

## Transient Electroluminescence in the Light-Emitting Diodes of Poly (p-phenylene) Thin Films

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We have studied the temporal response of the electroluminescence (EL) emission in the light-emitting diodes fabricated with a vacuum-deposited poly (p-phenylene) (PPP) thin film as an emissive layer sandwiched between indium-tin-oxide (ITO) and Al electrodes. Upon application of a rectangular driving voltage with a forward bias, we observed a time delay between the onset of the bias voltage pulse and the EL emission. The EL time delay results from the charge carrier transport towards the recombination zone. Since the hole mobility is much larger than the electron mobility in PPP, the EL delay time is the transit time for holes in PPP thin films. The hole mobility is estimated to be  $\sim 1 \times 10^{-5} \text{ cm}^2/\text{Vs}$  in vacuum-deposited PPP films.

### I. INTRODUCTION

Light-emitting diodes (LEDs) with organic thin films of small molecules or  $\pi$ -conjugated polymers as active emissive layers have attracted considerable interest due to their potential application in flat-panel displays [1,2] and solid-state laser diodes [3,4]. Their high luminance efficiency in the full range of the visible spectrum and their lasing properties upon optical pumping have demonstrated the potential of organic LEDs [1-4]. The  $\pi$ -conjugated polymers are also very attractive in the scientific aspects.

Since  $\pi$ -electrons are coupled to distortions in the polymer backbone by a strong electron-phonon interaction, charge carriers injected in the  $\pi$ -conjugated polymers self-localize and form nonlinear excitations such as solitons, polarons, and bipolarons [5]. These nonlinear excitations have been intensively studied to understand the nature of primary photoexcitations and the mechanisms of carrier transport and recombination [5-9].

Electroluminescence (EL) from organic LEDs is the result of the radiative recombination of electrons and holes injected from the cathode and anode, respectively. Therefore, the time response of the LED is determined by the interplay of these processes. Upon application of short rectangular voltage pulses with forward biases the EL arises with a delay time  $\tau_d$  and then saturates when the electron and the hole distributions have been

interpenetrated and steady-state conditions have been achieved [10-14]. At the end of the voltage pulse, the EL decays to zero as the injected charge carriers deplete. The delay time  $\tau_d$  of the EL onset is considered as the time for the leading edges of the packets of injected electrons and holes to meet and undergo radiative recombination [10-12]. Therefore, one can study charge carrier dynamics, as well as estimate the charge carrier mobility, from the temporal response of the transient EL signal. In addition, the advantages of pulsed electrical excitation of organic LEDs with short rectangular voltage pulses over continuous wave (CW) operation are the minimization of the Joule heating effects and the operation of the device under a higher current density [14]. In this paper, we will study the transient EL response to understand the transport process of charge carriers and the origin of the EL time delay in blue-emitting LEDs fabricated with vacuum-deposited poly(p-phenylene) (PPP) thin films [15,16].

PPP has gained significant interest because of its high photoluminescence (PL) efficiency and good thermal stability [17]. However, it is infusible and insoluble so that it is not easy to use to fabricate a thin film. Grem *et al.* [18] first reported using a soluble PPP precursor and then thermally converting to the conjugated polymer to fabricate blue-emitting PPP LEDs with external quantum efficiencies of 0.01-0.05 %. Since the spin-coating method has disadvantages, such as the contamination of PPP with the various impurities in the solvent and difficulty in controlling film thickness and fabricating multilayer device structures, the vacuum deposition of

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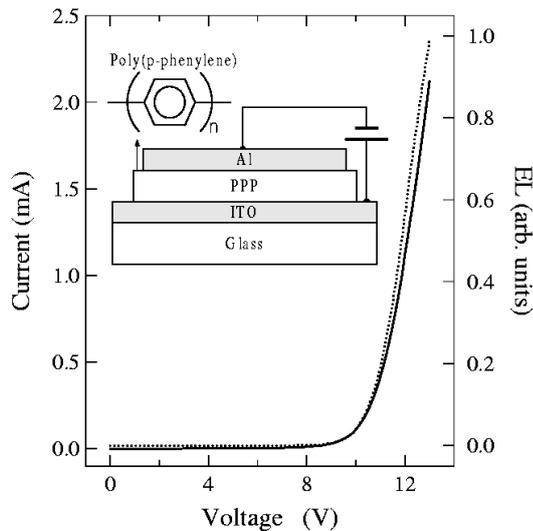


Fig. 1. The forward biased  $I$ - $V$  (solid line) and  $EL$ - $V$  (dotted line) characteristics of the ITO/PPP/Al device at room temperature. The inset shows the chemical structure of PPP and the device configuration.

PPP thin film has been investigated by several groups [19,20]. Here, we study the transient EL response of blue-emitting LEDs fabricated with vacuum-deposited PPP thin films. The temporal behavior of the EL from ITO/PPP/Al upon application of a rectangular driving voltage pulse is analyzed in terms of the electron-hole recombination. The EL time delay is attributed to the transit time of the holes with the hole mobility of  $\sim 1 \times 10^{-5}$  cm<sup>2</sup>/Vs in vacuum-deposited PPP films.

## II. EXPERIMENT

The details of the synthesis of poly (p-phenylene) used in this study are reported elsewhere [16]. The chemical structure of PPP is shown in the inset of Fig. 1. The degree of polymerization  $n$  was characterized by IR spectrum analysis [16,19]. We found that the average phenylene chain lengths of the parent PPP powder and the vacuum-deposited PPP thin films were about  $n=27-28$  and  $n=8-9$ , respectively [16]. This indicates that the shorter molecular weight portion evaporates predominantly and/or that the long chain segment in the parent PPP is broken upon heating. Indium tin oxide (ITO) glass with a sheet resistance of about 10  $\Omega/\square$ , supplied by Samsung Corning Co., Ltd., was cleaned in an ultrasonic bath of toluene, isopropyl alcohol, acetone, and methanol, successively, and then loaded into a vacuum-deposition chamber. The PPP thin film was deposited onto the ITO substrate by heating the parent PPP powder to 500 °C under a vacuum of about  $2 \times 10^{-6}$  Torr. On top of the PPP layer, the Al electrode was vacuum-deposited with an active area (the overlap of ITO and Al)

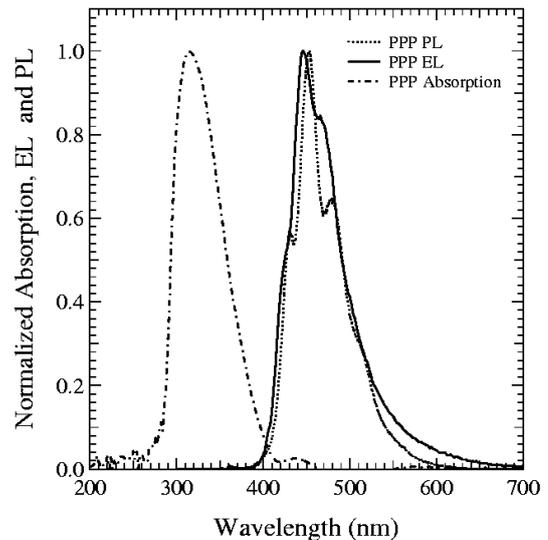


Fig. 2. The optical absorption spectrum and the PL spectrum of the vacuum-deposited PPP thin film compared with the EL spectrum of the ITO/PPP/Al device under 12 V at room temperature.

of about 4 mm<sup>2</sup>. The EL and the PL spectra were measured with a Shimadzu spectrofluorophotometer (RF-540) and the absorption spectra of the PPP thin films deposited onto quartz substrates were measured with a Scinco S-2140 UV-Vis spectrophotometer.

The ITO/PPP/Al devices were mounted in a cryostat under vacuum. The  $I$ - $V$  characteristics were measured with a Keithley 2400 source meter. The intensity of the EL emission was simultaneously measured with a Keithley 2000 multimeter equipped with a calibrated Si photodiode. For the transient EL measurement a Hewlett-Packard HP 214B pulse generator was used to apply rectangular voltage pulses of up to 100 V between the ITO and the Al electrodes. The voltage pulse width was varied between 50 ns and 10 ms. The temporal response of the EL was detected by using a fast photomultiplier tube (ARC P2 PMT) through an ARC 275 monochromator. The voltage pulse from the pulse generator, the voltage across the current-limiting resistor (50  $\Omega$ ) in series with the device, and the transient EL signal were simultaneously digitized with a 500-MHz digital storage oscilloscope (Tektronix TDS 644B). The overall RC time constant of the system was estimated to be less than 50 ns with an active electrode area of about 4 mm<sup>2</sup>.

## III. RESULTS AND DISCUSSION

Figure 1 shows the current-voltage-light ( $I$ - $V$ - $L$ ) characteristics of the ITO/PPP/Al device at room temperature, along with the device configuration and the chemical structure of PPP in the inset. The  $I$ - $V$  characteristics show a rectifying behavior with the forward bias defined

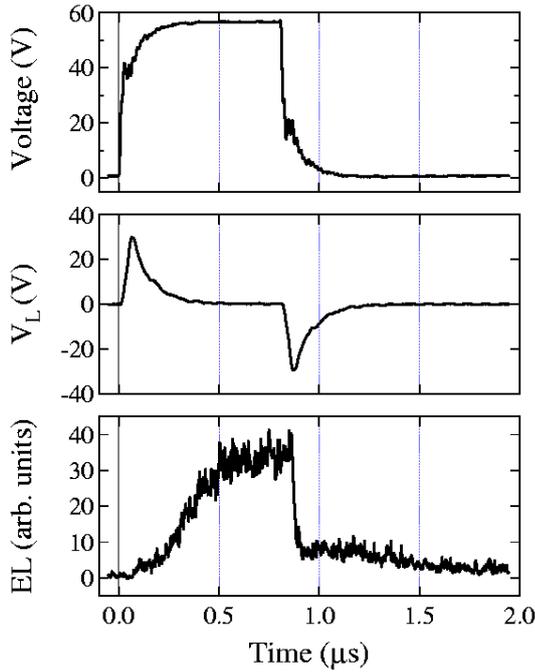


Fig. 3. Transient EL response (bottom) of the ITO/PPP(120 nm)/Al device to a rectangular voltage pulse from a HP 214B pulse generator (top) and the voltage response,  $V_L$ , (middle) across the current-limiting resistor ( $50 \Omega$ ) in series with the device.

as the positive voltage applied to the ITO electrode. The ITO/PPP/Al LED with a PPP layer thickness of about 120 nm turned on at approximately 8 V with an external quantum efficiency of about 0.02 %. The charge carrier injection was dominated by a tunneling process through an energy barrier of about 0.6~0.8 eV in ITO/PPP/Al [21].

Figure 2 compares the optical absorption spectrum, the PL spectrum of the vacuum-deposited PPP thin film with the EL spectrum of the ITO/PPP/Al device under 12 V at room temperature. All the spectra are normalized at the peak wavelength. The optical absorption spectrum shows a steep onset at about 410 nm (3.02 eV) and a peak at about 314 nm, assigned to the  $\pi$ - $\pi^*$  interband transition in PPP. The PL spectrum shows well-resolved vibronic structures. The EL spectrum exhibits a peak at 446 nm (2.78 eV), slightly blue-shifted compared with the PL peak at 453 nm (2.74 eV). A similar blue shift of the EL was observed previously in the ITO/PPP/Al devices fabricated with a soluble PPP precursor by Grem *et al.* [18]. The overall spectral shapes of the EL and the PL are very similar, implying that the excited states that lead to radiative recombination are the same.

Figure 3 shows the typical transient EL response of the ITO/PPP/Al device in comparison with the shape of the voltage pulse from the HP 214B pulse generator and the voltage response,  $V_L$ , across the current-limiting

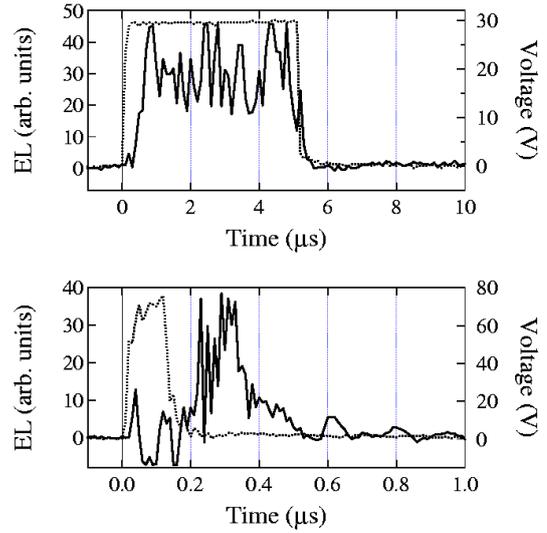


Fig. 4. Transient EL signal (solid line) of ITO/PPP/Al upon application of voltage pulses (dotted line) with the pulse duration of  $5 \mu\text{s}$  and 150 ns.

resistor ( $50 \Omega$ ) in series with the device. The voltage spikes in  $V_L$  at the rise and the fall of the pulse are due to the capacitive effect of the device with the RC time constant much less than the voltage pulse width. The EL emission arises with a time delay of  $\tau_d \sim 200$  ns after the onset of the bias voltage pulse and then saturates at  $\sim 500$  ns. The delay time and the rise time of the organic LED in the submicrosecond time region are important aspects for high-resolution display applications in which a fast response time is required of the EL pixel. The time delay between the EL and the voltage pulse is much clearer when the voltage pulse duration is reduced from  $5 \mu\text{s}$  to 150 ns, as shown in Fig. 4. The EL emission under the pulse with a width of 150 ns is observed after a time delay of  $\tau_d \sim 200$  ns even though the voltage pulse has already been reduced to zero at 200 ns.

The delay time  $\tau_d$  of the EL onset can be considered as the time for the leading edges of the packets of injected electrons and holes to meet and undergo radiative recombination [10–12]. Then, this time delay is given by

$$\tau_d \cong d/(\mu_n + \mu_p)F \cong d/\mu_p F, \quad (1)$$

where  $d$  is the thickness of the PPP layer, and  $\mu_n$  and  $\mu_p$  are the electron and the hole mobilities, respectively, at an average electric field  $F=V/d$ . In Eq. (1), we assume that the hole mobility is much larger than the electron mobility, which is typical in organic semiconductors. Thus, we can estimate the hole mobility from Eq. (1) [10–12].

Alternative interpretations have been reported for the EL delay time [22–24]. If the electron mobility is much smaller than the hole mobility, the leading edges of both carriers meet near the metallic cathode, where excited states would be quenched. Therefore, the EL can arise only when the leading edges of the electron packets can

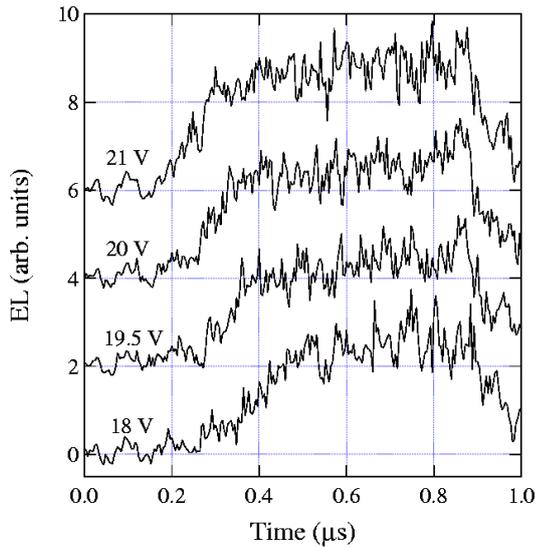


Fig. 5. The transient EL evolution in time from the ITO/PPP(120 nm)/Al device upon application of a rectangular voltage pulse with various pulse amplitudes.

migrate across the width of the quenching zone, on the order of 10~15 nm, near the cathode [22,23]. Within this interpretation, the transit time of the fast charge carriers (holes) is much shorter than the delay time  $\tau_d$  that is determined by the electron mobility and the width of the quenching zone at the cathode [22,23]. Recently, Ostergard *et al.* [24] also attributed the EL time delay to accumulation of space charges and build-up of an internal field. Holes move through the organic layer with large mobility. The injection rate of electrons increases as holes build up a space charge near the cathode, thereby increasing the internal electric field. When the field near the cathode becomes high enough, the electrons are injected and the EL is observed [24]. If the delay time were the transit time of holes across the PPP layer, we would expect the delay time to decrease with increasing field according to Eq. (1). On the contrary, if the delay time were the time for electrons to migrate across the quenching zone, we would expect the delay time to have no field dependence. In order to settle the controversy about the EL delay time  $\tau_d$ , we have measured the dependence of the transient EL response on the voltage and the film thickness.

The voltage dependence of the transient EL response of the ITO/PPP( $d=120$  nm)/Al device is shown in Fig. 5. Increasing the amplitude of the voltage pulse causes the delay time to decrease, and the steady-state EL level is reached at shorter time, consistent with Eq. (1). Therefore, the decrease in the delay time is due to the decrease in the hole transit time with increasing applied electric field.

Figure 6 shows the EL time delay as a function of  $1/V$  in the ITO/PPP/Al devices for different PPP layer thicknesses of about  $d_1=120$  nm and  $d_2=260$  nm. The

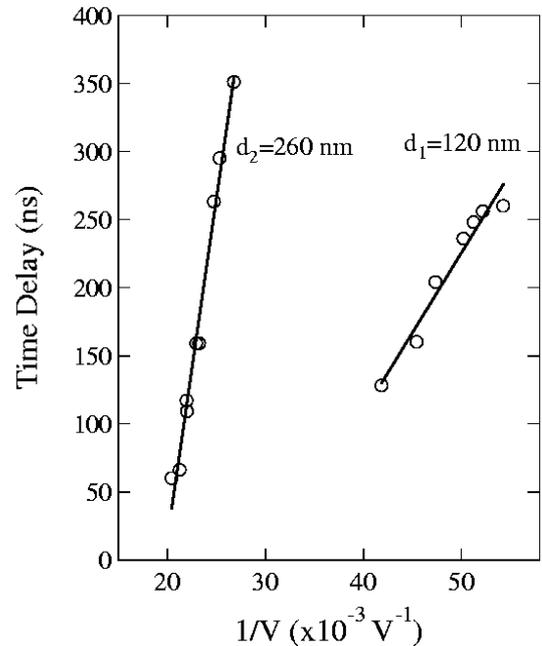


Fig. 6. The voltage dependence of the EL time delay in the ITO/PPP/Al devices for different PPP layer thicknesses of about  $d_1=120$  nm and  $d_2=260$  nm. The line through the data points is the straight-line approximation of  $\tau_d$  as a function of  $1/V$ .

EL delay time is longer for the thicker film under the same applied field, consistent with Eq. (1). We can calculate the hole mobility from the slope of the straight-line approximation of  $\tau_d$  as a function of  $1/V$  and the thickness of the PPP film by using Eq. (1). The hole mobility is  $\mu_p=d^2/\tau_d V \sim 1.2 \times 10^{-5}$  cm<sup>2</sup>/Vs and  $1.4 \times 10^{-5}$  cm<sup>2</sup>/Vs for the devices with  $d_1=120$  nm and  $d_2=260$  nm, respectively. Thus, similar mobility values are obtained for different film thicknesses, as expected from Eq. (1). This hole mobility value is consistent with that recently reported for organic LEDs based on para-hexaphenyl film [25]. This result again agrees with the assumption that the EL delay time is attributed to the transit time of holes across the PPP layer.

#### IV. CONCLUSIONS

The transient EL response of blue-emitting LEDs fabricated with vacuum-deposited PPP thin films has been studied to unravel the cause of the time delay between the onset of the voltage pulse and the EL onset. The dependence of the transient EL response on the amplitude of the voltage pulses and the film thickness indicates that the EL time delay results from the transit of holes across the PPP layer. However, the observed results are inconsistent with the model that the EL delay time corresponds to the time the electrons need to migrate through the quenching zone. The hole mobility is estimated to be

$\sim 1 \times 10^{-5}$  cm<sup>2</sup>/Vs in the vacuum-deposited PPP films. We also showed that the ITO/PPP(120 nm)/Al LED turned on at about 8 V with an external quantum efficiency of about 0.02 % and that it had a fast response time of less than a microsecond.

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