Pulsed excitation of low-mobility light-emitting diodes: Implication for organic lasers

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We present a theoretical and experimental study of electrical pulsed excitation in polymer light-emitting diodes (LEDs). We find that the low mobility results in a relatively high charge density within an electrically pumped structure. The broad spectrum of the charge-induced absorption and its overlap with the ground-state absorption pose a significant barrier for achieving net gain and lasing. We suggest an approach that might circumvent this problem using suitable emitters and an appropriate driving scheme. We also suggest methods for ultrafast modulation of LEDs as well as direct determination of the space charge within the recombination zone. © *1999 American Institute of Physics.* [S0003-6951(99)05019-6]

Ever since the realization of lasers in the early 1960s organic materials have been considered as lasing media.[1] Only in the 1990s have conjugated (semiconducting) polymers reached the necessary quality (and purity) to be used for lasers.[2–5] The realization of an optically pumped organic laser based on a material that could support current densities of kA cm^{-2} (Refs. 2 and 6) showed that these materials could now be considered for electrically pumped lasing. However, to the best of our knowledge an electrically pumped laser has not been reported yet. In this letter we highlight some of the issues relevant to electrically pumped structures.

We start by writing the equations that are considered to govern the operation of an electrically pumped light-emitting device (LED), assuming exciton generation is a Langevin process,[7,8]

$$\frac{\partial}{\partial t} n_e(z,t) = \frac{\partial}{\partial z}\left[D_e\frac{\partial}{\partial z}n_e(z,t) + \mu_e(E)n_e(z,t)E(z,t)\right]$$
$$- R_e(z,t)n_e(z,t), \tag{1}$$

$$\frac{\partial}{\partial t} S(z,t) = FR_e(z,t)n_e(z,t) + \frac{\partial}{\partial z}\left[D_s\frac{\partial}{\partial z}S(z,t)\right] - \frac{S}{\tau}, \tag{2}$$

$$n_e|_{z=0} = n_{e0}, \quad n_h|_{z=L} = n_{h0}, \quad n_e|_{z=L} = n_h|_{z=0} = 0, \tag{3}$$

$$R_e = \frac{q}{\epsilon\epsilon_0}\mu_{\text{eff}}n_h.$$

Here, n_e, n_h, and S are the electron, hole, and singlet exciton density, respectively. Equation (1) describes the electron dynamics and a similar equation describes the hole dynamics. D is the diffusion coefficient, μ is the mobility,[8] and R is the Langevin recombination rate which is field dependent through the field dependence of the mobility.[7,8] Equation (2) describes the dynamics of the singlet exciton density, which is generated through the Langevin recombination rate. F is the fraction of singlet excitons generated (we assume

that $F = 1/4$) and τ is the exciton lifetime. μ_{eff} is the effective mobility for recombination and we assume $\mu_{\text{eff}} = \mu_e + \mu_h$. Previous modeling of LEDs (Refs. 8 and 9) did not include Eq. (2). However, in the context of lasers it is essential to include the gain level.[10] The boundary conditions, Eq. (3), are written assuming an Ohmic contact. Neglecting the diffusion term in Eq. (2), it can be solved for steady state:

$$\frac{S}{n_e} = F\frac{q}{\epsilon\epsilon_0}\mu n_h\tau. \tag{4}$$

Using typical values for polymer LEDs under cw excitation ($\mu = 10^{-5}\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$, $n_h = 10^{16}\,\text{cm}^{-3}$, $\tau = 10^{-9}\,\text{s}$), we find that $n_e = 6.6\times 10^4\times S$. Namely, the typical low-mobility LED contains many more charges (polarons) than light-emitting (gain) excitons. Moreover, if the injection/mobility is unbalanced, then $n_h \gg n_e$. The implication for lasers is that the Langevin recombination is a bottleneck[11] for exciton generation.[12] The effect on internal absorption is shown in Fig. 1, which describes on a logarithmic scale the ground-state absorption [measured using the photodeflection spectra (PDS) technique], excitonic gain (measured using an optical pump probe[13]), and charge-induced absorption [measured in a LED (Ref. 6)] for poly (p-phenylenevinylene) (PPV). This gain–loss balance (Fig. 1) shows that the broad polaronic (charge) absorption, having a cross section similar to that of the excitonic gain ($5 - 10\times 10^{-16}\,\text{cm}^2$), will make
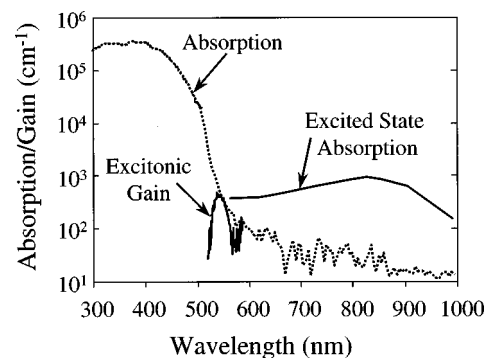

FIG. 1. Absorption gain and excited-state absorption coefficients. The gain (produced by exciton) and the absorption (produced by excited states) is shown for an equal density of $10^{18}\,\text{cm}^{-3}$.

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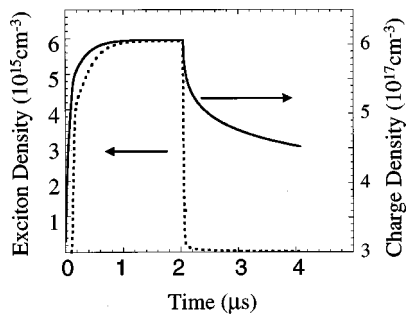FIG. 2. Calculated time response of the average exciton and charge density in a PPV LED.
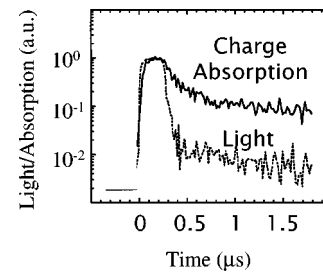

FIG. 3. Measured time response of light and charge-induced absorption in an ITO/PPV/Ca LED. The applied voltage was 27 V and the device was cooled to −170 °C.

it impossible to observe net gain in the cw-driven LED described here. These features are not unique to PPV and broad charge-induced absorption has been reported for other materials.[14]

There could be several approaches for avoiding the problem associated with Eq. (4). First, use a material with high mobility so that the exciton density would be enhanced. Second, find a material system where the absorption is negligible, at least in a small spectral range, so that the method of shifting the emission[15] (gain) to a desired spectral position may prove useful. Third, operate the device in non-cw conditions. In the following, we explore the potential advantages of using a pulsed operation. A pulsed operation has several advantages: avoiding heating[16] and allowing current density of kA cm^{-2}.[6] For the present discussion the most relevant results, reported in Ref. 6, are that under pulsed excitation, mobility values reach 10^{-2}–10^{-1} cm^2 V^{-1} s^{-1} and the charge density can be as high as 5×10^{17} cm^{-3}. Inserting these values into Eq. (4) we find that $n_e \cong S$ at the high excitation regime.

To check if further improvement can be reached through the use of non-steady-state conditions [where Eq. (4) does not hold], we simulate the response of a LED to a short-pulse excitation focusing on the turn-on and turn-off of the device. We solve Eqs. (1) and (2) coupled to the Poisson equation. We assume here $n_{e0} = n_{h0} = 10^{19}$ cm^{-3}, and $\mu_e = 0.1 \mu_h$.

Figure 2 shows the calculated time response of the exciton density ($\propto$ light), and the average charge density [neglecting the diffusion in Eq. (2)]. Focusing on the turn-on, we note that the rise time is composed of two time constants. Based on the simulation, we attribute the first to the holes moving towards the slow electrons and the second to effects due to transport of electrons away from the contact. If the excitons are first generated close to the quenching electrode, the magnitude of the first time constant may be suppressed. Since the exciton density rises slower than the charge density, we conclude that during the turn-on, the charge-induced absorption is relatively higher, and hence, this part of the pulse is not useful. Examining the turn-off of the device, the exciton density shows an instantaneous drop. When the voltage is turned off, the field-dependent mobility drops instantaneously, which results in almost a complete switch off of the Langevin recombination rate. The size of the drop is determined by the remaining space charge, and will be addressed elsewhere. To verify experimentally the effect of the field-dependent Langevin rate we measured both the carrier-induced absorption and the light intensity in a Ca/PPV/ITO

LED, shown in Fig. 3. Figure 3 shows that the light intensity drops instantaneously (within experimental resolution) as the voltage is turned off. On a longer time scale, both the carrier density and light intensity show similar time dependence. Namely, in this type of LED the situation at turn-off is not beneficial with respect to Eq. (4).

A closer examination of the turn-off of the exciton density (Fig. 2) shows that the decay is not instantaneous but reflects the radiative lifetime of the excitons. Therefore, we conclude that by using a long-lived emitter the situation at turn-off is much improved, and that it is possible to overcome the charge-induced losses by regarding the device operation as a two-step process: (1) Charge injection and a buildup of high exciton density. (2) Charge extraction in reverse bias. In this case at the end of the cycle the structure is free of charges but still contains high exciton density capable of producing gain. To demonstrate this idea we have made a LED with a long-lived emitter [platinum octaethyl-porphyrin (PtOEP)],[17,18] blended into a polymer host (poly [4-(*N*-4 vinylbenzyloxyethyl, *N*-methylamino)-*N*-(2,5-di-tertbutylphenyl naphthalimide)]-PNP).[17] Figure 4 shows the response of such a LED to a 500 ns, 22 V pulse superimposed on a −8 V dc bias. The response shows an initial fast ($<\mu$s) rise, as in any LED, followed by a long ($\gg\mu$s) rise. This long rise was shown to be indicative of the capture of triplets generated in the polymer host by the PtOEP.[17] The most important point here is that the emission (exciton) lifetime can be made much longer (75 μs) than the time charges reside in the structure (this 75 μs lifetime is similar to the photoexcited lifetime). The nature of the emitter (singlet or triplet; molecule or atom) is irrelevant to the concept we wish to illustrate, which relies on the interplay between loss (charge) and gain (exciton) lifetime.

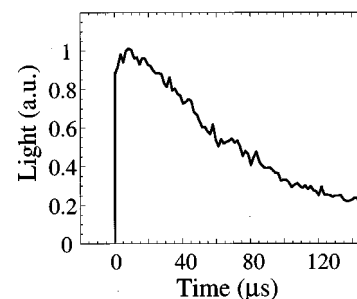To conclude, we have analyzed the operation of polymer

FIG. 4. Time response of the light in a polymer LED doped with a long-lived emitter (PtOEP) emitting at ~640 nm.

LEDs under pulsed excitation. We found that the presence of a high charge density is an inherent property of low-mobility organic materials and that it may prevent net gain in electrically pumped devices. We found that by using pulsed excitation in combination with a long-lived emitter this problem may be practically eliminated. Our analysis also resulted in a few interesting results not necessarily related to lasing: (1) The turn-on of a device contains the information of both hole and electron mobility. (2) The turn-off of the device contains information regarding the amount of space charge in the device. (3) Light intensity can be modulated much faster than the transport time.

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