Photoinduced doping effect of pentacene field effect transistor in oxygen atmosphere studied by displacement current measurement

著者	庭野　道夫
journal or publication title	Applied Physics Letters
volume	86
number	25
page range	252104-1-252104-3
year	2005
URL	http://hdl.handle.net/10097/47704

doi: 10.1063/1.1949281

APPLIED PHYSICS LETTERS **86**, 252104 (2005)

Photoinduced doping effect of pentacene field effect transistor in oxygen atmosphere studied by displacement current measurement

Satoshi Ogawa,[a] Tatsuo Naijo, Yasuo Kimura, Hisao Ishii, and Michio Niwano
Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST) 4-1-8 Hon-cho, Kawaguchi 332-0012, Japan

(Received 14 December 2004; accepted 10 May 2005; published online 13 June 2005)

It is widely accepted that atmospheric oxygen can work as an electron-accepting dopant mainly to *p*-type organic semiconductors. We have examined the effect of oxygen on a pentacene field effect transistor (FET) with and without exposure to light using the displacement current measurement. Under vacuum conditions, the change in the displacement current due to hole injection from the source and drain electrodes to the pentacene layer is clearly observed, suggesting that the origin of the mobile carriers in the pentacene FET is carrier injection. When the FET is exposed to oxygen under dark conditions, a very small change in the threshold gate voltage for hole injection is observed. In contrast, with exposure to both oxygen and light, we observed that the threshold voltage is lowered and shifted across the zero bias and even to the polarity against hole injection. This *photoinduced doping effect* induces a distinct increase in the drain current of the FET, and it is maintained for at least several hours even after the irradiation is turned off. This finding suggests that the performance of organic semiconductor devices is affected not only by atmospheric oxygen but also by ambient light even during the processing and storage of the devices. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1949281]

It is well known that the properties of electronic devices using organic semiconductors (OSCs) such as sensors, transistors, and light-emitting diodes are affected by ambient gases.[1–3] Especially, atmospheric oxygen gas has been known as a doping agent. It has been widely accepted that holes are created in a *p*-type OSC by charge transfer to the electron-accepting oxygen molecule analogous to the picture of impurity doping for inorganic semiconductors.[4]

However, the details of the doping mechanism of oxygen to *p*-type OSCs is not yet well understood. For example, when we consider the energy diagram of an OSC and an oxygen molecule system, the energy separation between the highest occupied molecular orbital of the OSC and the lowest unoccupied molecular orbital of an oxygen molecule is much larger than the thermal energy at room temperature; the electron affinity of an oxygen molecule $[\chi(O_2)]$ is 0.45 eV in the gas phase,[5] and the typical ionization potential (I_s) of *p*-type OSCs is in the range from 5 to 6 eV. Even if the energy difference in $\chi(O_2)$ between in gas phase and in OSC solids is taken into account, the energy required for the electron transfer from the OSC to oxygen is still much larger than kT. When the oxygen anion and the cation of the OSC can be bound to gain an attractive Coulomb potential, the energy barrier for electron transfer can become smaller, making electron transfer possible. However, the formed cation is strongly bound by the oxygen anion due to the large Coulomb potential, resulting in no effective generation of mobile holes. This point suggests that excess energy is necessary for effectively creating mobile carriers.

In this study, we have investigated the oxygen effect on the pentacene field effect transistor (FET) by using the displacement current measurement (DCM). This technique has been applied to model interfaces of organic light-emitting diodes by Egusa *et al.*[6,7] Recently, we applied the DCM to organic FETs, and reported that the DCM can give us useful information about the behavior of carriers in organic FETs, such as the occurrence of carrier injection, the total amount of charges accumulated in the FET, the area of the charge sheet formed in the channel, the trap effect and so on.[8] In the present study, by using this technique, we found that the charge transfer between pentacene and oxygen molecules is significantly enhanced by exposure to both oxygen gas and light. This *photoinduced doping effect* induces a drastic shift in the threshold gate voltage for hole accumulation at the channel along with a distinct change in the FET properties, suggesting that the electron transfer from a pentacene molecule to an oxygen molecule effectively occurs through the excitation of the pentacene molecule by light absorption.

The structure of the FET fabricated in this study was the top contact type. Pentacene was purchased from Wako Pure Chemical Industries, Ltd. The nominal purity was 99.9%. The sample was purified once by vacuum sublimation. A *p*-type Si(100) wafer with an electric resistivity of $<0.01\ \Omega\,\mathrm{cm}$ was thermally oxidized and used as the substrate of the FET structures. The thickness of the oxide layer was 100 nm. A 100 nm thick pentacene layer was deposited on it by vacuum vapor deposition. Finally, the source and drain electrodes were fabricated by depositing Au metal on the organic layer through a metal mask. The channel length was 200 μm. The device was quickly moved to a small vacuum chamber to measure the electric properties. During the transfer, the device was exposed to air. Although the atmospheric gases, such as oxygen and water, were included in the pentacene layer, most of them were removed by pumping for several hours. The working pressure during the measurements was on the order of 10^{-3} Pa.

For the displacement current measurements of FET structures, a current through the FET is measured under a

---

[a] Electronic mail: s-ogawa@riec.tohoku.ac.jp

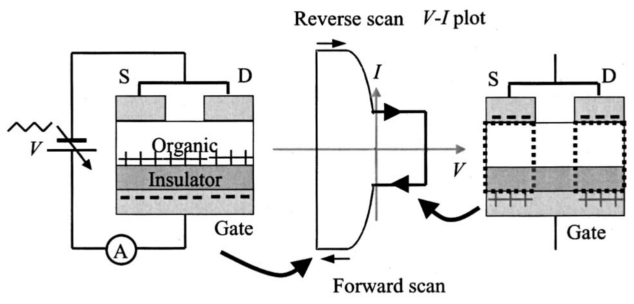


FIG. 1. The principle of displacement current measurement. Center: A typical voltage-current curve for a *p*-type semiconductor with hole injection. Right: The distribution of carriers in the FET at a positive bias. Left: The distribution of carriers at a negative bias with hole injection.

triangular wave from an external bias voltage. The source and drain electrodes were connected to ground, and the gate electrode was biased relative to the ground. Oxygen dosing was performed by introducing oxygen gas (1 atm, purity 99.999%) into the measurement chamber. A light-emitting diode (the central wavelength is 430 nm) was used to irradiate the FET.

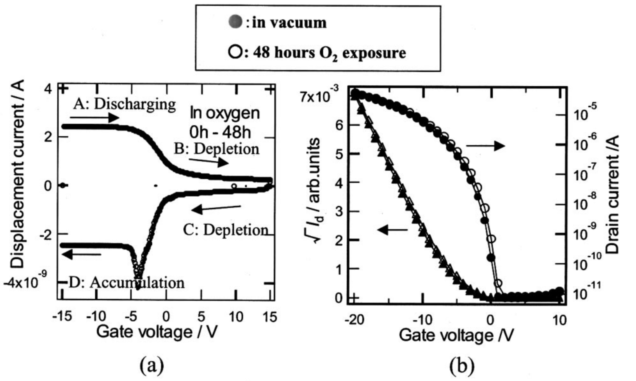
Before discussing the results, let us briefly explain the principle of DCM for *p*-type organic FETs shown in Fig. 1. We discuss only the cases without impurity carriers. The general principle of the DCM for a FET structure was described in Ref. 8. The device can be regarded as a capacitor with an effective capacitance C_{eff}. When a ramp voltage, $V,(dV/dt=constant)$ is applied to the device, the current through the device, (I_d), can be expressed as

$$I_d = C_{\mathrm{eff}} \cdot \frac{dV}{dt}. \tag{1}$$

When no carrier injection occurs at the positive gate voltage, the region of both the organic and insulator layers beneath the source and drain electrodes, which is denoted by the dotted rectangle, works as a combined capacitor, and a constant displacement current is observed for a positive gate bias. When hole injection occurs on the negative voltage side, the injected holes are accumulated at the organic/insulator interface, and only the insulator layer works as a capacitor. Since the capacitance of the insulator is greater than the combined capacitance, a current increase is observed with hole injection.

Figure 2 shows the change in the DCM curve and transfer characteristics of the pentacene FET structure in a vacuum and during exposure to oxygen under dark conditions. In a vacuum, the output characteristics exhibit the typical performance of a pentacene FET; the mobility obtained from the measured saturation current was 0.21 cm^2 V^{-1} s^{-1}, and the on/off ratio was 10^6.

At the start of the DCM measurement, a bias of −15 V was applied to the device, and holes are injected from the source and drain electrodes. In the negative bias region (Region A) during the reverse scan (upper half of the DCM curve), a constant current was observed at $V_g < -5$ V. The effective capacitance calculated from the saturated current at $V_g < -5$ V is similar to that of the SiO_2 layer, indicating that the holes are well delocalized at the pentacene/SiO_2 interface. The current exhibits a decrease at $-5 < V_g < 0$, and it becomes constant at a positive bias in the reverse scan (Region B). The effective capacitance calculated from the observed current at $V_g > 5$ V was similar to that of the combined capacitance of the pentacene and SiO_2 layers, indicating that no carrier injection occurs and the carriers in the pentacene layer become depleted. Next, the direction of the voltage sweep is switched to the forward scan (lower half of the curve). In the positive bias region during the forward voltage scan (bottom curve)(Region C), the magnitude of the current is similar to that in Region B, indicating the depletion of the hole again. For the negative bias (Region D) in the forward scan, the current starts to increase around zero bias, shows a peak around −4 V, and then becomes constant at $V_g < -5$ V. This increase in the current is due to hole injection from the source and drain electrodes. The peak is probably due to the displacement current of the term, $V \cdot dC/dt$, which reflects transient change of the effective capacitance during the growth of the charge sheet at pentacene/insulator interface. After the completion of the extension of the charge sheet, the component of $V \cdot dC/dt$ vanishes. The threshold voltage of the hole injection in the DCM is very close to the onset voltage (V_{onset}) of the transfer characteristics of the pentacene FET. Concerning the threshold voltage, V_T, which is determined as the threshold of the linear part of $\sqrt{I_d}$, the transient change in DCM in the region of $-5 < V_g < 0$ V is completed near the V_T. The voltage region, where the effective capacitance becomes constant, corresponds well with that where $\sqrt{I_d}$ shows a good linearity. These results indicate that the carriers in the channel of the FET are supplied by the carrier injection from the source and drain electrodes.



(a) (b)

FIG. 2. The change in the DCM curve (a) and transfer characteristics (b) for the pentacene FET structure upon oxygen exposure without light irradiation. ● denotes the data measured in a vacuum, while ○ indicates that measured after a 48 h exposure to 1 atm oxygen gas.

The FET is exposed to an oxygen atmosphere (1 atm, 48 h) and the DCM and FET properties are measured. Concerning the DCM result, the exposure to oxygen under dark conditions induced a very small voltage shift on the order of a few tenth V. Accordingly, the transfer characteristics of the FET exhibited a similar voltage shift of a few tenths V. No significant change in the mobility was observed. These results suggest that the doping effect due to only oxygen in pentacene induces no effective change in the performance of the FET.

Next, the FET was irradiated by light (430 nm) in the oxygen atmosphere. As shown in Fig. 3(a), the DCM curve shows voltage shift as a function of time. In contrast to the case of the exposure to oxygen under dark condition, the threshold voltage of the current increase is shifted from about −1 V in a vacuum even into positive bias region, about +6 V after a 40 h exposure. This shift indicates a change in

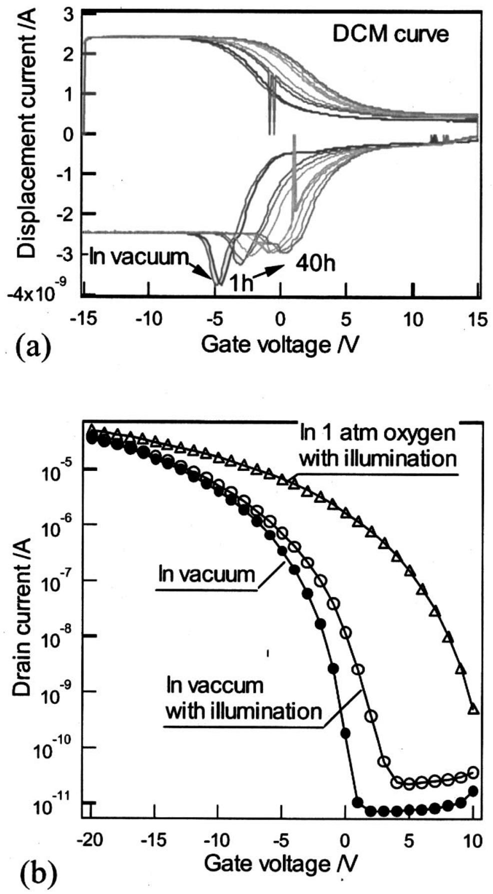


FIG. 3. (a) The changes in the displacement current curves as functions of light irradiation time in 1 atm oxygen atmosphere. The combination of irradiation and oxygen exposure induces the threshold voltage shift for hole accumulation at the channel. (b) A comparison of the transfer characteristics under three conditons: In a vacuum, in a vacuum with illumination, and in oxygen atmosphere with illumination.

the threshold voltage for hole accumulation at the channel. Accordingly, the onset voltage for the transfer characteristics of the FET is also shifted as shown in Fig. 3(b).

The combination of both oxygen and light is critical for the observed change in the FET performance. As shown in Fig. 3(b), the change in the transfer characteristics only by illumination in a vacuum is much smaller than that by exposure to both oxygen and light. The increase in the drain current and the shift in the onset voltage is also small, suggesting that illumination without oxygen does not induce many free carriers and that the performance of the FET under illumination is significantly affected by ambient oxygen.

Such a concerted effect by oxygen and light was also reported for the photocurrent of pentacene.[9] In this reference, the photocurrent of a pentacene film was measured. It was reported that no oxygen effect is observed in the dark current while an increase in the photocurrent is induced by dosing with oxygen during illumination. The author concluded that additional charge carriers are produced during illumination by photoexcitation of a surface complex. A similar result was also reported for anthracene.[10]

Photon absorption spectra are also known to be sensitive to oxygen. The contact charge transfer between an organic molecule and oxygen is proposed. In this model, photon absorption can induce electron transfer for a molecule-oxygen pair in which a charge transfer cannot occur in the ground state.[11]

Such a photoinduced charge transfer is one possible origin of the voltage shift as follows. When the pentacene film is irradiated by light, the photon is absorbed to form the excited pentacene molecule. Through the excited states, electron transfer to the oxygen molecule becomes effective, forming a pentacene cation and an O_2^- anion. The cation can transport within the pentacene film as a hole, while the O_2^- anion is almost immobile and forms a space-charge layer. The built-in potential due to the negative space charge can induce a shift in the threshold voltage for hole injection toward the positive gate voltage. Concerning the molecular doping system, similar photoinduced charge transfer was recently reported for C_{60} doped by leucocrystal violet.[12]

The observed voltage shift was maintained under an oxygen atmosphere even after turning off the light. We observed that the DCM curve shows a gradual shift toward the original position under an oxygen atmosphere without illumination, and that photoinduced doping effect can be maintained for at least several tens of hours. This suggests the stability of the oxygen anion in the pentacene layer. These findings suggest that the performance of organic semiconductor devices is affected not only by atmospheric oxygen but also ambient light even during the processing and the storage of the devices: The performance of the FET in the dark can be affected by the history of the photon absorption before the start of the measurement.

In conclusion, we have measured the displacement current and transfer characteristics of a pentacene FET under ambient conditions. We found a *photoinduced* oxygen doping effect in the pentacene FET. This finding forces us to reconsider the widely accepted mechanism in oxygen doping to *p*-type organic semiconductors. Our results demonstrate that the doping effect only by exposure to oxygen is not significant, but is also significantly enhanced by exposure to light, demonstrating that photoinduced doping is a new approach to controlling the carrier generation in organic semiconductors.

Part of this work was supported by Grants-in-Aid for Scientific Research (Nos. 15350075, 14205007, and 13640576) and Creative Scientific Research (No. 14GS0213) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

[1] G. Guillaud, J. Simon, and J. P. Germain, Coord. Chem. Rev. **178**, 1433(1998).
[2] S. Hoshino, M. Yoshida, S. Uemura, T. Kodzasa, N. Takada, T. Kamata, and K. Yase, J. Appl. Phys. **95**, 5088 (2004).
[3] M. S. A. Abdou, F. P. Orfino, Y. Son, and S. Holdcroft, J. Am. Chem. Soc. **119**, 4518 (1997).
[4] J. D. Wright, *Molecular Crystals*, 2nd ed. (Cambridge Unviersity Press, Cambridge, UK, 1995).
[5] For example, R. J. Celotta, R. A. Bennett, J. L. Hall, M. W. Siegel, and J. Levine, Phys. Rev. A **6**, 631 (1972).
[6] S. Egusa, N. Gemma, A. Miura, K. Mizushima, and M. Azuma, J. Appl. Phys. **71**, 2042 (1992).
[7] S. Egusa, A. Miura, N. Gemma, A. Miura, and M. Azuma, Jpn. J. Appl. Phys., Part 1 **33** 2741 (1994).
[8] S. Ogawa, Y. Kimura, H. Ishii, and M. Niwano, Jpn. J. Appl. Phys., Part 2 **42**, L1275 (2003).
[9] H. Kuroda and E. A. Flood, Can. J. Chem. **39**, 1981 (1961).
[10] A. G. Chynoweth, J. Chem. Phys. **22**, 1029 (1954).
[11] R. S. Mulliken, Recl. Trav. Chim. Pays-Bas **75**, 845 (1956); L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc. **79**, 4839 (1957).
[12] F. Li, A. Werner, M. Pfeiffer, and K. Leo, J. Phys. Chem. **108**, 17076 (2004).