

The field-dependent interface recombination velocity for organic-inorganic heterojunction

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Abstract

We have derived an analytical formula which describes the field-dependent interface recombination velocity for the boundary of two materials characterized by different permittivities. The interface recombination of charge carriers has been considered in the presence of image force Schottky barrier. We suggest that this effect may play an important role in the loss of current for organic-inorganic hybrid heterojunctions. It has been proved that the presented method is a generalization of the Scott-Malliaras model of surface recombination at the organic/metal interface. We also discuss that this model is intuitively similar but not analogous to the Langevin mechanism of bulk recombination.

Key words: Hybrid structures, Organic electronics, Recombination

1 Introduction

The hybrid structures consisting of organic and inorganic materials are currently of an intense interest due to their potential applications in electronics and optoelectronics. Recently, the role of hybrid devices, like the perovskite-based solar cells [1] and the dye-sensitized solar cells [2], has greatly increased. Heterojunctions play a key role in such systems, therefore a special attention is paid to an explanation of all interfacial processes.

Predominantly, permittivities of inorganic compounds are higher than for organic ones. The differences between the dielectric constants should lead to an electrostatic polarization at the heterojunctions. A theoretical description of an image force effect, which occurs at the boundary of two materials characterized by different permittivities, is known in classical electrodynamics for many years [3,4]. The existence of this phenomenon has been discussed in literature to explain experimental results observed in semiconductor-semiconductor and semiconductor-insulator structures [5-13].

Recently, we have proposed a new recombination mechanism which takes place for heterojunctions [11]. For this type of recombination, charge carriers located in a material characterized by a lower dielectric constant are attracted to the boundary with the second material with a higher permittivity and recombine there. This model has been successfully applied to explain a non-Langevin

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nongeminate recombination observed in organic donor–acceptor bulk hetero-junction solar cells [14,15] and to describe the increasing of recombination order in disordered organic heterostructures [16].

The aim of this work is to consider this type of interface recombination in the presence of an image force Schottky barrier which appears when an external electric field is applied to the hybrid organic–inorganic heterojunction.

2 Problem statement

2.1 The model

It is well known that two opposite sign charge carriers can recombine bimolecularly in an organic material if their electrostatic potential energy is of the order of kT [17,18]. Comparing these two energies, we obtain a capture distance for both carriers, called the Coulomb (or Onsager) radius

$$r_c = \frac{e^2}{4\pi\epsilon_0\epsilon_1kT}, \quad (1)$$

where e is an electron charge, ϵ_0 is a permittivity of a vacuum, ϵ_1 represents a dielectric constant of organic material, k is a Boltzmann constant and T is a temperature.

First, let us consider an interface between metal and an organic material characterized by permittivity ϵ_1 . When a charge carrier e is located at a distance x to the metallic surface, then an attractive force acting between the charge

and its image can be found from equation [19]

$$F = \frac{e^2}{4\pi\epsilon_0\epsilon_1(2x)^2}. \quad (2)$$

In order to determine a capture distance for an interface recombination in such system ($x = x_c$), one should compare the thermal energy kT to an electrostatic potential energy of the carrier and its image. Scott and Malliaras found that [20]

$$x_c = \frac{r_c}{4}. \quad (3)$$

Let us now analyze an interface of two materials characterized by different permittivities ϵ_1 and ϵ_2 ($\epsilon_1 < \epsilon_2$). If a charge carrier e is located in an organic material (a permittivity ϵ_1) near the interface with an inorganic compound (a permittivity ϵ_2), then two image charges appear at both sides of the boundary [3,4]

$$e' = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}e, \quad e'' = \frac{2\epsilon_2}{\epsilon_1 + \epsilon_2}e, \quad (4)$$

where e' represents an image charge situated in the material with dielectric constant ϵ_2 and e'' is a charge located in the position of e .

When a distance from the charge carrier e to the interface is x , then a force acting between the charges e and e' can be calculated from equation

$$F = \left| \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right| \frac{e^2}{4\pi\epsilon_0\epsilon_1(2x)^2}. \quad (5)$$

In order to avoid a problem with the minus sign, we decided to use an absolute value.



If an electrostatic potential energy of e and e' is equal to kT , then a capture distance for an interface recombination is in the form

$$x_c = \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \frac{r_c}{4}. \quad (6)$$

When an external electric field E is applied across the compound described by ε_1 , one may observe a lowering of the interfacial barrier height Φ_B . For a charge e located in an organic material, an expression for the potential energy looks as follows [5]

$$U(x) = e\Phi_B - eEx - \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \frac{e^2}{16\pi\varepsilon_0\varepsilon_1 x}. \quad (7)$$

The position of an extremum in potential energy is situated at the distance [8]

$$x_{ext} = \left(\left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \frac{e}{16\pi\varepsilon_0\varepsilon_1 E} \right)^{1/2} \quad (8)$$

from the interface.

The value of this extremum is expressed by relation

$$U(x_{ext}) = e\Phi_B - e \left(\left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \frac{eE}{4\pi\varepsilon_0\varepsilon_1} \right)^{1/2}. \quad (9)$$

The density of an interface recombination current may be defined as [20]

$$J_{rec} = en(x_c)S(E), \quad (10)$$

where $n(x_c)$ is an interfacial charge density at a capture distance x_c to the interface and $S(E)$ represents a field-dependent interface (surface) recombination velocity.

It should be mentioned that the real charge carrier e does not recombine bimolecularly with its image charge e' , because such a process is physically impossible. After reaching the boundary between organic and inorganic compounds, the real charge e may be trapped near the interface and then waits for an opposite sign (real) charge carrier to recombine bimolecularly. The presented mechanism of recombination is considered in temperatures much greater than an absolute zero, thus we expect a sufficient amount of free charge carriers thermally created in the bulk of inorganic material. If a layer of the inorganic material is thin, what is typical for structures used in organic electronics, then some of these thermally generated carriers should spend an enough long time near the interface. It causes that the probability of their bimolecular recombination with the trapped charge carriers increases. Certainly, some of these trapped carriers may be detrapped before recombination and then a total amount of recombining carriers n_{rec} decreases ($n_{rec} < n(x_c)$). Therefore, the density of a recombination current given by Eq. (10) should be treated as its maximal value. However, the detrapping process does not influence on the final derivation of a formula describing the field-dependent interface recombination velocity $S(E)$ which is presented in the following.

It is evident from Eq. (10), that the interface recombination velocity may be expressed as

$$S(E) = \mu E(x_c), \quad (11)$$

where μ is a mobility of charge carriers in organic material. The electric field $E(x_c)$ at a distance x_c is

$$E(x_c) = -E + \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \frac{e}{16\pi\varepsilon_0\varepsilon_1 x_c^2}. \quad (12)$$

Analogously to the method presented by Scott and Malliaras [20], the potential energy at the capture radius x_c may be estimated from an expression

$$U(x_c) = U(x_{ext}) - kT. \quad (13)$$

From the above equations, we can derive the formula for the field-dependent interface recombination velocity

$$S(E) = \frac{S(0)}{4} \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \left(\left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \frac{1}{\Psi^2} - f \right), \quad (14)$$

where the recombination velocity at a zero electric field is

$$S(0) = \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right|^{-1} \frac{16\pi\varepsilon_0\varepsilon_1(kT)^2\mu}{e^3} \quad (15)$$

and f denotes a reduced electric field defined as [20]

$$f = \frac{eEr_c}{kT}. \quad (16)$$

The parameter Ψ is given by

$$\Psi = f^{-1} + f^{-1/2} \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right|^{1/2} - f^{-1} \left[1 + 2 \left(f \left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| \right)^{1/2} \right]^{1/2}. \quad (17)$$

2.2 Approximation

For an organic/metal interface, the permittivity of metal $\varepsilon_2 \rightarrow \infty$. In order to analyze this case, it is convenient to rearrange the ratio

$$\left| \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right| = \left| \frac{(\varepsilon_1/\varepsilon_2) - 1}{(\varepsilon_1/\varepsilon_2) + 1} \right|. \quad (18)$$

One may easily check that Eqs. (14), (15) and (17) are transformed to formulas

$$S(E) = \frac{S(0)}{4} \left(\frac{1}{\Psi^2} - f \right), \quad (19)$$

$$S(0) = \frac{16\pi\varepsilon_0\varepsilon_1(kT)^2\mu}{e^3}, \quad (20)$$

and

$$\Psi = f^{-1} + f^{-1/2} - f^{-1} \left(1 + 2f^{1/2} \right)^{1/2}, \quad (21)$$

respectively, which are exact expressions derived by Scott and Malliaras for a recombination of charge carriers at the organic/metal interface [20].

2.3 Discussion

As mentioned earlier, a starting assumption is that a capture distance R is associated with a case when an electrostatic potential energy of two opposite signed charge carriers is comparable to the thermal energy. Such an idea is usually used to explain the Langevin mechanism of bulk recombination [17]. Thus, in their paper, Scott and Malliaras [20] decided to treat their model analogously to the Langevin theory.

Recently, it has been reported that a Langevin equation for the bulk rate constant can be obtained from a general theory of bulk recombination [21,22], when the capture distance $R = 0$. This result suggests that the Langevin theory does not correspond to the case $R = r_c$ (an Onsager radius), what is usually taken into account in literature. It leads to conclusion that the Scott and Malliaras model (and the presented generalization) are only intuitively similar but not analogous to the Langevin mechanism.

We should mention that an additional electrostatic effect, which may play a role in the recombination of charge carriers, has not been considered in this paper. The recombining positive and negative (real) charges can interact with a medium through the charge-dielectric interaction [23]. In order to estimate of the influence of this effect, one should calculate the solvation energy of both oppositely signed real carriers in the medium composed of two materials characterized by different permittivities [24].

3 Summary

To conclude, we have derived an analytical expression which describes the field-dependent interface recombination velocity for the heterojunction of two compounds characterized by different dielectric constants. The process of recombination has been considered for the case when an image force Schottky barrier is forming at the interface of both materials. We have proved that our model is a generalization of the Scott-Malliaras model which describes the surface recombination of charge carriers at the organic/metal interface.

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