and its magnitude can be lowered by reducing the film thickness. If the Al is replaced by the metal with the lower work function, for example Mg, Ca, it is expected that EL intensity will be improved.

Figure 5 shows the time dependence of PDSM-EL spectra at 250K. The injected current was kept constant at 28• A. The decrease of the peak intensity is small after the initial fast decay in the first 15 min. The lifetime defined at a half-of-initial intensity value is estimated to be about 6 hours; this value is much longer if the initial decay is excluded. At 300K the lifetime decreases to less than one hour.

Figure 6 shows the PL spectra of the phosphors excited by UV-light emitted from PDMS-EL diode at 250K. The excitation light of 350 nm is completely absorbed by the phosphor layer, because of high absorbance of phosphor layer in UV range. These spectra have a peak in the red, green and blue regions, respectively. Each peak is a slightly broader than the PL peak of phosphor. This is most likely due to the visible light emission from PDMS-EL and its transmittance through the phosphor layer. The intensity of the red emitted light is the smallest. This may be due to a poor conversion efficiency of the red phosphor.

Figure 7 shows the relation between the injected current and the luminance of the green light-emitting device at 250K. The luminance increases linearly with the injection current, and the luminance of 0.2 cd/m^2 can be obtained from the green phosphor at 250K. The current density at the maximum luminance is 0.8 mA/cm^2. This value appears to be much lower in comparison with the • -conjugated polymer based devices. If a large current density can be applied to our device without the device breakdown, we could expect a much larger luminance. The calculated external quantum efficiency for our device is 0.0054%. This value is consistent with the external quantum efficiency of PDMS-EL diode which is about 0.01% [7] and the conversion efficiency of phosphor is about 10%. The value of the external efficiency is very low, but this

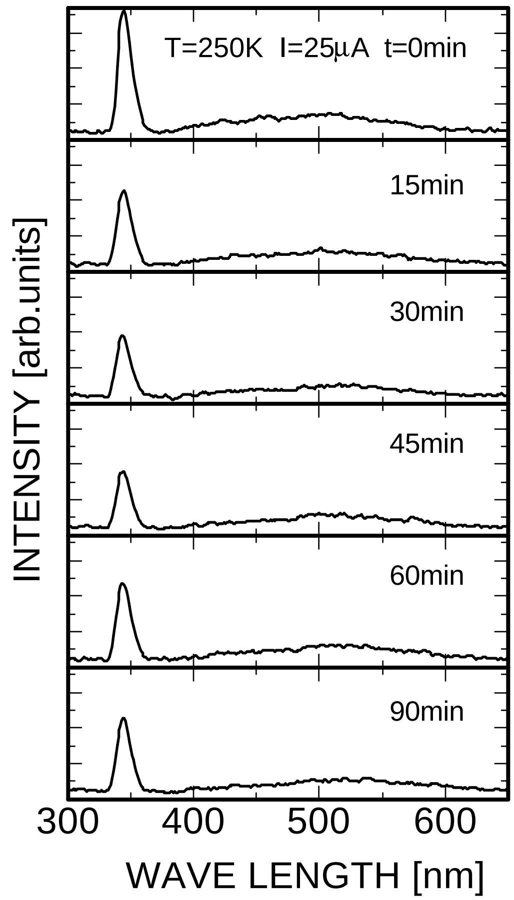


Fig.5 Time-dependence of PDMS-EL diode emission spectra at 250K.

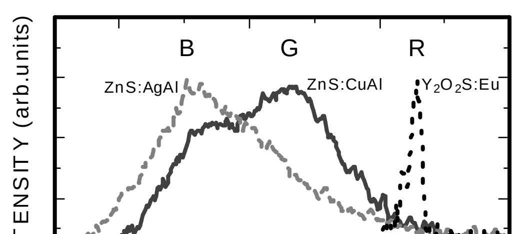


Fig. 6. Spectra of the light emitted from different phosphors excited with UV-light emitted from PDMS-EL diode at 250K.

ISSN0098-0966X/98/2901-$1.00 + .00 (c) 1998 SID

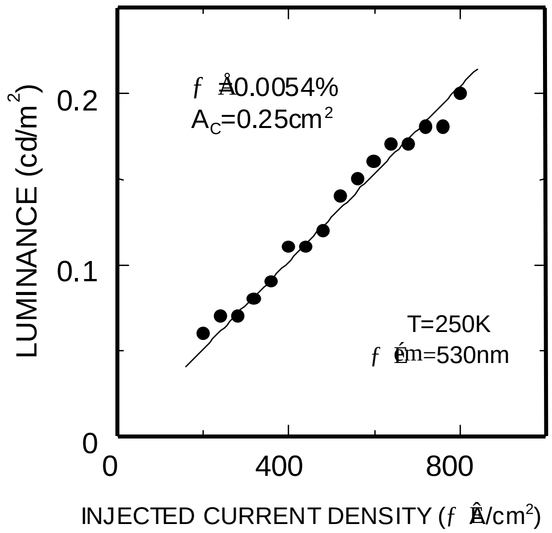


Fig.7 Relationship between luminance and injected current density of the green light-emitting device at 250K.

value can be improved, for example, by using a heterolayer structure and a lower work function metal electrod.

Figures 8 show photographs of the light emission from these devices. Though the shape of electrode is square, the emitting arias are very blurred. This is due to the scattering of the emitted light from PDMS-EL diode in a thick glass substrate.

Summary

We have fabricated two kinds of full-color light-emitting devices based on π- and σ-conjugated polymers. The EL diode using poly(bithiazole), a new class of π-conjugated polymers, emits the light in the blue, green and red regions at room temperature under ambient conditions. The diode using PDMS evaporated film emits UV-light (350 nm) which converted to a full-color light by phosphors. The device lifetime is estimated to be more than 6 hours at 250K and about one hour at room temperature. The device has an external quantum efficiency of about 0.0054%.

References

[1] T.Wakimoto, H.Ochi, S.Kawami, H.Ohata, K.Nagayama, R.Murayama, Y.Okuda, H.Nakata, T.Tohma, T.Naito, H.Abiko, Journal of the SID **5/3** (1997) 235.

[2] Yi He, Jeffery K. Politis, Haitao Cheng, M. David Curtis and Jerzy Kanicki, IEEE Transactions on Electron Devices, **44** (1997) 1282.

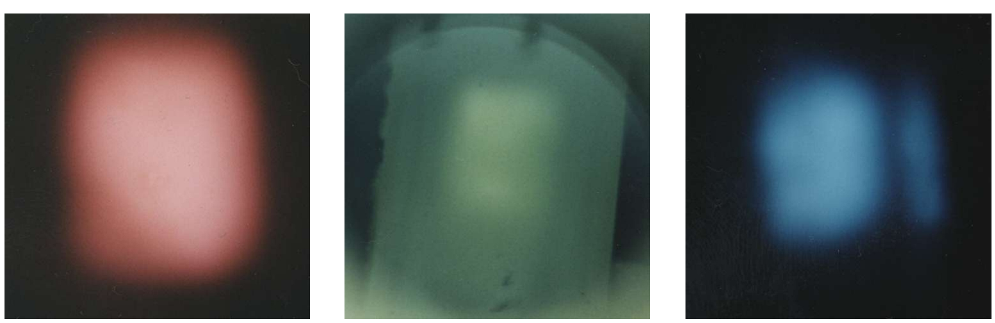
[3] Y.Majima, K.Kawata, Y.Nakano and S.Hayase, *J. Polym. Sci. Polym. Chem.*, A35 (1997) 427.

[4] A.Fujii, K.Yoshimoto, M.Yoshida, Y.Omori and K.Yoshino, *Jpn. J. Appl. Phys.* **34** (1995) L1365.

[5] H. Suzuki, *Adv. Mater.* **8** (1996) 657.

[6] K.Ebihara, S.Koshihara, T.Mayazawa, M.Kira, *Jpn. J. Appl. Phys.*, **35** (1996) 1278.

[7] R.Hattori, T. Sugano, J. Shirafuji, T.Fujiki, *Jpn. J. Appl. Phys.*, **35** (1996) L1509.



(a) (b) (c)

Fig.8 Photographs of the light emitted from the PDMS-EL diode combined with (a) Y_2O_2S:Eu, (b) ZnS:CuAl, (c) ZnS:AgAl.

ISSN0098-0966X/98/2901-$1.00 + .00 (c) 1998 SID