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Characteristics of [6]phenacene thin film field-effect transistor

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Transistor characteristics are studied for field-effect transistors (FETs) with thin films of [6]phenacene, which has six benzene rings and W-shape structure. The molecular alignment preferable for FET transport is found to be formed in [6]phenacene thin films. The transistor shows clear p-channel FET characteristics with field-effect mobility μ as high as $3.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The similar O_2 sensing properties to picene FET are observed in [6]phenacene thin film FET. The bias stress properties are observed in [6]phenacene thin film FET. The pulse-voltage application suppresses the bias-stress effect and it enables a continuous O_2 sensing in [6]phenacene FET. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4747201>]

Field-effect transistors (FETs) with thin films of aromatic phenacene molecules, which consist of benzene rings and show W-shape molecular structure, have attracted much attention owing to their good FET characteristics.^{1–7} First, the picene thin film FET was fabricated¹ and the field-effect mobility, μ , reached the value as high as $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under O_2 atmosphere.² Various characteristics such as O_2 sensing and bias-stress properties in picene thin film FET were clarified and the device performance was improved by the interface control between source/drain electrodes and picene thin films as well as between gate dielectric and picene thin films.^{1–7} Thus, picene thin film FET showed a potential application of picene molecule toward active layer of practical FET devices. The FET performance is comparable to that of thin film FET with acene type molecule, pentacene;^{8–12} pentacene has the same number of benzene rings as picene and it takes a liner molecular structure. The electronic structure determined for picene thin films showed a wide gap (3.3 eV) between highest occupied molecular orbital (HOMO; -5.5 eV) and lowest unoccupied molecular orbital (LUMO; -2.2 eV).^{1,13} This electronic structure suggests lower reactivity than in acene-type molecules such as pentacene.¹³

We second reported the characteristics of FET device with thin films of another phenacene molecule, [7]phenacene, which has seven benzene rings, and it showed clear p-channel FET characteristics with the μ being as high as $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁴ The electronic structure is similar to that of picene, and the HOMO level and HOMO-LUMO gap was -5.7 eV and 3.1 eV , respectively. The O_2 sensing properties are not so high, contrary to picene FET.^{1–7,14} Thus, regardless of similarity in electronic structure, the O_2 sensing behavior is different between two phenacene molecules, picene and [7]phenacene.

In this paper, we report the FET characteristics of transistor with thin films of phenacene molecule, [6]phenacene. [6]phenacene has six benzene rings and the number of benzene rings is an intermediate between picene and [7]phenacene. Very recently, we determined the electronic structure of [6]phenacene by use of photoelectron yield and optical absorption spectra for [6]phenacene thin films.¹⁵ The HOMO level and HOMO-LUMO gap were -5.5 and 3.1 eV , respectively, which are similar to those of picene and [7]phenacene described above. Therefore, the clarification of FET characteristics of [6]phenacene transistor is of interest from the expectation of the high p-channel FET performance.

[6]phenacene was synthesized according to the method described in Refs. 16 and 17, and it was sublimed to be $>99.5\%$ in purity under vacuum. SiO_2 and Ta_2O_5 were used as gate dielectrics. The surface of SiO_2 was coated by either hexamethyldisilazane (HMDS) or parylene, while that of Ta_2O_5 was coated by parylene. HMDS and parylene can provide hydrophobic surface. Especially, parylene with thickness of 25–35 nm is effective to avoid leak of gate current I_G and to make hydrophobic surface. [6]phenacene thin films were 35 nm thick, and Au source/drain electrodes were 50 nm. Thin films of [6]phenacene and Au electrodes were formed by thermal evaporation at 10^{-7} Torr. Device structure (top-contact type) is shown in Fig. 1(a). The capacitance per area, C_o , for SiO_2 (300 nm) and Ta_2O_5 (50 nm) measured by LCR meter were 11 and 64 nF cm^{-2} , respectively. The C_o was estimated by an extrapolation of the capacitance measured at 1 kHz–1000 kHz to 0 Hz. The channel L and width W were $30 \mu\text{m}$ and $1.5\text{--}3.4 \text{ mm}$, respectively. The μ values were evaluated from the saturation transfer curve with the general MOS formula. The FET characteristics were recorded by semiconductor parametric analyzer (Agilent B1500A) in an Ar-filled glove box or vacuum or O_2 atmospheric condition. The x-ray diffraction pattern and atomic force microscope (AFM) image were measured with x-ray

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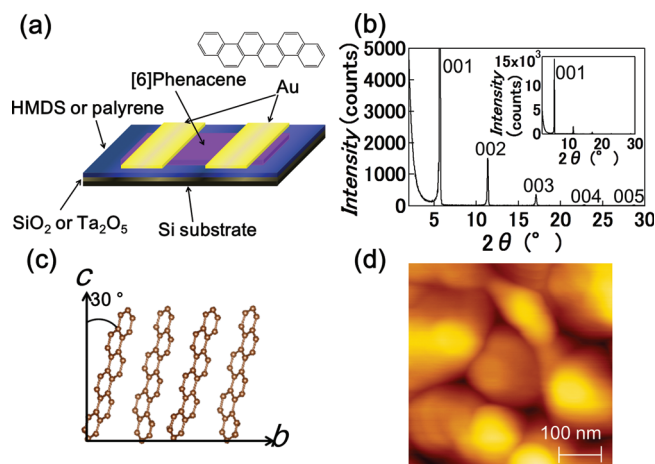


FIG. 1. (a) Device structure of [6]phenacene thin film FET and molecular structure of [6]phenacene. (b) X-ray diffraction pattern of [6]phenacene thin films on Si substrate. The wavelength of x-ray beam is 1.5418 Å. Inset: X-ray diffraction pattern expanded for showing the whole shape of 001 reflection. (c) Schematic representation of molecular alignment of [6]phenacene in the thin films formed on SiO₂. (d) AFM image of [6]phenacene thin films on Si surface.

diffractometer (Rigaku Smartlab-pro) and AFM measurement system (SII Nano Technology SPA400), respectively.

X-ray diffraction pattern of [6]phenacene thin films is shown in Fig. 1(b); thin films (35 nm) of [6]phenacene are formed on SiO₂/Si substrate. The diffraction pattern shows only 00 l reflections in the same manner as picene and [7]phenacene,^{4,14} implying that ab -plane (ab -layer) in [6]phenacene thin films are parallel grown on the SiO₂ surface. The distance between layers substantially corresponds to the lattice constant c which is estimated to be 15.55(1) Å from the 00 l reflections. In Fig. 1(c), the schematic alignment of [6]phenacene molecule on the SiO₂ surface is drawn by considering the lattice constant c and van der Waals length (18.1 Å) of the long axis of [6]phenacene molecule. The molecular alignment shown in Fig. 1(c) is the same as that of picene and [7]phenacene.^{4,14} The inclined angle is estimated to be 30° respective to [001] axis, which is the same as picene and larger than that, 20°, of [7]phenacene.^{4,14} As it can be assumed that [6]phenacene crystals take herringbone structure as in picene, the above growth that the ab -plane forming herringbone stacking produces the layer parallel to the SiO₂ surface is preferable for the channel transport in FET device. Actual channel region in [6]phenacene thin film FET is considered to be the one-layer (15.55 Å) on SiO₂ gate dielectric, and the π -overlap between [6]phenacene molecules along b -axis should mainly contribute to the p-channel transport, which is concluded from the analogy with the calculation of transfer integral of picene molecules. The size of crystallite is estimated to be 56(8) nm from the full width at half maximum (FWHM) for diffraction peaks with Scherrer formula, whose value is the same order as those of picene, 35(5) nm.⁴

The AFM image of [6]phenacene thin films (35 nm) is shown in Fig. 1(d). The AFM image shows the closely packed granules in which each granule has the size as large as 80 nm. The root mean square (RMS) roughness in thin films is 60 Å, showing the flat surface as in picene and [7]phenacene: 31 Å for picene and 48 Å for [7]phenacene.^{4,14} Thus, the grain size and roughness for [6]phenacene thin

films evaluated from AFM image are also consistent with those for picene and [7]phenacene, predicting the high FET characteristics in [6]phenacene thin film FET. Later we will discuss briefly the correlation between the μ and RMS roughness.

Output and transfer curves of [6]phenacene thin film FET with SiO₂ (300 nm) gate dielectric are shown in Figs. 2(a) and 2(b), respectively. The clear p-channel characteristics are observed in the output curves (Fig. 2(a)), exhibiting a linear behavior in plots of absolute drain current $|I_D|$ versus absolute drain voltage $|V_D|$ at low $|V_D|$ region and a saturation behavior at high $|V_D|$ region. Here, source electrode is grounded ($V_S = 0$) and drain/source voltage V_{DS} is equal to V_D . The field-effect mobility, μ , and on-off ratio were estimated to be 3.7 cm² V⁻¹ s⁻¹ and 1.6×10^9 , respectively, from the forward transfer curve (Fig. 2(b)), which is relatively high in the organic thin film FETs; the μ value is higher than, 1.4 cm² V⁻¹ s⁻¹, that of picene thin film FET.² As the μ value higher than 3.5 cm² V⁻¹ s⁻¹ was recorded in three [6]phenacene thin film FETs, the reproducibility of high mobility is confirmed. The absolute threshold voltage, $|V_{TH}|$, was determined to be 62 V from the transfer curve (Fig. 2(b)). The $|V_{TH}|$ is too high because of the use of SiO₂ with low dielectric constant ϵ_x (~ 3.9). As seen from Fig. 2(b), the hysteresis between forward and reverse transfer curves is small regardless of a simple hydrophobic treatment with HMDS, in contrary to picene thin film FET.¹⁻⁵

Fig. 2(c) shows the transfer curve of [6]phenacene thin film FET with high ϵ_x Ta₂O₅ (50 nm, $\epsilon_x \sim 20$) gate dielectric of which the surface is covered with parylene (35 nm). The μ

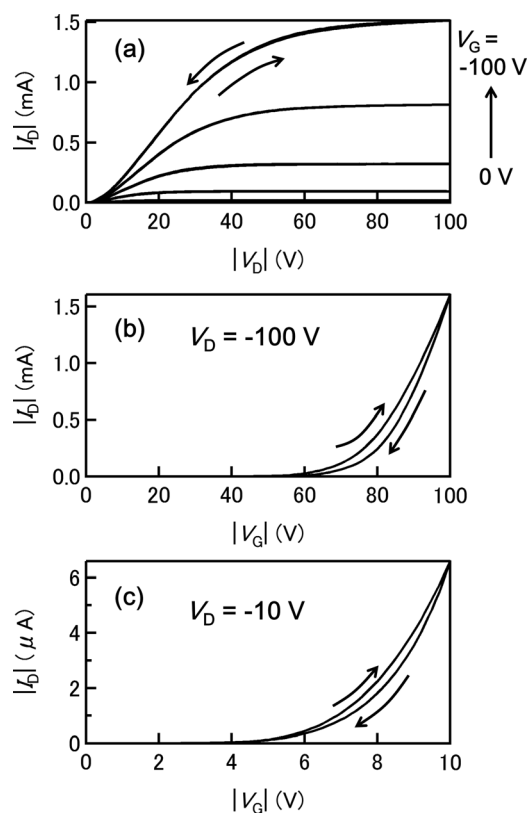


FIG. 2. (a) Output and (b) transfer curves of [6]phenacene thin film FET with SiO₂ gate dielectric. (c) Transfer curves of [6]phenacene thin film FET with Ta₂O₅ gate dielectric.

and $|V_{TH}|$ are estimated to be $9.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 5.4 V, respectively, from the transfer curve. This μ is smaller than that ($=3.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in [6]phenacene thin film FET with SiO_2 gate dielectric shown in Figs. 2(a) and 2(b). The $|V_{TH}|$ is smaller by one order of magnitude than that in Figs. 2(a) and 2(b). This implies that the use of gate dielectric with high ϵ_x is preferable for low-voltage operation in FET device.

Fig. 3(a) shows the I_D evolution as a function of time, t , for [6]phenacene thin film FET with SiO_2 (300 nm) gate dielectric under a dynamical pumping condition (4.5×10^{-2} Torr) and O_2 atmosphere (760 Torr). The transfer curves are measured at 1 h step and the maximum drain current, $|I_D|^{\text{max}}$, which corresponds to $|I_D|$ measured at $|V_D|=|V_G|=100 \text{ V}$, is plotted as a function of t in Fig. 3(a). As seen from Fig. 3(a), the $|I_D|^{\text{max}}$ increases rapidly by exposing the FET to O_2 , and under vacuum (4.5×10^{-2} Torr) the $|I_D|^{\text{max}}$ clearly decreases. These results show that [6]phenacene thin film FET has an ability for O_2 sensing in the same manner as picene thin film FET. This finding is of significance because it has been found that O_2 sensing properties are not unique in picene FET but universal in phenacene FETs. Namely, [6]phenacene can be sufficiently utilized as the active layer in FET-type O_2 gas sensor and the high-speed O_2 gas sensor may be realized because of higher μ value than picene FET. Here, we discuss the correlation of

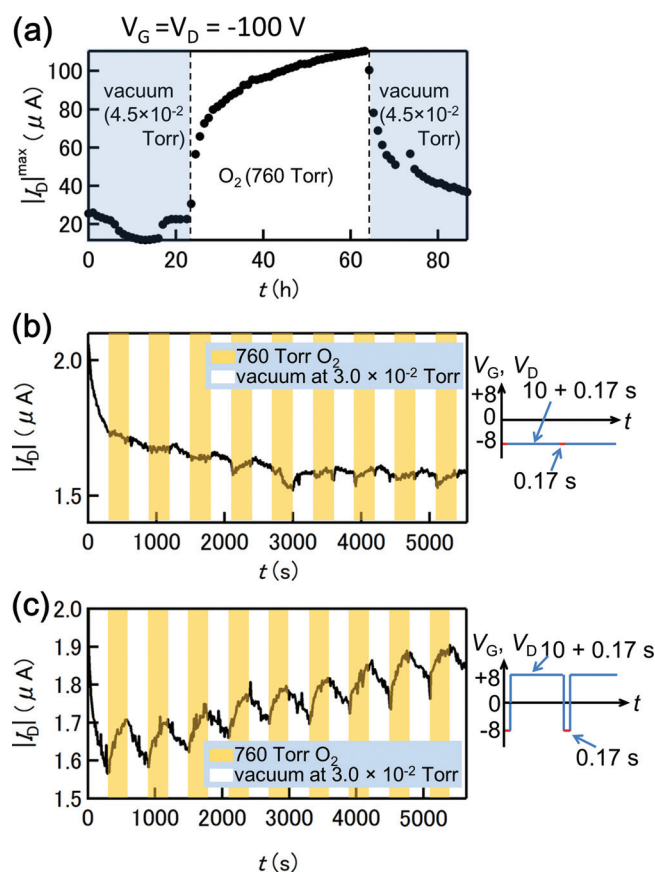


FIG. 3. (a) $|I_D|^{\text{max}}$ evolution of as a function of t for [6]phenacene thin film FET with SiO_2 gate dielectric. (b) Plots of $|I_D|$ measured at continuous application of $V_D=V_G=-8 \text{ V}$ as a function of t . (c) Plots of $|I_D|$ measured at pulse application of V_D and V_G as a function of t ; the applied bias is schematically shown in (b) and (c). The bias voltage is applied in time shown in blue and red line and the I_D is detected in time shown in red line (0.17 s).

high μ and RMS roughness of thin films. We did not previously pay much attention to the correlation between the μ and RMS, but if the difference in RMS roughness for each thin film is considered to be significant, the larger RMS (6.0 nm in [6]phenacene) may be preferable owing to the formation of effective O_2 penetration path into channel region, which may lead to the high μ value. Actually, our preliminary investigation showed the lower μ value in [6]phenacene single crystal FET than that in its thin film FET,¹⁵ although the smaller RMS roughness was expected in single crystal FET, suggesting the necessary of the effective O_2 penetration path into channel region, *i.e.*, the larger RMS value. However, we cannot clearly conclude the correlation between the μ and RMS roughness at the present stage, *i.e.*, the more detailed investigation on the correlation is indispensable.

We tried to continuously apply V_D and V_G to [6]phenacene thin film FET with Ta_2O_5 gate dielectric. As seen from Fig. 3(b), the $|I_D|$ gradually decreases with an increase in t , which is also observed in picene thin film FET. Such a behavior originates from bias-stress effect, caused by emergence of trap associated closely with existence of H_2O .^{18–21} The $|I_D|$ at continuous application of $V_D=V_G=-8 \text{ V}$ was recorded as a function of t under dynamic pumping and O_2 atmosphere (760 Torr). As seen from Fig. 3(b), the continuous application of V_D and V_G does not increase $|I_D|$ by an exposure of [6]phenacene thin film FET to 760 Torr O_2 . Actually, the $|I_D|$ fluctuates by O_2 exposure and pumping, but the clear response for O_2 is not observed. That is, the O_2 sensing ability in [6]phenacene thin film FET disappears in this detection mode.

To recover the O_2 sensing properties in [6]phenacene thin film FET, we altered the detection mode of $|I_D|$ from continuous bias-voltage (Fig. 3(b)) to pulse bias-voltage application (Fig. 3(c)), because the latter application mode may suppress the bias-stress effect. Fig. 3(c) shows the $|I_D|$ as a function of t , which is recorded at pulse V_D and V_G application. The dynamical pumping and O_2 -exposure are repeated at 5 min step. In contrary to the graph shown in Fig. 3(b), the $|I_D|$ increases rapidly under O_2 atmosphere and decreases by dynamical pumping. Thus, the clear O_2 sensing properties are found in this graph, implying that the pulse bias-voltage application is effective for suppression of bias-stress effect.

In conclusion, the [6]phenacene thin film FET has been fabricated and its p-channel FET characteristics have been confirmed. As expected from the molecular alignment in [6]phenacene thin films on SiO_2 surface, the μ value as high as $3.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been realized, which is one of the highest in organic thin film FETs. The clear O_2 sensing properties are observed as in picene thin film FET. The high μ and clear O_2 sensing properties suggest that [6]phenacene is a promising material for practical high-performance organic FET.

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