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Transient uv electroluminescence from poly(*p*-phenylenevinylene) conjugated polymer induced by strong voltage pulses

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We present time-resolved and spectral measurements of electroluminescence from poly(*p*-phenylenevinylene) (PPV) thin films upon application of high-voltage pulses. Above some threshold voltage of 100 V, we observe an uv-violet emission centered at 390 nm, in addition to the characteristic yellow-green luminescence of PPV. We explain this emission as being induced by a generation of hot carriers in the strong electric field, which inhibits the formation of singlet excitons and enhances the probability for direct interband transitions of the relaxed carriers. [S0163-1829(97)50544-3]

The electroluminescence (EL) and photoluminescence (PL) properties of poly(*p*-phenylenevinylene) (PPV) conjugated polymer have been studied extensively during the past decade. Most of the theoretical and experimental evidence[1–4] suggests that the green EL and PL emission (at 510 nm ≈2.45 eV) in PPV is associated with radiative decay of singlet excitons. Singlet excitons can be generated either by photoexcitation or by electrical injection of negative and positive charge carriers to the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively. Due to exciton binding energy and the lattice relaxation[2] the luminescence energy of PPV is lower than the HOMO-LUMO band gap, which is around 3.1 eV. Recent PL studies of PPV in the presence of electric field[5] have indicated that the PL is partially quenched. This was attributed to exciton dissociation by the strong electric field. However, to the best of our knowledge, the effect of strong electric fields on the EL properties of PPV has not been studied yet. This communication reports on transient EL studies of PPV-based light-emitting diodes under strong and short voltage pulses. Application of short voltage pulses with low duty cycle minimizes heating and temperature accelerated chemical reactions, which are among the main reasons for device degradation and failure.

Pulsed EL studies are also of interest in view of the recent discovery of optically pumped lasing from PPV films[6,7] and the prospects for electrically pumped laser. As high current density is a prerequisite for electrically stimulated lasing the effect of high voltage and the nature of EL properties under electrically strained conditions are important. Pulsed EL in PPV were reported by several authors,[8–11] however, the highest current density reported[8] was 25 A/cm^2. Here we report on transient EL studies under strong pulsed voltage and current density up to 700 A/cm^2 and demonstrate new phenomena at such high fields and currents.

Films of poly(*p*-phenylenevinylene) (PPV) were prepared from either water or methanol solution spin cast on transparent and conductive ITO-coated glass and subsequently vacuum heated to 300 °C for 12 h. We have determined the thickness of the films by means of x-ray reflectivity to be approximately 500 Å. Aluminum was used as the counter-electrode with an active area of 5 mm^2. The RC time of the device, measured at 1 MHz, was approximately 110 ns. We have used the Velonex 350 as the high-voltage pulse generator and achieved a maximum of 800 V on the load impedance of our LED's. The voltage pulsewidth could be varied between 250 ns and 5 μs. However, in most of our measurements we have used pulses of 250-ns duration either in a single pulse mode, or, at a very low duty cycle (0.001%) in repetitive mode measurements. The EL through the ITO electrode was measured by a fast photomultipler and recorded with a 500-MHz digital oscilloscope. Spectral measurements were performed in repetitive mode using a monochromator and scanning the photomultipler (PMT) signal with a photon counter. These measurements were repeated by monitoring and averaging the PMT output on the digital oscilloscope, and calculating the area under the EL signal curve with consistent results. As will be demonstrated below, the transient EL signal at high applied voltage amplitude is a combination of green and uv luminescence. To distinguish between the two in the time-resolved measurements, we have utilized two sets of optical filters: (a) an uv filter consisting of an interference filter centered at 392 nm followed by a glass filter (with overall transmission less than 10^{-5} for $\lambda > 410$ nm); (b) a ''Green filter,'' a combination of filters blocking the wavelengths below 480 nm (transmission $< 0.5\times 10^{-4}$).

The current through the sample was monitored via a 1-Ω resistor in series with the sample and was also recorded by the digital oscilloscope. Simultaneously with the transient current and the transient EL signals we have also recorded the voltage pulse across the device. This voltage is composed of two components: the voltage across the PPV film, and the voltage drop on the external circuitry including the ITO electrode with a total resistance of 50 Ω. During measurements, samples were placed in a vacuum cell at room temperature.

Typical EL signal, current, and voltage oscillograms are shown in Fig. 1, upper panel, for a pulse amplitude of 120 V. The onset of EL (upper panel) is delayed relative to the voltage pulse. This delay has been interpreted as the time required for the leading front of injected positive and negative charge carriers to meet and recombine radiatively.[9,11,12] The delay time allows an estimate of mobility of positive carriers, to be $\mu_h = 1.8\times 10^{-5}$ cm^2 V^{-1} s^{-1}. We observe two dis-

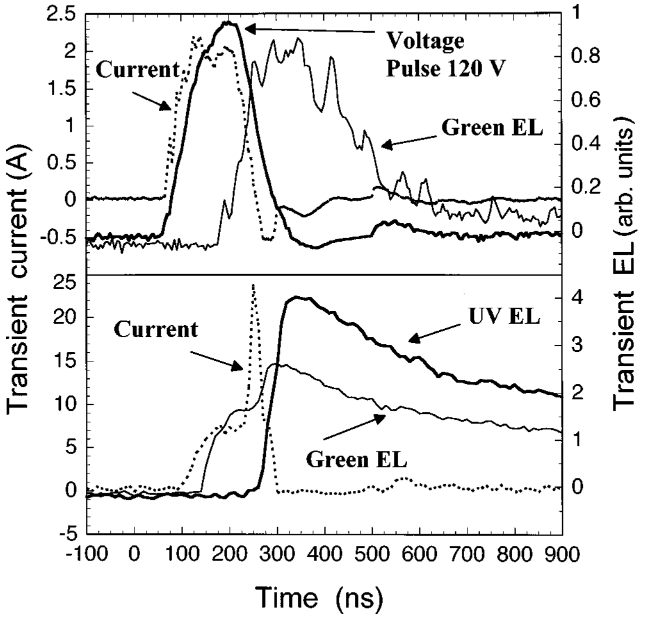

FIG. 1. Upper panel: Oscillogram of the voltage pulse (solid thick line), the transient EL response (solid thin line), and the transient current response (dotted line) of a Al-PPV-ITO device. The amplitude of the voltage pulse is 120 V, which corresponds to the threshold voltage for the appearance of the uv-violet emission. The EL signal is mostly green EL. Signals are obtained in a single acquisition mode. Note the delay between the voltage pulse and the onset of EL. Lower panel: Oscillogram describing the transient EL response (solid thick line is the EL response at 370–410 nm; solid thin line is the green EL response) and the transient current response to a 350 V voltage pulse. Signals are obtained in a single acquisition mode. Note the delay of the violet EL after the green EL and the larger intensity of the former. Note also the appearance of a spike on the current pulse due to avalanche (see text). This sharp current spike leads to a strong increase of the uv EL intensity and to an enhancement of the green EL.

tinct regimes of device operation depending on the pulse amplitude and the driving current. Below 100 v and current density up to 50 A/cm^2 the EL spectra under pulsed voltage (Fig. 2) reveal the typical yellow-green emission of PPV with no noticeable difference with respect to the EL spectra under dc bias except the significantly more intense EL in the former case. In Fig. 3 we have plotted the EL intensity and the current density through the device versus the applied voltage. Note the dramatic increase in the pulsed EL intensity with voltage (by three orders of magnitude at low voltages) up to 30 V. In this low voltage regime ($<$30 V), the current and the EL intensity are superlinear with the voltage, and the EL seems to saturate above some value of $\approx$30 V. Plotting the EL intensity versus the peak current (not shown here) reveal almost linear behavior up to voltage of 120 V followed by a saturation above this value. The total luminous intensity of our sample (5 mm^2) driven at 50 A/cm^2 was around 0.15 cd, which corresponds to a brightness of 30 $\times 10^3$ cd/m^2. Best results[1] using multilayer structure indicate 90$\times 10^3$ cd/m^2 under pulsed mode and 20 $\times 10^3$ cd/m^2 at dc operation. As anticipated the efficiency of approximately 0.02 lum/W of our samples is lower than those reported in multilayer samples[13] or even for single layers but using different electrodes.[13–15]

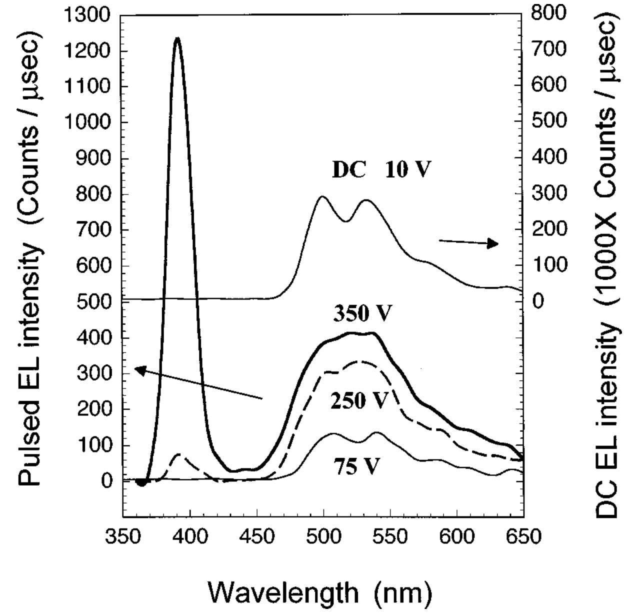

FIG. 2. EL spectra of a Al-PPV-ITO device under pulsed voltage with different amplitudes (indicated in the figure). The threshold voltage for the appearance of the uv EL spectra at 390 nm is ~100 V. For comparison the EL spectra (enhanced by a factor of 1000) of the same device but under dc voltage of 10 V is shown.

Probably, the most important observation is the appearance of additional ultraviolet (uv)-violet luminescence centered at 390 nm ($\approx$3.18 eV) at higher voltages. Figure 3 exhibits the EL intensity associated with the uv-violet emission, the green emission, and the current density as functions of the peak voltage. As clearly seen, the threshold voltage for the appearance of the uv EL is about 100 V. Above this voltage the intensity of the uv EL seems to increase in a

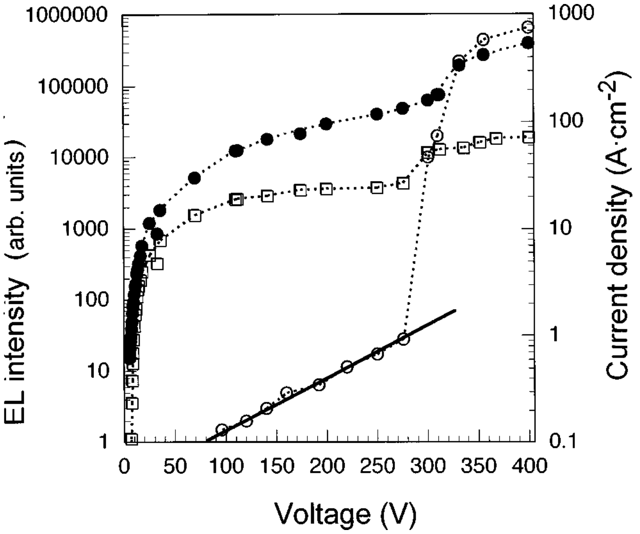

FIG. 3. EL peak intensity for the green emission (open squares), the uv-violet emission (open circles), and the peak transient current (closed circles) as a function of the voltage pulse height. The dashed lines are guides to the eye. The solid line represents an exponential fit to the uv EL for voltages below 350 V. (This is the threshold voltage for the appearance of the current spike.)

exponential-like fashion. The solid line in Fig. 3 represents an exponential fit to the data. Above 300 V the uv EL increases dramatically by roughly three orders of magnitude (Fig. 3), while the green EL exhibits only a moderate increase. In the time domain this dramatic increase occurs exactly at the emergence of the spike in the transient current (Fig. 1, lower panel). In Fig. 1, a lower panel, we show also the green transient EL and the uv transient EL for an applied voltage pulse of 350 V. It is clearly seen that at such high voltage the transient uv EL far exceeds the green one. It is also seen that the onset of the transient uv EL lags after the onset of the green EL. In addition, we notice a small enhancement of the green EL at the onset of the sharp current spike: the current spike leads to a strong increase of the uv EL emission and enhancement of the green emission.

All the effects described above are reversible, and were reproduced many times on different samples. At lower voltages up to 290 V we could apply 10^7 pulses without device degradation. However, at higher applied pulsed voltages (>400 V) we have witnessed a gradual degradation of our devices. Just before the complete failure of the device the luminescence from the light-emitting diode was highly unstable with the noisy spectrum in the red.[16] As clearly seen in Fig. 2, at a voltage of 290 V the uv EL intensity is comparable to the green one. For this voltage the current density is 140 A/cm^2 and the overall brightness is approximately 10^5 cd/m^2.

To the best of our knowledge this is the first observation of uv violet emission from PPV. Naturally, the question arises, what is the origin of the uv emission in PPV? We emphasize that EL studies of insulating nonconjugated polymers have demonstrated wide spectra with violet and uv EL emissions at high electric fields.[17–20] The high-energy photon emission in these systems was attributed to the so-called ''impact ionization,'' which occurs when the injected and thermally generated carriers are accelerated by strong electric field to cause collision excitations and subsequent radiative recombination. Theoretical models[20–24] suggest that the number of these collisions depends exponentially on the electric field. In stronger electric fields these collisions may produce avalanches that lead to electrical breakdown. Our results in Fig. 3 indeed indicate that the EL intensity associated with the uv emission increases exponentially with the increasing of the amplitude of the applied voltage pulse, in contrast to the linear increase of the green EL emission. This may suggest that the uv EL observed in the present experiment is also associated with the recombination of ''hot'' nonequilibrium carriers in the presence of large electric fields. To clarify the situation further, we have constructed a device in which an insulating nonconjugated polymer, namely, poly(vinyl alcohol) (PVA) is sandwiched between ITO and aluminum electrodes and have studied the device EL properties under pulsed electric fields. Similar to previous studies, we find a wide spectrum of EL emission including uv emission upon applying strong pulses. However, the intensity of this emission is at least two to three orders of magnitude smaller than the uv emission from our PPV-based devices. This may suggest that the uv EL from ITO/PPV/Al cells is associated with the PPV and *not* with the ITO or the Al electrodes. The delay time between the onset of green EL and uv emission is probably due to the time needed to establish the high current density within the PPV film.

To determine whether the uv emission from a ITO/PPV/Al light-emitting diode occurs in the vicinity of the ITO or the Al side of the device, we have carried out an additional measurement using semitransparent aluminum electrode and compared the intensity of the emission from the Al and the ITO sides. We have found that while the green El intensity did not vary appreciably, the uv EL from the aluminum side was at least 100 times more intense than that emitted from the ITO side. We conclude that the uv EL originates near the Al electrode and is strongly absorbed by the polymer even with the relative small thickness of 500 Å.

We propose the following explanation for the strong 390-nm uv-violet EL: at the first stage, impact excitation induced by the strong field produces a large number of excited carriers in excess of equilibrium (''hot'' carriers). At the second stage, these excited states decay approaching their number at equilibrium. The decay is realized via several competing mechanisms. Formation of singlet excitons, which then decay radiatively emitting green EL, is one such possible mechanism. However, the strong electric field inhibits this type of decay by dissociation of the excitons, thereby enhancing the direct HOMO-LUMO interband radiative transition with uv emission. Since in the depletion layer formed at the polymer-aluminum interface the electric field is the largest,[5,9] the uv EL originates at this side of the device, as observed in our samples. This model also agrees with previous time-resolved photoexcitation measurement[5] where quenching of PL upon application of electric field was observed when optical excitation was from the Al side, but not from the ITO side. The authors argued that the strong electric field at the polymer-Al interface quenches the luminescence due to exciton dissociation.

In conclusion, (a) we have demonstrated that LED devices based on a single PPV layer can be operated in a pulsed mode at high electrical fields pulses with considerable transient current densities without significant degradation of the device. Very high transient current density, more than 140 A/cm^2, was achieved which in turn leads to considerable enhancement of the EL by several orders of magnitude.

(b) Above some threshold voltage of ~100 V we have observed a new feature of uv emission (centered at 390 nm) that increases exponentially with the applied field. In our opinion this phenomenon is explained in the framework of the impact excitation model in strong electric fields by which hot electrons with large densities far exceeding the equilibrium state are created. Under such conditions direct radiative transition is favorable over exciton recombination. The saturation of the green EL signal around ~100 V is further evidence for the partial inhibition of exciton recombination.

(c) At even stronger voltage pulses of ~350 V, we see the appearance of a sharp spike on the transient current signal. This transient current spike is believed to be associated with electrical breakdown and avalanche. This is associated with a sharp increase (three orders of magnitude) of uv EL intensity (avalanche-mediated EL emission). The sharp uv EL following this current spike suggests that hot carriers in strong electric field are responsible for the uv emission. The observed small increase of the green luminescence with the onset of uv EL is readily explained as a secondary photoexcitation by the strong uv emission. The ability to reach such high field strength and such high current densities without significant device degradation is attributed to the remarkable dielectric strength of the PPV films.

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[1] R. H. Friend, G. J. Denton, J. J. M. Halls, N. T. Harrison, A. B. Holmes, A. Kohler, A. Lux, S. S. Moratti, K. Pichler, N. Tesler, and K. Towns, Synth. Met. **84**, 463 (1997).

[2] J-L. Bredas, J. Cornil, and A. J. Heeger, Adv. Mater. **8**, 447 (1996).

[3] M. Chandross, S. Mazumdar, S. Jeglinski, X. Wei, Z. V. Vardeny, E. W. Kwock, and T. M. Miller, Phys. Rev. B **50**, 14 702 (1994).

[4] S. V. Frolov, M. Liess, P. A. Lane, W. Gellermann, Z. V. Vardeny, M. Ozaki, and K. Yoshino, Phys. Rev. Lett. **78**, 4285 (1997).

[5] U. Kesting, U. Lemmer, M. Deussen, H. J. Bakker, R. F. Mahrt, A. Kurz, V. I. Arkhipov, H. Bassler, and E. O. Gobel, Phys. Rev. Lett. **73**, 1440 (1994); U. Lemmer, S. Karg, M. Scheidler, M. Deussen, W. Reiß, B. Cleve, P. Thomas, H. Bassler, M. Schwoerer, and E. O. Gobel, Synth. Met. **67**, 169 (1994).

[6] N. Tessler, G. J. Denton, and R. H. Friend, Nature (London) **382**, 695 (1996).

[7] F. Hide, M-A. Diaz-Garcia, B. J. Schwartz, M. R. Anderson, Q. Pei, and A. J. Heeger, Science **273**, 1833 (1996).

[8] D. Braun, D. Moses, C. Zhang, and A. J. Heeger, Appl. Phys. Lett. **61**, 3092 (1992); D. Braun, D. Moses, C. Zhang, and A. J. Heeger, Synth. Met. **55-57**, 4145 (1993).

[9] S. Karg, V. Dyakonov, M. Meier, W. Reiß, and G. Paasch, Synth. Met. **67**, 165 (1994).

[10] S. Kirstein, G. B. Cohen, D. Davidov, U. Scherf, M. Klapper, K. Chmil, and K. Mullen, Synth. Met. **69**, 415 (1995).

[11] H. Chayet, E. Z. Faraggi, H. Hong, V. N. Savvateev, R. Neumann, Y. Avni, and D. Davidov, Synth. Met. **84**, 621 (1997).

[12] C. Hosokawa, H. Tokailin, H. Higashi, and T. Husumoto, Appl. Phys. Lett. **60**, 1220 (1992).

[13] E. Buchwald, M. Meier, S. Karg, P. Posch, H-W. Schmidt, P. Strohriegl, W. Reiß, and M. Schwoerer, Adv. Mater. **7**, 839 (1995).

[14] S. Karg, J. C. Scott, J. R. Salem, and M. Angelopoulos, Synth. Met. **80**, 111 (1996).

[15] Y. Yang, E. Westerweele, C. Zhang, P. Smith, and A. J. Heeger, J. Appl. Phys. **77**, 694 (1995).

[16] V. N. Savvate'ev, A. Yakomov, R. Pogreb, and D. Davidov (unpublished).

[17] C. Laurent, C. Mayoux, and S. Noel, J. Appl. Phys. **58**, 4346 (1985); D. Mary, M. Albertini, and C. Laurent, J. Phys. D **30**, 171 (1997); F. Massines, P. Tiemblo, G. Teyssedre, and C. Laurent, J. Appl. Phys. **81**, 937 (1997).

[18] S. S. Bamji, A. T. Bulinski, and R. J. Densley, J. Appl. Phys. **61**, 694 (1987).

[19] K. Kojima, Y. Takai, and M. Ieda, J. Appl. Phys. **59**, 2655 (1986).

[20] J. V. Champion, S. J. Dodd, and G. C. Stevens, J. Phys. D **26**, 819 (1993).

[21] P. Fisher, in *Electrical Properties of Polymers*, edited by D. A. Seanor (Academic Press, London, 1982).

[22] N. Klein, Adv. Phys. **21**, 605 (1972).

[23] J. Artbauer, J. Phys. D **29**, 446 (1996).

[24] P. R. Thornton, *The Physics of Electroluminescence Devices* (E. & F. N. Spon, London, 1967).