Spectral narrowing of photoluminescence and improvement of electroluminescent properties in conducting polymers with Si atoms in main chains

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Optical properties of conducting polymers with Si atoms in main chains, such as optical absorption, photoluminescence (PL), and electroluminescence (EL), have been studied. The electronic energy structures have been determined by optical and electrochemical measurements. The strong PL with high quantum efficiency has been clarified, and spectral narrowing has been observed by pulse excitation of a nitrogen laser. Intense blue or red EL has also been demonstrated and the emission efficiency has been improved by anode surface modification and annealing. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1416863]

I. INTRODUCTION

The use of π-conjugated conducting polymers as functional materials has attracted much attention from the point of view of basic science and applications, because of their high processability, stability, and promising electrical and optical properties.[1] Among various conducting polymers, alkyl- or alkoxy-substituted polymers, such as poly(3-alkylthiophene),[2] poly(9,9-dialkylfluorene) (PDAF),[3,4] poly(p-phenylene) (PPP) derivative,[5] and poly(2,5-dialkoxy-p-phenylene vinylene)[6,7] are the most attractive materials, because of their high solubility in common organic solvents, their fusibility at relatively low temperatures, and their high luminescent quantum efficiency.

Utilizing conducting polymers with relatively large band gap, polymer blue light-emitting diodes (LEDs) could be realized. We have demonstrated the blue LEDs by utilizing PDAF,[3] PPP derivative,[5] or polyacetylene derivative[8] as emission layers.

On the other hand, copolymers with a π-conjugated segment and silicon (Si) atom in each monomer unit of polymer main chains are expected to possess unique characteristics and functionalities. Recently, copolymers such as poly(disilanyleneoligophenylene)s[9] and poly(disilanylene-oligothienylene)s[10] were synthesized and demonstrated the solubility in common solvents and the blue-to-red electroluminescent (EL) properties, since Si in main chains interrupts the π-conjugated chain and limits the π-conjugation length. Copolymers synthesized by the modified synthetic process should also have other π-conjugated segments and the pos-

sibility of exhibiting unique luminescent properties. Indeed, Kim *et al.* reported on their success in the synthesis of copolymers with Si atoms in main chains, and demonstrated color tuning of the emission to reduce the lowest unoccupied molecular orbital (LUMO) level.[11] In the case of the polymer LEDs utilizing such copolymers, suppression of the operating voltage to obtain blue emission might be realized. In addition, these copolymers promise to improve the thermal stability and possess high carrier mobility.

In this article, we report on the optical properties, such as photoluminescence (PL), spectral narrowing of PL, and the EL properties of conducting polymers with Si atoms in main chains, and methods for improvement of EL properties are also suggested.

II. EXPERIMENT

Four kinds of conducting polymers, poly(diphenyl-silylene-di-p-phenylene vinylene-p-phenylene) (SiPhPPV), poly(hexylmethylsilylene-p-phenylene vinylene-9,9-dihexylfluorene vinylene-p-phenylene) (SiHMFPV), poly(diphenylsilylene-p-phenylene vinylene-9,9-dihexyl-fluorene vinylene-p-phenylene) (SiPhFPV), and poly(diphenylsilylene-p-phenylene vinylene-thienylene vinylene-p-phenylene) (SiPhThV), the molecular structures of which are shown in Fig. 1, were studied in the present work. These polymers were synthesized and purified by the method already described.[11,12] In these polymers, π conjugations are regularly interrupted along the backbone by Si atoms, resulting in isolated chromophores that emit blue or red lights in color. These polymers are soluble in common organic solvents such as chloroform and toluene.

Absorption and PL spectra of polymer thin films prepared by a spin-coating method were measured at room tem-

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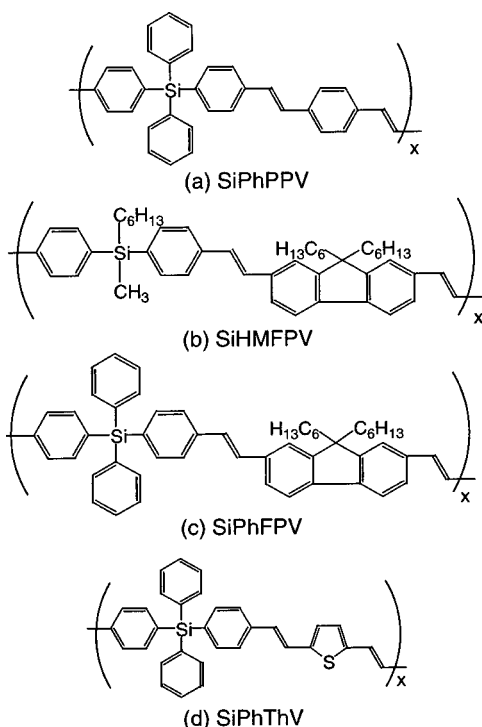
FIG. 1. Molecular structures of conducting polymers with Si atoms in the main chains.

FIG. 2. Absorption spectra of conducting polymers with Si atoms.

perature in an evacuated quartz vessel using a Hewlett Packard HP8452A spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. PL quantum efficiency was measured by a system consisting of an Ar^+ laser (363.7 nm) or blue semiconductor laser (402 nm), a mechanical light chopper, and an integrated sphere with a photodiode and a lock-in amplifier.

Electrochemical measurements, such as cyclic voltammetry, were carried out with a three-electrode system consisting of a working electrode with the sample, a platinum counter electrode, and a silver reference electrode in an electrolytic solution of tetrabutylammonium tetrafluoroborate/acetonitrile using a Hokuto Denko HB-105 function generator and the HA-105 potentiostat.

For the PL measurements at high excitation intensities, we used a nitrogen laser of 337.1 nm in wavelength, 600 ps in pulses, and $1–30$ μJ in the energy per pulse. The pump laser beam was focused by a cylindrical lens onto the polymer thin film and the emission from the side of the film was detected by a photonic multichannel analyzer (PMA) (PMA-11, Hamamatsu Photonics Co.).

Time resolved PL measurements were carried out utilizing a Ti–sapphire mode-lock laser pumped by a cw diode laser as a femtosecond pulse-laser system and a second harmonic generator unit. The pulse-laser beam had a pulse width of about 100 fs and pulse rate of 82 MHz. PL was observed using a streak camera, the time resolution of which is about 15 ps. This measurement was carried out at room temperature in an evacuated quartz vessel.

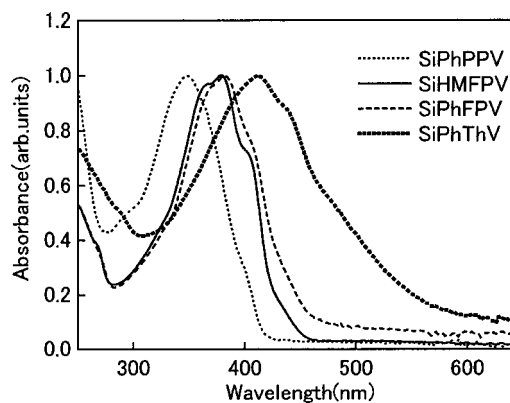EL devices with the structure of indium–tin–oxide (ITO)/polymer/aluminum (Al) were fabricated by vacuum deposition of the Al onto a polymer thin film on ITO-coated glass substrates. The active area of the EL devices was 4 mm^2. Electrical properties such as current–voltage-characteristics and EL spectra were measured using conventional methods.

III. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of SiPhPPV, SiHMFPV, SiPhFPV and SiPhThV in thin films. As evident from this figure, the absorption edges and peaks are shifted depending on the polymer components with π conjugation. The peak wavelengths of absorption in SiPhPPV, SiHMFPV, SiPhFPV, and SiPhThV were 348, 378, 382, and 412 nm, respectively, which corresponds to the $\pi–\pi^*$ transition of the polymers. That is, the absorption peak and edge wavelength are influenced by π conjugation length or conformation in the main chain. From an analysis of the absorption spectral edge corresponding to the highest occupied molecular orbital (HOMO)–LUMO gap of the polymers, using the relationship $(h\nu \times \alpha)^2$ versus $h\nu$ (α: absorption coefficient, h: Planck's constant, ν: frequency) under the assumption of direct transition, the band-gap energies of SiPhPPV, SiHMFPV, SiPhFPV, and SiPhThV are evaluated as 3.2, 2.95, 2.9, and 2.5 eV, respectively.

The top of the valence band, the HOMO, was determined from the observed threshold potential of the electrochemical oxidation in the cyclic voltammogram of the polymers. The threshold potentials of SiPhPPV, SiHMFPV, SiPhFPV, and SiPhThV are estimated to be about 1.3, 1.1, 1.0, and 0.8 eV below the workfunction of silver, respectively. From the analysis of the observed absorption spectral edge and the threshold potentials of the electrochemical oxidation, the electronic energy diagrams in these polymers were evaluated as shown in Fig. 3.

When the SiPhPPV, SiHMFPV, SiPhFPV, and SiPhThV films were excited by light from a Xe lamp, the wavelengths of which correspond to the absorption peaks, strong PL was observed. The PL spectra of SiPhPPV, SiHMFPV, SiPhFPV, and SiPhThV are shown in Fig. 4. The peak wavelengths were located at 444 nm for SiPhPPV, 482 nm for SiHMFPV, 496 nm for SiPhFPV, and 607 nm for SiPhThV. The emission colors were, therefore, blue for SiPhPPV and SiHMFPV, bluish green for SiPhFPV, and red for SiPhThV, respectively.
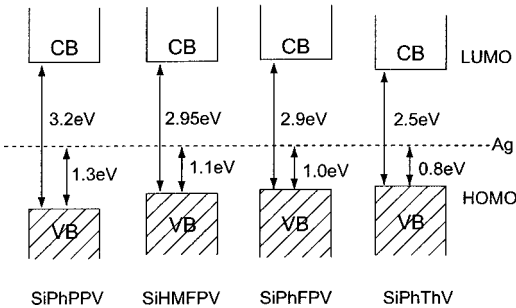
FIG. 3. Electronic energy band diagrams of conducting polymers with Si atoms.

TABLE I. Peak wavelengths of absorption and PL, PL efficiencies, and PL lifetimes of conducting polymers with Si atoms used in this study.

Polymer	Absorption peak (nm)	PL peak (nm)	PL efficiency (photon/photon)	PL liftime (ns)
SiPhPPV	348	444	26.4	0.68
SiHMFPV	378	482	12.7	0.21
SiPhFPV	382	496	11.6	0.15
SiPhThV	412	607	5.3	0.11

PL quantum efficiencies of the polymer films are evaluated as summarized in Table I, when the laser line at 363.7 nm of an Ar$^+$ laser or at 402 nm of an semiconductor laser were adopted as excitation sources. It should be noted that SiPhPPV demonstrated the highest efficiency, 26.4% (photon/photon), in these polymers in spite of the shortest peak wavelength of the emission. The efficiency is comparable with the previously reported efficiency of blue luminescent conducting polymers.[13,14]

From time resolved PL measurements, PL decay time at the PL peak wavelength could be approximated by single-exponential decay:[15] $I(t) = I_0 \exp(-t/\tau)$, where $I(t)$ is the PL intensity at time t, I_0 are the initial intensities, and τ are the lifetime constants, respectively. The evaluated PL lifetime constants of the polymers in films are also summarized in Table I. As is evident in this table, the polymer with longer lifetime exhibits higher PL quantum efficiency. For example, the PL decay times of SiPhThV at peak wavelengths were evaluated to be $\tau = 0.11$ ns, which was the shortest in these polymers as indicated in Table I. The short decay time and the low PL efficiency of SiPhThV might be due to the strong interchain interaction, resulting in the longer diffusion length of photoexcited excitons and nonradiative emission upon encountering the quenching center.

When the excitation intensity of the nitrogen laser pulse at 337.1 nm was increased, the emission spectra of the SiPhPPV film changed as shown in Fig. 5. It is seen that the broad PL spectrum of SiPhPPV obtained at low excitation intensities in Fig. 4 changes at high excitation intensities to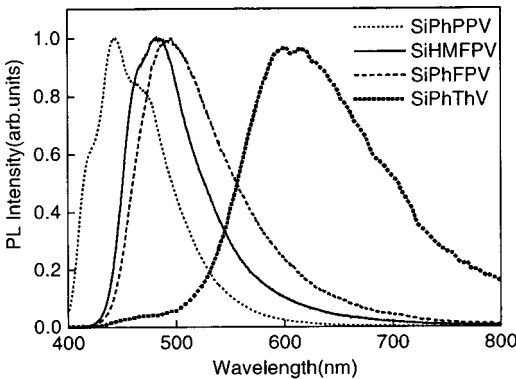 a much narrower and stronger emission band peaked at 444 nm with the spectral width of 5 nm. The emission spectral narrowing is accompanied by a nonlinear amplification as illustrated in the inset of Fig. 5. The sharp peak starts to be observed at the input energy of about 10 μJ/pulse and the intensity of the peak at 444 nm changes its dependence on excitation intensity to superlinear. The spectrally narrowed emission is interpreted as being caused by the amplified spontaneous emission[13,16,17] enhanced by the optical waveguiding in the SiPhPPV film.

In the case of LEDs utilizing SiPhPPV, SiHMFPV, SiPhFPV, and SiPhThV as emission layers, that is, with a structure of ITO/polymer/Al, strong EL was observed. The LEDs exhibit typical rectifying characteristics. In this case, ITO and Al layers act as hole and electron injecting electrodes, respectively. The emission intensity starts to increase at around 12 V. Each EL spectrum is shown in Fig. 6. The emission peak wavelengths of polymers coincide with those of PL.

Although some alternating copolymers have already been known as EL materials, such blue luminescent alternating copolymers with high quantum efficiencies[14] have hardly been reported. It should be emphasized that copolymers, such as SiPhPPV, could be candidates of blue luminescent materials for organic blue LEDs and blue lasers.

Improvement of emission efficiency is one of the most inevitable points in polymer LEDs for realization of the flat panel displays. In this study, two attempts to achieve higher efficiency were carried out. One of them was surface treatment effects of ITO by two silyl coupling materials, *N*-(2-aminoethyl-3-aminopropyl)trimethoxy silane (TMS) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS). The other was ef-

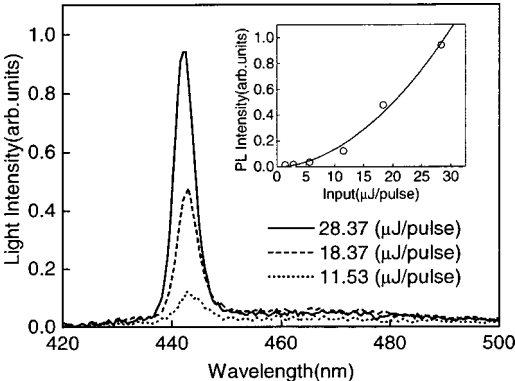FIG. 4. PL spectra of conducting polymers with Si atoms.

FIG. 5. Optical emission spectra at different excitation pulse energies in SiPhPPV thin film. Inset shows the emission peak intensity dependence on the excitation intensity in SiPhPPV thin film.
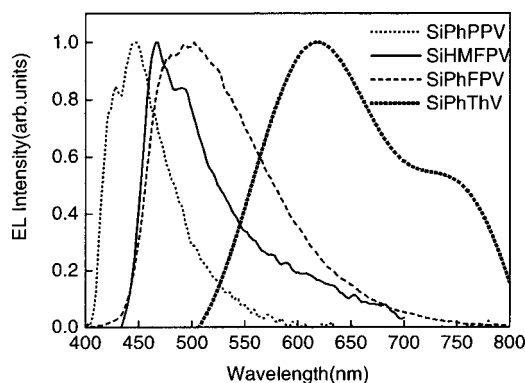
FIG. 6. EL spectra of conducting polymers with Si atoms.

FIG. 8. Current density EL intensity characteristics of SiPhPPV LEDs annealed with various annealing temperatures after Al deposition.

ficiency improvement by the annealing process after fabrication of LEDs.

The former method is described as follows: flat ITO glass substrates precleaned by oxygen plasma were immersed into a toluene solution of TMS of 5 vol % for 15 h. Then, the substrates were heated in toluene at 50 °C for 1 h and washed with toluene, a toluene–methanol mixture (1:1), and methanol to remove the excess TMS. The substrates were also ultrasonicated in distilled water for 10 min and dried at 55 °C in air for 30 min. The substrates were then coated by a TMS monolayer, on which polymer layers were spin coated.

In the case of surface modification by HMDS, ITO glass substrates precleaned by oxygen plasma were immersed into a *p*-xylene solution of HMDS of 10 vol % for 1 h. Then, the substrates were washed with toluene and methanol for 15 min each to remove the excess HMDS, dried in ambient atmosphere, then coated by a HMDS monolayer, on which polymer layers were spin coated.

Figure 7 shows current density EL intensity characteristics of LEDs with or without a silyl coupling layer on ITO surfaces pretreated by oxygen plasma. As can be seen in this figure, both LEDs with modified ITO demonstrated 1.5–2 times higher emission intensity at the same current than that with unmodified ITO. Since the current–voltage characteristics and the turn-on voltages of all LEDs were almost the same, it should be noted that the emission efficiency changed

markedly. By using the silyl coupling layer, such as TMS, which is utilized as a substrate surface treatment in polymer self-assembled techniques,[18–20] tight adhesion between the substrate surface and spin-coated polymer film might be obtained.

Indium atom diffusion from ITO in the polymer emission layer is one of the most serious problems in organic LEDs that has been reported by several groups previously.[21–23] However, the coating of silyl coupling layer could prevent the indium contamination from the ITO electrode, therefore the silyl coupling layer might play a role in polymer LEDs as a buffer to impede indium diffusion from ITO and thus enhance the emission efficiency. Furthermore, the coating of the silyl coupling layer needs a simple fabrication process in comparison with a thin buffer layer composed of an organic dye molecule, such as copper phthalocyanine, which has been reported to be adopted as a buffer layer on the anode of organic LEDs.[24] The surface treatments by TMS and HMDS were available and effective to improve the EL efficiency for normal EL materials such as PPV derivatives as well as copolymers with the Si atom. The EL enhancement factors were slightly different for each conducting polymer.

The annealing process was carried out after deposition of the Al cathode onto polymer films. The fabricated LEDs were loaded into a quartz tube and annealed by an electric furnace in vacuum at various temperatures for 1 h. Figure 8 shows current density EL intensity characteristics of EL devices annealed with various annealing temperatures after Al deposition. Comparing the light intensity at the same current density, LED annealed at 100 °C achieved twice stronger intensity than an unannealed one. However, in the case of LEDs annealed at 140 or 180 °C, the emission intensity was quenched markedly. Such annealing effects could not be observed in the annealing process before deposition of the Al cathode onto polymer films. The optimum annealing temperature also depends on polymer materials, for example, an optimum annealing temperature of LED with poly(2-methoxy-5-dodecyloxy-*p*-phenylene vinylene) emission layer was found around 140 °C. The thermal treatment might be effective for any conducting polymer LEDs with the Al cathode. In the case of polymer LEDs with a magnesium–
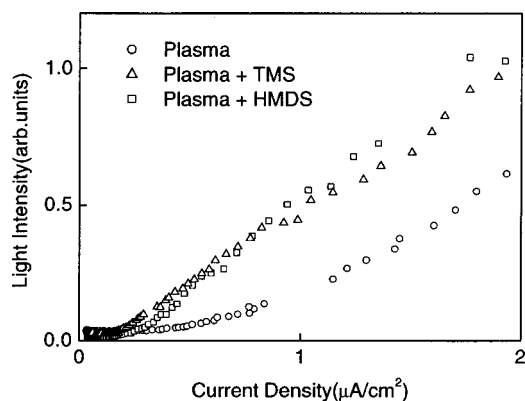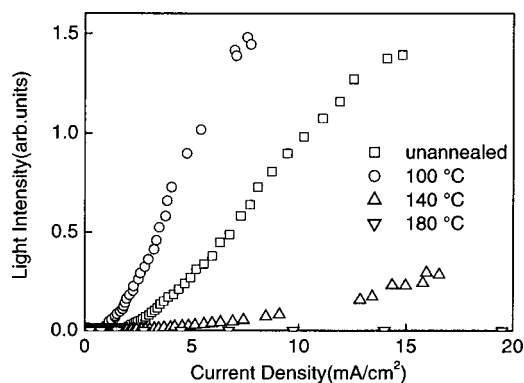

FIG. 7. Current density EL intensity characteristics of SiPhPPV LEDs with or without the silyl coupling layer on ITO surfaces pretreated by O₂ plasma.

silver alloy cathode, such improvement of EL efficiency could not be found.

As previously reported, Al diffusion into the polymer film at the interface between the polymer layer and the Al cathode has been known.[25] The deposited Al atoms tend to cause a covalent bond formation around the interface with polymer material. Thermal treatment after Al deposition promotes adhesion between the polymer layer and the Al cathode and formation of the chemical bond such as the C–Al or C–O–Al covalent bonds,[26] resulting in an efficient electron injection interface due to the interfacial adhesion. Thermal treatment over optimum temperature might enhance interchain interaction of polymers or degenerate the polymer film, resulting in the low emission efficiency.

IV. SUMMARY

Optical properties of conducting polymers with Si atoms in main chains, such as optical absorption, PL, and EL were studied. The electronic energy structures were determined by optical and electrochemical measurements. Strong PL with high quantum efficiency was clarified in the films, and spectral narrowing was observed by pulse excitation of a nitrogen laser. Intense blue or red EL was also demonstrated and the emission efficiency was improved by electrode surface modification and an annealing process.

ACKNOWLEDGMENTS

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