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Influence of Oxygen on Photocurrent Multiplication Phenomenon at Organic/Metal Interface

Kouji Suemori, Masahiro Hiramoto, and Masaaki Yokoyama

Material and Life Science, Graduate School of Engineering, Osaka University
Yamadaoka, Suita, Osaka 565-0871, Japan
Phone:+81-6-6879-7933 Fax:+81-6-6879-7237 E-mail:suemori@chem.eng.osaka-u.ac.jp

1. Introduction

We have observed large photocurrent multiplication phenomenon reaching 10^5-fold in vacuum-evaporated films of organic semiconductors both of n-type such as naphthalene derivative (NTCDA, Fig. 1)[1] and of p-type such as quinacridone (DQ, Fig. 1) [2]. During research on this phenomenon, we have accidentally found that the multiplication behaviors were affected by the atmosphere.

Here, we report the strong influence of oxygen on the multiplication characteristics of n-type NTCDA and p-type DQ.

2. Experiment

Sandwich-type cells (Fig. 2) were fabricated by the vacuum evaporation of organic semiconductors and Au on indium tin oxide (ITO) glass substrate. Photocurrent was measured by irradiating the monochromatic light to semi-transparent Au electrode. Measurements were performed in the cryostat evacuated to 10^{-1} Pa or filled by O_2 gas (1 atm). Photocurrent quantum efficiency, i.e., multiplication rate was calculated as the ratio of the number of carriers collected to the number of photons absorbed by the organic film.

3. Results

3.1 Influence of oxygen on p-type DQ cells

Figure 3 shows the dependence of multiplication rate on applied voltage for p-type DQ. Au electrode was positively biased with respect to ITO electrode. Though multiplication rate was only about 700-fold at 28 V under vacuum, it increased to 4,800-fold under O_2 atmosphere. Oxygen strongly enhanced the photocurrent multiplication for p-type organic semiconductor.

3.2 Influence of oxygen on n-type NTCDA cells

Figure 4 shows the dependence of multiplication rate on applied voltage for n-type NTCDA. Au electrode was negatively biased with respect to ITO electrode. Though multiplication rate exceeded 70,000-fold at 5 V under vacuum, it decreased to only about 500-fold under O_2 atmosphere. Figure 5 shows the response profile of multiplied photocurrent for O_2 introduction and evacuation. Response was reversible and could be repeated many times. Influence of O_2 introduction was opposite between p-type DQ and n-type NTCDA.

4. Discussion

In the case of p-type DQ, multiplication occurs at the positively biased interface by the photoinduced hole injection due to the accumulation of photogenerated electrons near the Au electrode, which causes the electric field concentration to the interface (Fig. 6(a)). By introducing oxygen, adsorbed O_2 molecules act as electron traps (O_2^-) and enhance the electron accumulation. This promotes the field concentration and the hole injection, and results in larger multiplication rate.

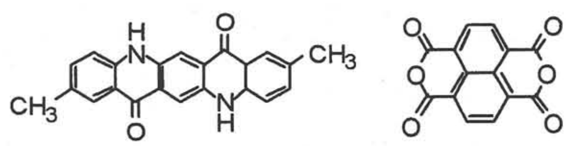
On the other hand, in the case of n-type NTCDA, multiplication occurs at the negatively biased interface by the opposite mechanism of photoinduced electron injection due to the accumulation of photogenerated holes (Fig. 6(b)). By introducing oxygen, adsorbed O_2 molecules act as electron traps (O_2^-) and decrease the substantial number of accumulated holes. This results in multiplication suppression.

Since oxygen induced the very large change of photocurrent density reaching 40 mAcm^{-2} (Fig. 5), very small amount of gas is expected to be detected by the change of multiplied current. This suggests that high sensitive gas sensor can be fablicated by making use of multiplication process.

References

[1] M. Hiramoto, K. Nakayama, T. Katsume, and M. Yokoyama, Chapter 18 in the book "Conjugated Polymer and Molecular Interfaces" edited by W. R. Salaneck, K. Seki, A. Kahn, J.-J. Pireaux published by Marcel Dekker Inc., pp 585-612 (2001) and references therein.

[2] M. Hiramoto, S. Kawase, and M. Yokoyama, Jpn. J. Appl. Phys., **35**, L349 (1996).



DQ NTCDA

Fig. 1 Chemical formulas of DQ and NTCDA.

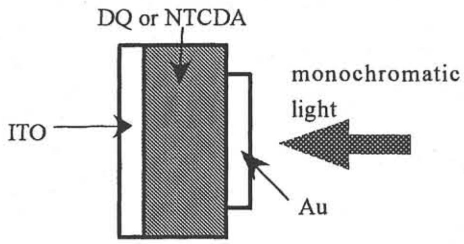


Fig. 2 Structure of sandwich-type cells.

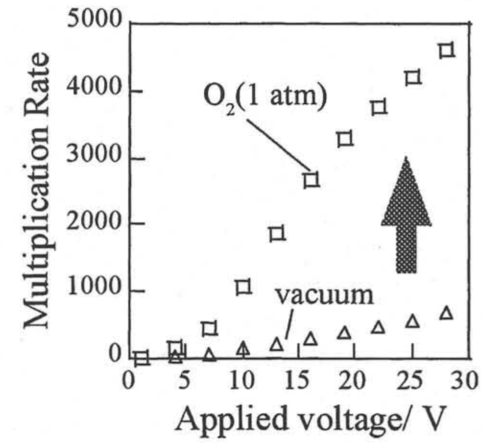


Fig. 3 Dependence of multiplication rate on applied voltage for ITO/DQ(600 nm)/Au cell. Au electrode was positively biased with respect to ITO electrode.

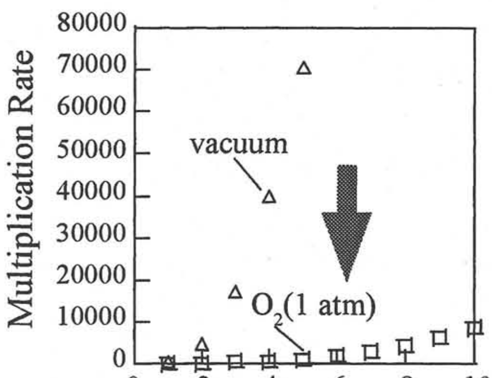


Fig. 4 Dependence of multiplication rate on applied voltage for ITO/NTCDA(500 nm)/Au cell. Au electrode was negatively biased with respect to ITO electrode.

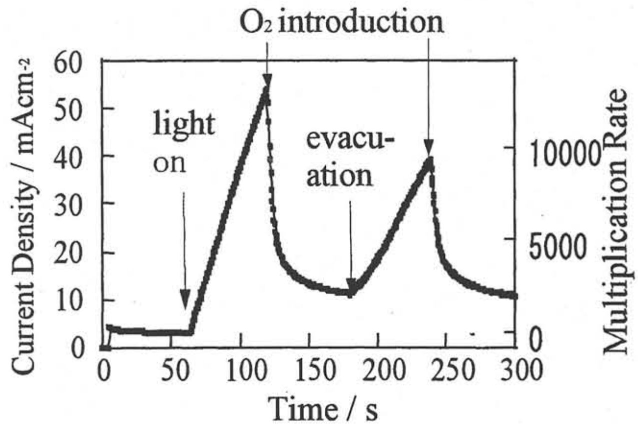


Fig. 5 Response of multiplied photocurrent for O_2 introduction and evacuation at 5 V. Cell was the same to Fig. 4.

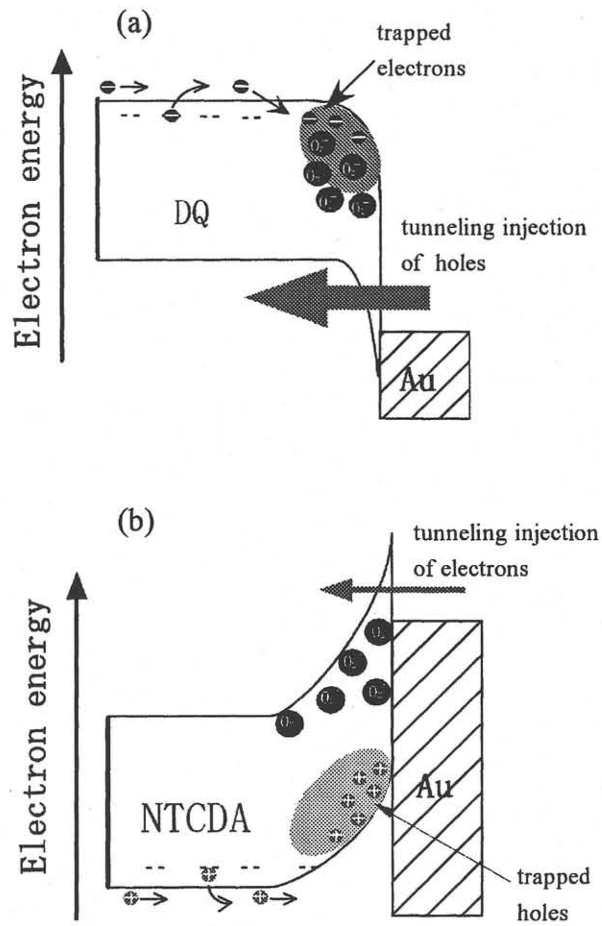


Fig. 6 Energy structure of organic/metal interface during multiplication under O_2 atmosphere. (a) p-type DQ/Au interface biased positively. (b) n-type NTCDA/Au interface biased negatively.