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Flexible picene thin film field-effect transistors with parylene gate dielectric and their physical properties

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Flexible picene thin film field-effect transistors (FETs) have been fabricated with parylene gate dielectric on polyethylene terephthalate substrates. The picene thin film FETs show p-channel output/transfer characteristics and the field-effect mobility μ reaches $\sim 1\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ in vacuum. The FET shows a clear O_2 gas sensing effect and negligible hysteresis in the transfer curves, indicating a possible application of the transistor as O_2 selective gas sensor. Furthermore, it has been found that the parylene gate dielectric can eliminate a reduction in on-state drain current caused by continuous bias-voltage application which is observed if a SiO_2 gate dielectric is used. © *2010 American Institute of Physics*. [doi:10.1063/1.3360223]

Organic thin film field-effect transistors (FETs) have many advantages such as mechanical flexibility, compatibility with large area substrates, low-temperature/low-cost fabrication, and many organic FETs have been developed all over the world. However, for the best organic thin film FETs the field-effect mobility, μ, is around $1\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$.[1–5] This is still lower by three orders of magnitude than the μ of $\sim 1000\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$, for inorganic FETs.[6] Recently, we fabricated FET devices with thin films of an aromatic hydrocarbon, picene, and the transistors have a very high μ of $2-3\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ under O_2 atmosphere.[4,5] In addition, the picene thin film FET devices show a clear O_2 gas sensing effect down to ~ 10 ppm of O_2.[7–9] However, the transfer curve in a picene thin film FET has a very large hysteresis which is attributed to H_2O.[4,5,7–9] These results suggest the possibility to simultaneously detect O_2 and H_2O with a picene thin film FET. An O_2 selective gas sensor, which would not be influenced by moisture, is indispensable from an application point of view.

We recently tried to fabricate O_2 selective gas sensors based on picene thin film FETs with SiO_2 gate dielectrics coated with highly hydrophobic polymers, Cytop™ and polystyrene.[8,9] The transfer curves in these picene FETs showed a drastic reduction in hysteresis in comparison with those employing a SiO_2 gate dielectric coated by hexamethyldisilazane (HMDS).[9] Nevertheless, a very small hysteresis was still observed in these picene FETs with Cytop™ and polystyrene coated SiO_2 gate dielectrics.[9] In this letter, we report on the fabrication of flexible picene thin film FETs with parylene gate dielectric which show hysteresis-free transfer curves. A high μ value of $\sim 1.0\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ is realized in the best transistors even under vacuum. This mobility is quite high for a flexible p-channel organic FET.[10–12]

Previous studies have shown that the continuous application of a gate voltage V_G and a drain voltage V_D to a picene thin film FET causes a drastic reduction of the absolute value of the on-state drain current, $|I_D^{on}|$; for this reason the O_2-exposure effect on $|I_D^{on}|$ was studied under an discontinuous application of V_G and V_D.[5,7–9] This phenomenon is also observed in pentacene thin film FETs.[13] It is a serious problem in the development of a practical O_2 gas sensor because a continuous bias voltage cannot be applied to the sensing device. In this study, we have suppressed the reduction of $|I_D^{on}|$ by use of a parylene gate dielectric which provides a very hydrophobic surface and a good surface for the growth of picene.

The picene thin film FETs were fabricated in a top-contact structure [Fig. 1(a)]. Commercially available polyethylene terephthalate (PET) was cleaned by the procedure described elsewhere.[14] Au thin films with a thickness of 50 nm were formed as gate electrode on the PET substrate. The parylene thin films were made on the Au gate electrode by polymerization of parylene-C. We used several methods to determine the capacitance of parylene films. For example, the thickness d of a parylene gate dielectric film was estimated to be 685 nm from the weight of the parylene film (the density $\rho = 1.289\ \mathrm{g\ cm}^{-3}$) formed on a glass substrate placed near the FET device in the parylene deposition process. The d was also directly measured to be 800 nm with an alpha-stepper (Tencor). The measured capacitance C was determined to be 26 pF with a circular gold electrode having a diameter of 1 mm. The capacitance per unit area, C_0, thus is $3.3 \times 10^{-9}\ \mathrm{F\ cm}^{-2}$ for this sample. If we assume a dielectric constant, ε_x, of 2.9 for parylene, the d estimated from C_0 is 775 nm. The d is in good agreement with the value from the alpha-stepper. Consequently, the thickness of this parylene gate dielectric film is ~ 800 nm. Consequently, a C_0 of $3.3 \times 10^{-9}\ \mathrm{F\ cm}^{-2}$ is used for this specific sample. The experimental details for the formation of parylene thin films are described elsewhere.[14] Picene films with a thickness of 50

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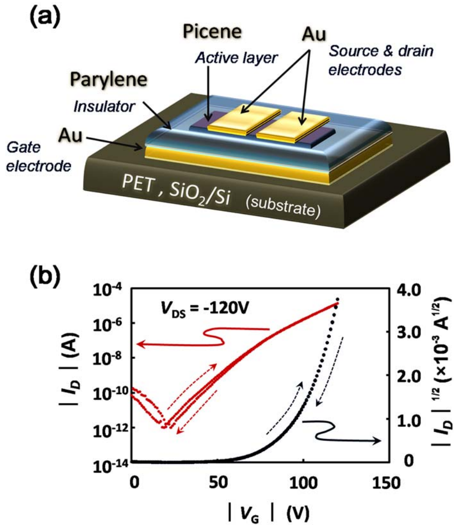

FIG. 1. (Color online) (a) Transistor structure of picene FETs used in the present study. Two types of PET substrates (black and transparent sheets) were used in the devices. (b) Transfer of a picene FET with parylene gate dielectric measured in vacuum. The mobility is as high as 1.1 $cm^2\ V^{-1}\ s^{-1}$ and the transistors have a negligible current hysteresis.

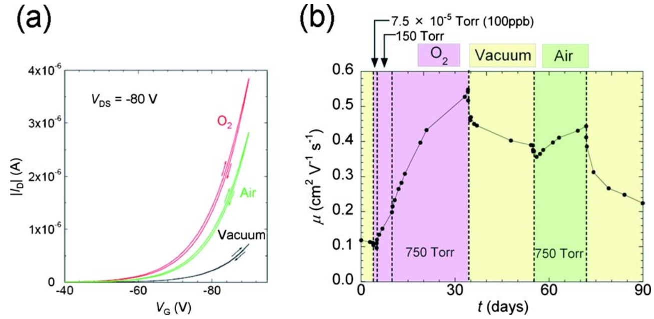

FIG. 2. (Color online) (a) Plots of $|I_D|-|V_G|$ curves under vacuum of $\sim 10^{-8}$ Torr, 750 Torr of air and 750 Torr of O_2. Even in O_2 or air, the transfer characteristics have a negligible current hysteresis. (b) Plot of μ as a function of time. The atmospheric conditions (vacuum, air and O_2) are indicated in the figure. The mobility in the transistor increased by as much as a factor of 5. The purity of O_2 was 99.9999 vol % and the concentration of H_2O in O_2 was <0.5 ppm in this experiment.

nm were then formed on the parylene coated PET substrates; picene was synthesized with a method reported previously.[4] Au source and drain electrodes with a thickness of 50 nm were formed on the picene thin films. Channel length and width were 50–300 and 500–600 μm, respectively. The FET characteristics were measured at room temperature in vacuum, air and O_2 atmosphere; the O_2 gas used in this study contains a trace of H_2O (<0.5 ppm or <0.014 ppm) and the purity of O_2 was 99.9999 vol % or 99.5 vol %.

Figure 1(b) shows transfer curves of a picene thin film FET with a parylene gate dielectric measured under vacuum of 10^{-5} Torr. Clear hole transporting (p-channel) behavior is observed in Fig. 1(b). The μ was determined to be 1.1 $cm^2\ V^{-1}\ s^{-1}$ from both the forward and reverse sweeps referring to the sweeps measured by increasing the absolute gate voltage $|V_G|$ and by decreasing $|V_G|$, respectively. The μ is high for an organic thin film FET with a flexible gate dielectric and substrate. Furthermore, it should be noted that the μ determined from the forward and reverse sweeps are the same. The μ values in previous picene thin film FETs with SiO_2 gate dielectric were largely different when estimated from the forward and reverse sweeps because of a large hysteresis.[4,5,7–9] Furthermore, from the transfer characteristics in Fig. 1(b), the absolute threshold voltage, $|V_{TH}|$, and the on-off ratio were determined to be 93 V and 10^7 for both the forward and reverse sweeps. The same values of μ and $|V_{TH}|$ are a direct result of a negligible hysteresis, as is clearly seen from the transfer curves in Fig. 1(b). By employing parylene as gate dielectric we have achieved transistors without hysteresis. A reduction in hysteresis was already observed in picene thin film FETs with SiO_2 gate dielectrics coated by hydrophobic polymers, Cytop™ and polystyrene,[9] but the hysteresis still remained in the transfer curves. Here it should be noted that Cytop™ is more hydrophobic than parylene or almost has the same hydrophobic nature as parylene because the contact angle on Cytop™ is 90°–110°, or frequently $>110°$.[15] The contact angle on parylene is $\sim 95°$. Consequently, the complete absence of hysteresis in a picene FET with parylene gate dielectric may be due to both the hydrophobic parylene surface and an improved growth of picene on the parylene surface.

Figure 2(a) shows transfer curves of a picene thin film FET with parylene gate dielectric under vacuum of $\sim 10^{-8}$ Torr, 750 Torr of air and 750 Torr of O_2. The slope of the transfer curve is drastically increased in air and O_2 in comparison with the slope in vacuum. Although the O_2 gas exposure effect on picene FETs was already reported,[4,5,7,8] the hysteresis in the present picene FETs with parylene gate dielectrics is very small even under air and O_2 [Fig. 2(a)].

In the following, we describe long-time O_2/air exposure experiments with a picene thin film FET. The μ is plotted as a function of time of the O_2/air exposure and dynamic pumping in Fig. 2(b). The dynamic pumping leads to a reduction in μ, while the O_2/air exposure enhances μ drastically in the same manner as for picene FETs with SiO_2 gate dielectric.[4,5,7–9] However, 7.5×10^{-5} Torr of O_2 gas exposure did not increase the μ of the transistor with parylene gate dielectric; this O_2 gas concentration corresponds to 100 ppb.

On the other hand, 150 and 750 Torr of O_2 gas enhance the μ with almost the same rate. We note that the mobility is increased by as much as a factor of 5 after ~ 30 days in O_2. Moreover, the effect is not at all saturated after 30 days and higher mobility should be possible after a longer O_2 exposure time. Furthermore, the rate of increase for air-exposure is less than 1/3 as compared to the rate for O_2 exposure [Fig. 2(b)]. These results clearly show that O_2 enhances the μ value. As evidenced in Fig. 2(b), the rate of the increase in μ caused by 750 Torr of air is smaller than the rate caused by 150 Torr of O_2, although 750 Torr of air exactly contains 150 Torr of O_2 (O_2 concentration in air: 21%). Possibly, the N_2 contained in air suppresses the enhancement of μ caused by O_2-exposure. We presented a model for O_2-induced μ-enhancement in a previous paper.[5] The essence of this model is that the polarized O_2 molecules, $O_2^{\delta-}$, screen positively charged trap centers and reduce their detrimental effect on charge transport.[5] In the frame of this model, the substitution of $O_2^{\delta-}$ by inert N_2 around the positively charged trap centers should reduce the screening effect and the positively charged traps centers are more effective in impeding the charge transport. Furthermore, the improvement of the device performance due to O_2 may be doping, i.e., the O_2 provides additional positive charge carriers. It is well known that the doping, particularly close to the contacts, leads to an

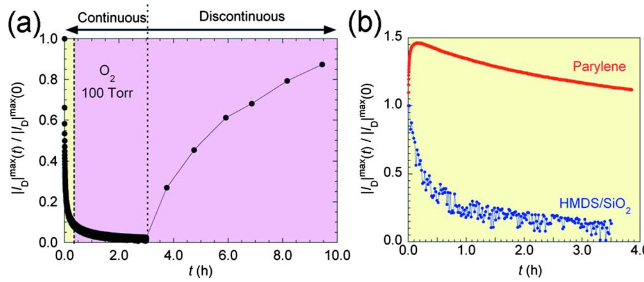

FIG. 3. (Color online) (a) $|I_D|^{max}(t)/|I_D|^{max}(0)$ of a picene thin film FET with SiO_2 gate dielectric coated with HMDS under continuous application of V_G and V_D, followed by discontinuous application of V_G and V_D. The yellow and pink regions refer to vacuum (10^{-5} Torr) and O_2 (100 Torr), respectively. (b) $|I_D|^{max}(t)/|I_D|^{max}(0)$ of picene thin film FETs with HMDS-coated SiO_2 and parylene gate dielectrics under continuous application of V_G and V_D in vacuum (10^{-5} Torr). The purity of O_2 was 99.5 vol % and the concentration of H_2O in O_2 was <0.014 ppm in this study. At $t>0.1$ h, the current decreases very slowly if a parylene gate dielectric is used.

increase in the transistor performance because of a lowering of the contact resistance. The N_2 may occupy the O_2 sites when the sample is exposed to air instead of pure O_2, which makes the doping less efficient. In any case, in spite of the same O_2 partial pressure the increase in μ may be suppressed for 750 Torr of air due to the inert N_2 gas as compared to 150 Torr of O_2.

As is seen from the transfer curves [Figs. 1(b) and 2(a)], a negligible hysteresis is observed for the picene thin film FET with parylene gate dielectric. In our previous picene thin film FETs with SiO_2 gate dielectric, the $|I_D^{on}|$ in the reverse transfer curve is lower than in the forward sweep.[4,5,7–9] This means that $|I_D^{on}|$ reduces after a prolonged application of a high $|V_G|$. Figure 3(a) shows the ratio of the maximum drain current $|I_D|^{max}$ at any time t relative to $|I_D|^{max}$ at $t=0$, i.e., the ratio $|I_D|^{max}(t)/|I_D|^{max}(0)$ for a picene FET with SiO_2 coated by HMDS as gate dielectric. Here, V_G (=−100 V) and V_D (=−100 V) are continuously applied in a vacuum of 10^{-5} Torr and then in 100 Torr of O_2. As seen from Fig. 3(a), $|I_D|^{max}(t)/|I_D|^{max}(0)$ for a picene FET with SiO_2 coated by HMDS exponentially decreases with time t in a vacuum of 10^{-5} Torr, if V_G and V_D are continuously applied. This is due to the bias-stress effect caused by the continuous application of V_G and V_D. Actually, even when the picene FET was exposed to 100 Torr of O_2, the $|I_D|^{max}$ did not enhance under continuous application of V_G and V_D but continued to decreases exponentially, as is seen from Fig. 3(a); the enhancement of $|I_D|^{max}$ by O_2-exposure is completely cancelled out by the rapid decrease due to continuous bias-voltage application.

Such a bias-induced reduction of the drain current was also observed for pentacene FETs with SiO_2 gate dielectric,[13] and in this case $|I_D|^{max}$ rapidly decreases under 2 mbar of H_2O. Consequently, H_2O seems to be responsible for the reduction of $|I_D|^{max}$ under continuous bias application. As is seen from Fig. 3(a), when the continuous application of V_G and V_D to the picene FET was stopped and the measurements of $|I_D|^{max}$ were performed at 1 h intervals, $|I_D|^{max}$ increased gradually. These results clearly show that the continuous application of V_G and V_D suppress the O_2 sensing effect, i.e., the O_2 induced enhancement of $|I_D|^{max}$, if a SiO_2 gate dielectric coated with HMDS is used.

We can focus on the $|I_D|^{max}(t)/|I_D|^{max}(0)$ plots for picene FETs as measured in vacuum of 10^{-5} Torr. In contrast to the $|I_D|^{max}(t)/|I_D|^{max}(0)$ plots for picene FETs with SiO_2 gate dielectric coated with HMDS [Fig. 3(b)] and polystyrene (not shown), the plot for picene FET with parylene gate dielectric shows no rapid decrease, despite of the continuous application of V_G and V_D [Fig. 3(b)]. These results can be understood by the fact that H_2O scarcely exists on the parylene surface. Interestingly, the $|I_D|^{max}(t)/|I_D|^{max}(0)$ increases by a factor of 1.6 during t of 0–0.1 h, and at $t>0.1$ h the ratio decreases very slowly in contrast to the drastic decrease for picene FETs with SiO_2 gate dielectrics coated with HMDS. Although the origin of the initial increase in $|I_D|^{max}(t)/|I_D|^{max}(0)$ remains to be clarified, the observation of a very slow decay of $|I_D|^{max}(t)/|I_D|^{max}(0)$ under continuous application of a bias voltage is very important from viewpoints of gas sensor application. If $|I_D|^{max}(t)/|I_D|^{max}(0)$ decreases rapidly under a continuous bias voltage, the O_2 gas sensing is practically impossible. The realization of an almost constant $|I_D|^{max}$ under continuous application of V_G and V_D is of crucial importance for the application of organic field-effect transistors as O_2 gas sensors.

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