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Polysilane LEDs Emitting Ultraviolet Light at Room Temperature

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1. Introduction

Polysilanes are quasi-one-dimensional (1D) Si-backbone polymers that have alkyl or aryl groups in their side chains. Unlike crystalline silicon, polysilanes show 1D direct-gap nature, attributed primarily to the quantum confinement effect on the conjugated electrons delocalized in polymer backbone chains. They have a sharp photoluminescent (PL) band with a high quantum efficiency in the UV region. [1] Recently, the characteristics of polysilane light-emitting-diodes (LEDs) have been studied because of their potential application to large-area flat full-color displays and high density optical recording systems by virtue of their UV emission. However, the external quantum efficiencies of polysilane LEDs were very low, and UV EL was observed only at low temperatures, while a broad and strong visible emission was also observed. [2,3] It was pointed out that the visible emission was mainly attributed to the defects existing at the interface between the polysilane and the cathode, and the low external quantum efficiency may be attributed to the poor electron injection due to the low electron mobility.

Very recently, for the first time we have successfully fabricated PMPS LEDs which emit UV light at room temperature using carefully purified poly(methylphenyl silane) (PMPS) as an emission material. [4] In order to make the UV emission stronger and to increase the external quantum efficiency, we tried to fabricated multilayer-structure PMPS LEDs. We found that it was an effective way to improve the emission characteristics of PMPS LEDs to introduce a thin SiO_x layer between the PMPS layer and the cathode. The characteristics of these LEDs are reported here.

2. Experimental

PMPS was synthesized by Wurtz-type coupling reaction, and purified by repeated precipitation. PMPS LEDs were fabricated with a Mg:Ag/PMPS/ITO structure or a Mg:Ag/ SiO_x/PMPS/ ITO structure. The PMPS layer was prepared by spin-coating. The SiO_x thin layer was formed at the surfaces of PMPS films by O_2 plasma treatment. The thickness of SiO_x layer was controlled by the treatment time. The Mg:Ag layer was then vacuum deposited on the PMPS layer or the SiO_x layer at a pressure less than 2×10^{-6} Torr.

Current (I)-voltage (V)-EL intensity characteristics were measured using a Keithley 2400 type digital sourcemeter coupled with a photomultiplier. EL and PL spectra were measured with a fluorescence spectrometer.

3. Results and Discussion

Figure 1 shows the I-V-EL intensity curves of PMPS LEDs at 298 K. The turn-on voltage is about 28 V which
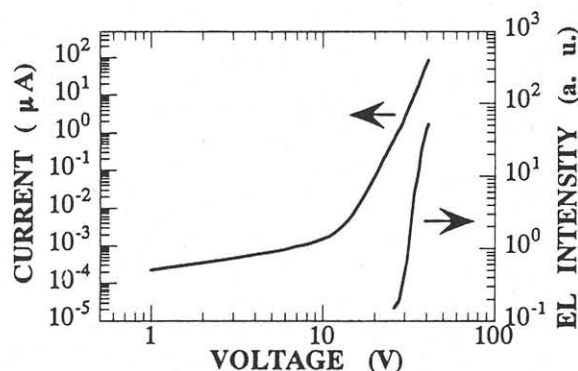

Fig. 1 I-V-EL intensity characteristics of PMPS LEDs at 298 K.

corresponds to an electric field of about 1.0×10^6 V/cm. We found that the voltage dependence of current appeared to follow the power law: $I \propto V^m$ (m≈8) at high current region. Thus we consider that Trapped-Charge-Limited (TCL) currents dominate the charge transport in PMPS LEDs. [5]
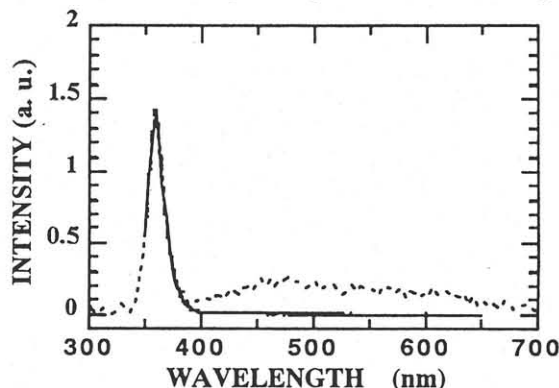

Fig. 2 EL (dotted line) and PL (solid line) spectra of PMPS LEDs at 298 K.

The EL and PL spectra of PMPS LEDs are shown in Figure 2. The PL intensity at visible region is shown to be very low. This indicates that Si-based defects such as branching points scarcely exist in our sample. [6] And as shown in Figure 2, a sharp UV emission band from PMPS LEDs has been successfully observed at room temperature. [4] The EL emission peak of 360 nm is in good agreement with the PL peak of PMPS films. Thus, this sharp UV EL emission from PMPS is attributed to the σ*-σ transition in the Si backbone. [1]

The successful fabrication of PMPS LEDs emitting UV light at room temperature is most probably attributed to the high purity of PMPS being used. However, a broad visible emission was also observed in the EL spectrum, although its intensity was very low compared with the previously reported spectra. [2,3] Moreover, the external quantum

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efficiencies of PMPS LEDs fabricated here were still very low, being about 10^{-5} %. PMPS is a good hole transport material with a hole drift mobility of about 10^{-4} cm²/(Vs) at room temperature, [7] while an electron mobility in PMPS is so low that it can not be measured by the standard time-of-flight technique. So, the electrons injected from the cathode are much less than the holes injected from the anode. Balanced injection of electrons and holes has not been achieved. Furthermore, we can also expect that it is in a region very near the cathode that holes recombine with electrons. 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. These defects may probably be induced by high-temperature metal particles during vacuum deposition processes of Mg and Ag. In order to improve the UV intensity and the external quantum efficiency of PMPS LEDs , it is important to introduce an electron transport layer between the PMPS and the cathode.

Because it is quite difficult to find an electron transport material with a wider bandgap than that of PMPS (about 3.6 eV), otherwise excitons (σ^*) will be quenched by the electron transport layer, we tried to improve the characteristics of PMPS LEDs by inserting a thin insulating layer between the PMPS and the cathode. The thin insulating layer was prepared by O_2 plasma treatment of the PMPS films. We confirmed that Si-O-Si bonds were formed in the O_2 plasma treated PMPS films by the FT-IR spectroscopy, and calculated the thickness of an SiO_x layer to be about 4.0 nm based on the UV absorption reduction after 40 seconds of O_2 plasma treatment. The I-V characteristics of PMPS/SiO_x is shown in Figure 3. Experiments show that the current density decreases with the introduction of a thin SiO_x layer. The behavior can be expected because the blocking of the hole transport by the SiO_x layer becomes effective. And as shown in Figure 4, the external quantum efficiency of the PMPS/SiO_x LEDs was enhanced by more than 8 times compared to the PMPS-only-device. One of the reasons is that electron injection was enhanced by the tunneling effect while hole current reduced due to the blocking effect, when a thin SiO_x layer was introduced. Another reason is that the quenching of the excitons by the cathode may have been effectively avoided by inserting a SiO_x layer between the PMPS and the cathode.
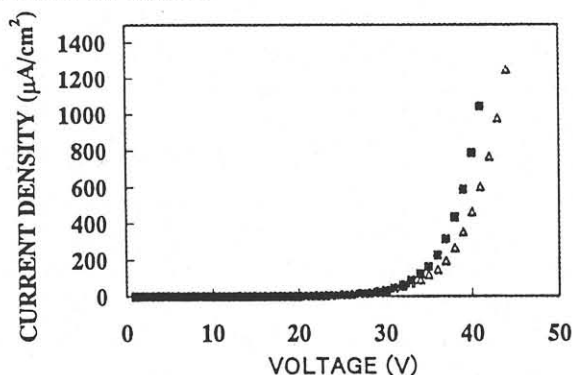

Fig. 3 I-V characteristics of PMPS LEDs (square) and PMPS/SiO_x LEDs (triangle).
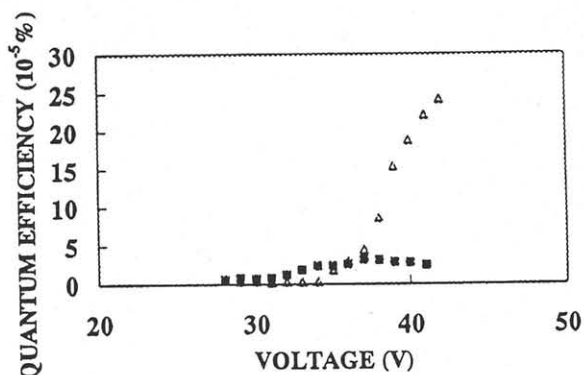

Fig. 4 External quantum efficiency of PMPS LEDs (square) and PMPS/SiO_x LEDs (triangle).
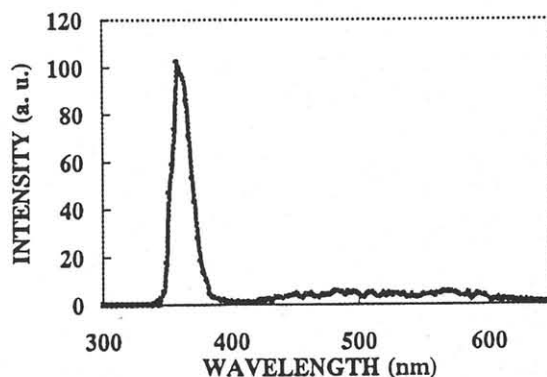

Fig. 5 EL spectrum of PMPS/SiO_x LEDs at 298 K.

Figure 5 shows the EL spectrum of PMPS/SiO_x LEDs. The ratio of the UV emission to the visible emission increased apparently, and almost only a sharp UV emission band was observed. This is because that the eroding effects of heated metal particles on PMPS surfaces during vacuum deposition processes can be eliminated by the introduction of a thin SiO_x layer, and the defects relating to the visible emission at the emission region are reduced.

4. Conclusion

We have successfully fabricated PMPS LEDs which emit UV light at room temperature, and found that the UV emission intensity and the external quantum efficiency of PMPS LEDs are significantly improved by simple O_2 plasma treatment of the PMPS film surfaces.

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