Nanosecond transients in the electroluminescence from multilayer blue organic light-emitting devices based on 4,4′-bis(2,2′diphenyl vinyl)-1,1′-biphenyl

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Nanosecond electroluminescence (EL) overshoots observed when multilayer blue 4,4′-bis(2,2′-diphenyl vinyl)-1,1′-biphenyl (DPVBi)-based organic light-emitting devices (OLEDs) are excited by rectangular voltage pulses are described. The overshoots occur at the voltage turn-off and exceed the cw brightness by up to an order of magnitude. Time-resolved images of the OLEDs demonstrate that the emission from most of the sample surface decays with a single time constant $\tau_1 = 13 \pm 3$ ns. This decay is attributed to recombination of charges which accumulate at the interface of the electron and hole transporting layers, possibly at intrinsic trapping sites. In areas of increased electron injection and EL, such as cathode edges and morphological defects, a second slower decay time $20\,\text{ns} < \tau_2 < 1\ \mu s$ is observed, apparently due to release of carriers from localized trap states in the organic/cathode interface. Only marginal variations in τ_1 are found between bright and dim areas of the devices. At a bias of 10 V, the amplitude of the overshoot is found to peak at a pulse duration of $\sim 20\ \mu s$. Its behavior is believed to result from increased quenching of singlet excitons by the accumulated charges. © *2000 American Institute of Physics.*
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Recent progress in organic light-emitting devices (OLEDs) has resulted in commercial-quality multicolor displays,[1] but low external quantum yields and the quest for an electrically pumped organic diode laser have motivated studies of these devices under pulsed bias.[2–4] Some of these described light flashes observed at the turn-off of the voltage pulse (termed ''overshoots'') in the green and yellow ranges of the visible spectrum,[2–4] with a characteristic duration of $\sim 10\ \mu s$ to a few ms. The studies were conducted on thick single-layer or bilayer polymer OLEDs. In the latter case, the two layers were deposited by consecutive spin coating of precursor solutions or solutions in which the solvents were mutually incompatible, so as to exclude the dissolution of the first layer by the second solvent. However, slight interpenetration of the organic layers may have occurred and a thin transition layer, in fact a blend, may have been formed. It was proposed that the charge accumulation that occurs in the transition layer during the pulse is responsible for the overshoot.[4]

This work describes the overshoots in multilayer small-molecular vacuum-evaporated blue-emitting devices based on 4,4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl (DPVBi),[5] which is a distyrylarylene (DSA) derivative that has attracted considerable attention due to its impressive performance in OLEDs.[6] Besides the use in electroluminescence (EL) displays, fast switching of blue OLEDs may be of special interest for telecommunications.

Figure 1 shows the device structure and the organic mol-

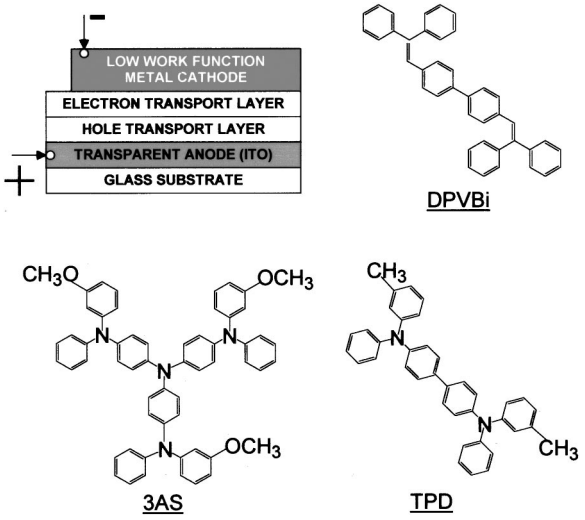

FIG. 1. OLED structure and the materials used to fabricate the devices.

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ecules used in device preparation. The core of the multilayer device are hole (h^+)- and electron (e^-) transporting layers (HTL and ETL, respectively) sandwiched between the h^+-injecting indium–tin oxide (ITO) or other anode and the e^--injecting Al cathode, respectively. In the ETL, the e^- and h^+ mobilities (μ_e and μ_h, respectively) are comparable but much lower than μ_h in the HTL. The ETL increases the steady-state majority-carrier density, reduces the number of h^+ being discharged nonradiatively at the cathode, and promotes e^- injection by generating an internal space charge that redistributes the internal electric field.[4] The injected electrons and holes migrate in opposite directions. About 75% of the recombination events yield the generally nonemissive triplet excitons, and ~25% the radiative singlet excitons, mostly at the HTL/ETL interface. Due to the mobility offset, majority-carrier accumulation also occurs at the HTL/ETL interface and leads to field redistribution across the bilayer device.[4] In particular, the field becomes concentrated in the region adjacent to the cathode that gives rise to enhanced electron injection.[4,7] To promote carrier injection, additional layers are often introduced between the ITO and the HTL, and between the ETL and the cathode. In this study, the HTL consisted of a 150-Å-thick 4,4′,4″-tris[*N*-[3-methoxyphenyl-*N*-phenyl-amine-triphenylamine], dubbed a ''three-armed star'' (3-AS) or Cu phthalocyanine (CuPc) followed by a 200-Å-thick layer of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) (see Fig. 1). The blue-emitting ETL was a 500-Å-thick DPVBi. A~15 Å buffer layer of Al_2O_3 was deposited between the ETL and the Al cathode.[8] The resultant steady-state EL spectrum peaked at 475 nm with a full width at half maximum of ~60 nm, similar to that reported earlier.[6] The samples were prepared as an array of 1.5 mm aluminum disk electrodes evaporated on the organic layers. Each 5×5 cm^2 substrate contained ~250 devices. The low capacitance of the small-area devices, typically, ~0.1 nF, and the ~1 Ω parallel load resistor, lead to a time constant ≤1 ns.

The EL was excited with a 1 ns fall time square pulse output of an Avtek AVL-C pulse generator. The measurements consisted of (i) an integrated transient EL wave form using a Hamamatsu 3456 photomultiplier tube (PMT), and (ii) time-resolved EL imaging using a TE300 Quantum Nikon Corp. inverted research microscope, and a 10 ×/0.13 NA Olympus Corp. objective coupled to a Picostar HR, LaVision GmbH gated camera. This 200 ps resolution camera uses a GEN II-type S20 photocathode and P43 phosphor intensifier lens coupled to a 640×480 pixel charge-coupled device with 12-bit dynamic range. In all the measurements the gate width was set at 2 ns.

Figure 2 shows the light output (EL) of a DPVBi-based OLED when addressed with a rectangular voltage pulse in the forward direction, i.e., ITO electrode biased positively. Upon bias application the EL gradually rises and reaches the steady-state level; the rise time τ_r decreases with increasing voltage. Earlier studies unanimously attributed it to interface charge buildup and the consequent electric-field redistribution. For the 10 V pulse shown in Fig. 2, $\tau_r\sim100\,\mu s$. At the end of the voltage pulse, an EL overshoot lasting <100 ns is observed. In Fig. 2, the peak amplitude of the overshoot is five times greater than the steady-state EL. The overall intensity overshoot measured from the whole sample is dominated by a single decay time $\tau_1=13\pm3$ ns, i.e., demonstrating that only one mechanism dominates the decay of the overshoot.

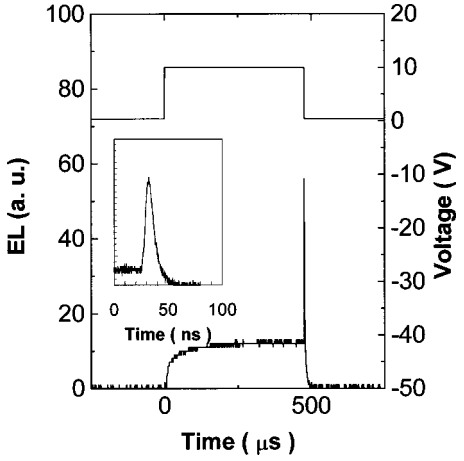

FIG. 2. Exciting voltage (upper trace) and transient EL (lower trace) vs time in the bilayer devices. Note that the EL, excited by a 14.4 V pulse, saturates to the same level as the steady-state dc EL. Inset: The resolved EL overshoot at the end of the voltage pulse.

The images shown in Fig. 3, which compare the overshoot brightness patterns with the steady-state emission, demonstrate a strong correlation between the pattern and the intensity of the overshoot. In order to analyze the decay of the overshoot intensity from different parts of the sample, the decay of the emission from the three rectangularly framed regions shown in Fig. 3(b) were measured. Several hundred pixels were averaged from the background-subtracted images and the intensity averages were plotted versus delay time where time zero was the peak intensity from the off pulse. These curves were then fit to a single- or double-exponential decay. The results are plotted in Fig. 3. The decay curves from the areas of increased injection are clearly biexponen-

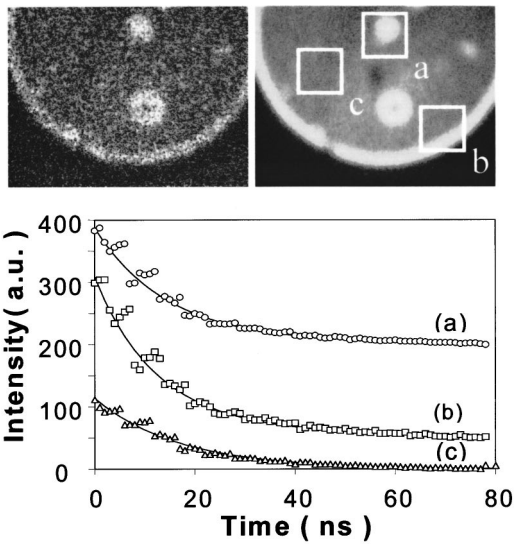

FIG. 3. Top-left image: the brightness pattern of the emitting surface of a DPVBi OLED in steady-state operation. Top right: the brightness of the overshoot. Bottom: The decay of the emission from the three frames in the right image. The islet (a) and edge (b) features required two-lifetime fits, with (a) $\tau_1=14.7$ ns, $\tau_2=435$ ns and (b) $\tau_1=11.7$ ns, $\tau_2=28$ ns. The ''featureless'' frame (c) followed a single decay time $\tau_1=16.9$ ns.

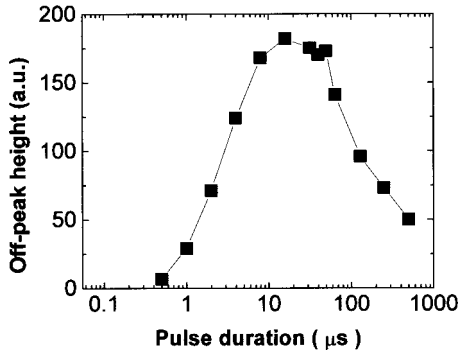

FIG. 4. Overshoot magnitude as a function of the duration of a 10 V pulse.

tial, with a shorter time $\tau_1 = 13 \pm 2$ ns, and a longer $\tau_2 \approx 28$ and 435 ns. We note that τ_2 increases with increased intensity.

Figure 4 shows the dependence of the overshoot amplitude on the duration of a 10 V pulse from 0.5 to 500 μs; the dependence on the bias amplitude was sublinear. The nonmonotonic dependence on the pulse duration, with the overshoot amplitude decreasing as the pulse length increases beyond ~ 30 μs, is in sharp contrast to that described in previous observations.[3] Note that this duration of ~ 30 μs coincides with the pulse rise time (see Fig. 2).

We now consider the present results in light of the overshoot mechanisms suggested previously:

(i) Upon onset of a forward bias pulse, positive and negative space-charge layers build up at the opposite faces of the HTL/ETL interface. Charge recombination preferentially occurs with the incoming flux of injected carriers of opposite polarity. Upon removal of the external electric field, the charges accumulated at the HTL/ETL interface attract each other and recombine, giving rise to the overshoot. The sublinear dependence of the overshoot amplitude on the bias amplitude suggests that the accumulated charges fill a limited number of sites at the HTL/ETL interface.

(ii) The other possible mechanism is the release of carriers stored in traps during the pulse [a variant of ''stored EL'' (Ref. 9)].

The weak variation of the fast decay process with τ_1 over the sample surface suggests that it is related to the HTL/ETL interface, as it is clearly independent of the details of the charge injection at the electrode interfaces. On the other hand, the wide variations in the longer τ_2 and its correlation with the bright spots with visible morphology or edges of the aluminum cathode suggest that emission is due to carrier release from traps at the ETL/cathode interface after turn-off of the pulse. The correlation also suggests that the inhomogeneity in electron injection is the key to the observed variations in the light output across the device. The local increased local electron injection leads to local increase of the quasi-Fermi level during the pulse turn-on. The higher local steady-state electron concentration leads to the filling of the deeper states in the gap. After the voltage turn-off, the carrier release from deeper lying states occurs with longer times, resulting in emission with lifetme τ_2. Therefore, the slow time scale characterizes the coupling between the localized states which trap the electrons, and the states in the lowest unoccupied molecular orbital (LUMO) band, to which the electrons must be released in order to participate in the formation of the radiative singlet excitons.

The other manifestation of the coupling between the trap and LUMO states is the nonmonotonic dependence of the overshoot on pulse duration. Indeed, as hole injection increases the density of positive charge stored at the ETL side of the HTL/ETL interface, these holes increasingly quench the singlet excitons responsible for the EL.[10]

In summary, the behavior of vacuum-evaporated multilayer blue OLEDs based on 4,4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl under pulsed bias was described. A strong overshoot in the EL at the voltage pulse turn-off, which exceeded the steady-state brightness by up to an order of magnitude, was observed. The decay of the overshoot from most of the sample is a simple exponential with a decay time $\tau_1 = 13 \pm 3$ ns. It is believed to result from recombination of carriers accumulated at the interface of the electron and hole transporting layers. However, in areas of increased injection, notably at morphological defects and edges of the cathode, a second longer overshoot decay time τ_2 appears. This longer decay is believed to result from detrapping of charges from the localized trap states at the cathode/organic interface after the voltage turn-off. We note that these overshoots in vacuum-vaporated small molecular OLEDs decay much more quickly than those observed in polymer-based devices. Finally, the dependence of the overshoot amplitude on the pulse duration is nonmonotonic, peaking at ~ 20 μs at $V = 10$ V. This behavior is suspected to result from increased quenching of singlet excitons by trapped charges.

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