<table>
<thead>
<tr>
<th>Title</th>
<th>Trap states and transport characteristics in picene thin film field-effect transistor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Kawasaki, Naoko; Kubozono, Yoshihiro; Okamoto, Hideki; Fujiwara, Akihiko; Yamaji, Minoru</td>
</tr>
<tr>
<td>Citation</td>
<td>Applied Physics Letters, 94: 043310-1-043310-3</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2009-01-29</td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Text version</td>
<td>publisher</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10119/7865">http://hdl.handle.net/10119/7865</a></td>
</tr>
<tr>
<td>Rights</td>
<td>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 <a href="http://link.aip.org/link/?APPLAB/94/043310/1">http://link.aip.org/link/?APPLAB/94/043310/1</a></td>
</tr>
</tbody>
</table>

**Description**

**JAIST**

**Japan Advanced Institute of Science and Technology**
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 Yamaji4

1Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan
2Division of Chemistry and Biochemistry, Okayama University, Okayama 700-8530, Japan
3Japan Advanced Institute of Science and Technology, Ishikawa 923-1292, Japan
4Department 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 O2 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 O2-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 O2-exposure never caused an increase in hole carrier density. Actually, a very high μ value of 3.2 cm2 V−1 s−1 is realized under 500 Torr of O2.

© 2009 American Institute of Physics. [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. However, the field-effect mobility μ for FET with thin films of organic material, ∼1 cm2 V−1 s−1 is still lower by three to four orders of magnitude than those in Si/inorganic materials metal-oxide-semiconductor FETs. Therefore, the improvement of performance in thin film FETs is a very important and urgent research subject in organic electronics. Very recently, we have discovered that an organic material such as picene, exhibits a very high μ of ∼2 cm2 V−1 s−1. The μ value is comparable to those, 1–5 cm2 V−1 s−1, in pentacene thin film FET. Furthermore, the μ and on-off ratio of picene thin film FET are remarkably improved by O2-exposure. However, the mechanism for improvement of FET performance caused by O2-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. In this study, we have clarified the mechanism for improvement of FET characteristics in picene thin film FET caused by O2-exposure on the basis of multiple shallow trap and release (MTR) model. The channel region in the picene thin film FET has been found to contain extremely small amounts of shallow trap states. Furthermore, the O2-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. Commercially available SiO2/Si wafer was washed by the procedure described elsewhere. The C0 of SiO2 was 8.63 × 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. Channel length and width were 30 μm and 3.0 mm, respectively.

Figures 1(b) and 1(c) show typical output (drain current ID versus drain-source voltage VDS plots) and transfer curves (ID versus gate voltage VG plots at VDS = −120 V) of picene thin film FET under 500 Torr of O2, which show hole-transporting (p-channel) enhancement-type characteristics; the O2 gas contains 0.014 ppm of H2O. The best μ value was 1.4 cm2 V−1 s−1 in the transfer curve measured for an increase in absolute value of gate voltage, [VG] (forward transfer curve), while it reached 3.2 cm2 V−1 s−1 in the transfer curve measured for a decrease in [VG] (reverse transfer curve). These values were higher than those under 160 Torr of O2 reported previously. Furthermore, on-currents of the FET under 500 Torr of O2 increased more rapidly for applied

---

a)Electronic mail: kubozono@cc.okayama-u.ac.jp.
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 $\mu$ and on-off ratio. The $\mu$ 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 $\mu$s 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 $\mu$s increase with an increase in temperature up to 300 K. The $\mu$ value follows clearly Eq. (1) based on the MTR model11,13–17

$$\mu(T) = \frac{\mu_0}{1 + \frac{N_f}{N_v} \exp \left( \frac{e_f - e_v}{k_B T} \right)},$$

where $T$, $\mu_0$, $N_f$, $N_v$, 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 $\mu_0$ value corresponds to the $\mu(T)$ in trap-free FET device, i.e., intrinsic crystal mobility. The $e_f$ and $e_v$ refer to the energy level of the trap state and the edge energy of valence band, respectively. Therefore, $e_f - e_v$ refers to the trap depth. The values of $\mu_0$, $N_f/N_v$, and $e_f - e_v$ were determined to be 0.43 cm$^2$ V$^{-1}$ s$^{-1}$, 9 $\times$ 10$^{-7}$, and 0.31 eV, respectively, from the temperature dependence of $\mu$ obtained from the forward transfer curve, and 0.62 cm$^2$ V$^{-1}$ s$^{-1}$, 5 $\times$ 10$^{-6}$ and 0.28 eV, respectively, from the temperature dependence of $\mu$ obtained from the reverse transfer curve under 160 Torr of O$_2$. These $\mu$s values are relatively high among organic thin film FETs.13,14,16 The large $\mu_0$ value implies that an extended $\sigma$-conduction network is formed in the channel region. Furthermore, the values of $N_f/N_v$ 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, 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 $\mu$ of picene thin film FET under vacuum of 10$^{-6}$ Torr, the $\mu_0$, $N_f/N_v$, and $e_f - e_v$ were determined to be 0.13 cm$^2$ V$^{-1}$ s$^{-1}$, 4.6 $\times$ 10$^{-5}$, and 0.18 eV, respectively, for the forward transfer curve, and 0.16 cm$^2$ V$^{-1}$ s$^{-1}$, 6.3 $\times$ 10$^{-4}$, and 0.13 eV for the reverse transfer curve.14 As a consequence, the O$_2$-exposure causes an enhancement of $\mu_0$ and a drastic reduction in $N_f/N_v$. These results can lead to the increase in $\mu$, as expected from Eq. (1), which is consistent with the experimental result that the $\mu$ values under 160 Torr of O$_2$ (Fig. 2) are larger than those found for temperature dependence of $\mu$ under vacuum of 10$^{-6}$ Torr.14 Contrary to a simple expectation, the trap depth, $e_f - e_v$, was not reduced by O$_2$-exposure, which cannot produce the increase in $\mu$.

The $\mu$ 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 $\mu$, on-off ratio, and absolute value of saturation drain on-current $|I_{DS}^{\text{max}}|$ measured at $V_{GS}=-120$ V and $V_{DS}=-120$ V are shown in Figs. 3(a)–3(c). As seen from Figs. 3(a) and 3(b), the $\mu$ 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 $|I_{DS}^{\text{max}}|$ drastically increases with an increase in $t$.

The $I_D$ can be generally expressed as follows,

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

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, $Q(y)E(y) = |I_{D}^{\text{max}}|/W\mu$, 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 $|I_{D}^{\text{max}}|$. [Fig. 3(e)]
caused by O2-exposure. This result shows clearly that the increase in $I_{D\max}$ or the increase in on-current by O2-exposure is produced by only an increase in $\mu$.

The picene thin film FET possesses extremely small shallow trap density ($N_t/N_e \sim 10^{-4}$ under vacuum$^7$ and $N_t/N_e \sim 10^{-6}$ under 160 Torr of O2). In this study, it has been found that the enhancement of $\mu$ by O2-exposure is associated with the increase in $\mu_0$ and the reduction in $N_t/N_e$. Especially, the rapid reduction in $N_t/N_e$ (or rapid reduction in shallow trap states) can be closely associated with a remarkable enhancement of $\mu$ caused by O2-exposure in picene thin film FET. Here, we discuss the mechanism of reduction in shallow trap states by O2-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 aromatics can act as Rutherford scattering centers for hole carriers, which lower the $\mu$ 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 O2 gas was introduced into picene thin films, the positively charged aromatics may be neutralized or shielded by the partly ionized oxygen molecule, $O_2^+$, 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 O2-exposure found in our analyses for the transport properties in hole carrier density by NO2 gas exposure. Since the electron affinity of NO2, $\sim 2.1$ eV, is higher than that of O2, $\sim 0.5$ eV, the NO2 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 NO2 gas exposure on picene FET is different from that of O2, namely, the O2-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 H2O and the very large hysteresis observed by NO2 gas exposure suggests that the strength of hysteresis may be discussed on the basis of the electron affinity of each gas.

In conclusion, the O2-exposure reduces the shallow trap states to enhance the $\mu$ 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 O2-exposure effect on FET performance is closely associated with the shallow trap reduction. In this study, the high $\mu$ value of $3.2 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ was realized through a drastic reduction in shallow trap states by an exposure of picene thin film FET to large amounts of O2 (500 Torr). The $\mu$ values more than $3.0 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ 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 O2 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.