Title	Trap states and transport characteristics in picene thin film field-effect transistor
Author(s)	Kawasaki, Naoko; Kubozono, Yoshihiro; Okamoto, Hideki; Fujiwara, Akihiko; Yamaji, Minoru
Citation	Applied Physics Letters, 94: 043310-1-043310-3
Issue Date	2009-01-29
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/7865
Rights	Copyright 2009 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in Naoko Kawasaki, Yoshihiro Kubozono, Hideki Okamoto, Akihiko Fujiwara, and Minoru Yamaji, Applied Physics Letters, 94, 043310 (2009) and may be found at http://link.aip.org/link/?APPLAB/94/043310/1
Description	

Trap states and transport characteristics in picene thin film field-effect transistor

Naoko Kawasaki,[1] Yoshihiro Kubozono,[1,a)] Hideki Okamoto,[2] Akihiko Fujiwara,[3] and Minoru Yamaji[4]

[1]*Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan*
[2]*Division of Chemistry and Biochemistry, Okayama University, Okayama 700-8530, Japan*
[3]*Japan Advanced Institute of Science and Technology, Ishikawa 923-1292, Japan*
[4]*Department of Chemistry and Chemical Biology, Gunma University, Kiryu 376-8515, Japan*

(Received 25 October 2008; accepted 6 January 2009; published online 29 January 2009)

Transport characteristics and trap states are investigated in picene thin film field-effect transistor under O_2 atmosphere on the basis of multiple shallow trap and release (MTR) model. The channel transport is dominated by MTR below 300 K. It has been clarified on the basis of MTR model that the O_2-exposure induces a drastic reduction in shallow trap density to increase both the field-effect mobility μ and on-off ratio. We also found that the O_2-exposure never caused an increase in hole carrier density. Actually, a very high μ value of 3.2 $cm^2 V^{-1} s^{-1}$ is realized under 500 Torr of O_2.
 [DOI: 10.1063/1.3076124]

Organic materials attract much attention as active layer in field-effect transistor (FET) because of their mechanical flexibility, light weight, large-area coverage, ambipolar property, and low-cost/low-temperature fabrication process.[1–6] However, the field-effect mobility μ for FET with thin films of organic material, ~ 1 $cm^2 V^{-1} s^{-1}$ is still lower by three to four orders of magnitude than those in Si/inorganic materials metal-oxide-semiconductor FETs.[1–6] Therefore, the improvement of performance in thin film FETs is a very important and urgent research subject in organic electronics. Very recently, we discovered that an organic material such as picene, exhibits a very high μ of ~ 2 $cm^2 V^{-1} s^{-1}$.[7] The μ value is comparable to those, 1–5 $cm^2 V^{-1} s^{-1}$, in pentacene thin film FET.[8–10] Furthermore, the μ and on-off ratio of picene thin film FET are remarkably improved by O_2-exposure. However, the mechanism for improvement of FET performance caused by O_2-exposure has not yet been clarified, regardless of the expectation that the picene thin film FET is promising for practical organic FETs and for their sensing applications.[7] In this study, we have clarified the mechanism for improvement of FET characteristics in picene thin film FET caused by O_2-exposure on the basis of multiple shallow trap and release (MTR) model.[11] The channel region in the picene thin film FET has been found to contain extremely small amounts of shallow trap states. Furthermore, the O_2-induced improvement of FET characteristics can be reasonably explained by a drastic reduction in shallow trap states.

The picene thin film FET used in this study is top-contact structure [Fig. 1(a)], as in the previous report.[7] Commercially available SiO_2/Si wafer was washed by the procedure described elsewhere.[12] The C_0 of SiO_2 was 8.63 $\times 10^{-9}$ F cm^{-2}. The picene thin films with thickness of 21 nm were formed by a thermal evaporation under base pressure of 10^{-7} Torr and Au source/drain electrodes (thickness of 34 nm) were formed by the thermal evaporation. The picene sample was synthesized by our group according to a new synthesis method.[7] Channel length and width were 30 μm and 3.0 mm, respectively.

Figures 1(b) and 1(c) show typical output (drain current I_D versus drain-source voltage V_{DS} plots) and transfer curves (I_D versus gate voltage V_G plots at $V_{DS} = -120$ V) of picene thin film FET under 500 Torr of O_2, which show hole-transporting (p-channel) enhancement-type characteristics; the O_2 gas contains 0.014 ppm of H_2O. The best μ value was 1.4 $cm^2 V^{-1} s^{-1}$ in the transfer curve measured for an increase in absolute value of gate voltage, $|V_G|$ (forward transfer curve), while it reached 3.2 $cm^2 V^{-1} s^{-1}$ in the transfer curve measured for a decrease in $|V_G|$ (reverse transfer curve). These values were higher than those under 160 Torr of O_2 reported previously.[7] Furthermore, on-currents of the FET under 500 Torr of O_2 increased more rapidly for applied

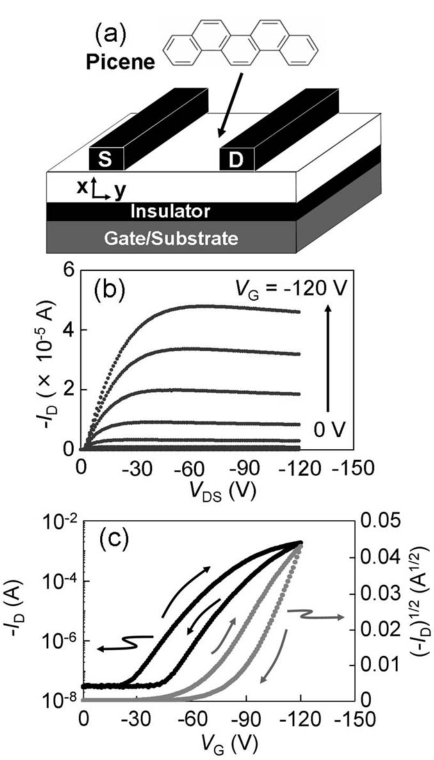

FIG. 1. (a) Device structure of picene thin film FET. (b) Output and (c) transfer curves of picene thin film FET under 500 Torr of O_2.

[a)]Electronic mail: kubozono@cc.okayama-u.ac.jp.

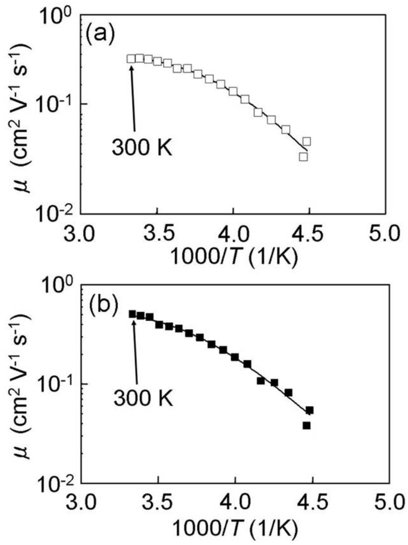

FIG. 2. μ vs T plots determined from (a) forward and (b) reverse transfer curves in picene thin film FET under 160 Torr of O_2.

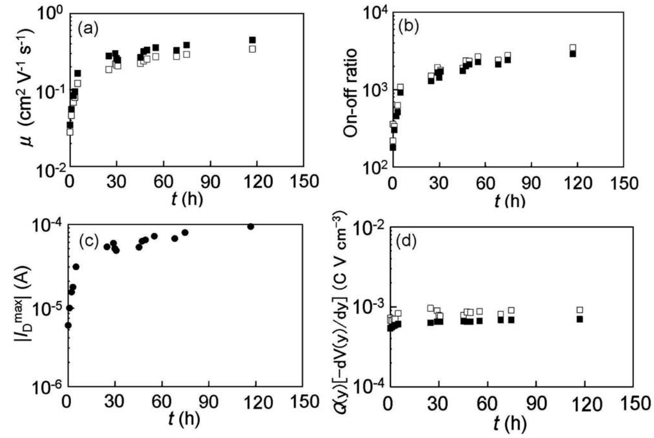

FIG. 3. Plots of (a) μ, (b) on-off ratio, (c) $|I_D^{max}|$, and (d) $Q(y)E(y)$ as a function of t in picene thin film FET under 16 Torr of O_2. In (a), (b), and (c), the open and close squares correspond to parameters estimated from forward and reverse transfer curves.

$|V_G|$ in both transfer curves than those under 160 Torr of O_2, and the off-current was the same as those under 160 Torr of O_2 and vacuum of 10^{-6} Torr. These results clearly show that O_2 is a main origin for the increase in μ and on-off ratio. The μ value, 3.2 $cm^2\ V^{-1}\ s^{-1}$, recorded in the reverse transfer curve is comparable to the best value, 3–5 $cm^2\ V^{-1}\ s^{-1}$, of pentacene thin film FET.[9,10]

Temperature dependences of μs obtained from the forward and reverse transfer curves for picene thin film FET under 160 Torr of O_2 are shown in Figs. 2(a) and 2(b). These μ values increase with an increase in temperature up to 300 K. The μ value follows clearly Eq. (1) based on the MTR model[11,13–17]

$$\mu(T) = \frac{\mu_0}{1 + \frac{N_t}{N_v}\exp\left(\frac{\varepsilon_t - \varepsilon_v}{k_B T}\right)}, \tag{1}$$

where T, μ_0, N_t, N_v, and k_B are temperature, intrinsic mobility, the total density of states (DOS) for the shallow trap states, the effective DOS at valence band edge, and the Boltzmann constant, respectively. The μ_0 value corresponds to the $\mu(T)$ in trap-free FET device, i.e., intrinsic crystal mobility. The ε_t and ε_v refer to the energy level of the trap state and the edge energy of valence band, respectively. Therefore, $\varepsilon_t - \varepsilon_v$ refers to the trap depth. The values of μ_0, N_t/N_v, and $\varepsilon_t - \varepsilon_v$ were determined to be 0.43 $cm^2\ V^{-1}\ s^{-1}$, 9×10^{-7}, and 0.31 eV, respectively, from the temperature dependence of μ obtained from the forward transfer curve, and 0.62 $cm^2\ V^{-1}\ s^{-1}$, 5×10^{-6} and 0.28 eV, respectively, from the temperature dependence of μ obtained from the reverse transfer curve under 160 Torr of O_2. These μ values are relatively high among organic thin film FETs.[13,14,16] The large μ_0 value implies that an extended π-conduction network is formed in the channel region. Furthermore, the values of N_t/N_v are remarkably smaller than that, 10^{-1}–10^{-2}, for organic thin film FETs,[14,16] and they are comparable to that, 10^{-6}, for the single crystal FETs (Ref. 17). These results show that the channel region of the picene thin films contains extremely few trap states, which is consistent with the results that picene is very stable and contains smaller amounts of impurity aromatics other than picene,[7] which act as trapped centers for carriers. The electron spin resonance of picene sample used in this study also shows the existence of extremely small amounts of impurity spins.

From the temperature dependence of μ of picene thin film FET under vacuum of 10^{-6} Torr, the μ_0, N_t/N_v, and $\varepsilon_t - \varepsilon_v$ are determined to be 0.13 $cm^2\ V^{-1}\ s^{-1}$, 4.6×10^{-5}, and 0.18 eV, respectively, for the forward transfer curve, and 0.16 $cm^2\ V^{-1}\ s^{-1}$, 6.3×10^{-4}, and 0.13 eV for the reverse transfer curve.[7] As a consequence, the O_2-exposure causes an enhancement of μ_0 and a drastic reduction in N_t/N_v. These results can lead to the increase in μ, as expected from Eq. (1), which is consistent with the experimental result that the μ values under 160 Torr of O_2 (Fig. 2) are larger than those found for temperature dependence of μ under vacuum of 10^{-6} Torr.[7] Contrary to a simple expectation, the trap depth, $\varepsilon_t - \varepsilon_v$ was not reduced by O_2-exposure, which cannot produce the increase in μ.

The μ and on-off ratio were increased by two to three orders of magnitude immediately after 160 or 500 Torr of O_2-exposure to picene thin film FET in comparison with those under 10^{-6} Torr of vacuum. To investigate a detail change in FET properties as a function of O_2-exposure time, we exposed the picene thin film FET to small amounts of O_2, i.e., 16 Torr of O_2. The O_2-exposure time (t) dependences of μ, on-off ratio, and absolute value of saturation drain on-current $|I_D^{max}|$ measured at $V_{DS}=-120$ V and $V_G=-120$ V are shown in Figs. 3(a)–3(c). As seen from Figs. 3(a) and 3(b), the μ and on-off ratio rapidly increase with an increase in t. Here it should be noted that the off-current is unchanged by O_2-exposure. Therefore, the increase in on-off ratio implies the enhancement of on-current. Actually, as seen from Fig. 3(c), the $|I_D^{max}|$ drastically increases with an increase in t.

The I_D can be generally expressed as follows,

$$I_D = WQ(y)\mu E(y) = WQ(y)\mu\left[-\frac{dV(y)}{dy}\right], \tag{2}$$

where $Q(y)$, $E(y)$, and $V(y)$ refer to charge carrier density, electric field, and bias voltage at position y in channel region of picene FET [Fig. 1(a)]. Therefore, the value, $Q(y)E(y) = I_D^{max}/W\mu$ should be proportional to hole density in saturation regime, assuming that $E(y)$ is constant. The $Q(y)E(y)$ versus t plots are shown in Fig. 3(d). The $Q(y)E(y)$ is almost constant regardless of a rapid increase in $|I_D^{max}|$ [Fig. 3(c)]

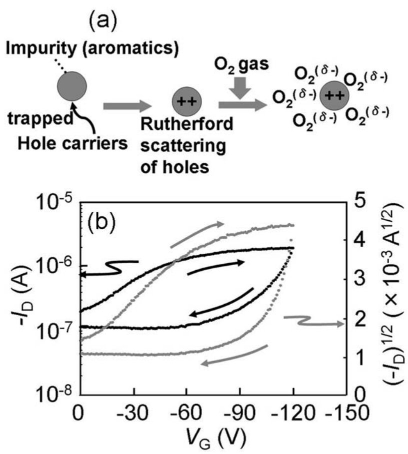

FIG. 4. (a) A model for the shallow trap reduction. (b) Transfer curves of picene thin film FET under 120 Torr of NO_2.

caused by O_2-exposure. This result shows clearly that the increase in $|I_D^{max}|$ or the increase in on-current by O_2-exposure is produced by only an increase in μ.

The picene thin film FET possesses extremely small shallow trap density ($N_t/N_v \sim 10^{-4}$ under vacuum[7] and $N_t/N_v \sim 10^{-6}$ under 160 Torr of O_2). In this study, it has been found that the enhancement of μ by O_2-exposure is associated with the increase in μ_0 and the reduction in N_t/N_v. Especially, the rapid reduction in N_t/N_v (or rapid reduction in shallow trap states) can be closely associated with a remarkable enhancement of μ caused by O_2-exposure in picene thin film FET. Here, we discuss the mechanism of reduction in shallow trap states by O_2-exposure. The proposed mechanism is shown in Fig. 4(a). The picene thin films should contain a trace of impurity aromatics. The impurity aromatics can act as trapped centers for mobile holes and the impurity aromatics are positively charged. The positively charged impurity aromatics act as Rutherford scattering centers for mobile hole, which lowers the μ in FET. This mechanism is already proposed in Ref. 18 and the impurity aromatics are generally recognized as a main origin of the trap. When O_2 gas was introduced into picene thin films, the positively charged aromatics may be neutralized or shielded by the partly ionized oxygen molecule, $O_2^{\delta-}$, to reduce the charged centers, as shown in Fig. 4(a). If the neutralization or shielding occurs for the positively charged impurity aromatics, this corresponds to a lowering of shallow trap density in MTR model. The drastic shallow trap reduction by O_2-exposure found in our analyses for the transport properties can be well explained by this model [Fig. 4(a)].

We briefly comment about the variation of μ_0 and trap depth, $\varepsilon_t - \varepsilon_v$ caused by O_2-exposure. The raise of μ_0 found by O_2-exposure implies that the crystallinity of picene thin films relating to formation of π-conduction network is never lowered by O_2-exposure. Further, the enhancement of trap depth by O_2-exposure may reflect a selective disappearance of shallow trap states because it corresponds to a mean depth for whole distribution of trap states. If it is the case, the increase in trap depth is reasonably connected with the reduction in shallow trap states. Finally, the effect of NO_2 gas exposure on picene thin film FET was investigated. The transfer curves are shown in Fig. 4(b). The on-current is lower than that under 500 Torr of O_2 but the off-current is significantly enhanced. This result implies a drastic increase in hole carrier density by NO_2 gas exposure. Since the electron affinity of NO_2, ~2.1 eV, is higher than that of O_2, ~0.5 eV, the NO_2 gas exposure may easily cause the chemical doping of holes into the picene thin films. The transfer curves at $V_{DS} = -120$ V [Fig. 4(b)] clearly shows that the effect of NO_2 gas exposure on picene FET is different from that of O_2, namely, the O_2-exposure effect on picene FET is never associated with the chemical doping. The hysteresis appeared in transfer curves [Fig. 4(b)] is larger than that for H_2O and the very large hysteresis observed by NO_2 gas exposure suggests that the strength of hysteresis may be discussed on the basis of the electron affinity of each gas.

In conclusion, the O_2-exposure reduces the shallow trap states to enhance the μ in picene thin film FET. In this process, the hole density in valence band is unchanged so that the enhancement of off-current is suppressed. The O_2-exposure effect on FET performance is closely associated with the shallow trap reduction. In this study, the high μ value of 3.2 $cm^2\ V^{-1}\ s^{-1}$ was realized through a drastic reduction in shallow trap states by an exposure of picene thin film FET to large amounts of O_2 (500 Torr). The μ values more than 3.0 $cm^2\ V^{-1}\ s^{-1}$ are always observed without any interface control for the surface of gate dielectric and electrodes in all devices of three picene FETs used for an investigation of the effect for 500 Torr of O_2 exposure. This study shows a possible application of picene FET toward practical gas sensor.

This work was partly supported by a Grant-in-Aid (Grant No. 18340104) from MEXT, Japan.

[1] D. Dimitrakopoulos and D. J. Mascaro, IBM J. Res. Dev. **45**, 11 (2001).
[2] C. D. Dimitrakopoulos and P. R. L. Malenfant, Adv. Mater. (Weinheim, Ger.) **14**, 99 (2002).
[3] C. R. Newman, C. D. Frisbie, D. A. da S. Filho, J.-L. Bredas, P. C. Ewbank, and K. R. Mann, Chem. Mater. **16**, 4436 (2004).
[4] J. Zaumseil and H. Sirringhaus, Chem. Rev. (Washington, D.C.) **107**, 1296 (2007).
[5] S.-S. Sun and L. R. Dalton, *Introduction to Organic Electronics and Optoelectronic Materials and Devices* (CRC, Boca Raton, 2008).
[6] D. A. Bernards, R. M. Owens, and G. G. Malliaras, *Organic Semiconductors in Sensor Applications* (Springer, Berlin, 2008).
[7] H. Okamoto, N. Kawasaki, Y. Kaji, Y. Kubozono, A. Fujiwara, and M. Yamaji, J. Am. Chem. Soc. **130**, 10470 (2008).
[8] Y.-Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, IEEE Electron Device Lett. **18**, 606 (1997).
[9] H. Klauk, M. Halik, U. Zschieschang, G. Schmidf, W. Radlik, and W. Weber, J. Appl. Phys. **92**, 5259 (2002).
[10] T. W. Kelly, D. V. Muyres, P. F. Baude, T. P. Smith, T. D. Jones, Mater. Res. Soc. Symp. Proc. **771**, L6.5.1 (2003).
[11] D. C. Hoesterey and G. M. Letson, J. Phys. Chem. Solids **24**, 1609 (1963).
[12] T. Kanbara, K. Shibata, S. Fujiki, Y. Kubozono, S. Kashino, T. Urisu, M. Sakai, A. Fujiwara, R. Kumashiro, and K. Tanigaki, Chem. Phys. Lett. **379**, 223 (2003).
[13] D. Knipp, R. A. Street, and A. R. Volkel, Appl. Phys. Lett. **82**, 3907 (2003).
[14] N. Kawasaki, Y. Ohta, Y. Kubozono, A. Konishi, and A. Fujiwara, Appl. Phys. Lett. **92**, 163307 (2008).
[15] R. W. I. de Boer, M. Jochemsen, T. M. Klapwijk, A. F. Morpurgo, J. Niemax, A. K. Tripathi, and J. Pflaum, J. Appl. Phys. **95**, 1196 (2004).
[16] R. J. Chesterfield, J. C. McKeen, C. R. Newman, P. C. Ewbank, D. A. da S. Filho, J.-L. Bredas, L. L. Miller, K. R. Mann, and C. D. Frisbie, J. Phys. Chem. B **108**, 19281 (2004).
[17] A. K. Tripathi, M. Heinrich, T. Siegrist, and J. Pflaum, Adv. Mater. (Weinheim, Ger.) **19**, 2097 (2007).
[18] M. Schwoerer and H. C. Wolf, *Organic Molecular Solids* (Wiley, Weinheim, 2007) Chap. 8.