Numerical Simulations of Photocurrent Multiplication Phenomenon at Organic/Metal Interface

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Abstract

In order to elucidate the photocurrent multiplication mechanism observed in the photoconducting organic pigment films, the electric field distribution formed by the space charges accumulated near organic/metal interface having imperfect contact and the flow of photogenerated carriers were numerically simulated. It was found that high density of surface charges, namely, charge accumulation appears in the steady state when the photogenerated carriers are supplied continuously, and that the accumulated charges staying at the non-contact organic film interface can provide enough high field for tunneling charge injection leading to multiplication process. These results indicate the validity of our previously proposed "structural trap model" that the charge accumulation occurs at blind alleys lying on the rough film surface of the organic/metal interface. Indeed, by introducing lower surface mobility based on the concept of rough surface of the orgainc film, the typically observed multiplied photocurrent response was well reproduced.

Introduction

Photocurrent multiplication phenomenon at the organic/metal interface is the phenomenon in that the quantum efficiency of the photocurrent exceeds unity. We have already reported that this phenomenon is observed in various kinds of organic semiconductors such as perylene[1], phthalocyanine and quinacridone pigments. The quantum efficiency, namely, photon-electron conversion rate exceeds 10^5 in some cases. Combining with organic EL in a layered structure, this distinctive feature of the photoinduced large current has been applied to various opto-electronic devices such as the light transducer, wavelength converter, light amplifier[2] and optical computing system.

Our previously proposed mechanism of this phenomenon is as follows. The photogenerated charges are accumulated at some interfacial traps and build up a high electric field at the organic/metal interface. Consequently, a large number of electrons are injected from the metal electrode by tunneling process, thus resulting in current multiplication exceeding unity of quantum efficiency. For the interfacial traps, we have proposed "field activated structural trap model" (see Fig.1), that is, a part of photogenerated charges is trapped at blind alleys due to the nm-scale rough surface of the vacuum deposited pigment film, at which imperfect contact occurs with the metal electrode[3]. Actually, it has been shown that the multiplication characteristics are strongly affected by the morphologies of organic film surface and deposited metal electrode on it. However, the accumulated charge distribution can hardly be observed directly.

In this paper, therefore, we have tried to simulate the photogenerated carrier flow at such an imperfectly contacting organic/metal interface by calculating electrostatic potential for a modeled organic/metal interface based on the AFM images observed for photocurrent multiplication devices. As the results, the validity of the proposed "structural trap model" for the charge accumulation at the organic/metal interface has been proved

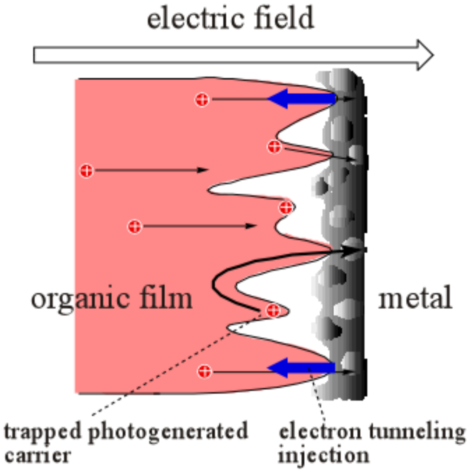

Fig. 1 Schematic illustration of the structural trap model for organic/metal interface in photocurrent multiplication device.

and the typically observed multiplied photocurrent response has been well reproduced.

Experimental

Figure 2 shows the AFM images of NTCDA (naphthalene tetracrboxylic dianhydride) film and Au electrode on it. NTCDA is a typical material showing a large multiplication rate[4]. In the NTCDA film, many grains of more than 100 nm size are grown and the surface seems to be rather smooth. On the other hand, the Au electrode deposited on the NTCDA film is composed of the gathering of spherical fine particles having diameter of about 20 nm. Based on these observed AFM images, we have modeled the structure of the organic/metal interface as shown in Fig. 2. The imperfect contact at the organic/metal interface in "structural trap model" is replaced with the even surface of organic film and electrode spherical particles covering the surface periodically and closely for simple and easy calculations.

The electrostatic potential calculation was performed by solving Poisson's equation for this modeled organic/metal interface. The boundary conditions used in this calculation are shown in Fig. 3. The calculation was carried for one electrode particle under the periodic boundary condition. The size of the calculating system in the z direction, namely, the film thickness was 50 nm. The potential of the metal electrode was assumed to be zero and that of the opposite side of the organic film was kept to the applied voltage.

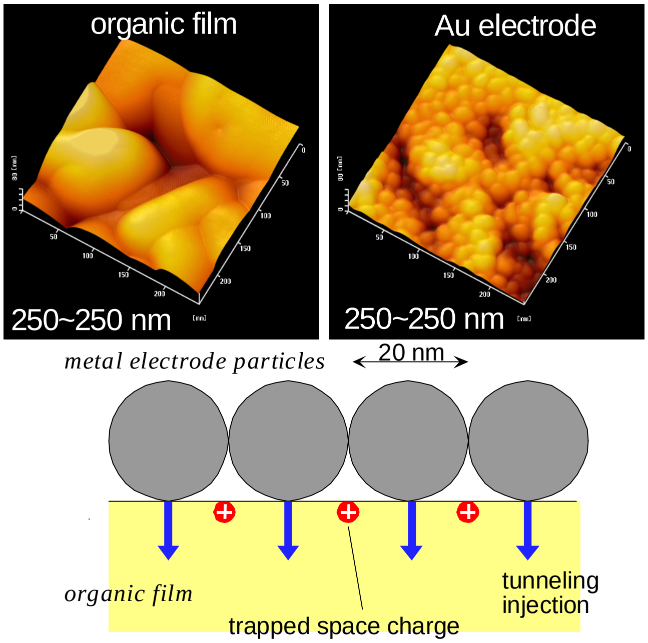

Fig. 2 AFM images of vacuum deposited films for photocurrent multiplication device and simplified interface model for electric field calculation based on the structural trap model is also shown..

First, the electrostatic potentials at the organic/metal interface were calculated when an appropriate amount of space charge density, i.e., the accumulated charge distribution, was assumed at the non-contact position between two electrode particles with Gaussian distribution. The amount of the accumulated charges was limited at the maximum amount of charges with no Coulombic repulsion. The electrostatic potential was obtained from the assumed charge distribution and the boundary condition by solving Poisson's equation by applying differential finite method to the divided system into 1 angstrom mesh. The local injection current density was obtained from the local electric field at the contact point of organic film and electrode fine particle by means of Fowler-Nordheim equation. Finally, we can obtain a mean current density that can be compared with the current density observed experimentally.

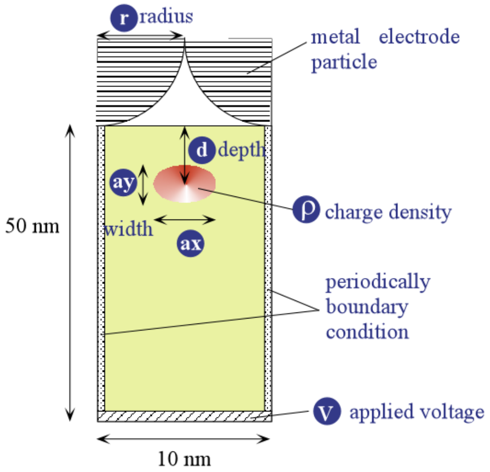

Fig. 3 Boundary conditions for calculation of electrostatic potential at organic/metal interface.

Next, the calculation was extended to simulating time-developing charge distribution at the organic/metal interface and the dynamic flow of the photogenerated carriers as shown in Fig. 4. Namely, for each time step, each charge within the pigment film was moved along the calculated electric field at a given time step. For the charge

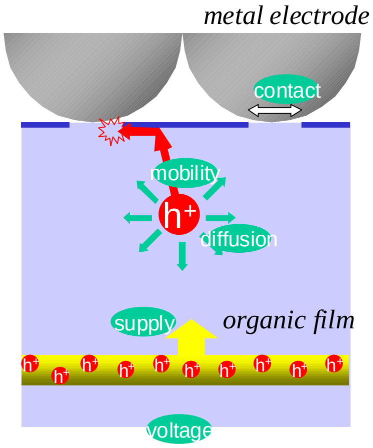

Fig. 4 Schematic illustration of the simulation model for the charge distribution dynamics at the modeled organic/metal interface.

movement the field drift and diffusion drift were taken into account. The time development of charge distribution was obtained one after another. The photogenerated carriers were supplied at film bulk in each time step. The photogenerated carriers were assumed to be able to vanish only at the contact point of organic/metal interface.

Results and Discussion

1. Electric field distribution at organic/metal interface

Figure 5 shows a typical result of the electrostatic potential calculations. It has been found that the charge accumulation at the non-contact point near the surface enhances the injection field intensity at the contact point. When the parameters were chosen so that the calculated current density is consistent with the observed current density, the injected field of 7×10^6 V/cm and the charge density of 90 nC/cm^2 were obtained, respectively. One of the questions for the "structural trap model" was whether the accumulated charge carriers could enhance the field intensity in the direction normal to the film or not, at the contact point where no accumulated charges exist. From the calculated field, it was found that the contact point at the interface can perceive the large enough electric field almost same as the point between two metal particles. This result comes from the nature of the electric force line which always stands perpendicularly on metal surface. The present result supports the validity of the "structural trap model" which insists on the separate positions of the organic/metal interface for charge accumulation and tunneling charge injection to occur, respectively.

Based on the present calculations, the energy diagram can be depicted as shown in Fig. 6. The energy band diagram of the organic/metal interface for the photocurrent multiplication can be discussed as follows. At the contact point of the organic/metal interface, where no accumulated charges exist, the conduction band of the organic pigment may bend gently and connects with the metal electrode directly. On the other hand, at the charge accumulating point, the conduction band bends sharply due to the accumulated charges, and furthermore, the vacuum level was inserted between the organic film and metal electrode. It should be noted that these two different kinds of energy diagram emerge periodically. It is clear that the place where the hole accumulates differs from the place which the electron flows by tunneling injection.

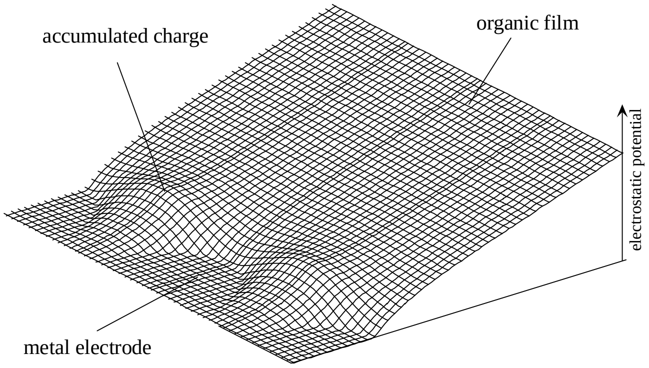

Fig. 5 Typical result of calculated electrostatic potential at modeled organic/metal interface.

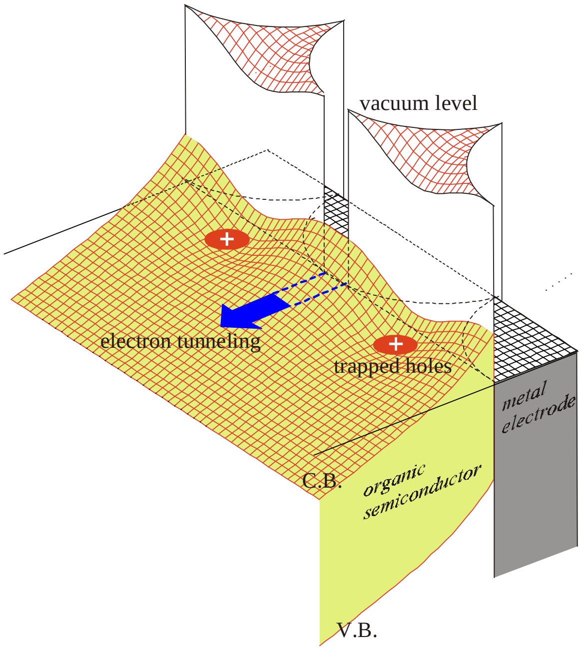

Fig. 6 Energy diagram for organic/metal interface based on the calculation results. The vacuum level is inserted between organic film and metal electrode at non-contact point.

These results tells us that similar behavior may occur not only in multiplication device but also in usual organic/metal interface if there exist imperfect contacts.

2. Simulation for charge accumulation process

Next, we have tried to simulate the charge accumulation process at the organic/metal interface. The simulation model for charge accumulation dynamics is illustrated in Fig. 3. Figure 7 shows a typical time development of charge distribution at the modeled organic/metal interface when the photogenerated carriers are supplied from the bulk of organic film continuously. The photogenerated carriers reaching the surface of organic film surface apparently piles up at the non-contact point between two electrode particles as the high density of surface charge until the charges vanish at the contact point. In the steady state, such the charge accumulation at the surface is balanced between the supply of photogenerated carriers from the bulk and the vanishing at the metal electrode. Thus, the excess space charges staying at the film surface give rise to inducing electron injection from the metal electrode for photocurrent multiplication. However, the amount of space charge accumulation at the organic film surface was limited by the

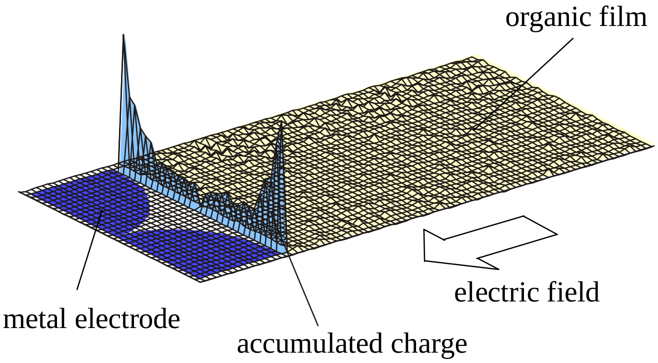

Fig. 7 Charge distribution at the organic/metal interface in the steady state when the photogenerated carriers are supplied continuously.

sojourn time of the surface charges, and the steady state emerge so quickly on the contrary to the fact that the multiplied photocurrent usually exhibits very slow response as shown in Fig. 8(a). Namely, Figure 8(a) shows the typical transient photocurrent of the photocurrent multiplication device[5]. The multiplied photocurrent clearly shows the two-step. The first component is primary photocurrent originating from the photogenerated carriers. The second component rising after several tens millisecond of light irradiation is the multiplied photocurrent due to the tunneling injection caused by charge accumulation.

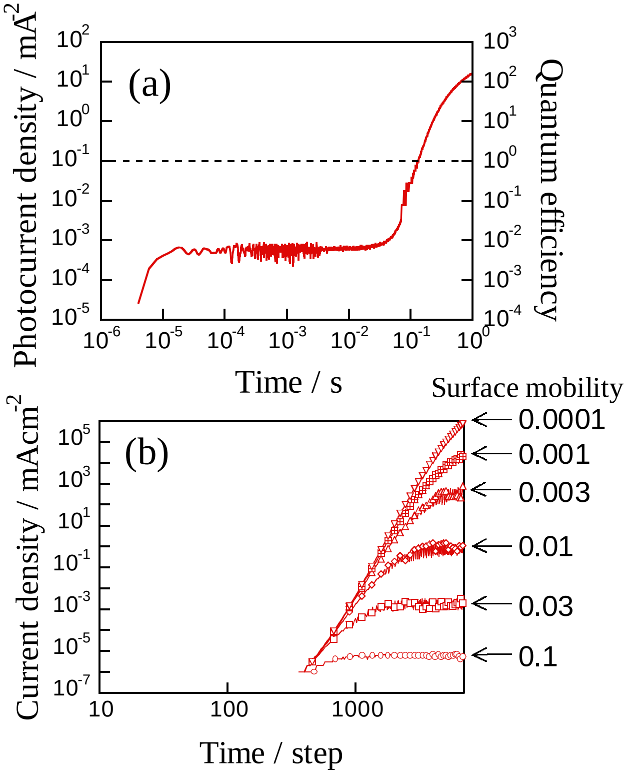

Fig. 8 Transient responses of the photocurrent observed in ITO/perylene/Au device experimentally (a). Simulated response of injected current density for various surface mobility (b). The surface mobility for each simulated response is shown in the figure.

Based on the image of rough surface of the organic film, therefore, we introduce the surface mobility, which is lower than that of the bulk. The concept of low surface mobility is an expression for the nm-scale disorder of the molecular stacking and/or the surface roughness. Figure 8(b) shows the calculated transient response of tunneling injection current calculated from the time developing electric field at the contact point with various mobility ratios of the surface and bulk mobilities. Interestingly, introducing the concept of low surface mobility successfully reproduces the multiplied current transients after onset time. The saturation current density also depends on the mobility ratio, in other words, depends on the sojourn time of photogenerated charges at the non-contact area of the organic/metal interface.

Conclusion

The charge accumulation process at the organic/metal interface having an imperfect contact was numerically simulated and the mechanism of the photocurrent multiplication phenomenon was discussed. It was found that an imperfect contact of the organic/metal interface necessarily causes the charge accumulation in the steady state of charge flow when the photogenerated carriers are supplied continuously. It is due to the sojourn time of photogenerated carriers at the surface layer. Furthermore, introducing low surface mobility that is much slower than transporting process based on the concept of rough surface of the organic film, we succeeded in reproducing the charge accumulation process, and also the transient response of photocurrent multiplication phenomenon qualitatively.

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Biography

Ken-ichi Nakayama received the B. Eng. in 1995 and the M. Eng. in 1997 from Osaka University in Applied Chemistry. He is now investigating photo-electrical properties of organic semi-conductors and their application as a Dr.course student under the direction of Prof. Masaaki Yokoyama in Graduate School of Engineering.