Time-delayed charge-injection effects on photocurrent shape in a double layer

A. Picos-Vega
Centro de Ciencias de la Materia Condensada, Universidad Nacional Autonoma de Mexico, Apartado Postal 2681, 22800 Ensenada, BC, Mexico

O. Zelaya-Angel
Departamento de Fisica, CINVESTAV-IPN, Apartado Postal 14-740, 07000 Mexico, DF, Mexico

R. Ramirez-Bon
Laboratorio de Investigacion en Materiales, CINVESTAV-IPN, Unidad Queretaro, Apartado Postal 1-1010, 76001 Queretaro, Qro., Mexico
(Received 12 November 1999)

Transient photocurrents of double-layer structures were simulated by a random walk through a cubic lattice in this work. The canonical technique of time of flight was simulated to find the characteristics of the photocurrents shape when each layer had a different mobility. The results reproduce the main features of the experimental data from similar real experiments reported in the literature. Also, the origin of the peak shape of photocurrents is discussed and it is shown that it is related to a stochastic process which forces the out-of-equilibrium charge carriers to be injected from one layer to the other within a period of time $(t,t+dt)$ as given by a time-dependent probability $\phi(t)dt$.

INTRODUCTION

Charge injection between disordered interfaces of amorphous organic materials has been a subject of interest during the last decade mainly motivated by the study of electroluminiscent, electrographic devices, etc. Recently some authors have reported studies on the dynamics of hole injection and the effect of energy barriers at interfaces on the photocurrent in two-layer systems.[1,2] In these works the analysis of charge transfer was done by the measurement of transient photocurrents induced by a packet of off-equilibrium charge carriers moving inside of an organic two-layer sample, using for this the time-of-flight (TOF) technique. Emphasis was placed on the lack of theoretical work on this topic even though it is an interesting problem. Also, the absence of a general model explaining the dynamics of charge injection or charge transfer at interfaces is mentioned.

Similar experiments were carried almost 20 years ago when other authors studied the time-dependent charge injection from Au contacts to a-As_2Se_3 samples.[3] The problem they studied was how the charge accumulation into the contact-sample interface affects the induced photocurrent in the TOF measurements. Instead of obtaining typical photocurrents as given by

$$i(t)\propto\begin{cases} t^{-(1-\alpha_1)}, & t\leqslant t_\tau, \\ t^{-(1+\alpha_2)}, & t>t_\tau, \end{cases} \tag{1}$$

where α_1 and α_2 are the dispersion parameters, and t_τ is the transit time, they measured peak-shape photocurrents whose origin was attributed to the time-dependent injection of carriers from the contact to the sample. These workers used a theoretical model for dispersive transport based on the continuous time random walk (CTRW),[4] which explained the origin of Eq. (1). A time-dependent function $\phi(t)$ was included in this model for the rate of charge injection at initial conditions:

$$\phi(t)=\frac{(t_1+t_2)}{t_2^2}(1-e^{-t/t_1})e^{-t/t_2}. \tag{2}$$

This distribution function $\phi(t)$ was chosen because it depends basically on two parameters that control its increasing (t_1) and decreasing (t_2), and it gives a peak shape to the transient photocurrents. Also, $\phi(t)$ was interpreted as the normalized probability for a carrier in a trap to reach a conduction state of the sample.

Recently, Picos-Vega *et al.*,[5] using a different model for the study of dispersive transient transport, found that a similar function $\phi(t)$ can be simulated by a random walk of particles into an incomplete lattice of sites (percolation cluster), i.e., by measuring the time distribution of arrivals for a set of particles crossing a disordered media. In this case a similar time-dependent distribution $\phi(t)$ for the carriers arriving at a sample was obtained. Also, they proposed that for a single layer showing peak-shape photocurrent in a TOF experiment the photogeneration region can be thought of as a thin layer of disordered and widely spaced states through which the off-equilibrium charge carriers must cross in order to arrive at the conduction states of the sample. This implicates that using a two-layer structure, with the first layer having a low mobility compared to the second layer, one can simulate a peak-shape photocurrent.

Experimental measurements on the same conditions as mentioned above were carried out recently by other physicists.[2] These workers reported experimental results of photocurrents measured by the TOF technique for a set of samples of organic-organic bylayers, each layer having a different mobility. From these results three types of photocur-

rent are relevant to show that effectively the peak shapes of photocurrents are due to the time delay of carriers at the interface contact sample[3,5] or in a reservoir layer.[5] Also, other authors[6] conclusions coincide with these results and they have proposed a use for the TOF technique using double-layer structures.

SIMULATION OF PHOTOCURRENTS

The transport model we used for the simulation of photocurrents as measured by the TOF technique is very simple, and a complete exposition can be found in Refs. 5 and 7. The off-equilibrium charge carriers move in a random walk across a disordered arrangement of sites, which represents a disordered distribution of localized states. The mean effect of the disordered environment and the drift force provided by the electrostatic potential is to disperse the charge packet as it moves across the sample. Here the dispersion of the charge packet is due to the waiting time of each carrier experiment in different sites due to the intricate connectivity of the system, which depends on the temperature of the system.[7]

For a single-layer experiment, as particles arrive at the contact in the opposite side of the sample, they are absorbed and its own contribution to the photocurrent is eliminated at the same time. The transient current shape is determined very well by Eq. (1) in this case. However, for a two-layer structure one can assume that each layer has a different drift mobility given by

$$\mu_i = v_i / E, \tag{3}$$

where $\mu_i \sim v_i$ for a constant field strength. Thus on each step a particle moves a distance given by the product (average velocity on the layer) $\times$ (steps interval). Also, we assume that when a carrier reaches the interface between layers, it then changes abruptly its mobility from μ_1 to μ_2. If necessary, one can also take into account, as we will see below, the effects of an energy mismatch between samples.

At initial conditions the packet of particles is injected at $x=0$ after $n=0$ steps, which means that all carriers move inside the sample immediately after they are generated. Also, the manner we measured the transient current induced by the random walk of particles through the percolation cluster is multiplying (the mean number of particles moving inside the sample after n steps) $\times$ (the mean velocity of the packet of particles at the same number of steps).[7]

For the simulation of photocurrents in bylayers, with mobility μ_1 and μ_2, respectively, we used a full lattice $p=1$, where p is the fraction of occupied sites for a percolation problem.[8] This helped us to calculate the transient current, saving computing time, and also gave us a flat constant current, while the carriers were moving inside the lattice ($\alpha_1 \sim 1$ *for Gaussian transport*).[4] For highly dispersive transport an incomplete lattice with $p \sim p_c$ can be used, with p_c the critical fraction of occupied sites for the existence of a spanning cluster over the entire system.[8]

TIME-DEPENDENT INJECTION RATE

The number of carriers inside the sample at time t can be computed by integration of the distribution of probability that a carrier reaches the sample after it is photogenerated. For simplicity, we take this probability distribution as Eq. (2), which integrated from 0 to t behaves as

$$\int_0^t \phi(t)\,dt = 1 - e^{-t/t_2}\left[\left(\frac{t_1}{t_2}\right)(1-e^{-t/t_1})+1\right]. \tag{4}$$

One can see that this equation has an exponential dependence on the parameter t_2 and a competence between t_2 and t_1 is established in the second term. Thus, in the limit of $t_2 \gg t_1$, Eq. (4) is well approximated by

$$\int_0^t \phi(t)\,dt \approx 1 - e^{-t/t_2}. \tag{5}$$

This means we have an exponential activation rate $(1/t_2)e^{-t/t_2}$ as the injection rate of carriers, which is the case for a step potential or a single trap state. A more detailed calculation of the current induced in a sample using Eq. (2) as the injection rate with $t_2 \gg t_1$ and $t_1 \ll t_\tau$ can be found in Ref. 3. Here the peak position (t_m) of $\phi(t)$ is very small, $t_m \sim t_1 \sim 0$. A plausible explanation for this function is that only one kind of trap or a step potential constrains the carrier injection into the sample. The temperature dependence is understood as due to the thermal activation of carriers from a potential barrier. However, other authors[5] have shown that the temperature dependence of transient currents with charge trapped effects can be simulated by changing the rate t_2/t_1 in Eq. (2), with the parameters t_1 and t_2 of the same order. The peak position for the time-dependent distribution $\phi(t)$ simulated by a random walk is proportional to the peak position of the simulated current, and it behaves as $t_m = e^{-E_{\rm act}/kT}$,[5] with $E_{\rm act}$ as the energy necessary to activate a carrier from an unique kind of trap.

For Eq. (2) the maximum occurs at

$$t_m = t_2\left(\frac{t_1}{t_2}\right)\ln\left(1+\frac{t_2}{t_1}\right), \tag{6}$$

and for times $t_2 \sim t_1$ the peak position depends linearly on the magnitude of t_2:

$$t_m \approx t_2 \quad \text{for} \begin{cases} t_2 < t_1, \\ t_2 = t_1. \end{cases} \tag{7}$$

Then when $t_2 \sim t_1$ the variation of t_m is proportional to the variation of t_2, which is the result obtained by Picos-Vega *et al.*[5] This means that effectively the temperature dependence of current is controlled through t_2, the characteristic time for activation of a carrier in a trap. With these results Eq. (2) can be considered as a weighted probability, with $(1-e^{-t/t_1})$ as the weight factor for the occurrence of trap events characterized by t_1, and e^{-t/t_2} the probability for the occurrence of release events with characteristic time t_2. Equation (2) is a density of probability properly normalized for the occurrence of only one characteristic trap event, which is a special case of a more general probability used for multiple trapping.[9]

RESULTS

We simulated different transient currents changing the values of mobility of each layer in a bilayer structure. The

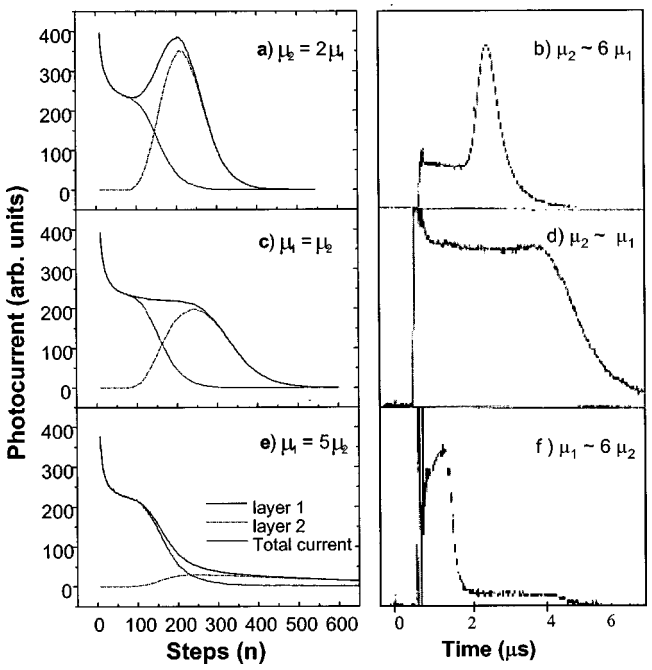

FIG. 1. Simulated photocurrents for a double-layer system with mobility rate of (a) $\mu_1/\mu_2=5/9$, (c) $\mu_1/\mu_2=1$, and (e) $\mu_1/\mu_2=5$, and the experimental counterpart for similar cases with mobility rates of (b) $\mu_1/\mu_2\sim 1/6$, (d) $\mu_1/\mu_2\sim 1$, and (f) $\mu_1/\mu_2\sim 6$. Experimental data were taken from Ref. 2.

induced current for each layer and the number of carriers participating after n steps were obtained independently. The total current for the double-layer structure is the sum of the independent currents. As expected, we found that the shape of the simulated transient currents is extremely dependent on the mobility in each layer, μ_1 and μ_2. The curves were classified as three different kinds depending on the mobility rate for both layers: (a) $\mu_1/\mu_2<1$, (b) $\mu_1/\mu_2=1$, and (c) $\mu_1/\mu_2>1$.

(a) In Fig. 1(a) the shape of the simulated photocurrent in layer 2 corresponds to a very well defined peak when $\mu_1/\mu_2<1$. The curve for current on layer 2 is similar to the current induced in a single layer when off-equilibrium charge carriers are injected from the interface contact sample at a rate similar to Eq. (2) with $t_1\sim t_2\sim t_t$. As can be seen, carriers through the first layer disperse and induce a current as given by Eq. (1) with $\alpha_1\sim 1$. However, they arrive at the next layer with a wide time distribution similar to Eq. (2), provoking a peak shape for the photocurrent of layer 2. It is important to remark that independently of the form adopted by the total current of the bilayer structure and for any case of mobility ratio μ_1/μ_2, the transient current induced in layer 2 will always be a peak shape. Figure 1(b) corresponds to the experimental photocurrent for an organic-organic bilayer with a mobility rate $\mu_1/\mu_2\sim 1/6$, approximately.[2]

(b) Figure 1(c) illustrates the case for a bilayer with mobility ratio $\mu_1/\mu_2=1$ without the existence of any trap or energy mismatch at the interface. This means that particles can cross the interface without any interruption or delay. As can be seen, the current remains constant until the first and faster carriers reach the opposite side of the sample. Also, the induced current in layer 1 behaves as Eq. (1) and the photocurrent in layer 2 has a peak shape with a maximum near the

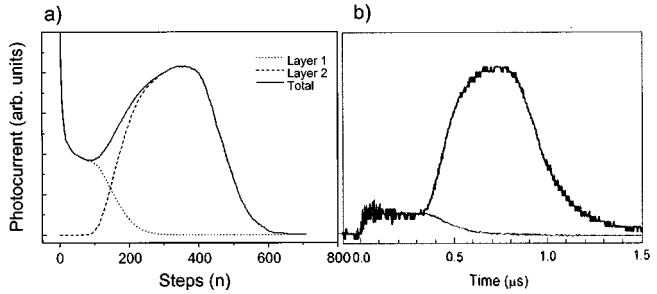

FIG. 2. (a) Simulated photocurrent for a double layer of thickness 30|120 sites and mobility rate $\mu_1/\mu_2=5/9$. (b) Experimental photocurrent for a 0.9 μm|9.6 μm organic-organic bilayer with mobility rate of $\mu_1/\mu_2\sim 1/6$.

transit time of layer 2. However, the sum of both currents can be expressed by Eq. (1). The experimental counterpart is shown in Fig. 1(d).

(c) In Fig. 1(e) a different case results when $\mu_1/\mu_2>1$. The charge packet initially moves in a region of high mobility, resulting in a high current for the first layer, but when carriers arrive at the second layer of lower mobility, suddenly the particles are slowed in such a manner that the photocurrent decreases too. The sum of individual currents from each layer has a double-step shape. Experimental results for an organic-organic bilayer with equal mobility but an energy mismatch of around 0.13 eV are shown in Fig. 1(f).

Good agreement between experimental data and simulated curves is evident in Figs. 1(a)–1(f) for the three cases of mobility rate, and also it is evident that the peak shape of the transient current in the second layer is due to the time delay of carriers when they are injected into the transport states of a single-layer sample. It means that the first layer acts as a time-dependent source of nonequilibrium charge carriers with a rate similar to Eq. (2) whose characteristic time parameters depend on its own physical properties. However, it is important to emphasize that only the raising of the induced photocurrent is due to the time-dependent injection of charge, as given by Eq. (4), and that the current decay is due to the recombination of carriers at the collector contact. Then the unique condition for the occurrence of a well-defined peak in the transient current is a competence between the injection of charge and the recombination of the same at the collector contact.

When the total charge is injected in a short period of time smaller than the transit time of the sample, no competence is then established between injection and recombination. So it leads to the appearance of a plateau in the photocurrent instead of a peak. This case can be obtained if we use $t_t \gg t_1, t_2$, such that the fraction of charge injected before the transit time is approximately 1. It means that all carriers move inside the sample before one of them is absorbed at the collector contact.

Figure 2(a) illustrates a simulation of what would happen if the charge packet moves first through layer 1 of mobility μ_1 and subsequently it moves through a layer 2 with mobility μ_2, for $\mu_1/\mu_2<1$. Current increases at a rate proportional to Eq. (4) due to the increase of carriers inside the sample. Then all carriers move inside layer 2 for a period of time Δt with the transient current induced as in Eq. (1) for

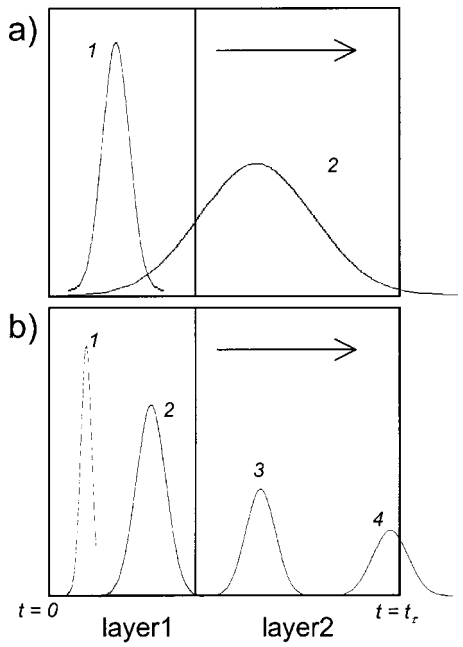

FIG. 3. Representative picture of a packet of particles moving inside a bilayer. (a) The packet can cross continuously the entire sample or (b) cross the layers one by one.

longer times. The beginning of the plateau delineates the end of the charge injection, and no peak will appear in the induced current. In Fig. 2(b) an experimental measurement of the photocurrent obtained from the literature for a wide double-layer sample is illustrated. It corresponds to a layer 1 of length L and a layer 2 of length $9L$, with mobility ratio $\mu_1/\mu_2 \sim 1/9$.[2] A correspondence of Figs. 2(a) and 2(b) is clear.

For clarity we illustrate, in Figs. 3(a) and 3(b), two cases of the different stages of dispersion of a charge packet inside of a double structure. In Fig. 3(a) the charge carriers have reached the collector contact when some carriers are still being injected from layer 1. This establishes a competence between injection and recombination given the origin of the peak-shape photocurrent. In Fig. 2(b) the complete packet crosses the interface layer 1–layer 2 and moves for a period of time Δt inside layer 2, giving rise to a plateau in the induced current of the double layer.

In principle, if the dielectric constant is the same for both layers and no differences in the conduction energy are present, then the transient current at the rising times must be

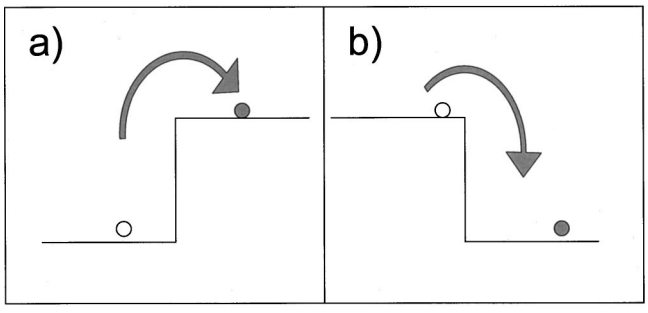

FIG. 4. Schematic picture of a particle crossing a step potential (a) from the lower level to the higher and (b) from a higher level to the lower.

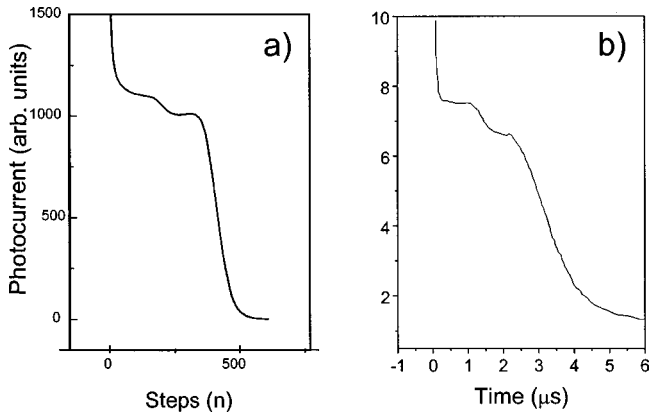

FIG. 5. (a) Simulated photocurrent for a bilayer with a time delay of charge at the interface. The mobility rate was $\mu_1/\mu_2=1$ and $t_1=150$ and $t_2=10$ for $\phi(t)$. (b) Experimental photocurrent for an organic-organic bilayer with mobility rate $\mu_1/\mu_2 \sim 1$ and energy mismatch of approximately 0.13 eV.

proportional to the rate of charge injection and its derivative equal to the time distribution of charge injection.

ENERGY BARRIER AT THE INTERFACE

There exist other cases of photocurrents when the material of layers have a different ionization potential or they present a mismatch in the mobility edge. In some cases one can see that even if the mobility is the same for both layers, the photocurrent could not be the same as that of Fig. 1(c) or 1(d). The effects of this phenomenon are visible in the curves of current as a step shape when charge carriers cross an interface from a lower-energy level to a higher-energy level, as in Fig. 4(a). For the inverse case, a jump from higher to lower energy, the charge carriers can jump without any effort into the new region as represented by Fig. 4(b). In terms of a random walk on a disordered arrangement of sites, crossing an interface with energy mismatch is similar to crossing a thin region where the localized energy levels are distributed with wider separation than in a single layer. The carriers must jump upward between states with more difficulty than in any layer, which causes a delay to the carriers in their trajectory. To include this effect in the simulation of photocurrents, it is necessary to introduce a time-dependent function for the ''activation'' of the carrier from the interface. In this case we choose the exponential dependence of $\phi(t)$ by taking $t_2 \gg t_1$ and the transit time $t_t \gg t_l$.

Figure 5(a) shows the transient photocurrent for a bilayer with mobility $\mu_1=\mu_2$, but considering the presence of a time delay for the carriers crossing the interface. The simulated photocurrent decreases for the second layer and even the mobility is the same, as is the case for an experiment under the same conditions, as shown in Fig. 4(b).

CONCLUSIONS

In this work we have simulated transient photocurrents in bilayer structures by means of a Monte Carlo transport model. We considered different mobility rates between both layers with and without an energy mismatch at the interface. From the results we conclude that it is necessary to have a time-dependent charge injection in order to have a peak-

shape photocurrent. The origin of such a time delay in charge injection can be associated with a stochastic process occurring at interfaces whose time distribution can be approximated by Eq. (2) in a raw manner. Besides, this work is a raw approximation to the problem of transient transport in disordered systems; it yields good results of the general characteristics of the transient current and explains how competition injection recombination is needed for the peak formation. Also, a theoretical model is necessary that includes the role of disorder in dispersive transport and the existence of two or more layers. The time scale invariance of this kind of transport must be a constant in this model due to its fractal characteristics and the size dependence of measurable quantities such as drift mobility.

ACKNOWLEDGMENT

This work was partially supported by Consejo Nacional de Ciencia y Tecnología (CONACyT), México.

[1] Liang-Bih Lin, S. A. Jenekhe, R. H. Young, and P. M. Borsenberger, Appl. Phys. Lett. **70**, 2052 (1997).
[2] Liang-Bih Lin, R. H. Young, M. G. Mason, S. A. Jenekhe, and P. M. Borsenberger, Appl. Phys. Lett. **72**, 864 (1998).
[3] M. Abkowitz and H. Scher, Philos. Mag. **35**, 1585 (1977).
[4] H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).
[5] A. Picos-Vega, O. Zelaya-Angel, R. Ramírez-Bon, and F. J. Espinoza-Beltrán, Phys. Rev. B **58**, 14 845 (1998).
[6] V. I. Mikla, Phys. Status Solidi A **165**, 427 (1998).
[7] K. Murayama and M. Mori, Philos. Mag. B **65**, 501 (1992).
[8] S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).
[9] H. Scher, M. F. Shlesinger, and J. T. Bendler, Phys. Today **44** (1), 26 (1991).