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Rough Electrode Surface: Effect on Charge Carrier Injection and Transport in Organic Devices

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Summary: The effect of electrode roughness on charge carrier injection and transport is considered. An explicit formula connecting the roughness profile of an electrode with the distribution of the electric field at its surface (and the electrostatic potential in the bulk of transport layer) is derived for the case of smooth roughness, when the typical height of roughness element is small in comparison with its size across the surface (this is a very typical situation). This formula gives us an opportunity to measure the electrode surface profile (e.g., by AFM) and then to calculate various injection properties of this particular electrode for any kind of injection. General properties of the electrode - organic layer interface in the case of significant (not smooth) roughness are considered and a suitable numeric procedure for the calculation of the surface electric field distribution is proposed. It is also shown that rough surface of electrodes generates an additional energy disorder in the bulk of transport layer. This principal result indicates that the electrode roughness affects not only carrier injection but carrier transport as well. Roughness-induced energetic disorder produces a channel-like structure in the vicinity of the electrode, thus providing separation of electrons and holes. Such separation should decrease the charge recombination rate and, hence, the emitting efficiency of light emitting devices. At the same time, the separation is favorable to solar cells.

Keywords: charge injection; charge transport; rough interfaces

Introduction

Morphology of the electrode surface and structure of the interface layer between the electrode and bulk of the organic transport layer significantly affect device performance: its efficiency, stability etc. A major aspect of this influence is the 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 a glass substrate, then a polymer solution is cast on it and dried, and then the top electrode is thermally deposited on the polymer layer. It is

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well known that these two interfaces have different structures, the bottom one having a rather sharp transition from the metal to organic layer, and the top one having a diffusive structure with the transition layer of 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 can 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 a typical height of the element is small in comparison with 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 also the charge transport across the organic layer. In the case of ideally flat electrodes, the surface charge accumulated at the surface if a 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,

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

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, 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 the more usual case of intrinsic structural disorder, the magnitude of this additional disorder should be proportional to E_0 decaying when going away from the electrode. Thus this presents 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); 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

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

where V_0 is a voltage applied to the device. 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

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

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 greater than the 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, the 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 of the distribution of $h(\rho)$, because many surface domains with size l^2 give contributions to $\delta U(\mathbf{r})$. Typical spatial distribution of φ in the vicinity of the rough electrode is shown in Fig. 1.

The rough surface of the electrode creates a channel-like disordered structure in the distribution of electrostatic potential. This structure leads to separation of electrons and holes (electrons tend to move along ridges of the potential, and holes tend to move along valleys). Typical scale of the structure in the direction perpendicular to the electrode plane is surface correlation length l. Such separation should decrease the charge recombination rate and, hence, the emitting efficiency of light emitting devices. At the same time, the separation is favorable to solar cells.

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

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

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

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

and in the opposite case, $\gamma \gg 1$

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

Equation 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 electrode 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 a Fowler-Nordheim (FN) [9]

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

or a Richardson-Schottky injection (RS) [10]

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

(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 [11], and parameter E_{RS} is small [12] in comparison with E_0; for this reason, even relatively small variation of $h(\rho)$ and $E(\rho)$ leads to a significant spatial variation of injection current (see Fig. 2). Small variations of $E(\rho)$ could even change completely the functional dependence of the total current $\langle J\rangle$ on E_0. For example, in the case of Gaussian distribution of $h_{0,L}$, the resulting distribution of δE has a Gaussian form with zero mean and variance $<(\delta E)^2> = 2(E_0 h / l)^2$, here $h^2 = < h^2(\rho)>$.

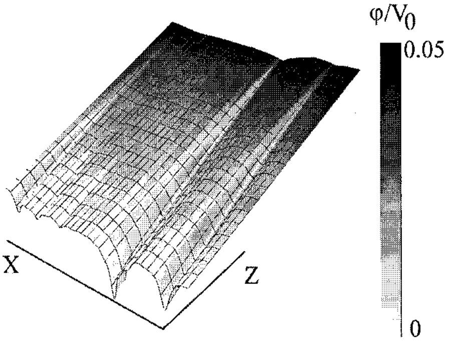


Figure 1. Spatial distribution of the potential in the vicinity of rough electrode (electrode plane is parallel to the XY plane, and the Z axis is directed to the bulk of the transport layer).

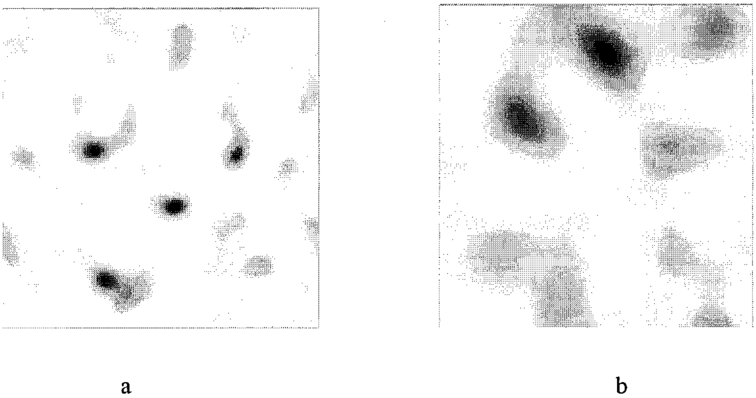


Figure 2. Spatial distribution of the FN injection rate in the case of Gaussian random surface profiles with the Gaussian surface correlation function $\Omega(\rho) = <h(\rho)h(0)> \propto \exp(-\rho^2/2l^2)$ and h = 1 nm: (a) h/l = 0.125 and (b) h/l = 0.062. We used $E_{FN} = 1\times10^7$ V/cm [11] and $E_0 = 1\times10^6$ V/cm. Darkness is proportional to the injection intensity. Note that in Fig. 2a the maximal intensity is approximately 70 times higher than the intensity for a flat electrode, and in Fig. 2b the maximal intensity is 14 times higher. The size of the area is approximately 0.1μ × 0.1μ.

A straightforward calculation of <*J*> gives

$$\ln\langle J_{\mathrm{FN}}\rangle \propto -\left(\frac{E_{\mathrm{FN}}}{E_0}\right)^{2/3} \lambda^{-1/3}, \qquad \lambda\frac{E_{\mathrm{FN}}}{E_0} >> 1, \tag{10}$$

$$\ln\langle J_{\mathrm{RS}}\rangle \propto \left(\frac{E_0}{E_{\mathrm{RS}}}\right)^{2/3} \lambda^{1/3}, \qquad \lambda\sqrt{\frac{E_0}{E_{\mathrm{RS}}}} >> 1.$$

Here $\lambda = <(\delta E)^2> / E_0^2 = 2(h/l)^2$.

Very rough electrodes

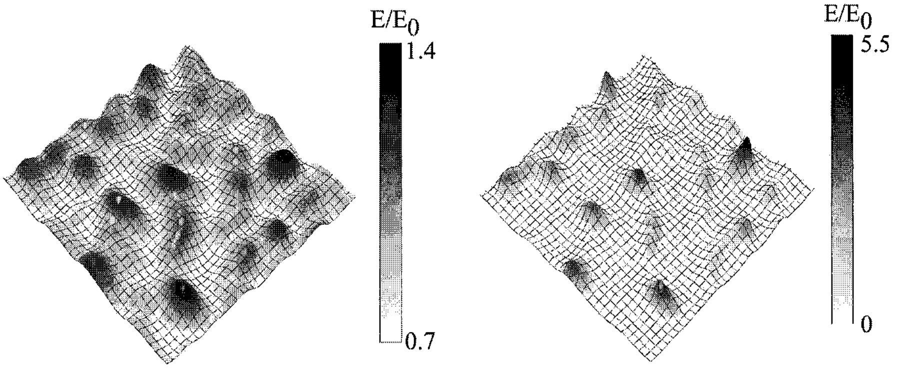
If $h/l \approx 1$, then the perturbation theory solution is not valid. In this case a better approach is numerical solution of the integral equation

$$\int d\rho e^{\mathrm{i}\mathbf{k}\rho - kh(\rho)} B(\rho) = 4\pi^2\delta(\mathbf{k}) \qquad \text{or} \qquad \int d\rho' \frac{h(\rho')}{\left[h^2(\rho') + |\rho - \rho'|^2\right]^{3/2}} B(\rho') = 2\pi \tag{11}$$

which describes the distribution of the charge density $B(\rho) = \sigma(\rho)/\sigma_0$ at the surface of rough electrode (we assume $l << L$, so the effect of the second electrode is negligible). Equation 11 was derived by the approach similar to that presented in [13]. Here $\sigma(\rho)$ is the surface charge density and σ_0 is the charge density for a flat electrode. Electric field may be calculated using equation

$$E(\rho) = \frac{E_0 B(\rho)}{\sqrt{1 + (\nabla h)^2}} \tag{12}$$

A suitable method to solve Eq. (11) is a solution of the corresponding lattice version of the problem, which turns out to be a very large system of linear equations. Resulting spatial field distributions for the Gaussian surface are shown in Fig. 3 and distribution of the magnitude of the electric field $P(E/E_0)$ is shown in Fig. 4. For smooth surface, the electric field magnitude fluctuates around E_0 but with increasing roughness, the electric field is effectively concentrated at the tops of surface peaks while the rest of the surface carries a very weak field. The exponential tail of the distribution for large E/E_0



a

b

Figure 3. Spatial distribution of the electric field at the surface of rough Gaussian electrodes with different roughness (area of $16l \times 16l$ is shown): (a) $h/l = 0.075$ and (b) $h/l = 0.75$.

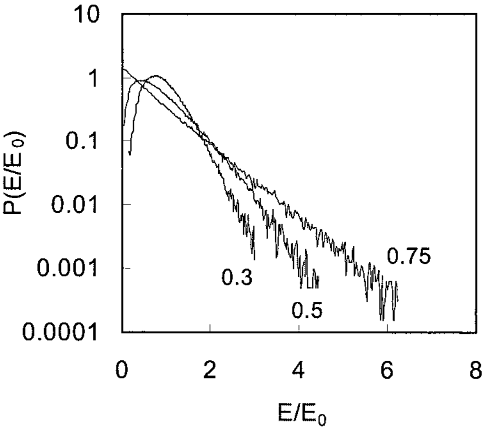


Figure 4. Distribution of the electric field magnitude at the surface of rough Gaussian electrodes with different roughness (values of h/l are indicated with corresponding curves).

$$\ln P = -bE/E_0 \tag{13}$$

seems to be a fingerprint of the Gaussian distribution of height (preliminary simulation data suggest that the development of the exponential tail does not depend on the functional form of the surface correlation function, but the tail has a different form for a non-Gaussian height distribution). The dependence of parameter b on h/l may be approximated by $b \propto (h/l)^{-\alpha}$ with $\alpha = 1.3 \pm 0.2$ (quality of this approximation can be seen in Fig. 5). The exponential tail of the distribution leads to the dependences: $\ln\langle J_{FN}\rangle \propto -(E_{FN}/E_0)^{1/2}$ for the FN injection and $\ln\langle J_{RS}\rangle \propto E_0/E_{RS}$ for the RS injection.

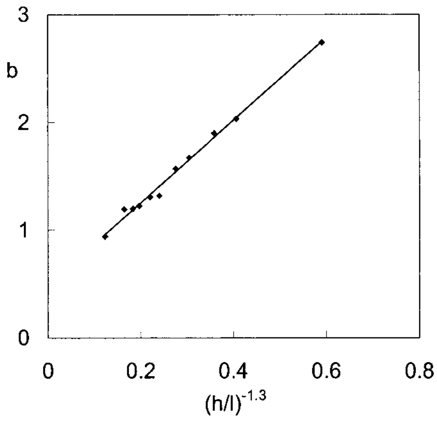


Figure 5. Dependence of parameter b on h/l.

Surface of real ITO samples

Data of AFM scans for different indium tin oxide (ITO) samples indicate that the model of Gaussian random surface may be a good approximation of the ITO electrode surfaces [14-16] (with the surface correlation function having the Gaussian form, too). Statistical properties of ITO electrodes are summarized in Table 1. It is reasonable to expect that the AFM data underestimate the actual roughness of the interface because of the ultrathin water layer effects (such layer frequently covers the sample surface), non-ideal deconvolution of the contribution of cantilever tip shape, non-ideal alignment of the organic material at the electrode surface (possible presence of the empty space), etc. For this reason the calculated values of parameter h/l should be considered as a lower bound on actual values. A comparison of Table 1 and Fig. 4 suggests that we should expect the evolution of the exponential tail of the electric field distribution at least for some of ITO electrodes. Thus, the electric field dependence of the total injection current should significantly differ from the field dependence of the proper microscopic injection rate (see Fig. 6). Quite frequently, such complicated field dependence of the injection current is attributed to the contribution of several injection mechanisms [11]. Our result indicates that it may be attributed to the roughness effect as well.

Table 1. Statistical properties of different ITO samples

ITO sample	*h*, nm	*l*, nm	*h*/*l*
Cornell group [14]	0.41	38	0.011
Minsk group [15]	1.8	18	0.1
Potsdam group, polished [16]	4.1	24	0.17
Potsdam group, unpolished [16]	4.1	14	0.3

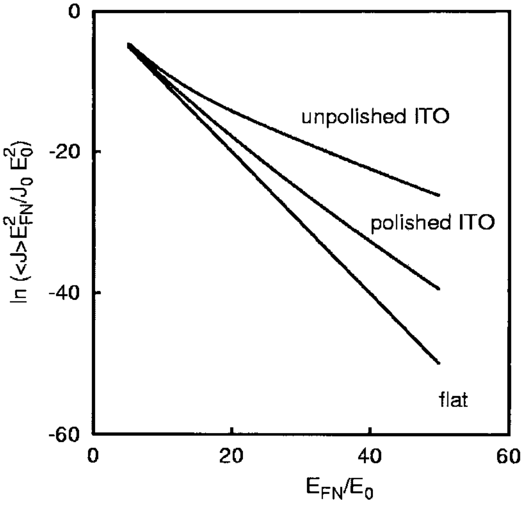


Figure 6. Calculated field dependence of the FN injection rate for the Gaussian electrode having parameters of the Potsdam ITO electrodes. We assume $E_{FN} = 1\times10^7$ V/cm [11].

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 statistical properties of the profile. In the bulk of the layer, the magnitude of the roughness-induced energetic disorder decays as the inverse distance when going away from the electrode, thus providing the case of spatially inhomogeneous disorder. Calculation of the distribution of the electric field offers an opportunity to study various aspects of charge injection.

Acknowledgments

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