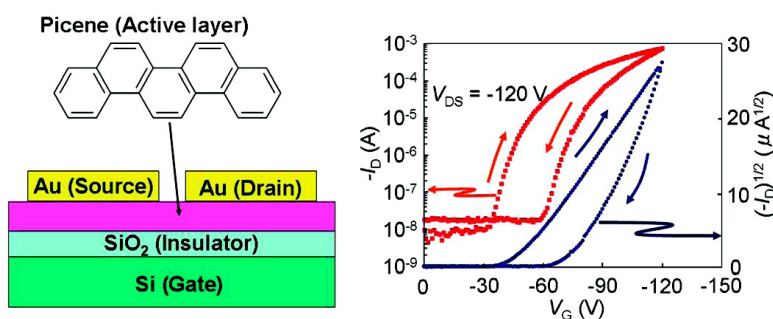


Air-assisted High-performance Field-effect Transistor with Thin Films of Picene

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Air-assisted High-performance Field-effect Transistor with Thin Films of Picene

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Field-effect transistors (FETs) with thin films of organic molecules have many advantages such as large-area coverage, mechanical flexibility, lightweight, and a low-temperature/low-cost fabrication process. The field-effect mobility, μ , value has been still lower than the values for inorganic MOS FETs,¹ but that of FET with single crystals of organic molecules reached up to $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.² The μ values of FETs with thin films of some organic molecules are also comparable to those of amorphous Si FETs, approximately $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.³ Currently, pentacene molecule is generally used for active layer of p-channel thin film FET because it can realize a high μ value of approximately $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁴ Nevertheless, instability or degradation of pentacene under atmospheric conditions causes severe problems for FET performance. Therefore, post-pentacene molecules, materials more suitable as active layer of FETs, have been searched.⁵ The aromatic hydrocarbon of picene possesses the same number of benzene rings as pentacene (Figure 1a), and the expanded and delocalized π -system exists within the molecule. Furthermore, picene should be more chemically stable than pentacene because of the large energy band gap of picene (3.3 eV) and large ionization potential (5.5 eV) (Supporting Information). This may guarantee a stable FET operation under atmospheric conditions. Herein, we report the first FET device with thin films of "old" polycyclic aromatic hydrocarbon, picene. Excellent p-channel enhancement-type FET characteristics with a μ value of $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on–off ratio of 1.6×10^5 have been observed under O_2 atmosphere.

The top-contact device structure of picene thin film FET is shown in Figure 1a. The picene sample was synthesized by our group according to a new synthesis method (Supporting Information), and the ¹H NMR spectrum shows no impurities (Figure S1 in Supporting Information). The details of device fabrication and dimension of device are described in Supporting Information.

The fabricated device was transferred from evaporation chamber to measurement vessel; that is, the device was exposed to air for more than 30 min. First, the FET performance at room temperature was measured under vacuum of 10^{-6} Torr without any annealing, and the temperature dependence of FET performance was investigated from 230 to 295 K under vacuum. Second, stability of device performance was investigated for a long time, more than 20 days, at 300 K. Third, after the device was once exposed to air for 1 h, the FET performance was again investigated under vacuum of 10^{-6} Torr and under atmospheric conditions. The surface topological image and photoemission spectrum were measured with an atomic force microscope (AFM: Seiko Instruments SPA-400) and a photoemission spectrometer (Riken AC-2).

Panels b and c of Figure 1 show p-channel enhancement-type output and transfer curves ($V_{\text{DS}} = -100 \text{ V}$) of picene FET at 290 K. The μ

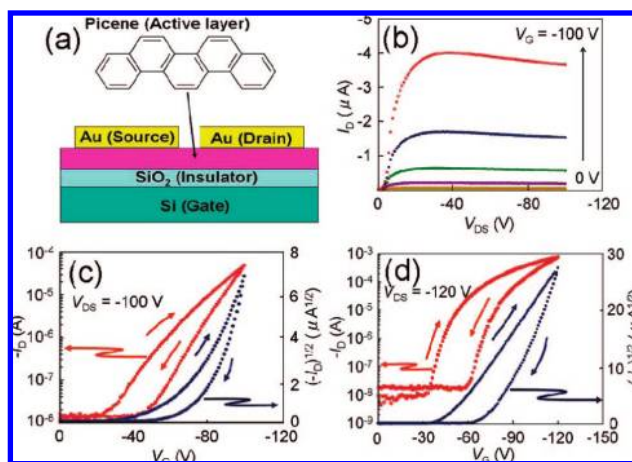


Figure 1. (a) Device structure of picene thin film FET. (b) Output and (c) transfer curves under vacuum, and (d) transfer curve after exposure to 160 Torr of O_2 for 4 h. In (b), V_G is varied at -10 V step from 0 to -100 V .

was determined to be $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from the transfer curve in forward measurement mode (forward transfer curve; Figure 1c), while the μ value estimated from the transfer curve in reverse measurement mode (reverse transfer curve; Figure 1c) was $0.27 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; the average value of μ values estimated from the forward transfer curves for three devices are described in Supporting Information so as to show a precision of the determined μ value. The on–off ratio was approximately 10^4 . This FET showed very high threshold voltages, V_{TH} , of 67 V (forward mode) and 80 V (reverse mode).

As shown in Figure 2a, the μ increases with an increase in temperature in the low temperature region under vacuum of 10^{-6} Torr, indicating a thermally activated hopping like transport for the channel conduction. However, the μ decreases with an increase in temperature above 275 K. This result may imply a different transport mechanism, such as a Drude-type conduction, which is found for organic single crystal FETs and thin film FETs with high μ value.^{6,7} The intrinsic mobility, μ_0 , activation energy, ϵ_a , and the ratio of total density of states (DOS) for trap states, N_t , to the total DOS of valence band (highest occupied molecular orbital (HOMO)), N_v , were determined to be $0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 180 meV, and 4.6×10^{-5} , respectively, from the μ – T plot for the forward transfer curve using a formula based on multiple trap and release (MTR) model.⁸ Here, the ϵ_a corresponds to the energy difference between the energy, ϵ_t , of trap states and that, ϵ_v (or ϵ_{HOMO}), of valence band (i.e., $\epsilon_a = \epsilon_t - \epsilon_v$). The μ_0 is relatively high, and the ϵ_a is close to those for organic FETs reported so far (100–200 meV).^{8–10} Furthermore, the N_t/N_v is extremely small in comparison with those reported so far for thin film FET devices (10^{-1} – 10^{-2}),¹⁰ and the value is close to that for single crystal FET (4×10^{-6}).⁹ The above values for μ_0 , ϵ_a , and N_t/N_v are almost the same as those estimated from the μ – T plot for the reverse transfer

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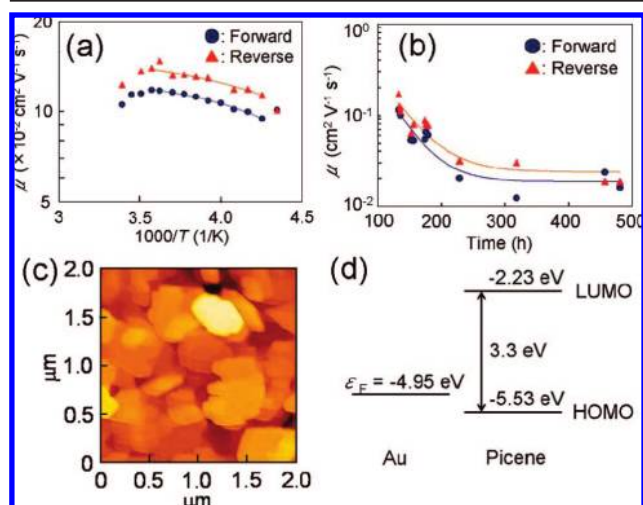


Figure 2. (a) μ - T and (b) μ - t of picene thin film FET under vacuum. (c) AFM and (d) energy diagram of picene thin films. Fitting lines in (a) and (b) are drawn on the basis of MTR model and exponential decay, respectively.

curve ($\mu_0 = 0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\varepsilon_a = 130 \text{ meV}$, and $N_t/N_v = 6.3 \times 10^{-4}$). These results indicate that the total DOS of trap states is very small under vacuum.

Time dependence of μ at 300 K for picene thin film FET under vacuum is shown in Figure 2b. The μ decreases exponentially with an increase in t , and it dropped down to approximately $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $t = 480 \text{ h}$. The FET device was exposed to air for 1 h after being kept under vacuum of 10^{-6} Torr for 480 h, and then the FET characteristics were measured under vacuum. The μ recovered from 1.6×10^{-2} to $0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the forward transfer curve and from 1.9×10^{-2} to $0.47 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the reverse transfer curve. The recovery of μ was also confirmed in the measurement under atmospheric conditions. The other FET devices with picene thin films recorded high μ values of $1.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the reverse transfer curve after air exposure for around 1000 h (Figure S2 in Supporting Information) and $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the reverse transfer curve after O_2 exposure for 4 h (Figure 1d). The on-off ratio of 1.6×10^5 is recorded in the forward transfer curve of the picene FET device exposed to O_2 for 4 h (Figure 1d). The very high μ value of $1.75 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is also observed in the reverse transfer curve of picene FET exposed to O_2 for 70 h (Figure S3). Typical output characteristics after O_2 exposure are shown in Figure S4. Thus, air (or O_2) exposure to FET produced a remarkable increase in both values of μ and on-off ratio. This is contrast to that in the other FETs where air exposure produced an increase in μ and a decrease in on-off ratio.¹¹ This implies that air (or O_2) really assists the channel transport in picene FET. Furthermore, it presents possible applications toward O_2 or H_2O sensor of picene FET.

The hysteresis in the transfer curve becomes larger under air than that under vacuum, as shown in Figure 1c and Figure S2 in Supporting Information. The air exposure of organic FET may enhance bias-stressed trap states, as suggested by pentacene FET.¹² This effect can explain well the enhancement of hysteresis under atmospheric conditions. Therefore, the small N_t/N_v found from the μ - T plots (Figure 2a) may be confined to the interface between active layer and gate dielectric under vacuum; that is, the larger N_t/N_v may be observed under atmospheric conditions. The pure O_2 exposure did not show a clear enhancement of hysteresis (Figure 1d and Figures S3 and S4). This fact suggests that the origin of hysteresis is not O_2 but H_2O in air.

When an FET device is exposed to air or O_2 , holes should be doped into the trap states at the interface between picene and SiO_2 gate dielectric because O_2 (or O) and H_2O (or OH) are electron

acceptors. This can produce small ε_a because of hole filling into trap states, leading to high effective field-effect mobility. In addition, charge neutrality between doped acceptor ions (O_2^- or OH^-) and filled holes may reduce scattering of carriers in the channel, which would produce high μ value. It is interesting to identify which the channel transport is assisted by, O_2 or H_2O . Judging from the increases in μ and on-off ratio found for pure O_2 -exposed picene FET, the channel transport in picene FET may be assisted by O_2 (Supporting Information).

The AFM image of picene thin film on SiO_2/Si substrate shows a dense packing of large grains (approximately 500 nm; Figure 2c). These grains show a very flat surface within the roughness of approximately 1 nm. Thus, the topological image suggests that the picene molecules are well ordered in the grains, and that thin films of picene are preferable for formation of π -conduction network. The energy diagram of picene (Figure 2d) shows energy difference of 0.6 eV between the Fermi energy, ε_F , of Au and $\varepsilon_{\text{HOMO}}$ of picene, while that between the ε_F and the energy, $\varepsilon_{\text{LUMO}}$, of lowest unoccupied molecular orbital (LUMO) is very large (approximately 2.7 eV); the ε_F and $\varepsilon_{\text{HOMO}}$ are determined from the onset of photoemission from picene thin film. The $\varepsilon_{\text{HOMO}}$ is consistent with that estimated by DFT calculation with basis set of B3LYP/6-31G. The $\varepsilon_{\text{LUMO}}$ is determined by consideration of the HOMO-LUMO gap, 3.3 eV, determined from the onset of absorption spectrum (not shown). The small energy difference between ε_F and $\varepsilon_{\text{HOMO}}$ can explain well p-channel conduction in picene FET with Au electrodes and lack of n-channel conduction.

In conclusion, high performance p-channel FET with μ more than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been realized with picene thin films, and the FET properties are clearly improved under air/ O_2 conditions. This shows that the picene FET is an air (or O_2)-assisted device.

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Supporting Information Available: Details of stability and synthesis of picene, ^1H NMR, device fabrication, transfer/output curves of FET device, and O_2 exposure effect. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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