Photocurrent Multiplication in Pigment Dispersion Films and Its Application to Optoelectronic Devices

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Abstract

Photocurrent multiplication in pigment-dispersed polymer films has been observed for the first time. The multiplication rate reached more than 2×10^4 rivaling the usual devices prepared by vacuum deposition. Based on the advantage of film uniformity and easy process originating in polymers, three kinds of applications of photocurrent multiplication to optoelectronic devices were demonstrated. First, we developed amplified photoreceptor devices with photogeneration efficiency exceeding unity, which have a great potential for high-sensitive or high-γ photoreceptors. Next, we fabricated organic light transducer combined with organic EL and achieved wavelength conversion from near-infrared to visible light and light amplification of input light. Finally, we suggested the organic optical logic gate by the light transducer with designed relationship between input and output light intensity, and demonstrated operation "OR" for two input images.

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.

For the mechanism of multiplication, we have proposed photo-induced charge injection mechanism[2] (Fig. 1) 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.

Such a multiplication phenomenon in organic films has been observed only in vacuum deposited films1-3. However, deposited films of crystalline pigment have difficulty to fabricate large area devices due to unavoidable pinholes. To solve these problems, in this study, we tried to apply pigment-dispersed polymer films to the multiplication devices. The film uniformity and easy process of polymer films enable us to fabricate more practical and large area devices. Based on this advantage, we applied photocurrent multiplication to three optoelectronic devices, amplified photoreceptors, organic light transducer, and optical logic gate.

Experimental

Pigment molecules used in this study are shown in figure 1. These molecules are known to be good charge generation molecules in OPC and show a large photocurrent multiplication in vacuum deposited films. Pigment-dispersed polymer films were fabricated by spin-coating or bar-coating method on the substrates. The pigment was ball-milled in THF solvent and mixed with polycarbonate (PC-Z). Typical concentration of pigment was 50% and film thickness was 0.7μm.

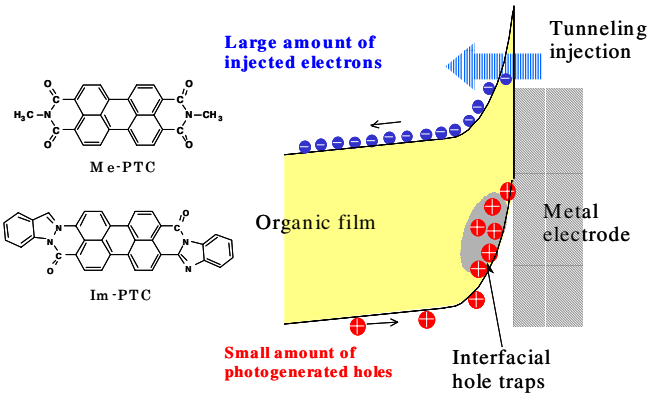

Figure 1. Energy diagram of organic/metal interface during photocurrent multiplication. Chemical structures of organic pigment showing large multiplication are also shown.

The simple multiplication device was composed of a single pigment-polymer film spin-coated on an ITO glass substrate and a semi-transparent gold electrode with thickness of 20nm. The quantum efficiency of photocurrent was evaluated by ratio of the number of incident photons and current carriers flowing through the device.

The device structures and measurement method for the each application are depicted in results and discussion.

Results and Discussion

1. Photocurrent Multiplication in Pigment-Dispersed Polymer Films

First, we measured the characteristics of the single-layered device of Me-PTC/PC-Z film sandwiched by two electrodes. Figure 2 shows the voltage dependence of quantum efficiency for various concentration of Me-PTC. The quantum efficiency exceeded 2×10^4 at 55 V in the case of 60% of pigment concentration and it showed that photocurrent multiplication occurred even in the pigment-dispersed polymer films alike vacuum deposited films. Since the current-voltage characteristics and transient responses were also similar to those in the case of vacuum deposited films, the multiplication mechanism in pigment-dispersed polymer films seems to be the same as the usual deposited films. Namely, photogenerated carriers accumulate to the structural traps at the organic/metal interface and cause high concentration of electric field at the interface. As a result, a large amount of electrons are injected from a metal electrode, resulting in multiplication.

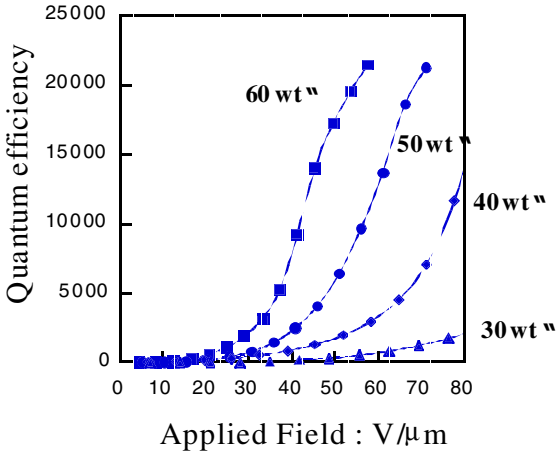

Figure 2. Voltage dependence of quantum efficiency in pigment-dispersed polymer device ITO/Me-PTC:PC-Z/Au for various concentrations of pigment.

2. Amplified Photoreceptors

Pigment-dispersed polymer films showing large photocurrent multiplication can be applied to new-type photoreceptors in electrophotography. The sensitivity of usual photoreceptors has principle limitation that the number of surface charges neutralized cannot exceed the number of illuminated photons as so long as surface charges are neutralized by photogenerated carriers directly. However, if one can utilize a large amount of electrons injected from metal substrate triggered by photogenerated carriers, this limitation can be overcome. Therefore, we tried to develop amplified photoreceptors based on photocurrent multiplication.

The organic film of the photoreceptor device was composed of Me-PTC, PC-Z and electron transport molecules and bar-coated on Al substrate with thickness of 5μm. Photodecay curve was measured by electrostatic paper analyzer (Kawaguchi Electric Works, EPA-8100).

The photodecay curves showed relatively good sensitivity as a single-layered device. We intended to evaluate the quantum efficiency for neutralization of surface charges as follows. Assuming that the organic film composes a capacitor with metal substrate and surface charges, the relationship between surface potential V and amount of surface charges Q was obtained as follows.

$$Q = \varepsilon_0 \varepsilon \frac{A}{d} V$$

Here, d is film thickness, ε and ε_0 is dielectric constant and relative one, A is device area. Thus, amount of neutralized charges for illuminated photons per unit time, that is, quantum efficiency was estimated from photodecay curves. Dependence of the quantum efficiency on applied field estimated from surface potential and film thickness is plotted in figure 3. It is revealed that the quantum efficiency exceeds 100% at 145 V/μm. This distinctive feature means that surface charges more than irradiated photons were neutralized, which is peculiar to photocurrent multiplication. In addition, the accelerative increase of the quantum efficiency in Fig. 3 is characteristic of multiplication. From these results, we concluded that injected electrons from metal substrate must neutralize the surface charges according to multiplication mechanism (Fig. 4). Such amplified photoreceptors suggest a new principle for high sensitive and high-γ photoreceptors.

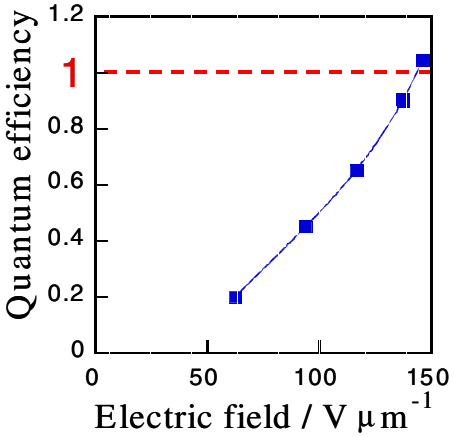

Figure 3. Electric field dependence of quantum efficiency of photogenerated carriers in pigment-dispersed polymer film composed of Me-PTC, MBDQ and PC-Z.

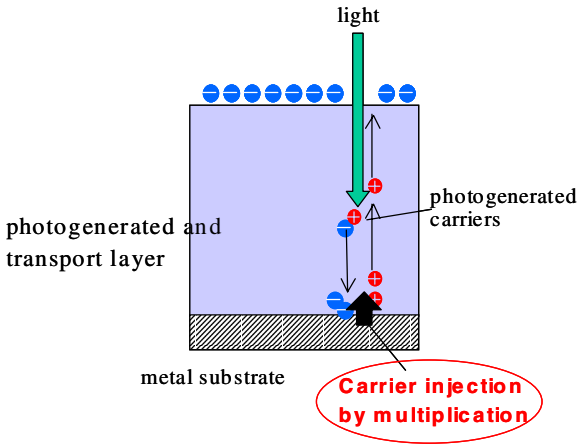

Figure 4. Concept of amplified photoreceptor utilizing photocurrent multiplication phenomenon. The injected carriers triggerd by photo irradiation decay the surface charge efficiently.

3. Organic Light Transducer Combined with EL

Next, we applied the polymer films to organic light transducer combined with organic EL. In this device, photocurrent multiplication layer acts as photo-controlled carrier injection layer and EL layer acts as an electron-photon conversion layer. Since EL layer is driven by large current due to multiplied photocurrent, the high photon-photon conversion can be attained in total.[3]

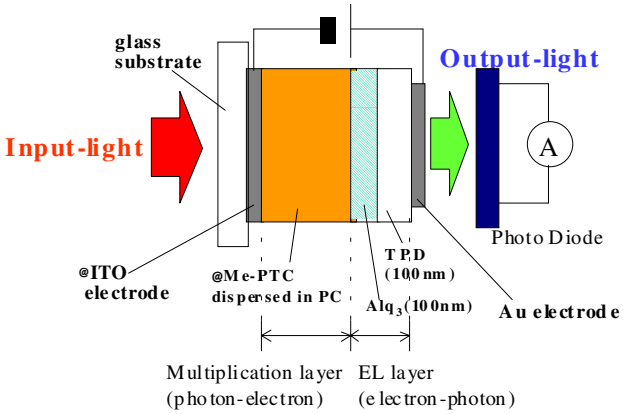

Figure 5. The device structure and measurement system for a light transducer combining photocurrent multiplication layer with organic EL

The devices structure is shown in figure 5. Organic EL layer composed of Alq3 and TPD were deposited on the polymer films. The monochromatic input light was shone onto the ITO glass. The output light from the EL layer was measured by a photodiode arranged near the Au electrode of the device. One of notable features of such a device is that the photon-electron conversion layer and electron-photon conversion layer can be tuned independently because the input light energy is once converted to electronic energy. Thus, we chose Im-PTC (Fig. 1) having wide absorption band reaching near-infrared region for multiplication layer and Alq3 showing green emission for emissive layer. This combination can be expected to realize wavelength converter from near-infrared to visible light. The quantum efficiency of Im-PTC single-layered device reached more than 2×10^4 similar to Me-PTC and good sensitivity even in near-infrared region over 700 nm.

EL output intensity was measured under voltage application and light illumination. While output was not observed only for voltage application, green EL emission driven by the multiplied photocurrent appeared upon the input irradiation. From the emission spectrum, visible light due to Alq[3] having a peak at 520 nm was observed in spite of near-infrared input light of 740 nm. This means that near-infrared input light was converted to visible light, namely, wavelength up-conversion of input light was achieved.

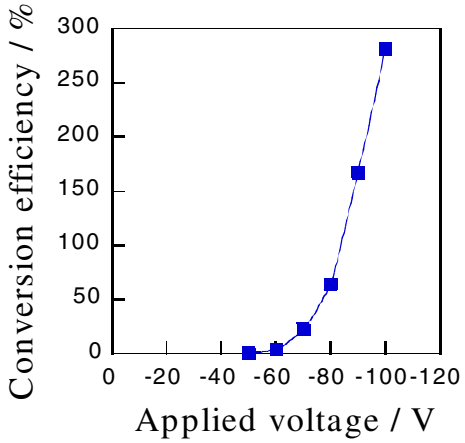

Figure 6. Voltage dependence of photon conversion efficiency defined as the ratio of input and output photons. The wavelength of incident light was 740 nm.

The performance of the light transducer was estimated by the photon-conversion efficiency defined as ratio of number of input photons absorbed in the organic films and output photons from the EL layer. The efficiency from near-infrared to visible light was revealed to rise up with increasing voltage and finally exceeds 100% at 80 V, as shown in Fig. 6. It means that output photons more than input photons are emitted from the EL layer, that is, light amplification was achieved. It is for the first time to attain both light amplification and up-conversion from near-infrared to visible light simultaneously. Furthermore, it should be noted that this performance was achieved at room temperature.

4. Optical Logic Gate

The light transducer mentioned previously has a distinctive feature that output light EL keeps spatial pattern of input light in spite of single large electrode, which indicates a great potential for an optical processor for 2-D input patterns.[4] In this study, we paid attention to the

relationship between input light and output light intensity. If the output intensity increases with some threshold and saturation for input intensity, optical logic gate of AND, OR can be performed. Figure 7 shows the measured relationship between input and output intensity in the device. It is revealed that output intensity shows strong saturation for input intensity. This means that output light intensity shows little change for increase of input intensity, and is very suitable for "OR" operation.

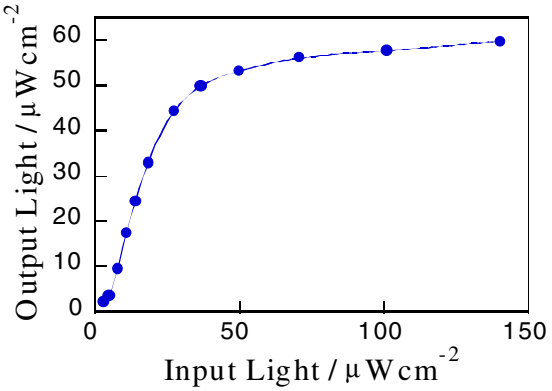

Figure 7. Relationship between input and output light intensity in the organic light transducer ITO/Me-PTC:PC-Z/Alq3/TPD/Au

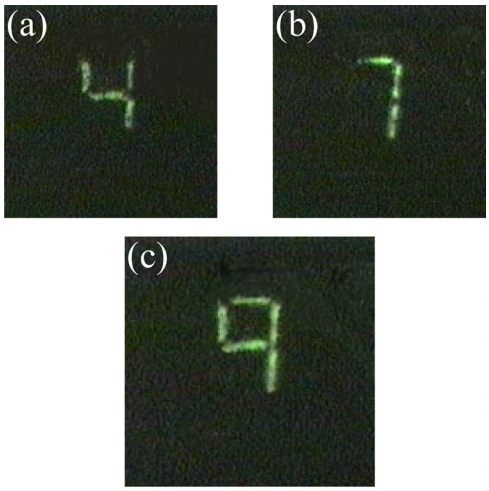

Figure 8. EL output images for various input images. (a) For input pattern of digit 4 (b)For input pattern of digit 7, (c) For overlapped patterns of digit 4 and 7. OR-operated pattern of digit 9 was obtained.

Based on this concept, we demonstrated an optical OR gate. Expanded and splitted two He-Ne laser beams through each photo mask patterned digit 4 and 7 were shone onto the organic light transducer. Obtained EL output pattern is shown in figure 8. EL output pattern of figure 9 was obtained as a result of OR operation of two input patterns.

Conclusion

Photocurrent multiplication in pigment-dispersed polymer films was observed for the first time. Based on the advantage of polymer films that large area devices can be fabricated with easy process, three kinds of applications for optoelectronic devices were demonstrated. The amplified photoreceptors which can neutralize surface charges more than illuminated photons was developed. The organic light transducer combined with EL achieved up-conversion from near-infrared light to visible light and light amplification of about 3 times. Furthermore, optical logic operator "OR" was demonstrated by paying attention to the relationship between input and output light intensity.

The technologies of photoelectric pigment materials and dispersed polymer films are developed in OPC field. In this study, we intend to demonstrate their new potential and application for organic electronics.

References

1. M. Hiramoto, T. Imahigashi, and M. Yokoyama, *Appl. Phys. Lett.*, **64**, 187, (1994) .
2. K. Nakayama, M. Hiramoto, and M. Yokoyama, *J. Appl. Phys.*, **87**, 3365, (2000).
3. T. Katsume, M. Hiramoto, and M. Yokoyama, *Appl. Phys. Lett.*, **66**, 2992, (1995) .
4. M. Hiramoto, H. Kumaoka, and M. Yokoyama, *Synthetic Metals*, **91**, 77, (1997) .

Biography

Ken-ichi Nakayama has worked as the research associate at Osaka University since 2000. He received the M. Eng. in 1997 and the Ph.D. Eng. in 2000 in Applied Chemistry from Osaka University. He is now investigating photo-electrical properties of organic semiconductors and their application. He is especially interested in structural and energetic properties of the organic/metal interface.