Recombination Process in Bilayer Polymer Electroluminescent Structures

Mariya P. Aleksandrova[1], Milka M. Rassovska[1], Georgy H. Dobrikov[1]

Abstract – In this article an analysis of the recombination process in bilayer polymer electroluminescent structure was presented, using simulations, made by program SimOLED Electrical. The aim of this study is to make reconstruction of the processes, arising at the junction between the hole transporting layer (HTL) and the electroluminescent layer (EL), where we could not receive information by direct measurements. The dependence of the recombination profile on the contact injection barriers at the polymer interface was estimated. The impact of the barriers height on the location of recombination peak and on the recombination rate was examined too. The mechanisms by which the recombination zone shifts from HTL side to the EL side were described in detail, according to the increases in conduction bands energy offset.

Keywords – Polymer electroluminescent structure, Recombination zone, Interface barriers.

I. INTRODUCTION

The polymer light-emitting devices (PLED) are intensively investigated as flat display technology of the future due to their several advantages including their own lightening, wide viewing angle, thin size and low cost [1]. The simplest PLED structure consists of a single polymer layer sandwiched between an anode and a cathode, but this structure suffers from poor efficiency [2]. In the most organic semiconductors inclusive conjugated polymers the hole mobility is larger than the electron mobility. This is the reason for charge carrier recombination near the cathode interface, where is more probable charge carriers trapping in the quenching centers formed during the cathode deposition. By insertion of additional buffer layer, decreasing of the anode injection barrier and recombination zone shifting away from the electrode interface could be achieved. As a result the quantum efficiency is increased.

Several studies are carried out for investigating the operation principle of bilayer polymer electroluminescent structures [3-5]. The authors explore the role of the electrode interfacial barriers height for the current balance in the electroluminescent thin film. Goliney first report data from modeling of performance characteristics of organic light-emitting device in the case of tunneling and thermionic injection through the electrodes into the emitting layer [6]. Paasch et al. conduct simulations to confirm the hypothesis for exponentially trap energy distribution and existence of localized charges in the vicinity of the anode or the cathode of organic light emitting devices [7]. Although it is known that the recombination process is dependent on the electrode contact barriers, there is no detail information about the charge carrier transport through the polymer heterojunction, according to the polymer interfacial barriers for the electrons and holes.

In the present article the radiative recombination rate and position in bilayer PLED structure ITO/PVK/PPV-D/Al is analyzed according to the polymer interface barriers. Indium-tin oxide (ITO) is transparent and conductive film, used as anode. Polyvinylcarbazole (PVK) is hole transporting buffer layer (HTL), polyphenylenevinylene derivative (PPV-D) - electroluminescent layer (EL) and aluminum film is used as cathode. The investigation aims to reconstruct the processes at the polymer layers interface, where it is not possible to receive information by direct experimental measurements.

II. EXPERIMENTAL

The analysis in this article is based on simulation results achieved with the specialized OLED/PLED simulation software SimOLED ELECTRIC [8], which considers processes like charge carrier injection and transport, radiative recombination, non-radiative decay etc. This program uses experimental measured data for input parameters, so the simulation results complement the data from the real measurement. The necessary parameters taken from the real prepared device are layer sequence and thickness d, highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energies, electrodes work function, main charge carrier mobility μ in the used polymer materials and relative permittivity. For the concretely investigated structure these material property's values are as follow: d_{ITO} = 180 nm, d_{PVK} = d_{PPV-D} = 100 nm, d_{Al} = 200 nm; the energy levels (HOMO, LUMO, work functions) could be seen in the energy diagram on Fig. 1; $\mu_{h\ PVK}$ = 5,4.10^{-3} cm^2/V.s, $\mu_{h\ PPV-D}$ = 3.10^{-5} cm^2/V.s; $\varepsilon_{r\ PVK}$ = 2,9, $\varepsilon_{r\ PPV-D}$ = 3, turn on voltage 10 V (from the forward current-voltage characteristic).

The current flow at the polymer interface is modeled in SimOLED ELECTRIC by thermoionic emission, according to the approved from Crone et al. model [9]. The assumption is for exponentially distribution of trap energies, which is the most widespread case in the organic semiconductors and in particular in the polymers.

[1]Mariya P. Aleksandrova is with the Faculty of Electronic Engineering and Technology, Technical University of Sofia, "Kl. Ohridski" str, 8, Bulgaria, E-mail: meri_7@abv.bg

[1]Milka M. Rassovska is with the Faculty of Electronic Engineering and Technology, Technical University of Sofia, "Kl. Ohridski" str, 8, Bulgaria, E-mail: rasovska_m@mail.bg

[1]Georgy H. Dobrikov is with the Faculty of Electronic Engineering and Technology, Technical University of Sofia, "Kl. Ohridski" str, 8, Bulgaria, E-mail: georgy_ddobrikov@abv.bg
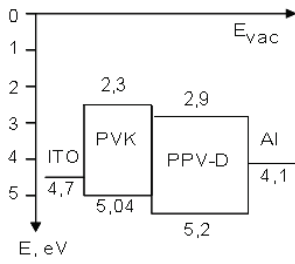
Fig. 1. Energy diagram of ITO/PVK/PPV-D/Al
electroluminescent structure.

The used approach for explaining of charge carrier motion in PLED is not appropriate for applying to hybrid organic/inorganic interface. The suitable for PLED inorganic buffer materials have mainly insulating properties and for that reason they must be deposited in form of ultrathin films (under ~6-8 nm) in the structure for prevention of charge carrier blocking. Injection through such interface is by tunnelling mechanism over triangular barrier, the material transport properties are neglected and they don't influence on the charge transportation. For simplicity, constant charge mobility in the bulk of the material is accepted. In our case this supposition is valid, because the metal/polymer contact is not Ohmic, so there is no disturbing field from space charge formation.

III. RESULTS AND DISCUSSION

A model of structure, consisting of polymer material – 1 (PVK), as hole transporting layer and polymer material – 2 (PPV-D), as electroluminescent layer, sandwiched between 2 electrodes is shown on Fig. 2a. Fig. 2b represents energy diagram with the corresponding polymer energy levels offsets relative to each other. Although at the cathode interface Schottky barrier is formed ($\approx$ 2 eV) during the simulations value of 0,2 eV was set to avoid restraints of the charge carrier injection. Thus the influence of the injection barriers height at the polymer interface on the device performance could be successfully demonstrated.
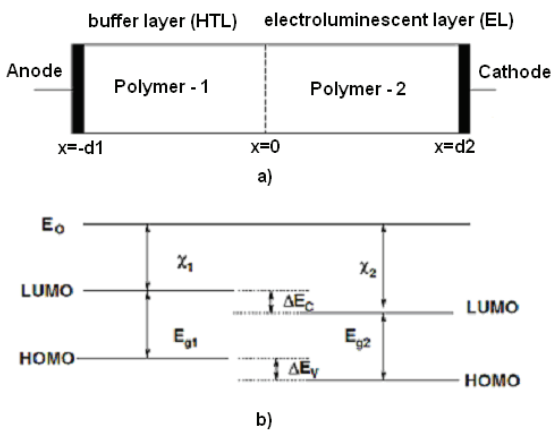

Fig. 2. a) Schematic diagram of a bilayer PLED and b) its associated energy band diagram.

Fig. 3 (up) illustrates the recombination profile in the bilayer PLED structure with ΔE_v=0,16 eV and ΔE_c=0,6 eV. It could be seen, that the recombination occurs predominantly at the polymer interface (zero position in relation to the junction). Some of the charge carriers, however, recombine in the HTL or EL layer. The situation of constant HOMO energy offset was considered first (ΔE_v=const) and LUMO energy offset varies from 0 to 0,8 eV. Fig. 3 (down) shows the recombination rate at the both side of polymer interface, depending on the electron injection barrier ΔE_c. Initially at small values of ΔE_c the charge carriers recombine in the HTL near the polymer interface. With ΔE_c increasing above certain value (~0,6 eV), the recombination zone is entirely shifted in EL layer. It seems that the holes already reach to the cathode interface, passing through the EL layer until the electrons overcome the ΔE_c barrier. The recombination rate in EL layer actually increase with electron injection barrier at the polymer interface as is shown on Fig. 3 (down). This effect probably arises, because of the accumulated electrons in the EL layer.
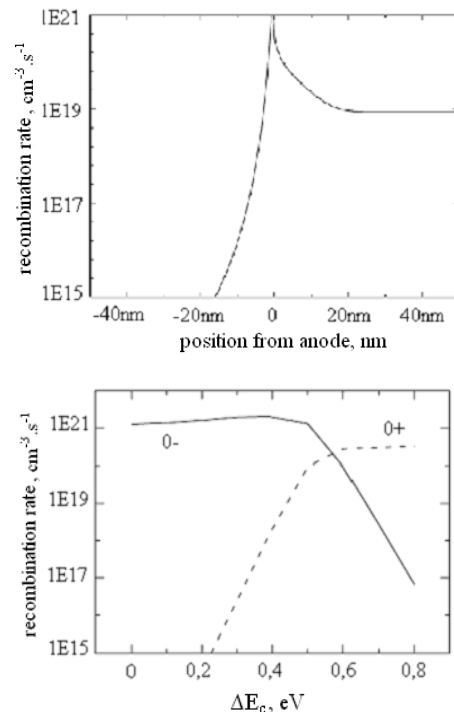

Fig. 3. A recombination profile in the bilayer structure (up); recombination rate immediately to the left (solid line) and to the right (broken line) of the polymer interface as a function of LUMO energy offset (down).

Situation of constant HOMO energy offset was considered first (ΔE_v=const) and LUMO energy offset varies from 0 to 0,8 eV. Fig. 3 down shows the recombination rate at the both side of polymer interface, depending on the electron injection barrier ΔE_c. Initially at small values of ΔE_c the charge carriers recombine in the HTL near the polymer interface. With ΔE_c increasing above certain value (~0,6 eV), the recombination zone is entirely shifted in EL layer. It seems that the holes already reach to the cathode interface, passing through the EL

layer until the electrons overcome the ΔE_c barrier. The recombination rate in EL layer actually increase with electron injection barrier at the polymer interface as is shown on Fig. 3. This effect probably arises, because of the accumulated electrons in the EL layer.

It is difficult to give a detailed explanation why the current through the structure remains almost constant by increasing of the LUMO offset (Fig. 4). Actually, all anode injected holes, which have been recombined in HTL before, recombining in the EL layer now. Consequently, the hole injection in the EL layer is expect to increase together with the electron injection barrier increasing, regardless of the unchanged applied voltage U.
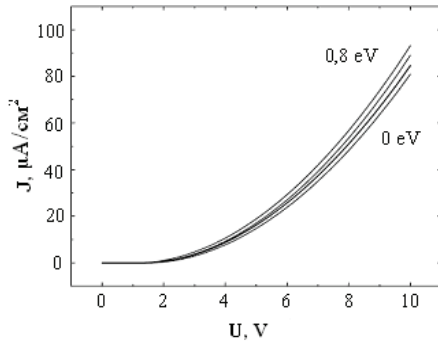

Fig. 4. Current density as a function of voltage obtained from numerical simulations for different values of LUMO energy offset (0; 0,2; 0,6; 0,8 eV) at the polymer interface.

Assuming that due to the large electric field at the interface, the drift component is predominant, the electron current in HTL at the polymer interface can be expressed as:

$$J \cong q\mu_{n1}E(0)n(0^-) \tag{1}$$

where E(0) is the electrical field at the interface, μ_{n1} – electron mobility in HTL (polymer – 1), $n(0^-)$ – electron density at the interface in HTL side. Using the relation

$$n(0^-) = n(0^+)\exp(-\frac{\Delta E_c}{kT}) \tag{2}$$

we can re-write Eq. 1 as

$$J \approx q\mu_{n1}E(0)n(0^+)\exp(-\frac{\Delta E_c}{kT}), \tag{3}$$

where k is the Boltzman's constant and T is temperature.

To estimate the increase in electric field or electron density separately, relation between both of them next to the interface is required. The results from simulation indicate that carrier density decrease exponentially away from the interface [10].

$$n(x > 0) = n(0^+)\exp(-\delta_2 x), \tag{4}$$

where δ_2 is the distance from interface to bulk region in the electroluminescent film.

The electron density in EL close to the interface is

$$Q_N = qn(0^+)\delta_2^{-1} \tag{5}$$

The accumulation of electrons close to the interface means that electron drift and diffusion currents must be almost equal and in opposition to each other. The assumption for quasi-equilibrium condition together with Eq. 4 can be used to obtain an expression of the electric field at the interface.

$$E(0) = \frac{kT}{q}\delta_2 \tag{6}$$

Using this expression, Eq. 5 can be written as

$$Q_N = n(0^+)\frac{kT}{E(0)} \tag{7}$$

Assuming that the region with accumulated charges acts as "shield" for further charge carrier transport, another expression can be applied, relating electric field and interface charge density [11]:

$$E(0) = \frac{Q_N}{\varepsilon} + E_{b2}, \tag{8}$$

where E_{b2} electric field in the EL bulk near the interface and ε is relative permittivity of the same layer. Substitution of Eq. 8 in Eq. 7 leads to quadratic equation in relation to E(0), whose solution is:

$$E(0) = 0,5E_{b2}\left\{1 + \sqrt{1 + \frac{n(0^+)}{n_2}}\right\}, \quad n_2 = (\frac{\varepsilon E_{b2}^2}{4kT}), \tag{9}$$

or Eq. 9 can be rewritten in a form, which is more handy for verification

$$\underbrace{\left\{\frac{2E(0) - E_{b2}}{E_{b2}}\right\}^2}_{Y_1} = 1 + \frac{n(0^+)}{n_2} \tag{10}$$

In order to verify Eq. 9, numerical simulations were carried out to obtain values of E(0) and $n(0^+)$ for electron barrier height in the range of 0–0,4 eV. Fig. 5 shows the left side of Eq. 10 as a function of the electron density, which is approximated with straight line.

Finally it is considered a bilayer PLED structure with $\Delta E_v=0,2$ eV and $\Delta E_c=0$ eV at the polymer interface. When forward bias is applied, holes are accumulate in the buffer layer side, because of the hole barrier. In the light-emitting layer the hole current is negligible. In the same time injected from the cathode electrons are transported to the buffer layer without barrier. The hole density in HTL at the interface is large and only a few electrons could penetrate into the buffer, so the recombination peak will be at the interface from the HTL side. Electron mobility in PPV-D is smaller than the hole mobility in PVK, so the applied voltage is distributed as voltage drop mainly over the EL layer. The current flow then

is determinate from the electrons which can reach the interface. Such behavior give us a reason for modeling of this bilayer structure as a single layer structure, where the cathode serves as first electrode and the accumulated holes serve as a second electrode. At these conditions in the organic semiconductor devices the current is described as:

$$J = \frac{9}{8} \varepsilon_o \varepsilon_r \mu \frac{U^2}{d_2^3} , \qquad (11)$$

where ε_r is relative material permittivity; ε_o is dielectric constant; μ – mobility of the main charge carriers in layer, having thickness d_2. Fig. 6 shows that the simulation results are in good agreement with the behavior according to Eq. 11.
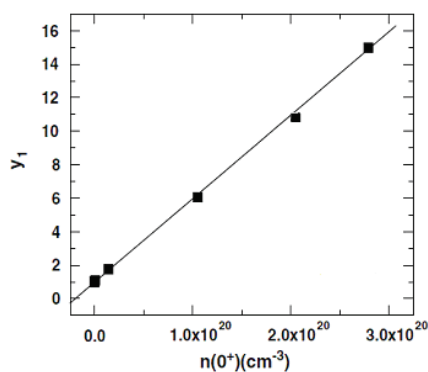

Fig. 5. Y_1 (left side of Eq. 10) plotted as a function of electron density in EL at the polymer interface.
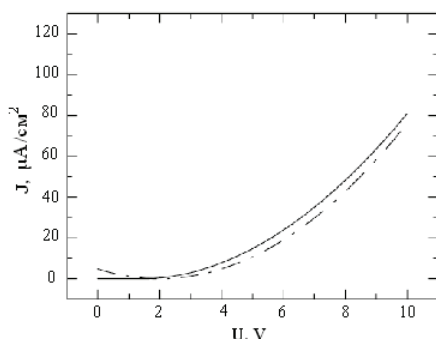

Fig. 6. Current density as a function of voltage obtained from numerical simulations (solid line) and the model (dotted line) described by Eq. 11 for ITO/PVK/PPV-D/Al bilayer structure.

IV. CONCLUSION

In this paper model of experimental bilayer polymer based electroluminescent structure was proposed. The real structure has configuration of ITO anode, PVK layer as hole transporting, PPV-D – as electroluminescent layer, and Al cathode. The model explains charge carrier recombination process in the electroluminescent layer. It was investigated the impact of interfacial barrier heights on the location of recombination peak and the recombination rate in such bilayer

device. The mechanism by which recombination shifts from HTL side of the polymer–polymer interface to the EL side with increase in LUMO energy offset is described in detail. It was established that the total current flow in the structure is not sensitive to the electron barrier height at the polymer interface.

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