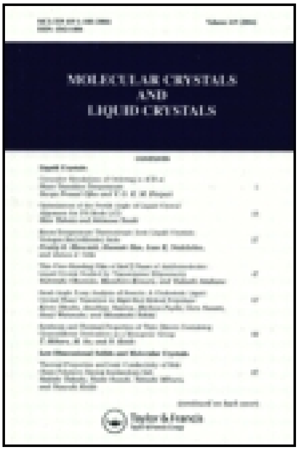

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LIGHT-EMITTING DIODES BASED ON SILICON-BACKBONE POLYMERS

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Abstract Recently near-ultraviolet electroluminescence (EL) was observed from a typical Si-backbone polymer, poly(methylphenylsilane) (PMPS). This study investigates the dependence of the EL characteristics on temperature, the electron injecting electrodes and the "*defect*" concentration at the interface between PMPS and electron injecting electrodes, in order to clarify the EL process in PMPS-LEDs.

INTRODUCTION

Si-backbone polymers exhibit electronic and optical properties which are markedly different from those of π-conjugated polymers because of their σ-conjugation.[1] Chain-like Si-backbone polymers (polysilanes) are of particular interest because they are *quasi*-one-dimensional (1-D) materials with delocalized σ-conjugated electrons along their polymer backbone chain.[2] Owing to their 1-D direct-gap nature, polysilanes possess sharp strong absorption and photoluminescence, usually in the near-ultraviolet (NUV) region. In almost all the light-emitting diodes (LEDs) utilizing polysilanes reported to date, poly(methylphenylsilane) (PMPS, see Figure 1 for the structure) has been used as a hole transporting material for multilayer LEDs.[3-8] This is mainly because PMPS exhibits trap-free hole transport with a rather high mobility ($\geq 10^{-3}$ cm^2/Vs) at room temperature (RT).[4,9] Recently NUV electroluminescence (EL) was observed from these *quasi*-1-D excitons in single-layer LEDs made from PMPS.[10,11] This provides two important opportunities: one is to use this EL as a sensitive probe in optical studies of the behavior of charge carriers and excitons in polysilanes, and the other is to utilize these polymers as emitting materials in LEDs.

In this study, EL characteristics were measured and analyzed as a function of temperature, electron injecting electrodes (EIEs), and the concentration of "*defects*" at the PMPS-EIE interface in order to study the EL process in PMPS-LEDs.

EXPERIMENTAL

The structure of the PMPS-LEDs fabricated in this study is shown in Figure 1. PMPS layers were prepared by spin-coating (thickness: 90 nm) from toluene. The EIEs were either Al (Al(vd)) or Mg:Ag(Ag: ~10 atom%) alloy (Mg:Ag(sp)) films, which were fabricated by the vacuum deposition or the rf magnetron sputtering technique, respectively.[12,13] The setups used for measuring the EL characteristics have been reported previously.[5,11]

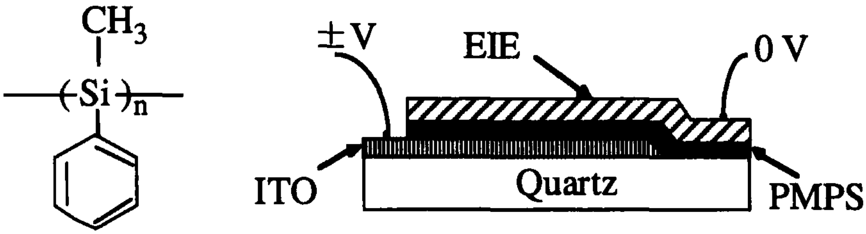

FIGURE 1 Structure of PMPS and PMPS-LEDs.

RESULTS AND DISCUSSION

Dependence on Temperature

PMPS-LEDs exhibit typical diode behavior (rectification ratio at 30 V: >10^3). Their various characteristics depend markedly on temperature. The EL spectrum consists only of broad visible emissions at RT. At lower temperatures, however, it also contains a sharp NUV band (peak: 353 nm).[10,11] The total EL intensity and the intensity distribution of these emissions both depend strongly on temperature (Figure 2).[11] With Al(vd) electrodes, the external quantum efficiency is in the 10^{-3}-10^{-4} and 10^{-5}-10^{-6} % range for visible and NUV EL, respectively, at temperatures between 110 and 240 K.[11] This temperature dependence of the EL spectrum is greatly different from that of the photoluminescence (PL) spectrum.[14] As the temperature is reduced, the visible PL intensity continuously increases, whereas the NUV PL intensity changes only slightly.

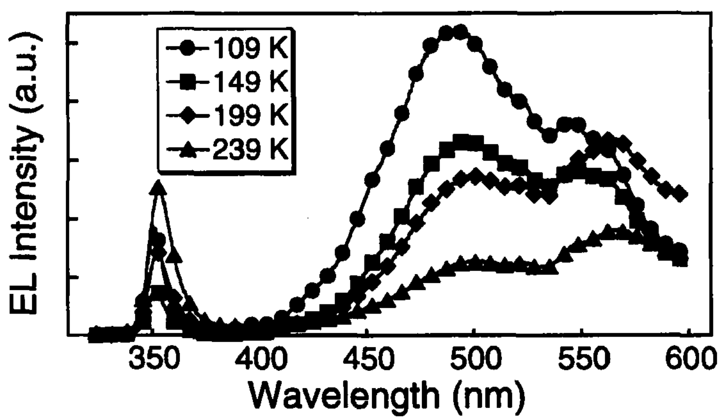

FIGURE 2 Temperature dependence of EL spectrum in PMPS-LEDs with Al(vd)

The EL turn-on voltage also depends on the temperature.[11] It increases from 9 V at RT to 15 V at 126 K without any noticeable change in the magnitude of the current. In PMPS-LEDs the current is dominated by holes, and the EL intensity is determined by the electron supply. Thus, electron injection into PMPS is a temperature dependent process with a finite barrier height. Current PMPS-LEDs are not very durable because of EIE degradation. Their lifetime is only several minutes at RT (operation: 6~7 mA/cm^2 at 30 V). At 120 K, however, it is about 30 min at a current density of 25 mA/cm^2 at 110 V.

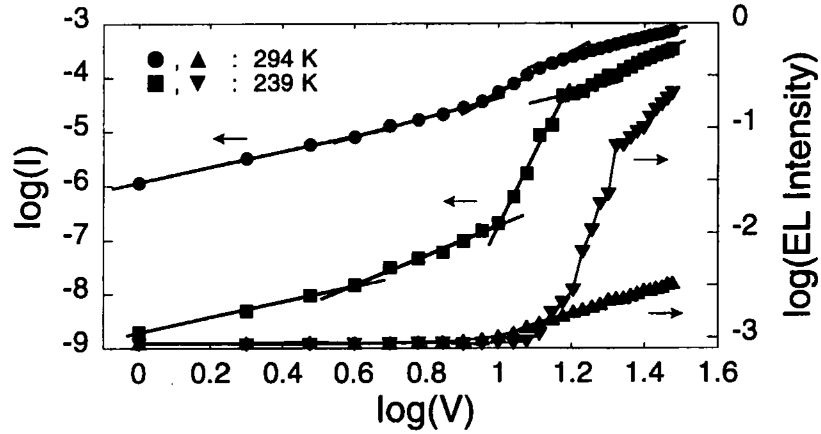

FIGURE 3 I-V-EL curves of PMPS-LEDs with Al(vd).

Analyses of I-V-EL Characteristics

I-V-EL curves of LEDs with Al(vd) electrodes can be described by the power law ($I \propto V^{m+1}$),[15] namely, the space-charge-limited current (SCLC) model (Figure 3).[16] Table I lists parameters obtained from these analyses of the data at 239 K and RT. At these temperatures the effective hole mobility (μ), a parameter needed for the analyses, was determined by the time-of-flight (TOF) technique.[5,9] The traps in Table I are the deepest that exist in PMPS bulk, and their depth (~0.4 eV) agrees well with the activation energy for μ in PMPS (0.36 ~ 0.37 eV).[5,9] The *I-V* curve at 239 K exhibits a current increase in the trap-free square law region upon EL emission. This is ascribable to the neutralization of positive space charges by the recombination of electrons with holes captured in the above traps, which accompanies the onset of NUV EL.[11,15] At RT the EL starts in accord with the onset of the trap-filling region and there is no accompanying current increase in the trap-free square law region. The EL at RT is, therefore, due to the recombination of electrons with holes captured not in the above traps, but in shallower traps at the PMPS-EIE interface. Since μ is larger at RT than at lower temperatures, the probability of holes being captured by shallower traps is larger at RT. The electron-hole recombination sites, therefore, depend on the temperature, and this explains why the EL spectrum at RT is composed only of visible emissions, whereas the NUV EL emerges at temperatures below 270 K.[11,15]

A similar analysis of I-V-EL data at 208 K revealed the presence of shallower traps (depth: 0.26 eV) in PMPS bulk. Quantitative analyses of *I-V* data at even lower temperatures are impossible due to the lack of μ data. However, the *I-V-EL* curves can also be described qualitatively by the SCLC model with multiple shallower traps.

TABLE I Parameters obtained from analyses using the SCLC model.

Temperature (K)	294	239
Trap depth (eV)	0.40	0.41
Trap density (cm^{-3})	$3.5x10^{17}$	$3.5x10^{17}$
quasi-Fermi energy (eV)	0.43	0.44
Free hole density (cm^{-3})	$3.6x10^{12}$	$4.4x10^{10}$
Trapped hole density (cm^{-3})	$9.2x10^{16}$	$6.9x10^{16}$

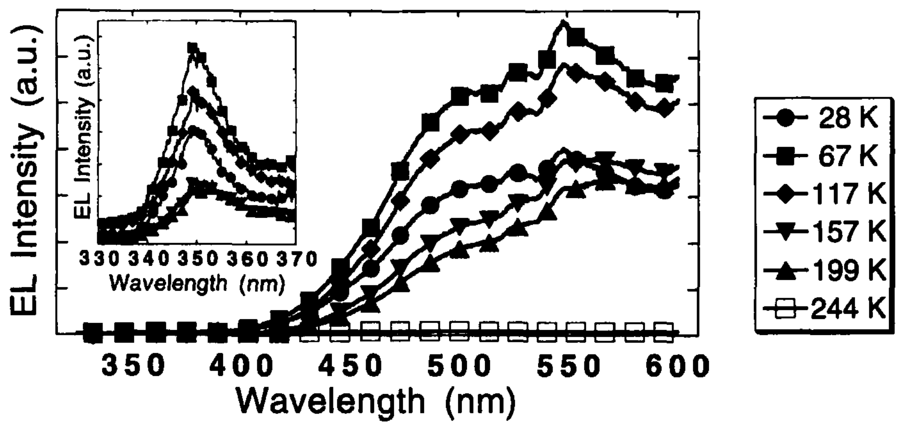

FIGURE 4 Temperature dependence of EL spectrum of PMPS-LEDs with Mg:Ag(sp).

Dependence on Electron Injecting Electrode and "Defect" Concentration

With Mg:Ag(sp) electrodes, LEDs exhibit a lower EL turn-on voltage (6 V at RT), and an EL intensity which is about two orders of magnitude larger than with Al(vd) electrodes.[11] The EL spectrum is, however, dominated by visible EL (Figure 4) because "*defects*", which act as radiative trapping centers, are produced at the PMPS-EIE interface during Mg:Ag(sp) electrode fabrication[15] because the energy of the metal particles used is higher with the sputtering technique (0.2~10 eV) than with the vacuum evaporation technique (0.1~0.2 eV). It should be noted that for LEDs in which the EL originates from the bulk of the emitting layers, the sputtering technique does not cause any noticeable change in the EL spectrum.[12,13] The marked change observed in the EL spectrum provides an additional indication that the EL is emitted from the vicinity of the PMPS-EIE interface.

These defects also act as energy acceptors for the *quasi*-1-D excitons responsible for NUV EL. The temperature at which NUV EL is detectable thus decreases from 270 K for Al(vd) to 244 K for Mg:Ag(sp).[15]

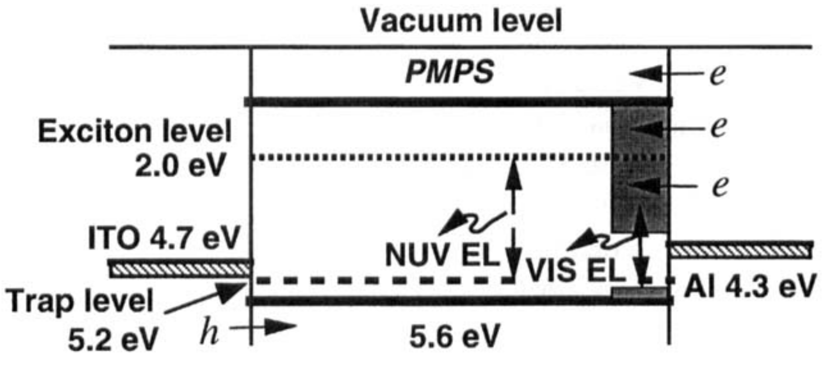

FIGURE 5 Schematic representation of the EL process in PMPS-LEDs.

<u>EL Process in PMPS-LEDs</u>

A schematic diagram of the EL process in PMPS-LEDs is shown in Figure 5. Because of the strong unipolar (hole conductive) nature of PMPS, the EL originates primarily from the vicinity of the PMPS-EIE interface, and so defects at this interface play a crucial role in the EL process. The marked difference between the EL and PL spectrum, of which the latter is emitted from the bulk polymer, is a manifestation of this assignment. The visible emission of the EL spectrum is greater in intensity with respect to the NUV emission than that of the PL spectrum, and the intensity of the visible EL becomes even larger because of damage at the interface caused by the Mg:Ag(sp) fabrication. These defects, which act as radiative trapping centers for the visible EL, exist predominantly near the interface, and some of them are generated during the EIE fabrication process. They also play a vital role with regard to the electron injection into PMPS. The barrier heights for electron injection into levels higher than the exciton level of PMPS, which is needed to observe the NUV EL, seem too large. However, positive space charges produced by trapped holes at these defects improve the electron injection from the electrodes to PMPS, resulting in a reduction in the EL turn-on voltage.[11] The electron-hole recombination sites depend on the temperature. At RT the EL is due to recombination at these defects, while at lower temperatures it is ascribable to the recombination between injected electrons and holes captured at the traps (depth: ~0.4 eV).[15]

Various processes such as the injection and trapping of charge carriers, and the radiative relaxation and energy transfer of excitons also play vital roles in the EL process.

The defects at the PMPS-EIE interface act, for instance, as energy acceptors for the *quasi*-1-D excitons. Since all these processes have their own temperature dependence, the strong temperature dependence observed for the LED characteristics is ascribable to competition between these processes.[11]

CONCLUSION

The EL process in PMPS-LEDs was clarified on the basis of the dependence of EL characteristics on temperature, EIEs and the concentration of defects at the PMPS-EIE interface. This study provides additional solid evidence that the EL originates from the vicinity of the PMPS-EIE interface, and that the defects at this interface play an essential role in the EL process. In LEDs made from polysilanes, the behavior of holes and electrons can be investigated separately because holes dominate the current, while the EL intensity reflects the electron supply. The EL also provides a novel sensitive tool with which to investigate optically the interface between polysilanes and EIEs. These two advantages are both based on the fact that polysilanes are strongly unipolar.

Further understanding of the EL process as well as improvements in such device characteristics as operating temperature and quantum efficiency in LEDs made from polysilanes should be realized as a result of work, currently under way, to develop materials and device structures.

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