Nanosecond electroluminescence spikes from multilayer blue 4,4′-bis(2,2′-diphenyl vinyl)-1,1′-biphenyl (DPVBi) organic light-emitting devices

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Abstract

Nanosecond electroluminescence (EL) spikes observed at the voltage turn-off when multilayer blue DPVBi-based organic light-emitting devices (OLEDs) are excited by rectangular voltage pulses are described. The spikes exceed the cw brightness by up to an order of magnitude. Time-resolved images of the devices 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 $20 \text{ ns} \leq \tau_2 \leq 1 \mu\text{s}$ is observed, apparently due to release of carriers from localized trap states in the organic/cathode interface. Only marginal variations in $\tau_1$ are found between bright and dim areas of the devices. At a bias of 10 V, the amplitude of the spike is found to peak at a pulse duration of $\sim 20 \mu\text{s}$. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

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 [1–3]. Some studies on thick yellow and green single- and bi-layer polymer LED’s described light flashes or spikes $\sim 10 \mu\text{s}$ to a few ms long observed at the turn-off of the voltage pulse [2–4]. In the case of bilayer devices, 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 charge accumulation in the transition layer was responsible for the spike [4].

This work describes the spikes 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 potential applications of the spikes sources as inexpensive versatile sources of pulsed light, fast switching of blue OLEDs may be of special interest for telecommunications.
2. Experimental procedure

Fig. 1 shows the device structure and the organic molecules 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 (\(\mu_{e}\) and \(\mu_{h}\), respectively,) are comparable but much lower than \(\mu_{h}\) 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 non-emissive triplet excitons, and \(~25\%\) the radiative singlet excitons, mostly at the HTL/ETL interface. Due to the mobility and HOMO and LUMO level offsets 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-ter-(N-(3-methoxyphenyl)-N-phenyl-triphenylamine) (MeO-MTDATA) or Cu phthalocyanine (CuPc) followed by 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\(_2\)O\(_3\) was deposited between the ETL and the Al cathode [8]. The resultant steady-state electroluminescence (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 a \(5 \times 5\) cm\(^2\) \(250\) pixel array of \(1.5\) mm aluminum disc electrodes evaporated on the organic layers. The \(~0.1\) nF capacitance of the small area devices and the \(~1\) \(\Omega\) parallel load resistor yielded 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 integrated transient EL waveform was measured using a Hamamatsu 3456 photomultiplier tube (PMT). The time resolved EL imaging was obtained from a TE300 Quantum Nikon Corp inverted research microscope and 10X/0.13 N.A. Olympus Corp. objective coupled to a 200 ps resolution Picostar HR, LaVision GmbH gated camera. This camera uses a GEN II type S20 photocathode and P43 phosphor intensifier lens coupled to a 640 \(\times\) 480 pixel CCD with 12-bit dynamic range. The gate width was set at \(2\) ns.

3. Results and discussion

Fig. 2 shows the EL of a device generated by a rectangular forward bias 10 V voltage pulse. The EL initially rises to the steady-state level with a rise time \(\tau_{r} \sim 100\) \(\mu\)s; \(\tau_{r}\) decreases with increasing voltage. Earlier studies unanimously attributed it to interface charge build-up and the consequent electric field redistribution.

At the end of the voltage pulse, an EL spike lasting \(<100\) ns is observed. In Fig. 2, the peak amplitude of the spike is five times greater than the steady-state EL. The overall intensity of the spike, measured from the whole sample, is dominated by a single decay time
The weak variation of the fast decay process at $\tau_1$ 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 $\tau_2$ and its correlation with the bright spots with visible morphology or edges of the aluminum cathode suggest that 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 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 lifetime $\tau_2$. Therefore, the slow time scale characterizes the coupling between the localized states which trap the electrons, and the states in the 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 the HOMO and/or LUMO states is the nonmonotonic dependence of the spike on pulse duration. This decrease in the spike amplitude at longer pulses is not clear, but it might reflect a growing imbalance between positive and negative charge accumulation at longer pulses.

Finally, we note that very recent measurements on ITO/CuPc/TPD/[Tris-(8-hydroxyquinoline Al) (Alq3)]/AlOx/Al OLEDs did not yield any detectable spikes [10]. These results are in agreement with a recent study on ITO/[N,N’-diphenyl-N,N’-bis(1-naphthyl)-(1,1’-biphenyl)-4,4’-diamine (NPB)]/Alq3/MgAg OLEDs, increases beyond $\sim 20 \mu s$, is in sharp contrast to that described in earlier observations [3]. Note that this optimal pulse length of $\sim 20 \mu s$ is comparable to the EL rise-time (see Fig. 2).

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

1. 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 spike. The sublinear dependence of the spike amplitude on the bias amplitude suggests that the accumulated charges fill a limited number of sites at the HTL/ETL interface.

2. The other possible mechanism is the release of carriers stored in traps during the pulse (a variant of ‘stored EL’) [9].

Fig. 3 shows that there is a strong correlation between the steady-state EL and spike images. In order to analyze the decay of the spike intensity from different parts of the sample, its decay from the three rectangularly framed regions was determined by averaging several hundred pixels from the background subtracted images and plotting this average versus delay time, as shown in Fig. 3b. The decay curves from the areas of increased injection are clearly biexponential, with a shorter time $\tau_1 = 13 \pm 2$ ns, and a longer $\tau_2 \approx 28$ and 435 ns.

Fig. 4 shows the dependence of the spike amplitude on the duration of a 10 V pulse from 0.5 to 500 $\mu$s; the dependence on the bias amplitude was sublinear. The nonmonotonic dependence on the pulse duration, with the spike amplitude decreasing as the pulse length

$\tau_1 = 13 \pm 3$ ns, demonstrating that it is dominated by one mechanism.

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sug[11] suggesting that Alq₃ does not promote the charge accumulation occurring in the DPVBi-based OLEDs, which is responsible for the spikes. This could be due to the difference between the HOMO and LUMO level offsets in the TPD/Alq₃ and NPB/Alq₃ interfaces, and those in the TPD/DPVBi interface, and to the different barriers and trap states in the Alq₃/MgAg and Alq₃/AlOₓ/Al interfaces, and those in the DPVBi/AlOₓ/Al interface. Additional studies attempting to confirm or refute these scenarios are underway and will be reported later.

4. Summary

In summary, the behavior of vacuum-evaporated multilayer blue OLEDs based on 4,4′-bis(2,2’-diphenylvinyl)-1,1′-biphenyl (DPVBi) under pulsed bias was described. A strong spike 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 spike 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 spike decay time $\tau_2$ 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 spikes, believed to be the first observed in vacuum-evaporated small molecular OLEDs, decay much more quickly than those observed in polymer-based devices. Finally, the dependence of the spike amplitude on the pulse duration is nonmonotonic, peaking at $\sim 20 \mu$s at $V = 10$ V.

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