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ELECTRODE ROUGHNESS EFFECT ON CHARGE CARRIER INJECTION AND TRANSPORT IN ORGANIC DEVICES

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Explicit formula connecting roughness profile of an electrode with the distribution of the electric field at its surface is derived for the case of smooth roughness, when typical height of roughness element is small in comparison to its size across a surface. An efficient numerical method is suggested for the calculation of the field distribution at the surface of very rough electrode. This gives us a possibility to calculate various injection properties of the electrode for a particular kind of injection rate: integral injection rate, surface distribution of injection peaks etc. It is shown also that rough surface of electrodes generates an additional energy disorder in the bulk of transport layer. This principal result indicates that electrode roughness affects not only carrier injection but carrier transport as well.

Keywords: charge transport; injection; rough electrode surface

INTRODUCTION

Morphology of the electrode surface and structure of the interface layer between the electrode and bulk of organic transport layer significantly affect device performance: its efficiency, stability etc. The major aspect of this influence is a dependence of the carrier injection rate on the structure of electrode surface. Rough surface creates a non-uniform distribution of the electric field, and, thus, non-uniform distribution of the injection rate. Usually, organic transport devices have a sandwich geometry (geometry of a flat capacitor): bottom electrode/organic (polymer) layer/top electrode. The bottom electrode is usually deposited on the glass substrate, then the

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polymer solution is cast on it and dried, and then the top electrode is thermally deposited on the polymer layer. It is well known that these two interfaces have different structures, with the bottom one having rather sharp transition from the metal to organic layer, and the top one having a diffusive structure with the transition layer having thickness of several nanometers [1,2]. This structural asymmetry of electrodes results in different injection properties. In this paper we focus our attention on the interface with the bottom electrode, because it may be approximately described as a rough (random) surface separating a metal (or another conducting material) and organic material. Mathematically, the rough surface may be described by setting its height $h(\rho)$ for a given position $\rho = (x, y)$. In many cases this surface is relatively smooth so that typical height of the element is small in comparison to its size across the surface [3–7]. In this situation it is possible to calculate distribution of the electric field at the surface knowing the surface profile function $h(\rho)$. In this paper we present the result of such calculation.

Roughness of the electrode surface affects not only injection, but the charge transport across the organic layer. In the case of ideally flat electrodes the surface charge, accumulated at the surface, if voltage is applied to the device, just produces a uniform electric field E_0 in the bulk of the device. In the case of rough surface electrostatic potential

$$\varphi(\mathbf{r}) = -E_0 z + \delta\varphi(\mathbf{r}) \tag{1}$$

attains a random component $\delta\varphi(\mathbf{r})$, thus giving an additional contribution $\delta U(\mathbf{r}) = e\ \delta\varphi(\mathbf{r})$ to the carrier random energy. Hence, a roughness of the electrode surface induces an additional energetic disorder in the bulk of organic transport layer, and, certainly, affects charge carrier transport. We should expect (and this is indeed the case) that in contrast to a more usual case of intrinsic structural disorder, the magnitude of this additional disorder should be proportional to E and decays when going away from the electrode, thus presenting a case of spatially inhomogeneous disorder.

ORGANIC LAYER BETWEEN ROUGH CONDUCTING ELECTRODES: SMOOTH ROUGHNESS

We model electrode surfaces by two random surfaces $z = h_0(\rho)$ and $z = L + h_L(\rho)$ assuming that $\langle h(\rho)\rangle = 0$ (here angular brackets denote a statistical average), and L is the transport layer thickness. To calculate $\varphi(\mathbf{r})$ we have to solve a Laplace equation $\Delta\varphi(\mathbf{r}) = 0$ inside the layer taking into account the boundary conditions

$$\varphi|_{z=h_0(\rho)} = 0, \quad \varphi|_{z=L+h_L(\rho)} = V_0, \tag{2}$$

where V_0 is a voltage applied to the device. To solve the Laplace equation it is convenient to make a transformation to new coordinates $X = x$, $Y = y$ and $Z = L(z - h_0)/(L + h_L - h_0)$, so the boundary conditions transform to $\varphi|_{Z=0} = 0$ and $\varphi|_{Z=L} = V_0$. For relatively smooth electrodes it is sufficient to take into account only terms up to $O(h)$. The actual solution is described elsewhere [8], here we show only the result

$$\varphi/V_0 = \frac{Z}{L} + \frac{1}{4\pi^2 L}\int d\mathbf{k}e^{i\mathbf{k}\rho}\left[\left(1 - \frac{Z}{L} - \frac{\sinh k(L-Z)}{\sinh kL}\right)h_0(\mathbf{k}) + \left(\frac{Z}{L} - \frac{\sinh kZ}{\sinh kL}\right)h_L(\mathbf{k})\right], \tag{3}$$

where $h(\mathbf{k})$ is a Fourier transform of $h(\rho)$. Direct calculation of the correlation function $C(\mathbf{r}, \mathbf{r}') = \langle \delta U(\mathbf{r})\delta U(\mathbf{r}')\rangle$ (back in the initial coordinates) gives for distances larger than surface correlation length l

$$C(\mathbf{r}, \mathbf{r}') \propto \frac{e^2 E_0^2 l^2 (z + z')}{\left[(z + z')^2 + (\rho - \rho')^2\right]^{3/2}}, \tag{4}$$

where E_0 is the applied electric field. Thus, magnitude of the disorder $[C(\mathbf{r}, \mathbf{r})]^{1/2}$ decays as $1/z$ for $z \gg l$. In this universal regime the distribution of $\delta U(\mathbf{r})$ is approximately Gaussian irrespectively to the distribution of h (ρ), because many surface domains with size l^2 give contributions to $\delta U(\mathbf{r})$.

Presently we do not know much about charge transport in devices having rough electrodes. Nonetheless, we may speculate that if a carrier is generated in the vicinity of the rough electrode and E_0 is strong enough, then the carrier must accelerate when going away from the electrode to the region of smaller disorder. In this case for a time-of-flight (TOF) method the usual plateau region of the photocurrent transient $I(t)$ where $I(t) \approx$ const should transform with the increase of E_0 to the region where $I(t)$ increases with time t. The same behavior may be caused by selective injection [9], but in the latter case the same transformation takes place with the increase of temperature as well, while in the case of roughness effect quite the opposite is true, i.e. the low temperature facilitates observation of the transformation.

Electric field $E(\rho)$ at the electrode surface at $Z = 0$ is

$$E(\rho) = E_0\left\{1 + \frac{1}{4\pi^2}\int d\mathbf{k}e^{i\mathbf{k}\rho}\frac{k}{\sinh kL}\left[h_0(\mathbf{k})\cosh kL - h_L(\mathbf{k})\right]\right\} \tag{5}$$

Distribution $h(\mathbf{k})$ decays for $k \gg 1/l$, and behavior of Eq. (5) depends on parameter $\alpha = l/L$. If $\alpha \ll 1$, then

$$E(\rho)/E_0 \approx 1 + \frac{1}{4\pi^2}\int d\mathbf{k}e^{i\mathbf{k}\rho}kh_0(\mathbf{k}) = 1 + O(h/l), \tag{6}$$

and in the opposite case $\alpha \gg 1$

$$E(\rho)/E_0 \approx 1 + \frac{h_0(\rho) - h_L(\rho)}{L} = 1 + O(h/L). \tag{7}$$

Eq. (7) corresponds to first terms of the series expansion of equation $E = E_0 L/(L + h_L - h_0)$ which describes simple re-scaling of the electric field in the case of very smooth variation of electrodes' surfaces.

A non-uniform spatial distribution of $E(\rho) = E_0 + \delta E(\rho)$ leads to a significant spatial variation of the injection current J which has a nonlinear dependence on E, be it Fowler-Nordheim (FN) [10]

$$J_{\mathrm{FN}} = J_0 (E/E_{\mathrm{FN}})^2 \exp(-E_{\mathrm{FN}}/E) \tag{8}$$

or Richardson-Schottky injection (RS) [11]

$$J_{\mathrm{RS}} = J_0 \exp[(E/E_{\mathrm{RS}})^{1/2}] \tag{9}$$

(here E_{FN} and E_{RS} are parameters which depend on temperature and properties of materials and metal/organic interface). In typical cases parameter E_{FN} is large [12], and parameter E_{RS} is small [13] in comparison to E_0, for this reason even relatively small variation of $h(\rho)$ and $E(\rho)$ leads to a significant variation of injection current (see Fig. 1). Small variations of $E(\rho)$ could even change completely a functional dependence of the total

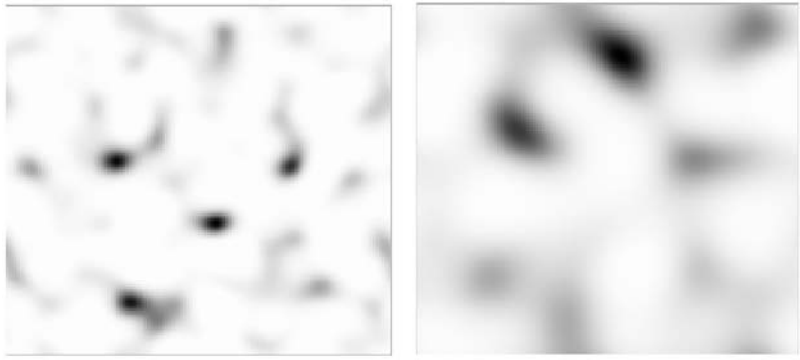

FIGURE 1 Spatial distribution of the FN injection rate in the case of Gaussian random surface profiles with the Gaussian surface correlation function $\Omega(\rho) \propto \exp(-\rho^2/2l^2)$: a) $h/l = 0.125$ and b) $h/l = 0.062$, correspondingly. We used $E_{\mathrm{FN}} = 1 \times 10^7$ V/cm [12] and $E_0 = 1 \times 10^6$ V/cm. Darkness is proportional to the injection intensity. Note that in (Figure 1a) the maximal intensity is approximately 70 times higher than the intensity for a flat electrode, and in (Figure 1b) the maximal intensity is 14 times higher. The show area is approximately $0.1\,\mu \times 0.1\,\mu$.

current $\boldsymbol{J}$ on $\boldsymbol{E}_0$. For example, in the case of Gaussian distribution of $h_{0,\mathrm{L}}$ the resulting distribution of $\delta\boldsymbol{E}$ has a Gaussian form with zero mean and variance $\langle(\delta\boldsymbol{E})^2\rangle = 2(\boldsymbol{E}_0 h/l)^2$, here h is a rms roughness. A straightforward calculation of $\langle\boldsymbol{J}\rangle$ gives

$$\begin{aligned} \ln\langle\boldsymbol{J}_{\mathrm{FN}}\rangle &\propto -\left(\frac{\boldsymbol{E}_{\mathrm{FN}}}{\boldsymbol{E}_0}\right)^{2/3}\lambda^{-1/3}, \quad \lambda\frac{\boldsymbol{E}_{\mathrm{FN}}}{\boldsymbol{E}_0} \gg 1, \\ \ln\langle\boldsymbol{J}_{\mathrm{RS}}\rangle &\propto \left(\frac{\boldsymbol{E}_0}{\boldsymbol{E}_{\mathrm{RS}}}\right)^{2/3}\lambda^{1/3}, \quad \lambda\sqrt{\frac{\boldsymbol{E}_0}{\boldsymbol{E}_{\mathrm{RS}}}} \gg 1. \end{aligned} \tag{10}$$

Here $\lambda = \langle(\delta\boldsymbol{E})^2\rangle/\boldsymbol{E}_0^2 = 2(h/l)^2$.

VERY ROUGH ELECTRODES

If $h/l \approx 1$, then the perturbation theory solution is not valid. In this case a better approach is the numerical solution of the integral equation

$$\int d\rho e^{i\mathbf{k}\rho - kh(\rho)} B(\rho) = 4\pi^2\delta(\mathbf{k}) \quad \text{or} \tag{11}$$

$$\int d\rho' \frac{h(\rho')}{\left[h^2(\rho') + |\rho - \rho'|^2\right]^{3/2}} B(\rho') = 2\pi \tag{12}$$

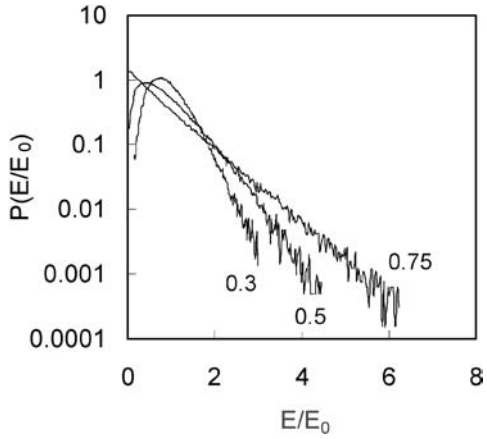

FIGURE 2 Distribution of the electric field at the surface of rough Gaussian electrodes with different roughness (values of h/l are indicated near corresponding curves).

which describe the distribution of the charge $B(\rho) = \sigma(\rho)/\sigma_0$ at the surface of rough electrode. This equation was derived by the approach similar to presented in [14]. Here $\sigma(\rho)$ is the surface charge density and σ_0 is the corresponding density for a flat electrode. A suitable method to solve (11) or (12) is to solve the corresponding lattice version of the problem which turns out to be a very large system of linear equations.

Resulting field distributions for the Gaussian surface are shown in (Fig. 2). Exponential tail of the distribution is a fingerprint of the Gaussian distribution of height. It leads to dependencies: $\ln\langle J_{\mathrm{FN}}\rangle \propto -(E_{\mathrm{FN}}/E)^{1/2}$ for FN injection and $\ln\langle J_{\mathrm{FN}}\rangle \propto E/E_{\mathrm{RS}}$ for RS injection.

CONCLUSION

We presented results of the calculation of the distribution of electrostatic potential in the bulk of organic layer and electric field at the surface of rough electrodes. For very rough electrodes the form of the distribution of E depends on the profile statistical properties. In the bulk of the layer a magnitude of roughness-induced energetic disorder decays as inverse distance when going away from the electrode, thus providing the case of spatially inhomogeneous disorder. This kind of disorder should transform the shape of photocurrent transient in TOF experiments. Calculation of the distribution of the electric field offers a possibility to study various aspects of charge injection.

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