Room Temperature Ultraviolet Electroluminescence from Poly(methylphenylsilane)

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Using carefully purified poly(methylphenylsilane) (PMPS), we have successfully fabricated PMPS LEDs which emit UV light at room temperature for the first time. The study of I-V characteristics of PMPS LEDs indicates that Trapped-Charge-Limited (TCL) currents dominate the charge transport in LEDs at high current region.

Recently polysilanes have attracted growing interest because of their unique electronic and optical properties attributed to the delocalization of σ-electrons along the Si-Si main chains.[1] It is shown that polysilanes have a very sharp photoluminescent (PL) band with a high quantum efficiency in the UV region, which corresponds to the σ^*-σ transition in the silicon skeleton. Very recently, the characteristics of organic polysilanes light-emitting diodes (LEDs) have been studied because of their potential application to large-area flat full-color displays by virtue of their UV emission.[2-6] However, their LED-emission quantum efficiencies were still very low, and the UV EL was observed only at temperature below 270 K except for poly(dimethylsilane), while a broad visible emission was well observed.[2-5] Although the origin of visible emission of PMPS is still controversial,[7] many studies showed that it was most probably associated with the Si-based defects such as branching points in the Si main chains.[8-10] It has also been reported that no visible emission was observed from the polysilane LEDs fabricated using carefully synthesized and purified poly(dihexylsilane) as an emission material, which gave a UV emission at temperature below 230 K.[6]

In this study, polysilane LEDs were fabricated using poly(methylphenylsilane) (PMPS) as an emission material, and for the first time room-temperature UV emission was successfully observed from PMPS. The characteristics of the PMPS LEDs is reported here.

PMPS used in this study was synthesized by Wurtz-type coupling reaction with sodium metal, CuCN being used as a catalyst to control the molecular weight.[11] The monomer of dichloromethylphenylsilane was carefully purified by distillation under reduced pressure, and the content of trichlorophenylsilane which is considered as the source of branching points in PMPS was determined as less than 0.1 % by GC-MS analysis. The toluene solution of the obtained PMPS was washed with distilled water for more than ten times to remove NaCl. Then, PMPS with high molecular weight ($> 5.0 \times 10^5$) and low molecular weight ($< 1.0 \times 10^5$) was removed by repeated precipitation from a toluene solution with 2-propanol. The molecular weight (M_w) was determined as *ca.* 2.7×10^5 from gel-permeation-chromatography using polystyrene as a standard. Photoluminescence spectrum was measured using a fluorescence spectrometer (Shimadzu RF-5300PC) at ambient atmosphere. As shown in Figure 1, the light intensity at visible region is very low and the peak intensity ratio of the sharp UV PL to the visible PL (at 450 nm) is as large as 180. This indicates that the Si-based defects scarcely exist in our sample.[9]

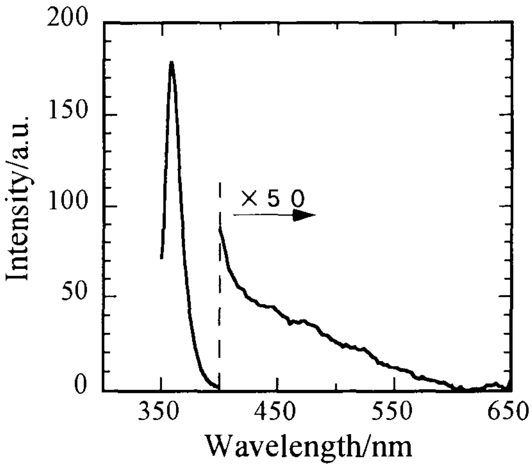

Figure 1. PL spectrum of PMPS films at 298 K (λ_{ex}=340 nm).

PMPS LEDs were fabricated with a simple Mg:Ag/PMPS/ITO glass structure. ITO (indium-tin-oxide) glass plates with a sheet resistance of 30 Ω/□ were used as substrates, and cleaned by ultrasonic treatments and an Ar plasma treatment, and kept in an oven at 100 ℃ until being used. The PMPS thin layer (thickness: 260 nm) was prepared by spin-coating from a toluene solution which was filtered through a 0.2 μm PTFE filter before use. The Mg:Ag layer (thickness: 100 nm) was then vacuum deposited on the PMPS layer at a pressure less than 2×10^{-6} Torr by simultaneous evaporation from separate sources. ITO and Mg:Ag layers were used as an anode and a cathode, respectively. The active area was 2.5×3 mm^2. All the above processes were performed in a clean room of class 1000. Current-voltage-EL intensity characteristics were measured using a photomultiplier tube (R928, Hamamatsu Photonics Co.) and a Keithley 2400 type digital sourcemeter. EL spectra were measured in vacuum with the fluorescence spectrometer mentioned above while the LEDs were operated at a pulse sweep mode with a pulse current of 20 μA.

Figure 2 shows the current-voltage-EL intensity curves of PMPS LEDs at 298 K. The turn-on voltage is about 28 V which corresponds to a field of about 1.1×10^6 Vcm^{-1}. This value is similar to those of reported organic LEDs.[12] We find that the voltage dependence of current appears to follow the power law: $I \propto V^m$ ($m \fallingdotseq 8$) at high currents ($> 10^{-3}$ μA). Thus we consider that Trapped-Charge-Limited (TCL) currents dominate the charge transport in PMPS LEDs.[13]

The EL spectrum of PMPS LEDs is shown in Figure 3. For the first time a sharp emission band in the UV region from PMPS LEDs has been successfully observed at room temperature, probably because of the high purity of PMPS being used. The emission peak at 360 nm in Figure 3 corresponds to

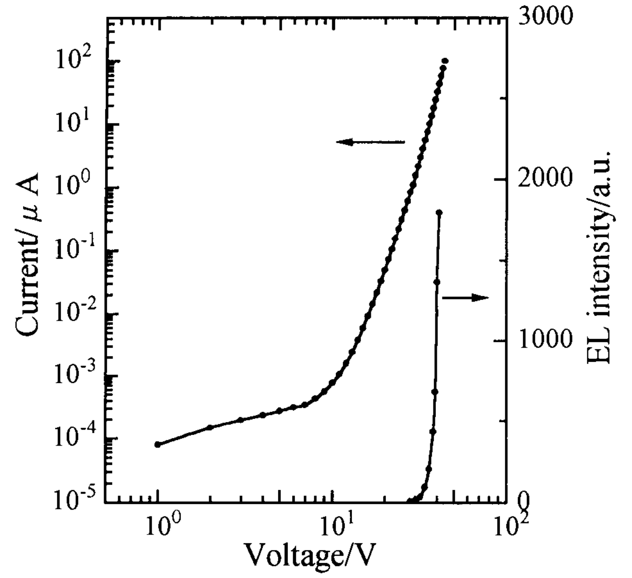

Figure 2. Current-voltage-EL intensity characteristics of PMPS LEDs at 298 K.

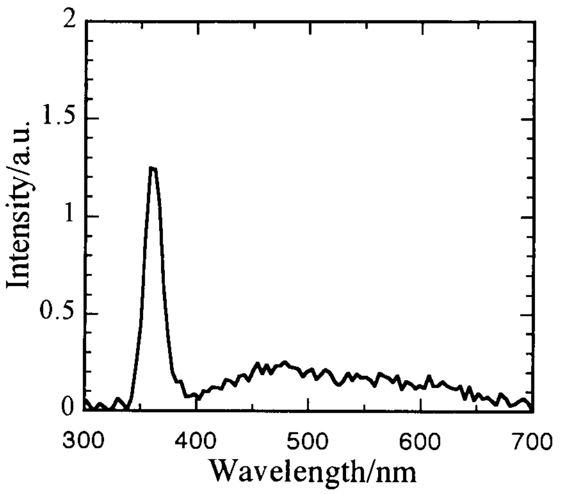

Figure 3. EL spectrum of PMPS LEDs at 298 K.

the peak of PL in Figure 1. Thus, this sharp UV emission band is attributed to the σ^*-σ transition in the Si backbone. Although a broad visible emission was also observed in the EL spectrum, the emission intensity was very low compared with the reported spectra.[4,5] PMPS is a good hole transport material with a hole drift mobility of about 10^{-4} $cm^2/(Vs)$ at room temperature,[14] While an electron mobility of PMPS is so low that it can not be measured by the standard time-of-flight technique. Then the holes injected from the anode recombine with the electrons injected from the cathode in a region very near the cathode. Therefore, the visible emission of PMPS LEDs is considered to be related to the defects existing at the interface between the PMPS and the cathode.

In conclusion, we have successfully fabricated PMPS LEDs, which emit UV light at room temperature. More understanding of PMPS LEDs characteristics and the introduction of multilayer structure are necessary in order to improve the device lifetime and LED-emission quantum efficiency for practical application. These studies are now in progress.

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 (1995).
3 A. Fujii, K. Yoshimoto, M. Yoshida, Y. Ohmori, K. Yoshino, H. Ueno, M. Kakimoto, and H. Kojima, *Jpn. J. Appl. Phys.*, **35**, 3914 (1996).
4 R. Hattori, T. Sugano, J. Shirafuji, and T. Kujiki, *Jpn. J. Appl. Phys.*, **11B**, L1509 (1996).
5 H. Suzuki, *Adv. Mater.*, **8**, 657 (1996).
6 K. Ebihara, S. Koshihara, T. Miyazawa, and M. Kira, *Jpn. J. Appl. Phys.*, **35**, L1278 (1996).
7 O. Ito, M. Terazima, T. Azumi, N. Matsumoto, K. Takeda, and M. Fujino, *Macromolecules*, **22**, 1718 (1989).
8 M. Fujiki, *Chem. Phys. Lett.*, **198**, 177 (1992).
9 H. Kishida, H. Tachibana, M. Matsumoto, and Y. Tokura, *J. Appl. Phys.*, **78**, 3362 (1995).
10 Y. Kanemitsu and K. Suzuki, *Phys. Rev.*, **B51**, 13103 (1995).
11 Presented at the 68th Annual Meeting of Chemical Society of Japan, Nagoya, 1994, Abstr., 3 B5 05.
12 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature*, **347**, 539 (1990).
13 P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A. Cronin, and M. E. Thompson, *J. Appl. Phys.*, **79**, 7991 (1996).
14 R. G. Kepler, T. M. Zeigler, L. A. Harrah, and S. R. Kurtz, *Phys. Rew.*, **B35**, 2818 (1987).