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

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1. Introduction

We have observed large photocurrent multiplication phenomenon reaching $10^4$-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 semitransparent 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 mA cm$^{-2}$ (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 fabricated by making use of multiplication process.

References


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\textsubscript{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\textsubscript{2} atmosphere. (a) p-type DQ/Au interface biased positively. (b) n-type NTCDA/Au interface biased negatively.