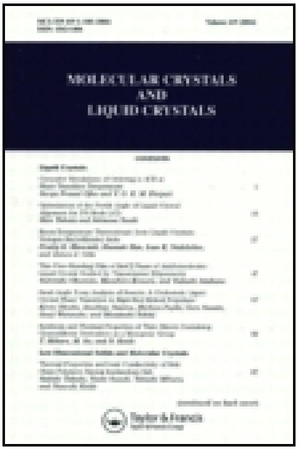

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Electroluminescent Properties of Dialkyl Substituted Polysilanes

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Electroluminescent Properties of Dialkyl Substituted Polysilanes

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We investigated the EL characteristics of a series of dialkyl substituted polysilanes to clarify the fundamental electroluminescent (EL) properties of σ-conjugated one dimensional Si polymers. The EL properties of these polysilanes were found to be strongly influenced by branch-like defects in the Si backbone from EL spectrum measurements and the energetics of carrier injection into the polysilanes. We also demonstrated the influence of a change in conformation on the EL spectrum of dialkyl polysilane-based light emitting diodes.

Keywords: polysilanes; electroluminescence; near-ultraviolet emission; conformation

INTRODUCTION

Since electroluminescence (EL) in the near-ultraviolet (NUV) region was reported from poly(methylphenylsilane) (PMPS)-based light emitting diodes (LEDs) (PMPS-LEDs),[1,2] much attention has focused on polymers with one dimensional (1D) Si backbones as LED emitting materials. In PMPS-LEDs, such device characteristics as carrier injection, transport, and EL spectrum are strongly influenced by structural defects, inevitably caused in the polymer during device fabrication, and branches in its backbone.[2-4] Since dialkyl polysilanes have a better chemical and/or thermal stability and a simpler electronic structure than PMPS, they are more suitable for use as an LED emitting material for investigating the fundamental EL properties of σ-conjugated 1D Si polymers. We have already investigated the EL properties of a series of symmetrically substituted dialkyl polysilanes.[5] Here, we report the influence of the branch-like defects in a Si backbone on the EL properties of poly(di-*n*-hexylsilane) (PDHS)- and poly(di-*n*-butylsilane) (PDBS)-based LEDs. We also studied the effect of Si backbone conformation on the EL properties of poly(di-*n*-pentylsilane) (PDPS)-based LEDs.

EXPERIMENTAL

Figure 1 shows the chemical structures of the polysilanes used in this study and the structure of the polysilane-based LEDs (PDBS-, PDPS- and PDHS-LED). In these LEDs, indium-tin-oxide (ITO) and Al electrodes were used for the injection of holes and electrons, respectively. Details of the polymer synthesis, device fabrication, and measurement of EL properties have been described previously.[2-5]

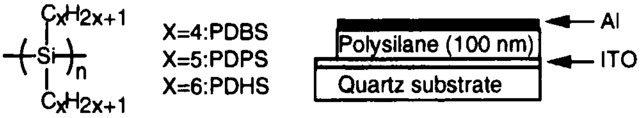

FIGURE 1 Chemical structure of polysilanes and device structure of LEDs.

RESULTS AND DISCUSSION

Influence of branch-like defects on EL characteristics

Figure 2(a) shows the PL spectra of PDHS and PDBS films prepared on quartz substrates at 100 K. These two polysilanes exhibit PL in the NUV region (NUV-PL) originating from the radiative relaxation of *quasi*-1D excitons delocalized along the Si backbone. The difference in the peak position of the PL indicates that the Si chains from which it is emitted have different conformations between PDHS and PDBS. The NUV-PL of PDHS corresponds to a typical emission originating from *quasi*-1D excitons delocalized along a polymer backbone with a *trans*-planar conformation,[6] whereas that of PDBS arises from those with a disordered conformation.[7] Although we observe no PL in the VIS region for the PDHS, the PDBS exhibits a weak PL as shown in the inset in Fig. 2(a). This indicates that there are defects at which the radiative relaxation of localized excitons occurs in the PDBS. The PDBS used in this study must have branches in its backbone because the dibutyldichlorosilane used as the monomer for the PDBS synthesis contains a very small amount of butyltrichlorosilane, which produces branches during polymerization. The PL in the VIS region is, therefore, due to the radiative relaxation of excitons localized at the branch-like defects of PDBS.

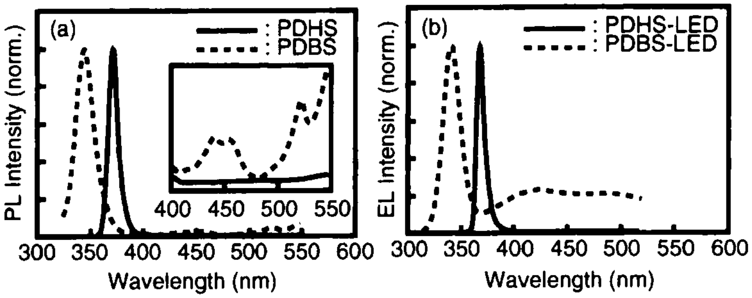

FIGURE 2 (a) PL spectra of PDHS and PDBS films, and
(b) EL spectra of PDHS- and PDBS-LEDs at 100 K.

Figure 2(b) shows EL spectra of the PDHS- and PDBS-LEDs at 100 K when the ITO electrode was positively biased. The EL spectrum of the PDHS-LED is composed only of the NUV emission and is identical to the PL spectrum of PDHS. The EL observed from the PDHS-LED is, therefore, due to the radiative relaxation of the *quasi*-1D excitons delocalized along the polymer backbone with a *trans*-planar conformation. By contrast, the EL spectrum of the PDBS-LED is composed of NUV-EL and broad EL in the VIS region (VIS-EL). This NUV-EL coincides with the PL in the NUV region while the VIS-EL is different from the PL observed in the VIS region in terms of intensity and spectral shape, as with the PMPS-LEDs.[2-4] In the PMPS-LEDs, the VIS-EL showed a different temperature dependence from that of the PL in the VIS region because the structural defects generated during device fabrication partly participated in the VIS-EL.[2-4] On the other hand, The PDBS-LED, in which far fewer structural defects are generated during device fabrication because of higher chemical and/or thermal stability of the polymer, exhibits no noticeable change either in the spectral shape or the intensity ratio between the NUV-EL and VIS-EL from 200 K to 100 K. We therefore conclude that the recombination sites for the VIS-EL are the branches that are inevitably generated during polymerization.

The effect of the branch-like defects on the device characteristics was also observed for the carrier injection process of these two LEDs. Our previous studies have revealed that the dominant carriers, observed as the device current, are injected holes and that the electron supply from the Al electrode to the polysilanes approximately determines the EL intensity.[2-5] Although the barrier heights for the electron injection from the Al electrode to the conduction bands or the quasi-1D exciton level have respectively been estimated to be 3.1 and 1.9 eV for PDHS, and 3.9 and 2.6 eV for PDBS,[5] the PDBS-LED exhibits a lower turn-on voltage (16 V) than the PDHS-LED (26 V). In the PMPS-LEDs, the positive space charges generated by injected holes trapped near the interface between PMPS and the electron injecting electrode improve the electron injection.[2-4] Therefore, the energetically inconsistent lower turn-on voltage of the PDBS-LED is due to the improvement in the electron injection by the positive space charges produced by the trapped holes at branch-like defects. We also observed that the device current of the PDBS-LED was almost four orders of magnitude larger than that of the PDHS-LED in spite of the small difference (0.1 eV) in the barrier height for the hole injection between the two LEDs.[5] This suggests that the carrier injection process of σ-conjugated Si polymers is determined by the barrier height for the carrier injection and the branch-like defects.

Dependence of EL characteristics on conformation

The electronic structure of dialkyl polysilanes is mainly determined by the backbone conformation. Therefore, any change in the Si backbone conformation is reflected strongly in such properties as photoabsorption or PL. We used PDPS-LEDs to investigate the dependence of the EL properties on conformation in a chemically identical polysilane. PDPS exhibits various solid state morphologies at a constant temperature. Figure 3 shows the change in the absorption spectra of a PDPS film at 260 K. A peak grows gradually at around 360 nm as the peak around 310 nm decreases, indicating that the backbone confor-

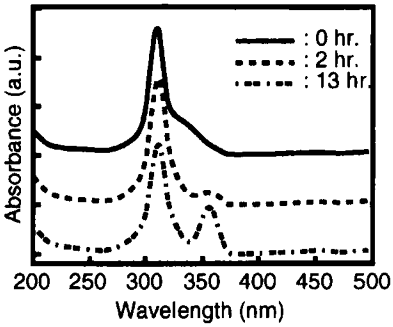

FIGURE 3 Change in absorption spectra of PDPS film treated for 0 hr. (top), 2 hr. (middle), and 13 hr 9bottom) at 260 K.

mation partly changes from a 7/3 helical to a *trans*-planar structure in a PDPS solid film. This change was hardly observed when the temperature was decreased below 250 K. In this way, three different conformations were introduced into the PDPS layer by treating the PDPS-LED at 260 K for 0, 2, and 13 hours, and then rapidly cooling it to 200 K. The EL properties of these PDPS-LEDs (LED-0, LED-2, and LED-13) are compared below.

Figure 4 shows PL and EL spectra observed for LED-0 and LED-13. The PL spectra were measured by photoexcitation ($\lambda ex=337$ nm) through an ITO electrode. Consistent with the PL spectrum, the peak position of the NUV-EL is 354 nm for LED-0 and 368 nm for LED-13, indicating that the emissive species are *quasi*-1D excitons delocalized along a 7/3 helical and a *trans*-planar structure, respectively. However, a small difference was observed between the NUV-EL and the PL in terms of spectral shape. In LED-0, the intensity of the lower energy component is smaller in the NUV-EL than the PL. By contrast, the higher energy component is weaker in the NUV-EL than the PL in LED-13. These observations indicate that the proportion of radiative recombination occurring at a 7/3 helical and a *trans*-planar structure is different for the EL and the PL. Since the EL of the PDPS-LEDs also occurs in the thin layer near the polysilane/Al electrode interface, as with other polysilane-based LEDs,[2-5] one explanation for the observed difference in the spectra may be that the conformation of the polymer in the thin layer is locally different from that of the whole PDPS layer.

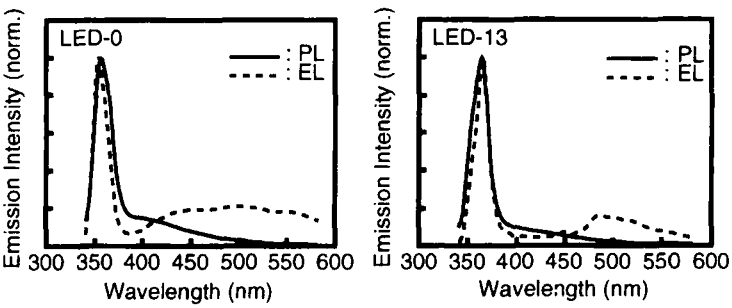

FIGURE 4 PL and EL spectra of PDPS-LEDs (LED-0 and LED13) at 200 K.

In contrast to the fact that the PL from the PDPS-LED is observed only in the NUV region, the EL is composed of NUV and VIS components. The VIS-EL spectrum varies as the *trans*-planar structure in the PDPS layer increases. The intensity of the VIS-EL between 400 nm and 450 nm decreases in the LED-2, and is hardly visible in LED-13 (see

Fig. 4). Since the VIS-EL of the PDPS-LED also has its origin in the radiative relaxation of excitons localized at defects in the Si backbone, this observation suggests that some of the defects are annihilated in LED-13 during the annealing process mentioned above. We consider that this VIS-EL originates from sites with specific conformations such as kinks, which are relieved by the propagation of a *trans*-planar phase in the PDPS layer. However, we observed no marked change in the VIS-EL above 450 nm, indicating that there are other kinds of defects which are insensitive to change in conformation and may have a different chemical structure from the regular backbone of PDPS.

SUMMARY

The EL characteristics of a series of dialkyl polysilanes were investigated for single-layer LEDs. The PDBS-LED showed different device characteristics from the PDHS-LED. Example included the observation of the VIS-EL and energetically inconsistent carrier injection. This is because PDBS has branch-like defects which act as low energy radiative recombination centers and hole traps for inner-device space charge formation. We studied the conformation dependence of the PDPS-LED and found there were structural defects which were sensitive to change in the conformation of the Si backbone. These structural defects acted as recombination centers for the VIS-EL.

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