Characteristics of field-effect transistors using the one-dimensional extended hydrocarbon [7]phenacene

Yasuyuki Sugawara, Yumiko Kaji, Keiko Ogawa, Ritsuko Eguchi, Shohei Oikawa, Hiroyuki Gohda, Akihiko Fujiwara, and Yoshihiro Kubozono

---

Articles you may be interested in

Quantitative analysis of the density of trap states at the semiconductor-dielectric interface in organic field-effect transistors
Appl. Phys. Lett. **107**, 103303 (2015); 10.1063/1.4930310

Thickness-dependent mobility in tetracene thin-film field-effect-transistors
J. Vac. Sci. Technol. B **33**, 050604 (2015); 10.1116/1.4931034

Probing bias stress effect and contact resistance in bilayer ambipolar organic field-effect transistors
Appl. Phys. Lett. **103**, 073303 (2013); 10.1063/1.4818644

Characteristics of [6]phenacene thin film field-effect transistor
Appl. Phys. Lett. **101**, 083301 (2012); 10.1063/1.4747201

Low voltage operation in picene thin film field-effect transistor and its physical characteristics
Appl. Phys. Lett. **95**, 183302 (2009); 10.1063/1.3257373

Characteristics of field-effect transistors using the one-dimensional extended hydrocarbon [7]phenacene

Yasuyuki Sugawara,[1,2] Yumiko Kaji,[1] Keiko Ogawa,[1] Ritsuko Eguchi,[1] Shohei Oikawa,[2] Hiroyuki Gohda,[3] Akihiko Fujiwara,[4] and Yoshihiro Kubozono[1,5,a)]

[1]*Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan*
[2]*Kuramoto Seisakusho Co. Ltd., Kurihara 989-5508, Japan*
[3]*NARD Co. Ltd., Amagasaki 660-0805, Japan*
[4]*Japan Synchrotron Radiation Research Institute, SPring-8, Hyogo 679-5198, Japan*
[5]*Research Center of New Functional Materials for Energy Production, Storage, and Transport, Okayama University, Okayama 700-8530, Japan*

Field-effect transistors (FETs) with solid gate dielectrics are fabricated with thin films of the one-dimensional (1D) extended hydrocarbon [7]phenacene, which contains seven benzene rings. p-channel FET characteristics are observed for these FETs, with a mobility of 0.75 cm^2 V^{-1} s^{-1} at 100 Torr of O$_2$. The O$_2$ gas-sensing effect is examined for the [7]phenacene FET and for the 1D hydrocarbon picene FET. These FETs' trap density and contact resistance are investigated with the multiple shallow trap and release model and the transfer line method. Unlike picene FETs, [7]phenacene FETs have few charge traps and are therefore air-stable. © *2011 American Institute of Physics*. [doi:10.1063/1.3540648]

Field-effect transistors (FETs) based on the one-dimensional (1D) extended hydrocarbon picene show attractive p-channel FET characteristics.[1–5] The field-effect mobility μ is as high as 3 cm^2 V^{-1} s^{-1}.[2] The absolute switch-on drain current $|I_D^{on}|$ and field-effect mobility μ of a picene thin film FET are drastically increased by O$_2$ exposure; $|I_D^{on}|$ represents the drain current at a gate voltage V_G above the threshold voltage V_{TH}. This phenomenon is explained by a decrease in the number of in-band traps under O$_2$.[2] Furthermore, it was found that the hysteresis in transfer curves was increased by the presence of H$_2$O.[5] We attempted to develop a practical O$_2$ gas sensor based on the above experimental results.[4,5]

In 1D extended hydrocarbons, [n]acene consists of a linear fusion of benzene rings, while [n]phenacene consists of a zigzag fusion of benzene rings, and [11]phenacene is currently the phenacene with the largest number of benzene rings that has been synthesized.[6] The band gap of an [n]phenacene is substantially wider than that of an [n]acene such as pentacene, and the highest occupied molecular orbital (HOMO) of an [n]phenacene is deeper.[1] This guarantees low reactivity and high stability for an [n]phenacene molecule, in contrast to an [n]acene such as pentacene; a pentacene FET shows degradation in air.[7] Therefore, [n]phenacenes may be important test materials for future stable and high-performance organic FETs. In this letter, we report the characteristics of a [7]phenacene FET with solid gate dielectrics; the molecular structure of [7]phenacene is shown in Fig. 1(a). The O$_2$ sensing effects are investigated at various O$_2$ concentrations, and the channel traps and the contact resistance of [7]phenacene are clarified based on the multiple shallow trap and release model (MTR) and the transmission line method (TLM), respectively.

[7]phenacene was synthesized as reported previously,[8] and a purified sample (99.9% purity) was obtained by sub-liming the crude sample at 573 K and 4×10^{-5} Torr. An SiO$_2$/Si wafer was used as the substrate for an FET device, with SiO$_2$ as gate dielectric. SiO$_2$ layers were 400 or 40 nm thick. One SiO$_2$ surface (400 nm) was coated with hexamethyldisilazane, while the other SiO$_2$ surface (40 nm) was coated with 1.8wt% of polystyrene to suppress leakage of gate current. Ta$_2$O$_5$ was also used as a gate dielectric and the Ta$_2$O$_5$ films were formed on the Si substrate by magnetron RF sputtering. The Ta$_2$O$_5$ was 200 nm thick, and 1.8 wt % of polystyrene was coated on the Ta$_2$O$_5$ surface to suppress gate current leakage. [7]phenacene thin film FETs were fabricated with the structure shown in Fig. 1(a). The [7]phenacene thin films were 30 nm thick, and the Au source/drain electrodes 50 nm. Thin films of [7]phenacene and the Au electrodes were formed by thermal evaporation at 10^{-7} Torr. The C_0
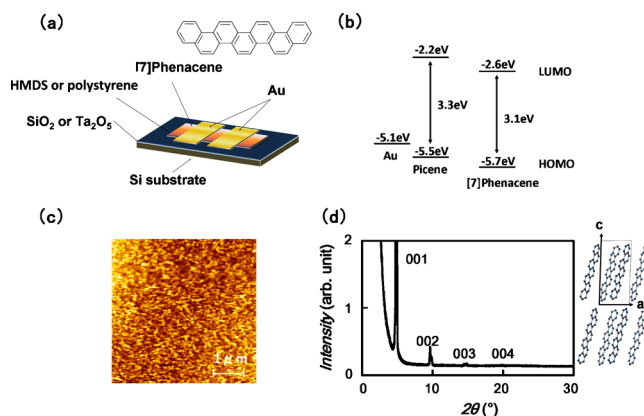

FIG. 1. (Color online) (a) Molecular structure of [7]phenacene and the structure of the [7]phenacene FET, and (b) energy diagram of [7]phenacene drawn by using the ionization potential determined by photoelectron yield measurement and band gap determined by optical absorption, which were measured in this study. In (b), the energy diagram of picene is shown for reference. (c) Atomic force microscope image and (d) x-ray diffraction pattern of [7]phenacene thin films. In (d), schematic representation of molecular stacking of [7]phenacene on SiO$_2$ surface is shown.

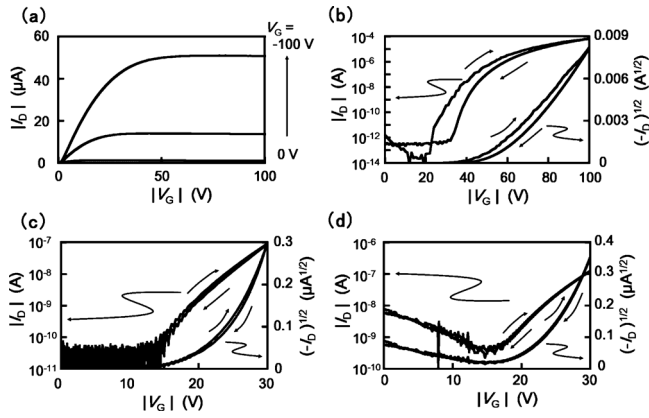a)Electronic mail: kubozono@cc.okayama-u.ac.jp.

FIG. 2. (a) Output and (b) transfer curves of [7]phenacene thin film FET with 400 nm thick SiO_2 gate dielectric. Transfer curves of [7]phenacene thin film FETs with (c) 40 nm thick SiO_2 and (d) 200 nm thick Ta_2O_5 gate dielectrics. All measurements were performed in an Ar-filled glove box.

values of the 400 and 40 nm SiO_2 gate dielectric were 8.1 and 16 nF cm^{-2}, respectively. The C_0 of the Ta_2O_5 gate dielectric was 23 nF cm^{-2}. The L and W were 30 μm and 2.0–3.5 mm, respectively.

The energy diagram of [7]phenacene is shown in Fig. 1(b). The band gap of [7]phenacene, 3.1 eV, is almost the same as that of picene, 3.3 eV. [7]phenacene and picene possess deep ionization potentials (or deep HOMOs) and shallow lowest unoccupied molecular orbitals (LUMOs). [7]phenacene shows a deeper HOMO ($\varepsilon_{HOMO} = -5.7$ eV) than picene ($\varepsilon_{HOMO} = -5.5$ eV), suggesting that a [7]phenacene FET with Au source/drain electrodes has a large injection barrier height even for holes. Nevertheless, the electronic structure of [7]phenacene is similar to that of picene and may produce an FET with characteristics similar to a picene FET.

An atomic force microscope image of [7]phenacene thin films shows dense packing of grains [Fig. 1(c)]. The root mean square thickness of the thin film was 4.8 nm. The x-ray diffraction pattern of the [7]phenacene thin films shows only (00l) reflections [Fig. 1(d)], indicating that the ab layer, with molecules stacked in herringbone fashion, is parallel to the SiO_2 surface in the same manner as in picene.[4] The lattice constant, c, of the thin films was determined to be 18.1(2) Å. The van der Waals distance of the long axis of [7]phenacene indicates that the molecule is inclined by 20° from the normal direction on the SiO_2 surface. The molecular stacking is shown schematically in Fig. 1(d). The topological features, i.e., that the grains are densely packed in [7]phenacene and the ab plane is parallel to SiO_2 surface, are also effective for channel conduction in the FET, as in picene FET.[1,4]

The output and transfer curves of the [7]phenacene thin film FET with a 400 nm thick SiO_2 gate dielectric are shown in Figs. 2(a) and 2(b), which were measured in an Ar-filled glove box. The p-channel FET characteristics are clearly observed and the maximum μ was 0.75 cm^2 V^{-1} s^{-1} at 100 Torr of O_2. The μ decreases gradually when the FET is stored in an Ar-filled glove box for a few days. This suggests an O_2 gas-sensing ability for [7]phenacene FET, similarly to a picene FET. Before the storage of the [7]phenacene FET in an Ar-filled glove box, the channel region of [7]phenacene should contain significant amounts of O_2 because the FET was exposed to air in transferring the device from the vacuum chamber (for the formation of [7]phenacene thin
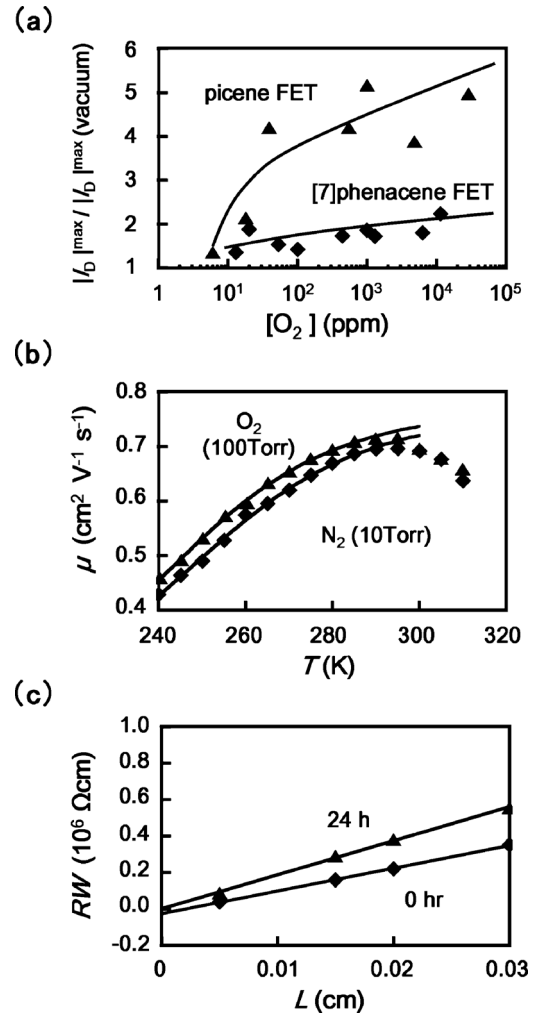

FIG. 3. (a) Ratio of $|I_D|^{max}$ with respect to the minimum $|I_D|^{max}$ measured under vacuum, $|I_D|^{max}/|I_D|^{max}$(vacuum), for [7]phenacene and picene FETs as a function of O_2 concentration. The eyes guides are drawn in (a). (b) μ $-T$ plots of the [7]phenacene thin film FET with 400 nm thick SiO_2 gate dielectric at 100 Torr of O_2 and 10 Torr of N_2, and the curves fitted with Eq. (1) (see text). (c) $RW-L$ plots of the [7]phenacene thin film FET with 400 nm thick SiO_2 gate dielectric in 0 h storage and 24 h storage (see text), and the fitted lines.

films and Au source/drain electrodes) to the glove box for FET characteristics measurements. The FET device operates at a value higher than the $|V_G|$ of 60 V, again similarly to a picene FET.[1–3,5]

For low-voltage operation, we fabricated [7]phenacene FETs with 40 nm thick SiO_2 and 200 nm thick Ta_2O_5 gate dielectrics. The transfer curves of the [7]phenacene FET with SiO_2 and Ta_2O_5 gate dielectrics are shown in Figs. 2(c) and 2(d), respectively. These FETs show p-channel operation. The μ values of these FETs were as high as 10^{-3} cm^2 V^{-1} s^{-1} but the $|V_{TH}|$ values were as low as 22 V in an Ar-filled glove box. Thus, low-voltage operation could be achieved by use of very thin SiO_2 (40 nm) or Ta_2O_5 (200 nm) with a high dielectric constant.

The maximum absolute I_D, $|I_D|^{max}$, for the [7]phenacene FET increases with its exposure time to O_2, and the value decreases after dynamical pumping at 10^{-6} Torr. As seen from Fig. 3(a), the responsiveness of the [7]phenacene FET to O_2 is lower than that of the picene FET; the data for picene FET are taken from our previous report.[5] The picene FET senses down to 10 ppm O_2, and the $|I_D|^{max}$ increases by

a factor of 4 at 1000 ppm of O_2, while in the [7]phenacene FET, the $|I_D|^{max}$ increases by a factor of 1.5 at 1000 ppm. Thus, the [7]phenacene FET can be a sensor for O_2 gas, but with lower sensitivity than the picene FET, suggesting the possible utility of a stable organic FET under O_2, or at least in dry air.

Here it is important to comment on the stability of the [7]phenacene FET to H_2O. Previous investigations found the criterion for stability to H_2O to be $\varepsilon_{LUMO}=-3.98$ eV.[9,10] Materials with $\varepsilon_{LUMO}>-3.98$ eV are unstable in an H_2O-rich environment, indicating that [7]phenacene ($\varepsilon_{LUMO}=-2.6$ eV) is not very stable. Nevertheless, the hysteresis emerging in transfer curves, which is closely related to H_2O, is very small for [7]phenacene FETs with polystyrene-coated gate dielectrics, implying that the influence of H_2O can be ameliorated by using hydrophobic polymer-coated gate dielectrics to fabricate air-stable organic FETs. Thus a [7]phenacene FET can be a candidate for a stable transistor under ambient atmosphere even in a high-humidity environment.

To explore the reason why the sensitivity of [7]phenacene is lower than picene, the temperature dependence of μ in [7]phenacene FET was investigated. As seen in Fig. 3(b), both μ values at 10 Torr of N_2 and 100 Torr of O_2 increase with increasing temperature up to 290 K, and then decrease above 300 K. The μ values at 100 Torr O_2 are slightly higher than those at 10 Torr of N_2 in the temperature region below 290 K, indicating a weak O_2 sensing effect in the [7]phenacene FET. We fitted the $\mu-T$ plots by using the expression of the MTR model,[2,11–16]

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

where μ_0, N_t, N_v, k_B, ε_t, and ε_v are intrinsic mobility, number of traps, total density of the valence band, Boltzmann constant, the mean trap energy and the edge energy level of the valence band, respectively. This expression was previously applied to the picene FET.[2] The values of μ_o, N_t/N_v and $\varepsilon_t-\varepsilon_v$ were determined to be 0.49 cm^2 V^{-1} s^{-1}, 5.8×10^{-7}, and 314 meV by least-squares fitting with Eq. (1) for the [7]phenacene FET at 10 Torr of N_2, while these values were 0.52 cm^2 V^{-1} s^{-1}, 5.1×10^{-7}, and 310 meV at 100 Torr of O_2. Here it is important to note that these parameters are almost the same for N_2 and O_2. In the picene FET the ratio N_t/N_v decreases by two orders of magnitude between vacuum and an O_2 atomosphere.[2] Thus, the traps in the [7]phenacene FET are not effectively reduced by the exposure of the [7]phenacene FET to O_2, in contrast to the picene FET.[2] This may be due to the extremely small number of traps ($N_t/N_v\sim5\times10^{-7}$) observed in the [7]phenacene FET under N_2, i.e., the [7] phenacene thin films are essentially trap-free; $N_t/N_v\sim5\times10^{-5}$ under vacuum in the picene FET.[2] The difference in the number of traps in [7]phenacene and picene remains to be clarified, but it may be due to the lower reactivity expected for the [7]phenacene molecule owing to its deeper HOMO level.

The product of resistance and channel width, RW, is plotted as a function of L in Fig. 3(c). The $RW-L$ plots were analyzed within the framework of TLM. The R was deter-

mined from output curves in the linear region ($|V_{DS}|<|V_G -V_{TH}|$) at $V_G=-100$ V with Ohm's law. The RW measured just after introducing the [7]phenacene FET into an Ar-filled glove box (0 h storage) shows a linear relationship, and the slope is smaller than the RW measured 24 h after introducing it (24 h storage). Since the [7]phenacene FET device was once exposed to O_2 after forming the [7]phenacene thin films and Au electrodes in the vacuum chamber, the channel region may have significant O_2 after 0 h storage, as mentioned previously. The increase in the slope of the $RW-L$ plot after 24 h storage implies that the sheet resistivity, $\rho_s(=RW/L)$, of [7]phenacene becomes large owing to the removal of O_2 caused by the 24 h storage in an Ar-filled glove box. The RW value at $L=0$ is the same in both $RW-L$ plots (0 h storage and 24 h storage), as seen from Fig. 3(c). The value is nearly equal to zero. Therefore, the contact resistance is very small in the [7]phenacene FET, and is not affected by O_2 gas. Even in the picene FET the contact resistance is very small, and is not affected by O_2 (figure not shown). Thus, the O_2 sensing properties of [7]phenacene and picene FETs are strictly related to channel resistance.

In conclusion, the [7]phenacene FET showed p-channel FET characteristics with a μ of 0.75 cm^2 V^{-1} s^{-1}, and low-voltage operation was achieved. The FET operation was not significantly affected by O_2, indicating its possible use in an air-stable organic FET device. We stress that these fundamental characteristics show that [7]phenacene may open an avenue for high-performance hydrocarbon FETs.

[1]H. Okamoto, N. Kawasaki, Y. Kaji, Y. Kubozono, A. Fujiwara, and M. Yamaji, J. Am. Chem. Soc. **130**, 10470 (2008).
[2]N. Kawasaki, Y. Kubozono, H. Okamoto, A. Fujiwara, and M. Yamaji, Appl. Phys. Lett. **94**, 043310 (2009).
[3]Y. Kaji, R. Mitsuhashi, X. Lee, H. Okamoto, T. Kambe, N. Ikeda, A. Fujiwara, M. Yamaji, K. Omote, and Y. Kubozono, Org. Electron. **10**, 432 (2009).
[4]Y. Kaji, N. Kawasaki, X. Lee, H. Okamoto, Y. Sugawara, S. Oikawa, A. Ito, H. Okazaki, T. Yokoya, A. Fujiwara, and Y. Kubozono, Appl. Phys. Lett. **95**, 183302 (2009).
[5]X. Lee, N. Kawasaki, M. Suekiyo, Y. Sugawara, A. Fujiwara, and Y. Kubozono, Org. Electron. **11**, 1394 (2010).
[6]F. B. Mallory, K. E. Butler, A. C. Evans, E. J. Brondyke, C. W. Mallory, C. Yang, and A. Ellenstein, J. Am. Chem. Soc. **119**, 2119 (1997).
[7]Y. Yamashita, Sci. Technol. Adv. Mater. **10**, 024313 (2009).
[8]F. B. Mallory, K. E. Butler, A. C. Evans, and C. W. Mallory, Tetrahedron Lett. **37**, 7173 (1996).
[9]D. M. de Leeuw, M. M. J. Simenon, A. R. Brown, and R. E. F. Einerhand, Synth. Met. **87**, 53 (1997).
[10]T. D. Anthopoulos, G. C. Anyfantis, G. C. Papavassiliou, and D. M. de Leeuw, Appl. Phys. Lett. **90**, 122105 (2007).
[11]D. C. Hoesterey and G. M. Letson, Phys. Chem. Solids **24**, 1609 (1963).
[12]D. Knipp, R. A. Street, and A. R. Volkel, Appl. Phys. Lett. **82**, 3907 (2003).
[13]N. Kawasaki, Y. Ohta, Y. Kubozono, A. Konishi, and A. Fujiwara, Appl. Phys. Lett. **92**, 163307 (2008).
[14]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).
[15]R. J. Chesterfield, J. C. McKeen, C. R. Newman, and 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).
[16]A. K. Tripathi, M. Heinrich, T. Siegrist, and J. Pflaum, Adv. Mater. (Weinheim, Ger.) **19**, 2097 (2007).