Transient Response of Multiplied Photocurrent Observed in Metal/Organic Pigment Film Interface

***Ken-ichi Nakayama, Masahiro Hiramoto, and Masaaki Yokoyama**[*1,*2]*
*[*1]**Material and Life Science, Faculty of Engineering, Osaka University,***
Yamadaoka, Suita, Osaka 565, Japan
*[*2]**CREST, Japan Science and Technology Corporation (JST)***

Abstract

Transient response of photocurrent multiplication phenomenon at organic/metal interface was revealed to have two components, which were identified as primary and subsequent multiplied photocurrents, respectively. Transient photocurrent directly traced the multiplication process, i.e., accumulation of photogenerated carriers near the interface, building up a high electric field at the interface, and tunneling electron injection from metal electrode to the organic layer. Amount of charges required for the multiplication onset was found to give a specific value of 30 nCcm^{-2}, implying that the increase of the carrier generation efficiency of primary photocurrent is expected to be effective to realize high speed multiplication. Based on these results, we developed the double-layered device which can be driven in high voltage through the increase of film uniformity. Consequently, large multiplication rate of 1.7 x 10^5 and short response time of 3.7 s was achieved.

Introduction

Recently, we discovered a large photocurrent multiplication phenomenon, in which the quantum efficiency of carrier yield exceeds unity, in perylene pigment,1) quinacridone pigment,2) and naphthalene tetracarboxylic anhydride3) films sandwiched simply with two metal electrodes, and as its mechanism we proposed tunneling electron injection from a metal electrode to the organic layer in a high electric field built up by the photo-accumulated space charges of trapped holes near the organic/metal interface.1,3) In the case of perylene pigment, for instance, the multiplication rate exceeded 10^5-fold. This means that more than 10^5 electrons flowed across the device by one input photon. Such a phenomenon comparable to a photo-multiplier tube seems to have large potential in its application to highly photo-sensitive devices.1-4) However, the multiplied photocurrent observed always exhibits slow transient response on the order of several tens second until the current saturation being attained. Based on our proposed model that the accumulation of trapped holes causes the multiplication1,3), slow response seems to be associated with the accumulation process of trapped holes at the interface. From this standpoint of view, to investigate the charge accumulation process of photogenerated holes by measuring the initial stage of transient photocurrent is very important, and may offer the guiding approach for accomplishing high-speed photocurrent multiplication for organic films, which are applicable to the practical photo-sensing devices. There have been a few reports on photocurrent multiplication for amorphous silicon-based materials,5,6) but no reports on the transient response measurement, especially for the newly observed organic photocurrent multiplication.

In this paper, we report the transient response of the photocurrent multiplication, which is firstly observed for the organic/metal junction between perylene pigment and gold. Observed photocurrent transients were revealed to follow the proposed photocurrent multiplication process faithfully. Furthermore, based on the results obtained, we fabricated a double-layered device and succeeded in achieving of the high-speed response with the large multiplication rate.

Experimental

Figure 1 shows the block diagram for the transient photocurrent measurements along with the cell structure. All the organic pigments used in this study were purified twice by the train sublimation technique. The thin film cell on an indium tin oxide (ITO) substrate was prepared by vacuum evaporation under 1x10^{-5} Torr. The deposition rates were 0.2 nms^{-1} for pigment and 0.05 nms^{-1} for Au, respectively. The cell was set in an optical cryostat (Janis Research Co. Inc., VPF-475) evacuated to 10^{-3} Torr. A light emitting diode (LED) which emits orange light of 620 nm having FWHM of 20 nm was used as a light source, which was driven by the step voltage from a function generator (Iwatsu Electric Co. Ltd., FG-330) in order to obtain the light source having sharp rise within 10 µs. LED light was irradiated on ITO electrode biased positively. Transient response of photocurrent was measured by a high speed current amplifier (Keithley Instruments, Inc., 428) connected to a digital oscilloscope (Nicolet 3091). Current-voltage characteristics were measured by source measure unit (Keithley Instruments, Inc., 238). Microscopic surface structures of pigment films were observed by atomic force microscopy (Seiko Instruments Inc., SPI3800). The photocurrent quantum efficiency, i.e., multiplication rate, was calculated as the ratio of the number of collected photoinduced carriers to the number of photons absorbed by the pigment film.

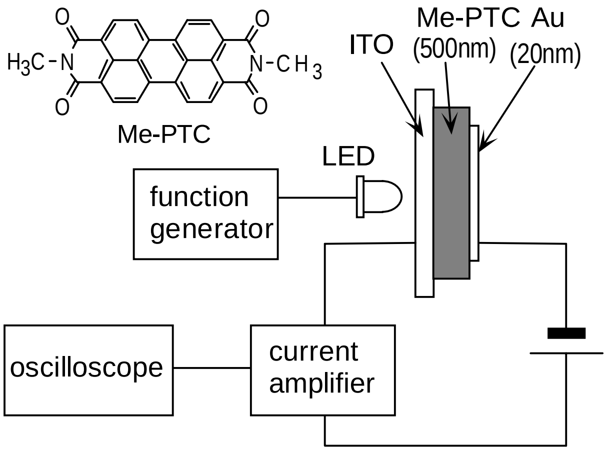

Figure 1. Block diagram for the transient photocurrent measurements. Structure of photocurrent multiplication device and chemical formula of perylene pigment (Me-PTC) are also shown.

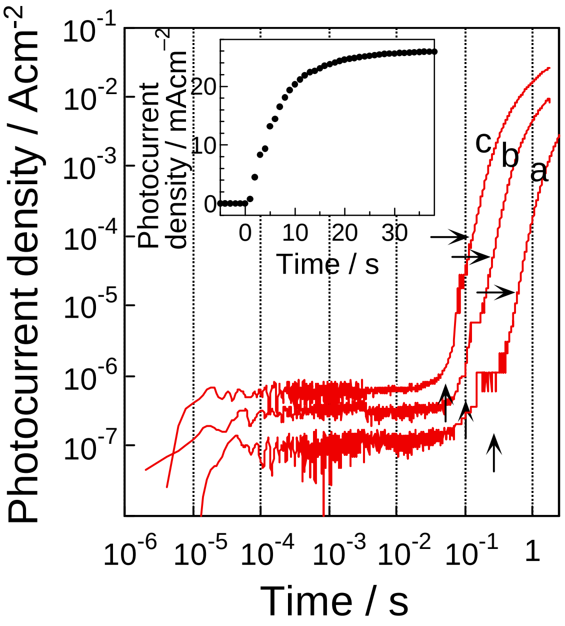

Figure 2. Initial stage of transient photocurrent curves for the light intensities of (a) 36, (b) 95 and (c) 190 μWcm^{-2}. Both axes are logarithmic scale. Measurements were performed at 203 K. Au electrode was negatively biased 15 V with respect to ITO electrode. Vertical and horizontal arrows in the figure indicate the onset time and the point of photocurrent quantum efficiency of unity, respectively. Inset is the linear scale plot of (b).

Results and Discussion

1. Initial Transient Response of the Photocurrent

Figure 2 shows the initial transient response of the photocurrent observed at 203 K for three light intensities, and the typical whole response reaching its saturation is also shown in the inset. Interestingly, transient photocurrent apparently consists of two components. First component rises within 10 µs and reaches plateau. Second component rises drastically after the onset time of 43 ms in the case of the light intensity of 0.19 mWcm^{-2} (curve c, indicated by a vertical arrow). Onset time of the 2nd component is defined simply as the inflection point of transient curve in which the second component rises.

Photocurrent quantum efficiency of the 1st component in the plateau region was found to be 0.65 %. Photocurrent density of the 1st component was proportional both to the applied voltage and the incident light intensity. On the contrary, photocurrent quantum efficiency of the 2nd component increased drastically after onset time exceeded unity at 130 ms (curve c, indicated by a horizontal arrow) and reached 180-fold at 1 s. Moreover, photocurrent density of the 2nd component drastically increased with applied voltage and obeyed the Fowler-Nordheim relation.

It is clearly shown that onset time becomes shorter with increasing light intensity (curves a, b and c). When the light intensity increased from 36 to 190 µWcm^{-2}, the onset time remarkably decreased from 250 to 43 ms.

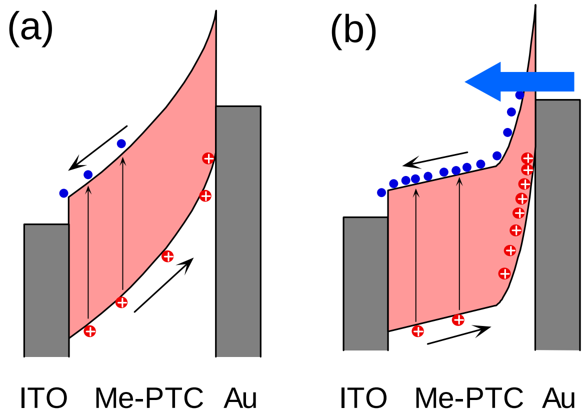

Figure 3. Energy structures of photocurrent multiplication device under light irradiation. Au electrode was negatively biased with respect to ITO electrode. (a) Before onset time. (b) After onset time.

Since the photocurrent observed before onset time was constant for given voltage and light intensity and showed the quantum efficiency far smaller than unity, this can be regarded as the primary photocurrent due to the photogeneration of carriers in the Me-PTC film. On the other hand, since the photocurrent observed after onset time showed remarkably large photocurrent quantum efficiency more than unity and obeyed Fowler-Nordheim relation, it can be regarded as the multiplied photocurrent due to the electron tunneling from Au electrode. Namely, the observed transient response clearly traces the multiplication process including the accumulation of trapped holes near the organic/metal interface during the primary photocurrent flow before onset (Fig. 3(a)) and the subsequent tunneling injection of electrons under the concentrated electric field due to the hole accumulation (Fig. 3(b)). Thus, the observed transient photocurrent behavior is well consistent with the proposed photo-induced electron tunneling mechanism for the photocurrent multiplication.

Based on the above consideration, the onset time can be regarded as the beginning of tunneling injection of electrons, namely, beginning of multiplication. In other words, it must be the completion of field concentration sufficient for multiplied current due to the trapped hole accumulation at the interface. The integration of the primary photocurrent till the onset time would give the total amount of charges flowed through the cell before onset time (onset charge), which relates to the total number of holes passed through the Me-PTC/Au interface. Figure 4 shows the light intensity dependence of such onset charge. Very interestingly, onset charge was found to be independent on the light intensity and were estimated to be 30 nCcm^{-2}. This means that required numbers of holes supplied to the organic/metal interface to induce the electron tunneling seems to have a specific value for the present Me-PTC/Au system. Therefore, effective supply of a given amount of holes to the Me-PTC/Au interface would bring about the decrease the onset time.

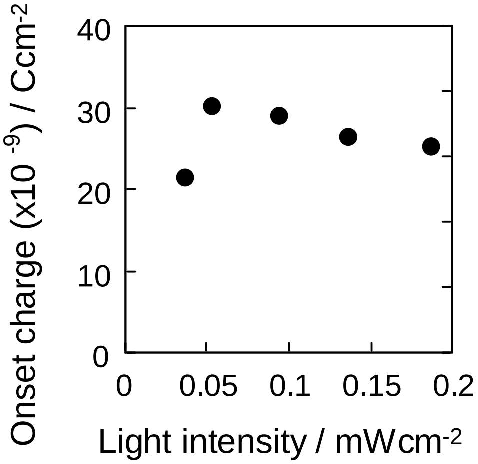

Figure 4. Light intensity dependence of the amount of onset charge. The onset charge is calculated by multiplying onset time by primary photocurrent density.

2. High-Speed Response in the Double-Layered Device

Based on the results obtained above, we developed a double-layered device which can be driven in high voltage for enhancing the carrier generation efficiency of primary photocurrent.

Figure 5 shows the cell structure of the double-layered device and AFM images of each layer deposited on ITO. NTCDA is the photoconductive material showing large multiplication rate as much as Me-PTC. In NTCDA film, many grains having the size of more than 100 nm were grown on ITO substrate, and the film surface is very uneven. PhEt-PTC is the photoconductive material but does not show multiplication. In PhEt-PTC film, the grain size was much smaller and the surface was relatively uniform. This difference is considered to come from the difference of substituents. NTCDA molecules having small substituents tend to stack and form large grains. PhEt-PTC molecules having bulky substituents hardly form molecular stacking, resulting in small grains and even surface. The combination of these two pigments in a layered structure would give the uniform film sample with better quality as a whole.

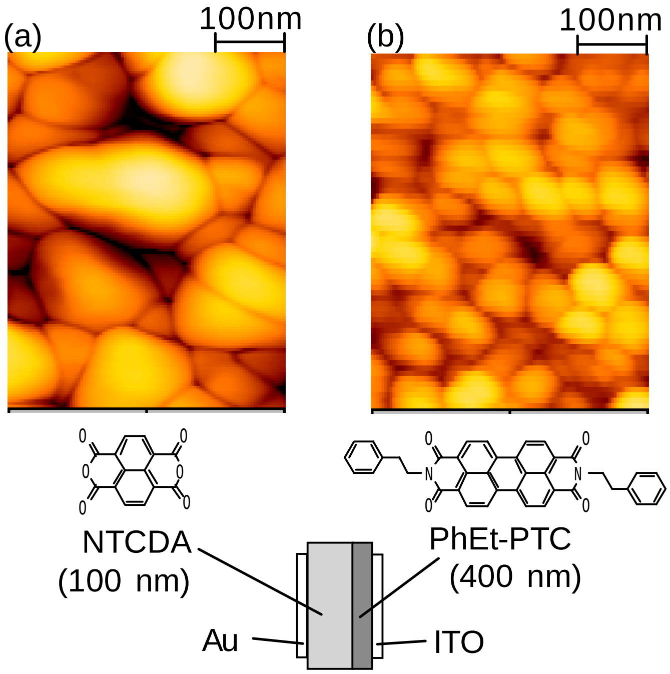

Figure 5. Cell structure of the double-layered device for high-speed response. AFM images of each film surface deposited on ITO are also shown.

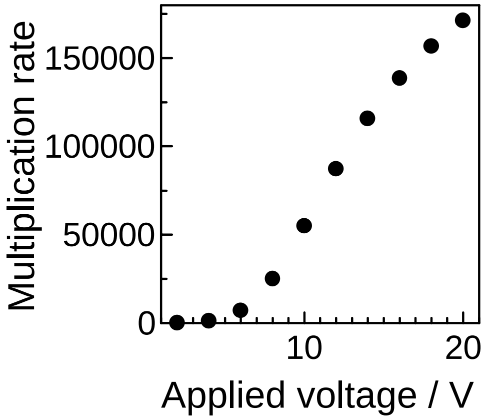

Figure 6. Voltage dependence of multiplication rate in the double-layered device. Continuous light (400 nm, 21 μWcm^{-2}) was irradiated on the Au electrode. Measurement was performed at room temperature.

We investigated voltage dependence of dark current in the single-layered and double-layered devices. In NTCDA single-layered device, dark current increased drastically with increasing voltage and reached 2.6 mAcm^{-2} at 18 V. On the other hand, in double-layered device, dark current was efficiently suppressed and limited to 0.12 mAcm^{-2} at 18 V. This result indicates that electric field applied to the device is distributed uniformly in the whole active area and pinpoint high electric field leading to breakdown was prevented by increase of film uniformity. Thus, by insertion of PhEt-PTC layer, the dark current is suppressed and high voltage application to the device can be performed.

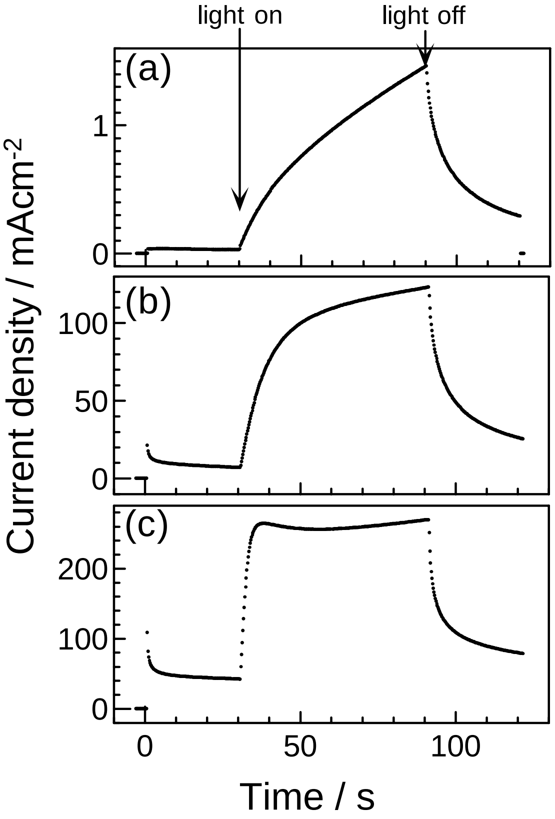

Figure 7. Transient responses of multiplied photocurrent in double-layered device at various applied voltage. a)4V, b)12V, c)20V

Figure 6 shows voltage dependence of multiplication rate in a double-layered device. Since the multiplication rate reached over 10^5-fold as same as the single-layered device, the underlying PhEt-PTC layer does not perturb the multiplication at the NTCDA/Au interface. Figure 7 shows transient responses of multiplied photocurrent at three voltages. In the low voltage region, the transient curve of photocurrent is similar to the usual single-layered devices showing slow response time. In the double-layered device, however, transient response becomes faster with increase of voltage, and interestingly, reached saturation at 18 V. Finally, the large multiplication rate of 1.7 x 10^5-fold and the short response time of 3.7 s was achieved at 20 V. Thus, we succeeded in achieving of high-speed response with large multiplication rate.

Conclusion

In conclusion, transient response of the present photocurrent multiplication was revealed to consist of two components. These components were identified as primary and multiplied photocurrents, respectively. Observed onset time was several tens ms. The transient response observed in the present study strongly supports our previously proposed photoinduced electron tunneling mechanism[1,3] for the photocurrent multiplication. Required amount of charges supplied to the organic/metal interface to induce the electron tunneling was estimated to 30 nCcm^{-2} for Me-PTC/Au system. These results imply that the increase of the carrier generation efficiency of primary photocurrent is expected to be effective to realize high speed multiplication. Furthermore, based on the results, we developed the double-layered device which can be driven in high voltage through the increase of film uniformity. Consequently, large multiplication rate of 1.7 x 10^5 and short response time of 3.7 s was achieved.

References

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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.