Variation of output properties of perylene field-effect transistors by work function of source/drain electrodes

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(Received 21 March 2006; accepted 14 June 2006; published online 2 August 2006)

Field-effect transistor (FET) devices with thin films of perylene have been fabricated with various metal electrodes exhibiting work function ϕ from 2.5 to 5.1 eV. All perylene FET devices show *p*-channel FET properties. The *p*-channel field-effect mobility μ_p and the on-off ratio in the perylene FET increase with an increase in ϕ of the metal electrodes. The *n*-channel conduction is also observed for the FET devices with Eu and Sr electrodes exhibiting small ϕ. These results can be reasonably explained on the basis of energy barrier for hole or electron. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2266596]

Field-effect transistor (FET) devices with thin films of fullerenes and organic molecules have attracted special attention because of structural flexibility, low-temperature/low-cost processing, and large-area coverage.[1,2] Most of organic thin-film FETs show either *n*- or *p*-channel property. The C_{60} thin-film FET device showed *n*-channel normally off FET properties exhibiting high *n*-channel field-effect mobility μ_n of 0.6 $cm^2\,V^{-1}\,s^{-1}$,[3,4] while the pentacene thin-film FET device showed *p*-channel normally off properties with the highest *p*-channel field-effect mobility μ_p of $\sim$1.5 $cm^2\,V^{-1}\,s^{-1}$ among all known FETs with organic thin films.[5]

Recently, the *n*-channel FET properties in the pentacene FET device were observed by using Ca metal for source/drain electrodes in the device.[6] Since the work function ϕ value of Ca metal is 2.87 eV,[7] electrons could go without energy barrier from the source electrode to the lowest unoccupied molecular orbital (LUMO) of pentacene with the energy level $E_{\rm LUMO}$ of -3.2 eV.[6] Furthermore, the *p*-channel operation in the C_{60} FET was realized with approaching the ϕ value of the electrodes to the highest occupied molecular orbital (HOMO) of C_{60} ($E_{\rm HOMO}=-6.17$ eV) (Ref. 8) by modifying Au electrodes with self-assembly monolayers (SAMs).[9] In this letter, we have studied the properties of perylene FET devices fabricated with source/drain metal electrodes exhibiting the ϕ value of 2.5–5.1 eV.

The SiO_2/Si substrate was cleaned and a hydrophobic treatment for the surface was performed based on the procedure reported elsewhere.[10] The thickness of SiO_2 layer and the capacitance C_0 were 400 nm and 8.6×10^{-9} F cm^{-2}, respectively. The thin films of perylene with a thickness of 150 nm were formed by a thermal deposition of commercially available perylene (Aldrich Co.: 99.5%) under 10^{-8} Torr. The metal electrodes of 50 nm thickness were attached as source/drain electrodes on the thin films of perylene. The device structure is the top-contact type [Fig. 1(a)] with channel length L and the channel width W of 30 and 6000 μm, respectively.

The plots of the drain current I_D versus the drain-source voltage $V_{\rm DS}$ in the perylene FET device with Cu source/drain electrodes show *p*-channel normally off properties [Fig. 1(b)], as in the perylene FET with Au source/drain electrodes reported previously.[11] The values of μ_p and threshold voltage V_T were determined to be 5.9×10^{-3} $cm^2\,V^{-1}\,s^{-1}$ and -28 V, respectively, from the $|I_D|^{1/2}$-$|V_G|$ plot [Fig. 1(c)] at $V_{\rm DS}=-100$ V (saturation region) with general equation for FET.[12] The μ_p value of 5.9×10^{-3} $cm^2\,V^{-1}\,s^{-1}$ is comparable to that

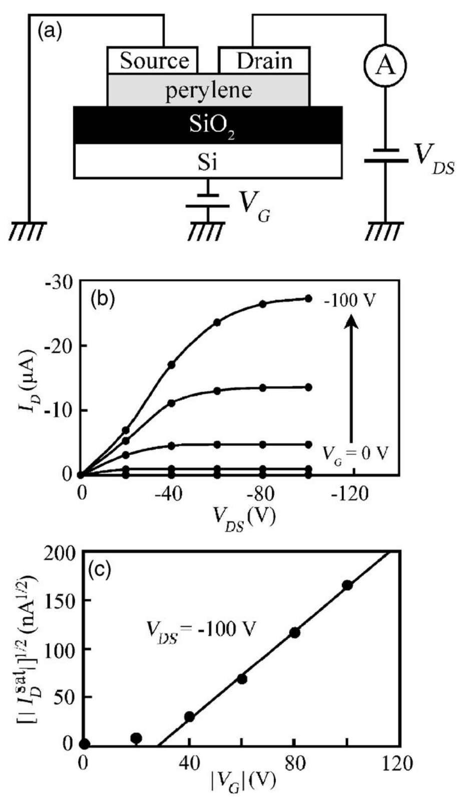

FIG. 1. (a) Device structures of perylene thin-film FET. The *p*-channel measurement mode is shown in (a). (b) I_D-$V_{\rm DS}$ plots measured in *p*-channel mode and (c) I_D-V_G plot ($V_{\rm DS}=-100$ V) of perylene thin-film FET device with source/drain electrodes of Cu.

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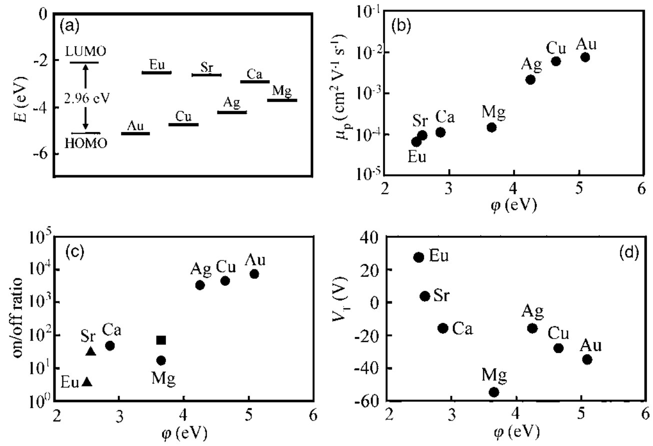

FIG. 2. (a) Energy level diagram of various metals used for source/drain electrodes and HOMO/LUMO of perylene; $E_F=-\phi$, and E_{LUMO} and E_{HOMO} are defined from photoemission data and optical gap (Refs. 13 and 14). ϕ dependence of (b) μ_p, (c) on-off ratio, and (d) V_T in perylene thin-film FET device. For Mg in (c), "■" refers to the ratio of I_D ($V_G=-100$ V) to I_D ($V_G=0$ V), respectively. See text for "●" and "▲."

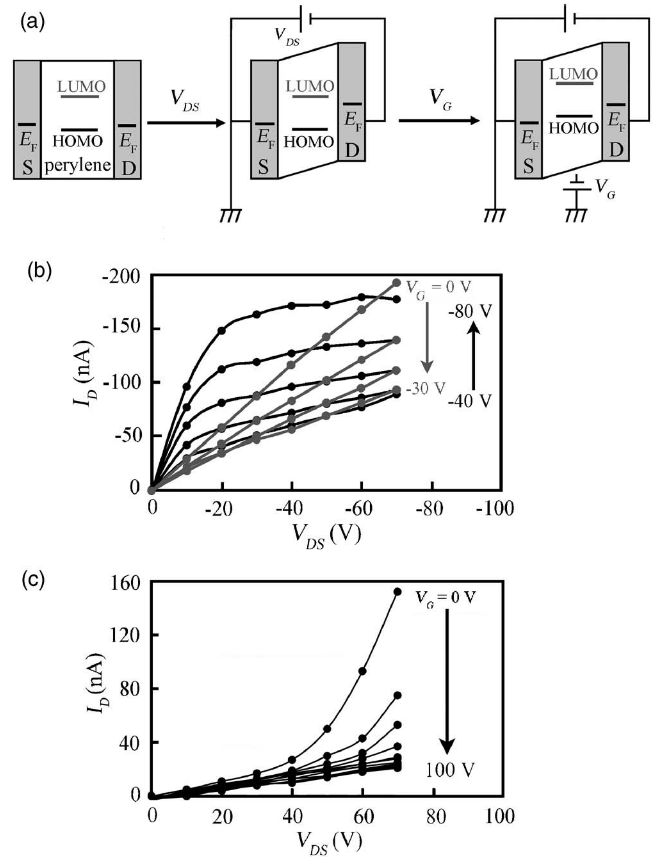

FIG. 3. (a) Schematic representation of FET operation in FET device with metal electrodes of large ϕ. Left: No application of V_{DS} and V_G. Center: Only application of V_{DS}. Right: Application of V_{DS} and V_G. I_D-V_{DS} plots of the FET device with Eu in the (b) *p*-channel measurement mode and (c) *n*-channel measurement mode.

for the device with Au electrodes, 7.0×10^{-3} cm^2 V^{-1} s^{-1}.[11]

Figure 2(a) shows the Fermi energy levels E_F $(=-\phi)$ of various metal electrodes[7] and the E_{HOMO} and E_{LUMO} of perylene. The E_{HOMO} and E_{LUMO} values were determined from photoemission spectrum and optical gap reported previously.[13–15] The carrier responsible for *p*-channel conduction is hole, and the energy difference between the E_F of metal electrodes and E_{HOMO} of perylene corresponds to the energy barrier for holes, when the E_F is higher than the E_{HOMO}. When the E_F of metal is lower than the E_{HOMO}, no energy barrier exists for hole in going from the metal electrode to the HOMO. On the other hand, the use of the metal electrodes with small ϕ such as Eu (ϕ=2.5 eV), Sr (ϕ =2.59 eV), and Ca (ϕ=2.87 eV) should lead to small energy barrier from the source electrode to the LUMO for electrons.

The schematic representation of energy diagram in the source electrode/perylene thin films/drain electrode is shown in Fig. 3(a); the energy difference between E_F of metal electrodes and E_{HOMO} is assumed to be small. When the V_{DS} (<0) was applied in *p*-channel measurement mode, the E_F of drain electrode rises. Furthermore, the HOMO rises and gets over the E_F of source electrode when the negative V_G was applied to perylene thin films. In this case, the channel conduction is realized from source to drain electrodes across perylene thin films. Consequently, the high efficiency for hole injection from source to HOMO should be realized when the difference between E_F and E_{HOMO} is small.

The μ_p values of the perylene FET devices are plotted in Fig. 2(b) as a function of ϕ; all μ_p values are determined from the $|I_D|^{1/2}$-$|V_G|$ plot in the saturation. The μ_p value increases drastically with an increase in ϕ from 2.5 eV for Eu electrode to 5.1 eV for Au electrode. Here it should be noted that the injection efficiency of holes from the source electrode to the HOMO of perylene increases with an increase in ϕ because of the lowering of the energy barrier for holes, as seen from Fig. 2(a). Therefore, the μ_p value seems to be closely associated with the injection efficiency of hole. Therefore, the μ_p estimated for the perylene FET may be the value containing the injection efficiency, i.e., the apparent increase in μ_p may be observed because of the increase in injection efficiency of hole produced by the lowering of the energy barrier.

The on-off ratio determined from the ratio of the I_D at $V_G=-60$ V to that at $V_G=0$ V for the FET devices with metal electrodes other than Sr and Eu is plotted in Fig. 2(c) as a function of ϕ: the ratio of the I_D at $V_G=-70$ V to that at $V_G=-30$ V for Sr and the ratio of the I_D at $V_G=-80$ V to that at $V_G=-40$ V for Eu. The value also increases with an increase in ϕ as in the case of the μ_p value [Fig. 2(b)]. The on-off ratio links with the channel current induced by V_G for the FET devices with Ca, Mg, Ag, Cu, and Au since these FET properties are normally off. On the other hand, the normally on properties, whose origin is described later, are responsible for the drastic decrease in the on-off ratio for the FET devices with Eu and Sr electrodes. Consequently, we can conclude that, for the FET devices with Ca, Mg, Ag, Cu, and Au electrodes, the increase in injection efficiency for hole accompanied by the increase in ϕ produces the increase in the on-off ratio, and that, for the FETs with Eu and Sr, the realization of *n*-channel conduction leads to the drastic decrease in the on-off ratio. Here, it is meaningful to notice that the relatively low on-off ratio for Mg originates from the high $|V_T|$ ($\sim$60 V) [Fig. 2(d)] in comparison with other metal electrodes (Ca, Ag, Cu, and Au). When the ratio of the I_D at $V_G=100$ V to that at $V_G=0$ V is plotted, the on-off ratio becomes the value between Ag and Ca [Fig. 2(c)], as is expected; the use of the I_D value at $V_G=100$ V is reasonable for the comparison with other on-off ratios because of the higher

$|V_T|$ by ~40 V in the FET device with Mg electrodes than those with other metal electrodes (Ca, Ag, Cu, and Au).

The V_T value is plotted in Fig. 2(d) as a function of ϕ. The correlation between V_T and ϕ could not clearly be observed in this plot, regardless of the expectation that the V_T will increase from the negative (normally off) to the positive value (normally on) with an increase in ϕ because of the decrease in the energy barrier for hole. Here it should be noted that the *n*-channel conduction occurs in the FET devices with Sr and Eu electrodes, as described later. Therefore, the positive V_T value in the FET devices with Sr and Eu electrodes originates from *n*-channel conduction, i.e., the V_T does not directly reflect the energy barrier of hole.

The large negative V_T for Mg can be explained by the large energy difference between the E_F and E_{HOMO}. Furthermore, the smaller negative V_T for the FETs with Ag, Cu, and Au than that with Mg is reasonable from viewpoints of the energy barrier for hole. On the other hand, the order of V_T among the FETs with metal electrodes of Ag, Cu, and Au cannot be explained only by the energy barrier. The other factors such as electron transfer from metal to perylene thin films and d-π interaction between metal electrodes and perylene may contribute to the V_T.

Figure 3(b) shows the I_D-V_{DS} plots for the perylene thin-film FET device with Eu electrodes (2.5 eV) in *p*-channel mode. The large $|I_D|$ is observed at V_G of 0 V. The $|I_D|$ value decreases by varying V_G from 0 to −30 V and increases by varying from −40 to −80 V. This suggests that the *n*-channel conduction is depleted by varying the V_G from 0 to −30 V, i.e., the ambipolar FET properties are induced. This result is also observed in the FET device with Sr electrodes (ϕ=2.59 eV), but the $|I_D|$ at V_G=0 V is lower than that with Eu electrodes. This reflects directly the energy difference between the E_F of metal and LUMO level, i.e., energy barrier for the electrons from source electrode to LUMO. The energy barrier is 0.36 eV for Eu and 0.45 eV for Sr. On the other hand, as seen from Fig. 3(c), only depletion of *p*-channel conduction was observed at V_G from 0 to 100 V in the FET devices with Eu and Sr. This implies that the ambipolar properties in the FET device are largely inclined to *p*-channel conduction.

The lowering of the V_T as well as the increase in μ_n were observed in the C_{60} FET with tetrakis(dimethylamino)ethylene (TDAE)-coated Au electrodes.[3] These originate from a lower energy barrier for electron in the C_{60} FET with TDAE-coated Au electrodes than that in the FET with Au electrodes. In this study, it has been found that the μ_p and the on-off ratio in the perylene thin-film FET device increase with an increase in ϕ of source/drain metal electrodes. This result can be reasonably explained by the reduction of energy barrier for hole, as in the C_{60} FET.[3] However, contrary to the case of C_{60},[3] the correlation between V_T and ϕ could not clearly be found because the V_T value was affected by various factors such as ambipolar property. The ambipolar properties were realized in the FET devices with Eu and Sr electrodes exhibiting small ϕ values. Consequently, we stress that the ϕ value of metals used for source and drain electrodes affects directly the FET properties.

The authors appreciate K. Yokoo and Y. Iwasa of Tohoku University and K. Seki of Nagoya University for their valuable suggestion. This study is partly supported by a Grant-in-Aid (18340104) from MEXT, Japan.

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