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Luminance and efficiency of a light-emitting diode with transport-blocking poly(methyl methacrylate) layers and quantum dots: theoretical model, experiment, optimization

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The results of studies of the influence of the thicknesses of the electron-blocking, hole-conducting and recombination layers on the luminance-voltage and other electrophysical characteristics of a multilayer light-emitting diode with an active layer based on semiconductor quantum dots are presented. Optimized thicknesses and voltages are determined to achieve the maximum efficiency of electroluminescence of the light-emitting diode.

Keywords: quantum dots, light-emitting diode, blocking layer.

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Semiconductor nanocrystals (quantum dots, QDs) are used more and more often in optoelectronic devices, and specifically in light-emitting diodes (QDLEDs) [1,2]. These devices are multilayer heterostructures with electroluminescent QD layers used in combination with organic layers of different functionality [3,4]. The introduction of layers blocking carrier transport into the structure of a light-emitting diode results in a manifold enhancement of the electroluminescence efficiency; this has already been demonstrated in organic LEDs with a hole transport layer (HTL) serving as an electron-blocking layer (EBL) [5,6]. However, the interaction of singlet excitons with charges accumulated at the interfaces between a QD layer and adjacent transport layers reduces the electroluminescence efficiency. This influence of charges may be suppressed if the recombination region (QD layer) is sufficiently thick and radiative recombination occurs deep within the indicated layer (i.e., away from excess QD charges accumulated in the near-surface layer). Another important problem related to QDLEDs consists in maintaining the balance between electron and hole currents in order to suppress the accumulation of excess charge within the bulk of an active QD layer. This bulk charge reduces the electroluminescence efficiency, due in particular to Auger recombination [7]. The introduction of an EBL, which restricts the electron flux between an electron transport layer (ETL) and a QD layer, into the LED structure is a promising approach to current balancing. Such a layer may be fabricated, e.g., from poly(methyl methacrylate) (PMMA) [8,9], since the positioning of energy levels of PMMA provides a high potential barrier for electron injection into a QD layer. A multilayer QDLED structure with PMMA electron-blocking layers of various thickness, which were located between a QD layer and an ETL, has been examined in [4]. It has been demonstrated that the QDLED parameters depend to a considerable extent on the EBL thickness.

In the present study, a simple theoretical model is used to analyze the effect of thicknesses of functional layers on the voltage dependences of the current density and the luminance of a QDLED structure. The ITO/PEDOT:PSS/*poly*-TPD/PVK/QDs/PMMA/ZnO/Al QDLED structure with a 40-nm-thick emission layer consisting of multishell QDs with a CdSe core and a ZnS/CdS/ZnS shell (see our earlier study [4] for a more detailed description of this structure) is modeled. Here, ITO is indium tin oxide, PEDOT:PSS is the hole-injecting poly(3,4-ethylenedioxythiophene) polystyrene sulfonate layer with a thickness of 40 nm, and *poly*-TPD and PVK are HTLs made from poly(N,N′-bis-4-butylphenyl-N,N′-bisphenyl) benzidine (30 nm in thickness) and poly(vinylcarbazole) (5 nm in thickness), respectively. The 50-nm-thick ETL was formed from ZnO nanoparticles. The energy diagram of the QDLED device is presented in Fig. 1. The typical electroluminescence spectrum is shown in the inset of Fig. 2. A high (about 0.5 eV) barrier for electrons forms at the interface between PMMA and ZnO, thus inducing the accumulation of negative near-surface charge with surface electron density Σ_e. A less significant barrier for holes at the interface between *poly*-TPD and PVK induces the accumulation of positive charge with surface hole density Σ_h at the HTL/QD interface. Since $\Sigma_e > \Sigma_h$, the electric field intensity in the ZnO layer is lower than the average value for the device as a whole ($F_0 = (V - V_{bi})/L$), while the field intensity in the *poly*-TPD layer exceeds the average one. Here, V_{bi} is the built-in potential, V is the applied voltage, and L is the interelectrode thickness of the device (Fig. 1).

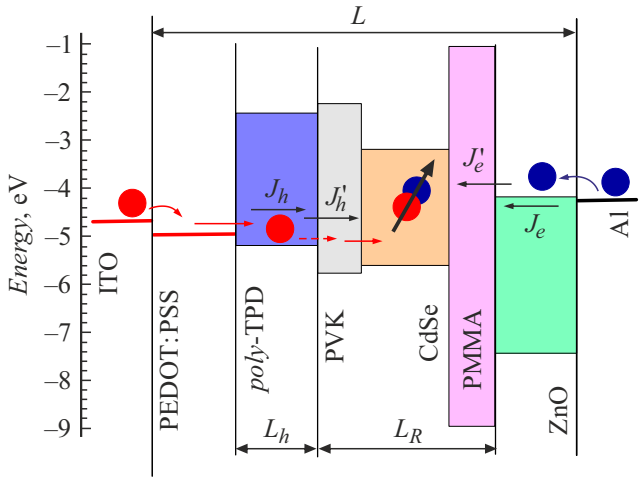

Figure 1. Energy diagram of the QDLED device and schematic representation of the electron (blue circles) and hole (red circles) transport processes and electron–hole recombination (black arrow) at QDs in the case when the egress of electrons and holes from the QD layer is negligible. The energy is measured from the vacuum level. A color version of the figure is provided in the online version of the paper.

Compared to the *poly*-TPD, PVK, PMMA, and QD layers, the PEDOT:PSS and ZnO layers are highly conductive; therefore, the voltage drop across them may be neglected in the model. The voltage drop across just the HTL (*poly*-TPD) with thickness L_h and the layer with effective thickness L_R, which is formed by the QD layer (with thickness L_{QD}) and the adjacent thin blocking polymer PVK (L_{PVK}) and PMMA (L_{PMMA}) layers, is considered below (Fig. 1). The field intensities in these layers (F_h and F_R, respectively) are related in the following way: $V - V_{bi} = F_R L_R + F_h L_h$. Taking the difference in dielectric permittivities of polymer layers and the QD layer (ε_p and $\varepsilon_{\mathrm{QD}}$, respectively) into account, we obtain $L_R = L_{\mathrm{QD}} + (L_{\mathrm{PMMA}} + L_{\mathrm{PVK}})\varepsilon_{\mathrm{QD}}/\varepsilon_p$. It follows from the Poisson's equation that $F_R = e\Sigma_e/(\varepsilon_{\mathrm{QD}}\varepsilon_0)$, $F_h = F_R - e\Sigma_h/(\varepsilon_p\varepsilon_0)$, where ε_0 is the electrical constant. Since the QD layer has a substantial thickness, it is fair to assume (just as in [10]) that recombination occurs primarily in the bulk of this layer and that recombination at the QD layer boundaries may be neglected, given that carriers do not leave the QD layer. Thus, the densities of currents in ZnO (J_e) and *poly*-TPD (J_h) are equal to the densities of currents flowing from these layers into the QD layer (J_e' and J_h', respectively). Therefore, current density J in the structure is $J = J_e' = J_h'$. Since high energy barriers are present in the structure, we used (following [10]) the modified Fowler–Nordheim injection model [11] to calculate J_e' and J_h': $J_e' = \nu_e\Sigma_e \exp(-\Delta_e/F_R)$, $J_h' = \nu_h\Sigma_h \exp(-\Delta_h/F_R)$, where factors ν_e and ν_h characterize the frequency of tunneling attempts. Quantities Δ_e and Δ_h are related to heights H_e and H_h of energy barriers at the PMMA/ZnO and *poly*-TPD/PVK interfaces, respectively, in the following way: $\Delta_i = \chi H_i^{3/2}\sqrt{2m}/(\hbar e)$, $i = e,\ h$. Here, factor χ accounts for the probable deviation of the barrier shape from the triangular one (as should be the case in the Fowler–Nordheim model); e is the elementary charge, $\hbar$ is the Planck constant, and m is the effective mass of the corresponding particle. The values of parameter χ are determined by fitting to the experimental current–voltage characteristics (CVCs) [4].

The following equation was derived from the above expressions for dimensionless quantities u and j that are related to current density J and voltage V as $J = uj\Delta_e\varepsilon_{\mathrm{QD}}\varepsilon_0\nu_e/[e(1 - pj^s)]$ and $V - V_{bi} = u\Delta_e(L_R + L_h)$: $j = \exp[-(1 - pj^s)/u]$. Solving it numerically, we find the QDLED CVCs. The CVD shape is defined by just two dimensionless parameters: $p = \varepsilon_{\mathrm{QD}}\nu_e L_h/[\varepsilon_p\nu_h(L_h + L_R)]$ and $s = (\Delta_e - \Delta_h)/\Delta_e < 1$. Figure 2 shows the calculated CVCs next to the experimental data for the QDLED structure obtained in [4] at different values of the PMMA layer thickness. These calculations were performed in Wolfram Mathematica. The following values of fitting parameters were used in the modeling: $\nu_e = 1.8 \cdot 10^5\ \mathrm{s}^{-1}$, $\nu_e/\nu_h = 0.68$, $H_e = 0.5$ eV, $H_h = 0.22$ eV, $L_h = 30$ nm, $L_{\mathrm{QD}} = 40$ nm, $L_{\mathrm{PVK}} = 5$ nm [4]; $\varepsilon_p = 3$, $\varepsilon_{\mathrm{QD}} = 10$. The values of all these parameters (except χ and ν_h) have been determined with a certain accuracy in earlier studies. The model agrees qualitatively with the experimental data if the value of factor χ for electrons increases with the PMMA thickness (apparently, due to changes in the electrophysical layer characteristics).

The developed model was used for further optimization of the QDLED structure parameters. Specifically, the voltage and thickness (L_h, L_{QD}, and L_{PMMA}) values corresponding to the maximum QDLED luminance and current efficiency were estimated. Voltage $V \approx 3.5$ V corresponding to the maximum current efficiency for LEDs with different EBL thickness values was determined by analyzing the experimental data presented in Fig. 3, *a*. The experimental values of the maximum efficiency and the current density values calculated using the model were used for comparative assessment of the luminance values for different thicknesses L_h and L_{QD}. Figures 3, *b*, *c* demonstrate the model dependence of luminance on thicknesses L_h and L_{QD} at $V \approx 3.5$ V for different values of the PMMA layer thickness. The simulated data revealed that the luminance value decreases exponentially as thickness L_h increases. At the same time, the luminance value increases as thickness L_h grows relative to thickness L_{QD} (Fig. 3, *c*). Thus, in order to maximize the QDLED luminance, one needs to minimize L_h (i.e., the *poly*-TPD layer thickness) while maintaining the $L_h/L_{\mathrm{QD}} \approx 1$ ratio. At very small values of L_{QD}, diffusing excitons will emerge at the boundaries of the QD layer, and nonradiative charge separation will occur. The model is also inapplicable to devices with small L_{QD} values, since the assumption of recombination occurring in the bulk of the QD layer (instead of at its boundaries) becomes invalid. The near-boundary recombination and the increased field intensity corresponding to a lower thickness of the emitting QD layer have a negative effect on the quantum

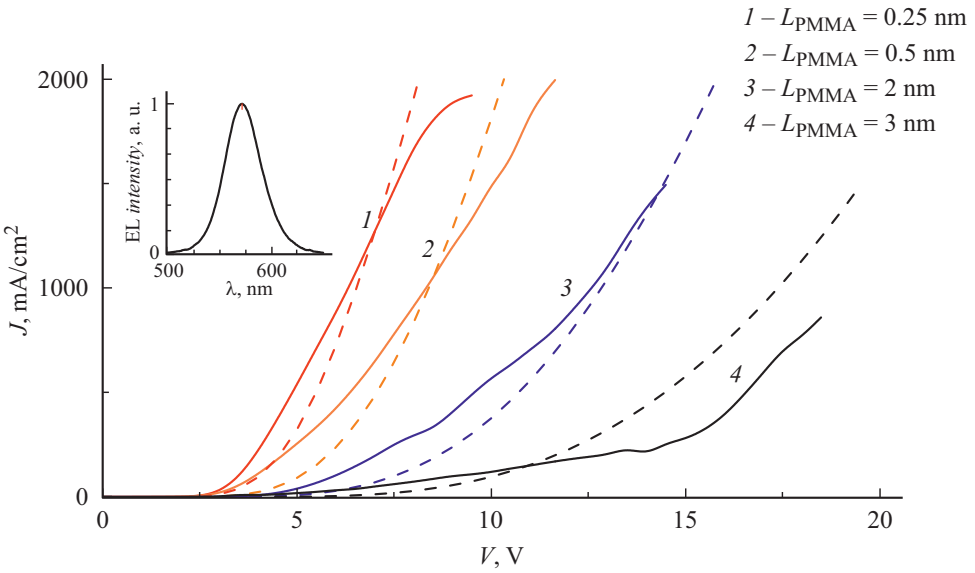

Figure 2. Results of simulation of the QDLED current-voltage characteristics (dashed curves) and experimental data [4] (solid curves) for various values of the PMMA layer thickness. The values of parameter χ (left to right): 0.044, 0.062, 0.1, 0.15. The corresponding values of parameter s: 0.7, 0.78, 0.87, 0.91. The typical QDLED electroluminescence spectrum [4] is shown in the inset.

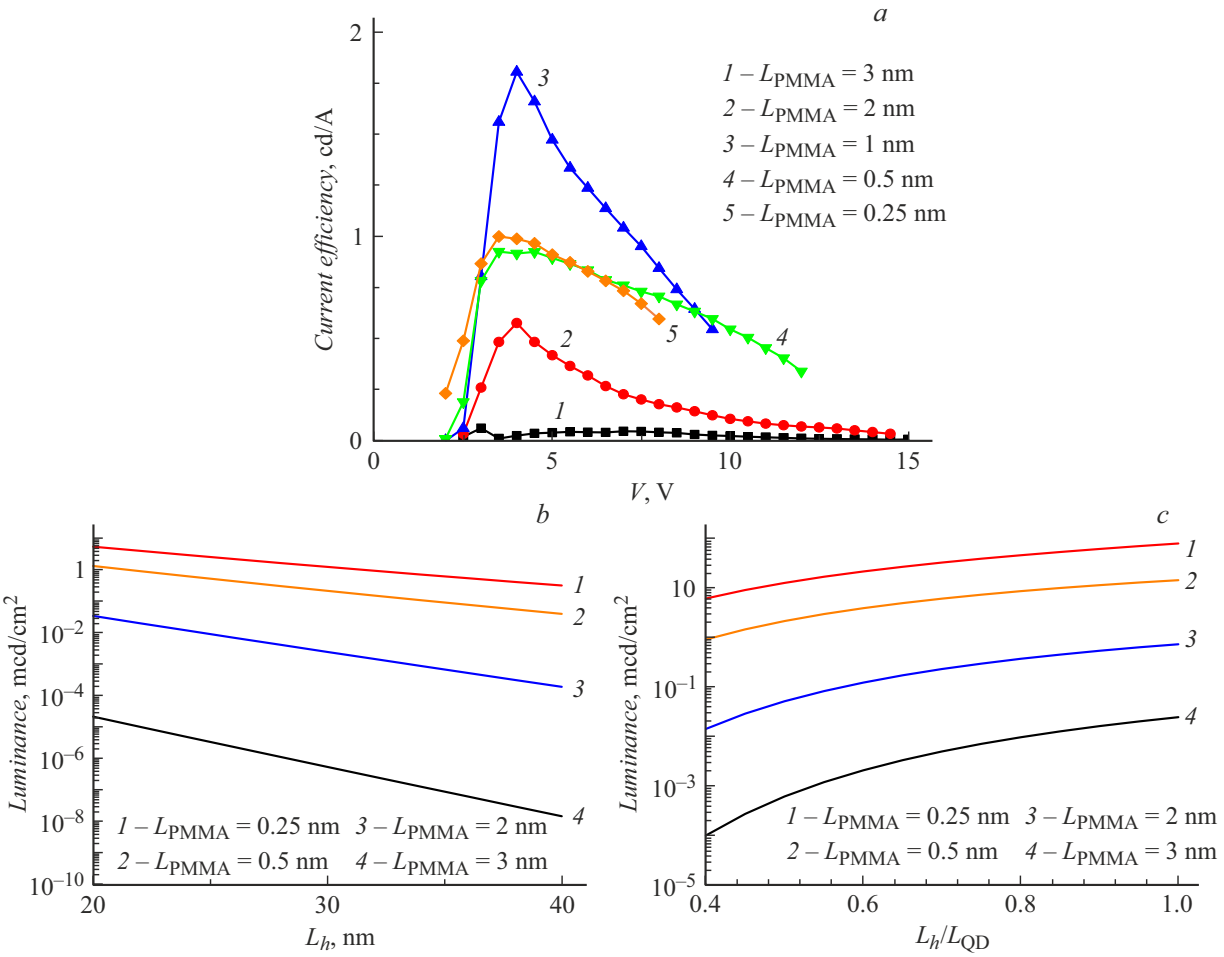

Figure 3. Experimental voltage dependences of the LED current efficiency at $L_h = 30$ nm, $L_{QD} = 40$ nm (a) and results of simulation of the dependence of the luminance at $V = 3.5$ V on the *poly*-TPD layer thickness at $L_h/L_{QD} = 0.5$ (b) and on the L_h/L_{QD} ratio at $L_h = 30$ nm (c). The other parameter values are the same as the ones in Fig. 2 (see text).

electroluminescence yield. Thus, since the exciton diffusion length in CdSe QD layers is as large as 20−30 nm [12], the luminance of QDLEDs based on such QDs should be maximized at $L_h \approx L_{QD} \approx 20$ nm.

The obtained results suggest that the current efficiency of the studied QDLED structure is maximized at an applied voltage of about 3.5 V and an effective thickness of the blocking PMMA layer of about 1 nm. The developed theoretical model agrees with the measured CVCs of the QDLED structure. At the indicated optimum parameters, the model predicts that the current (and luminance) of the QDLED structure should increase significantly as the HTL thickness grows relative to the QD layer thickness.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J. Lim, B.G. Jeong, M. Park, J.K. Kim, J.M. Pietryga, Y.-S. Park, V.I. Klimov, C. Lee, D.C. Lee, W.K. Bae, Adv. Mater., **26**, 8034 (2014). DOI: 10.1002/adma.201403620
[2] Y. Dai, Y. Deng, X. Peng, Y. Jin, Adv. Mater., **29**, 1607022 (2017). DOI: 10.1002/adma.201607022
[3] Y.Z. Sun, Y.B. Jiang, X.W. Sun, S. Zhang, S. Chen, Chem. Rec., **19**, 1729 (2019). DOI: 10.1002/tcr.201800191
[4] M. Zvaigzne, A. Alexandrov, A. Tkach, D. Lypenko, I. Nabiev, P. Samokhvalov, Nanomaterials, **11**, 2014 (2021). DOI: 10.3390/nano11082014
[5] Y. Kijima, N. Asai, S.-I. Tamura, Jpn. J. Appl. Phys., **38**, 5274 (1999). DOI: 10.1143/JJAP.38.5274
[6] V. Nikitenko, H. Bassler, J. Appl. Phys., **90**, 1823 (2001). DOI: 10.1063/1.1333028
[7] P.O. Anikeeva, C.F. Madigan, J.E. Halpert, M.G. Bawendi, V. Bulović, Phys. Rev. B, **78**, 085434 (2008). DOI: 10.1103/PhysRevB.78.085434
[8] X.L. Dai, Z.X. Zhang, Y.Z. Jin, Y. Niu, H. Cao, X. Liang, L. Chen, J. Wang, X. Peng, Nature, **515**, 96 (2014). DOI: 10.1038/nature13829
[9] M. Rahmati, S. Dayneko, M. Pahlevani, Y. Shi, Adv. Funct. Mater., **29**, 1906742 (2019). DOI: 10.1002/adfm.201906742
[10] S. Dayneko, D. Lypenko, P. Linkov, N. Sannikova, P. Samokhvalov, V. Nikitenko, A. Chistyakov, Mater. Today: Proc., **3**, 211 (2016). DOI: 10.1016/j.matpr.2016.01.059
[11] L.N. Dobretsov, M.V. Gomoyunova, *Emissionnaya elektronika* (Nauka, M., 1966), p. 406 (in Russian).
[12] G.M. Akselrod, F. Prins, L.V. Poulikakos, E.M.Y. Lee, M.C. Weidman, A.J. Mork, A.P. Willard, V. Bulović, W.A. Tisdale, Nano Lett., **14**, 3556 (2014). DOI: 10.1021/nl501190s