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Description	

# Hole-injection barrier in pentacene field-effect transistor with Au electrodes modified by $C_{16}H_{33}SH$

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Field-effect transistor with thin films of pentacene has been fabricated with Au electrodes modified by 1-hexadecanethiol ( $C_{16}H_{33}SH$ ), and the hole-injection barriers have been determined from the temperature dependence of output properties on the basis of the thermionic emission model for double Schottky barriers. The large tunneling barriers are formed by the insulating  $C_{16}H_{33}SH$  at the interfaces between the Au electrodes and pentacene thin films. © 2007 American Institute of Physics. [DOI: 10.1063/1.2789699]

Interface control is a very important technique for the realization of high-performance field-effect transistor (FET) devices. Recently, the Fermi level matching of the source/drain electrodes to the conduction/valence band of organic active layers produced *n*-, *p*-, and ambipolar FET properties.<sup>1-3</sup> These results opened the possibility of the FET devices with organic molecules. We also observed high  $\mu$  value of  $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the  $C_{60}$  FET with the Eu electrodes which possess low work function  $\phi$  of 2.5 eV.<sup>4</sup> This contact material has produced the Ohmic contact or effective carrier injection between the electrodes and  $C_{60}$  thin films.

In order to clarify the mechanism of carrier injection from electrodes to active layers, we analyzed the transport properties of the  $C_{60}$  FET devices with Au electrodes modified by 1-alkanethiols ( $C_nH_{2n+1}SH$ ) on the basis of the thermionic emission model for double Schottky barriers.<sup>5,6</sup> The effective Schottky barrier height  $\phi_B^{\text{eff}}$  and tunneling efficiency  $\beta$  of electron for alkyl chains were determined and the electronic structures at the interface between the electrodes and  $C_{60}$  thin films were fully investigated. The  $\phi_B^{\text{eff}}$  contains contributions from both Schottky barrier of pure Au- $C_{60}$  junction and additional tunneling barrier formed by  $C_nH_{2n+1}SH$ . However, the Schottky barrier and the tunneling of the hole through alkyl chains at the interface of the *p*-channel organic FET devices have not been investigated so far.

In this study, we have investigated hole injection from the Au electrodes to pentacene thin films within the framework of thermionic emission model for double Schottky barriers.<sup>5,6</sup> The pentacene thin-film FET device with Au electrodes modified by 1-hexadecanethiol ( $C_{16}H_{33}SH$ ), pentacene/ $C_{16}H_{33}SH$  FET, showed large effective hole-injection barrier  $\phi_{\text{bh}}^{\text{eff}}$  and it allowed us to provide useful information on Au-pentacene junctions in the FET device.

The device structure is shown in Fig. 1(a); the details of the dimensions are shown in the caption of Fig. 1(a). The processes for a cleaning of the surface of Si(100)/ $\text{SiO}_2$  wafers and for the formation of Au electrodes are described elsewhere.<sup>5,6</sup> The surface of Au electrodes was modified with  $C_{16}H_{33}SH$  by immersing the Si/ $\text{SiO}_2$ /Cr/Au substrates into the ethanol (EtOH) solution of  $C_{16}H_{33}SH$  ( $10^{-1} \text{ mol l}^{-1}$ ) for

47 h. The molecular structure of  $C_{16}H_{33}SH$  is shown in Fig. 1(b). The substrates were washed with EtOH and ultrapure  $\text{H}_2\text{O}$ . The expected structure of  $C_{16}H_{33}SH$  on the Au surface<sup>7,8</sup> is shown in Fig. 1(c). The thin films (50 nm) of pentacene were formed on the substrate maintained at room temperature  $T$  by a thermal deposition under vacuum of  $10^{-8}$  Torr. The transport characteristics of the FET devices were measured under vacuum of  $10^{-6}$  Torr without annealing of the devices.

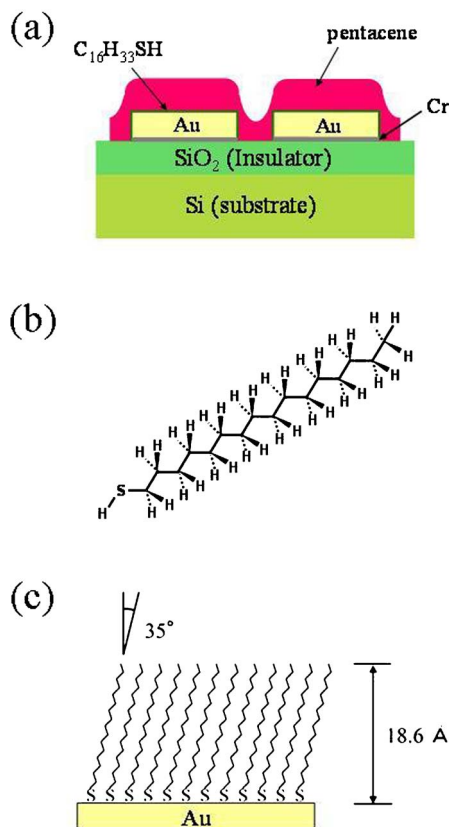


FIG. 1. (Color online) (a) Device structure of pentacene thin-film FET. The thicknesses of Cr, Au, and pentacene are 5, 50, and 50 nm, respectively. The channel width  $W$  and length  $L$  are 4000 and 30  $\mu\text{m}$ , respectively. The thickness and capacitance  $C_0$  of  $\text{SiO}_2$  are 400 nm and  $8.63 \times 10^{-9} \text{ F cm}^{-2}$ , respectively. (b) Molecular structures of  $C_{16}H_{33}SH$ . (c) Schematic representation of the surface of Au electrodes modified by  $C_{16}H_{33}SH$ .

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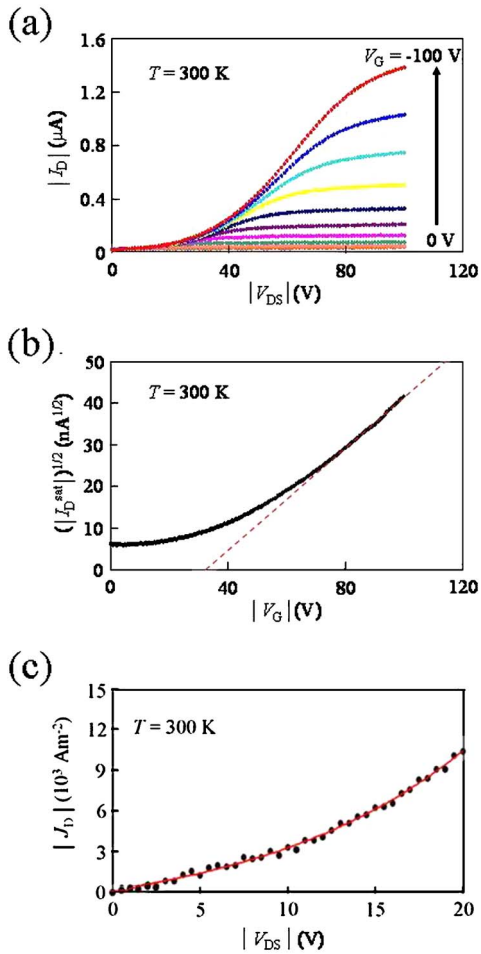


FIG. 2. (Color online) (a)  $|I_D|$ - $|V_{DS}|$ , (b)  $|I_D^{\text{sat}}|^{1/2}$ - $|V_G|$ , and (c)  $|I_D|$ - $|V_{DS}|$  plots of pentacene/ $C_{16}H_{33}SH$  FET at 300 K. The fitted lines are drawn for (b) with  $(|I_D^{\text{sat}}|)^{1/2} = (\mu WC_0/2L)^{1/2}(|V_G| - |V_T|)$  and for (c) with Eq. (3).

The absolute drain current  $|I_D|$  versus absolute source-drain voltage  $|V_{DS}|$  plots of the pentacene/ $C_{16}H_{33}SH$  FET device show  $p$ -channel normally off FET properties [Fig. 2(a)]. The  $|I_D|$ - $|V_{DS}|$  plots also show clear concave-up non-linear behaviors in the low  $V_{DS}$  region, which shows that the hole transport is strongly suppressed by the large effective hole-injection barrier  $\phi_{\text{bh}}^{\text{eff}}$ . The  $|I_D|$  increases linearly in the intermediate region for the pentacene/ $C_{16}H_{33}SH$  FET [Fig. 2(a)] and saturates in the high  $V_{DS}$  region.

The values of  $\mu$  and  $V_T$  were determined from the drain current  $|I_D^{\text{sat}}|$  in the saturation region ( $V_{DS}=100$  V), i.e.,  $|I_D^{\text{sat}}|^{1/2}$  versus absolute gate voltage  $|V_G|$  plot [Fig. 2(b)], to be  $6.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and 35 V at 300 K, respectively. The  $\mu$  value is lower by one order of magnitude than the value,  $5.9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , of  $C_{60}/C_{16}H_{33}SH$  FET.<sup>5</sup> The absolute drain current density  $|J_D|$  vs  $|V_{DS}|$  plot in the low  $V_{DS}$  region (0–20 V) at  $V_G=100$  V for the pentacene/ $C_{16}H_{33}SH$  FET device ( $T=300$  K) is shown in Fig. 2(c) together with the calculated (fitting) line. The fitting line was drawn according to Eq. (1) based on the thermionic emission model expanded to double Schottky barriers because this device possesses two Au-pentacene junctions modified by  $C_{16}H_{33}SH$  (source Au electrode-pentacene and pentacene-drain Au electrode),<sup>5</sup>

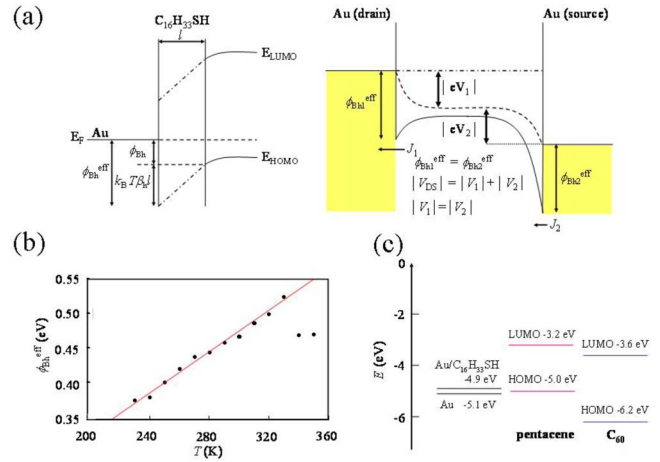


FIG. 3. (Color online) (a) (Left) Schematic representation of band bending for pentacene-Au junction modified by  $C_{16}H_{33}SH$  and (right) that of band bending (solid line) for double Schottky barriers in pentacene/ $C_{16}H_{33}SH$  FET. In the right figure, the additional tunneling barriers due to  $C_{16}H_{33}SH$  are not drawn. (b)  $\phi_{\text{bh}}^{\text{eff}}$ - $T$  plot for pentacene  $C_{16}H_{33}SH$ /FET. (c) Band diagram of  $E_F$  of Au,  $E_{\text{HOMO}}$ , and  $E_{\text{LUMO}}$  of pentacene and  $C_{60}$ .

$$J_D = A^* T^2 \times \exp(-\phi_{\text{bh}}^{\text{eff}}/k_B T) \sinh[eV_{DS}/(2k_B T)] / \cosh(eV_{DS}/2k_B T), \quad (1)$$

where  $A^*$ ,  $e$ , and  $k_B$  are the effective Richardson constant, electron charge, and Boltzmann constant, respectively. The  $A^*$  and  $\phi_{\text{bh}}^{\text{eff}}$  are given by Eqs. (2) and (3), respectively,

$$A^* = 4\pi e m_p^* k_B^2 / h^3 \quad (2)$$

and

$$\phi_{\text{bh}}^{\text{eff}} = \phi_{\text{bh}} + k_B T \beta_h l. \quad (3)$$

Here  $m_p^*$ ,  $h$ ,  $\phi_{\text{bh}}$ ,  $\beta_h$ , and  $l$  are the effective mass of hole, Planck's constant, hole-injection barrier height of pure Au-pentacene junction, tunneling efficiency of hole, and length of tunneling barrier, respectively. In the analyses, the  $m_p^*$  was fixed to be  $1.55m_0$  based on the value reported previously;<sup>9</sup>  $m_0$  is the electron rest mass. The term  $k_B T \beta_h l$  in Eq. (3) refers to the additional tunneling barrier produced by insertion of  $C_{16}H_{33}SH$ .

The energy band diagram for the Au-pentacene junction modified by  $C_{16}H_{33}SH$  and the simplified energy diagram for two junctions under the application of  $V_{DS}$  is shown in Fig. 3(a). In this model, most of  $V_{DS}$  is assumed to be applied to the interfaces of the two junctions because the channel resistance is small at  $V_G=100$  V ( $>V_T$  of 35 V) in comparison with the contact resistance. In the estimation of  $J_D$ , the thickness of channels is assumed to be 1 nm based on Ref. 10. The  $\phi_{\text{bh}}^{\text{eff}}$  value at 300 K was determined to be  $0.467 \pm 0.003$  eV by least-squares fitting to the  $J_D$ - $V_{DS}$  plot (0–20 V) with Eq. (1). The  $n$  value at 300 K was  $1.0043 \pm 0.0002$ . This value is close to the ideal value of unity, suggesting that two junctions of this device are almost ideal Schottky diodes. The  $\phi_{\text{bh}}^{\text{eff}}$  value is smaller than the  $\phi_B^{\text{eff}}$  ( $=0.51 \pm 0.02$  eV) determined for the  $C_{60}/C_{16}H_{33}SH$  FET.<sup>5,6</sup>

In the  $|I_D|$ - $|V_{DS}|$  plots ( $V_G=100$  V) at 230–350 K for pentacene/ $C_{16}H_{33}SH$  FET, the large concave-up nonlinearity in the low  $V_{DS}$  region is observed in the plots at low  $T$  region (not shown). The  $\phi_{\text{bh}}^{\text{eff}}$  value was determined from the  $J_D$ - $V_{DS}$  plot of  $V_{DS}=0$ –20 V at  $V_G$  of 100 V at each  $T$  with Eq. (1).

The  $\phi_{\text{bh}}^{\text{eff}}-T$  plot is shown in Fig. 3(b). As expected from Eq. (3), the linear relationship was observed in the  $\phi_{\text{bh}}^{\text{eff}}-T$  plot below 340 K. The values at 340 and 350 K deviate from the line. This corresponds to the variation from concave-up non-linear  $I_{\text{D}}-V_{\text{DS}}$  curve to linear line above 330 K, which suggests that the hole-injection barrier is gradually destroyed because of the thermal fluctuation of  $\text{C}_{16}\text{H}_{33}\text{SH}$  on Au electrodes.

The  $\phi_{\text{bh}}$  and  $\beta_h$  values for pentacene/ $\text{C}_{16}\text{H}_{33}\text{SH}$  FET have been determined by least-squares fit to  $\phi_{\text{bh}}^{\text{eff}}-T$  plot [Fig. 3(b)] with Eq. (3). When the  $l$ , 18.6 Å, of  $\text{C}_{16}\text{H}_{33}\text{S}-\text{Au}$  is used as the length to the tunneling barrier in this analysis [Figs. 1(c) and 3(a)],<sup>8</sup> the  $\beta_h$  value can be determined to be  $0.91 \pm 0.03 \text{ \AA}^{-1}$ , whose value is almost the same as the  $\beta$  value,  $1.12 \pm 0.06 \text{ \AA}^{-1}$ , for electron in  $\text{C}_{60}/\text{C}_{16}\text{H}_{33}\text{SH}$  FET.<sup>5,6</sup> This implies that the efficiency of the carrier tunneling across the  $\text{CH}_2$  chain is not much different for electrons and holes. If a vacuum barrier was assumed between Au and pentacene, the  $\beta_h$  would be estimated to be  $2.28 \text{ \AA}^{-1}$  since the highest occupied molecular orbital (HOMO) level,  $E_{\text{HOMO}}$ , of pentacene and the  $E_{\text{F}}$  of Au modified by  $\text{C}_{16}\text{H}_{33}\text{SH}$  is  $-5.0$  and  $-4.9$  eV, respectively, as seen from Fig. 3(c).<sup>1,5</sup> This  $\beta_h$  value of  $2.28 \text{ \AA}^{-1}$  is more than two times larger than the experimental value ( $0.91 \pm 0.03 \text{ \AA}^{-1}$ ). This result implies that the holes can pass through the  $\text{C}_{16}\text{H}_{33}\text{S}-\text{Au}$  more easily than through the vacuum barrier.

The  $\phi_{\text{bh}}$  value can be determined from the  $\phi_{\text{bh}}^{\text{eff}}-T$  plot [Fig. 3(b)] to be  $0.03 \pm 0.01$  eV. This value is smaller than that,  $0.09 \pm 0.03$  eV, determined from the  $\phi_b^{\text{eff}}-T$  plot for the  $\text{C}_{60}/\text{C}_{16}\text{H}_{33}\text{SH}$  FET.<sup>5</sup> From the band diagram of Au and pentacene, for holes, the Schottky barrier height between Au and pentacene can be expected to be 0.1 eV [Fig. 3(c)], whose value is slightly larger than the experimental  $\phi_{\text{bh}}$  value of  $0.03 \pm 0.01$  eV determined in this study. The deviation of experimental  $\phi_{\text{bh}}$  from the value expected from the simple band picture may be due to the lowering of actual Schottky barrier height produced by interface states, mirror charge effect, and electric double layer formed at the interface. However, this deviation is much smaller than the case of  $\text{Au}-\text{C}_{60}$  junctions

(experimental  $\phi_B$ : 0.09 eV, the Schottky barrier height expected from simple band picture: 1.5 eV).<sup>5</sup>

In conclusion, the  $J_{\text{D}}-V_{\text{DS}}$  curves of the pentacene/ $\text{C}_{16}\text{H}_{33}\text{SH}$  FET could be analyzed reasonably well within the thermionic emission model for double Schottky barriers, and the reliable values of  $\phi_{\text{bh}}$  and  $\beta_h$  have been determined for the FET device. In the pentacene/ $\text{C}_{16}\text{H}_{33}\text{SH}$  FET device, more than 90% in the  $\phi_{\text{bh}}^{\text{eff}}$  at 300 K is contributed from the additional tunneling barrier, which is associated with the tunneling of hole through  $\text{C}_{16}\text{H}_{33}\text{SH}$  insulators inserted into the Au-pentacene junctions. As the reliable parameters for the Schottky barrier heights in the  $p$ -channel pentacene FET devices are obtained by the application of thermionic emission model for double Schottky barriers to the  $J_{\text{D}}-V_{\text{DS}}$  curves in the same manner as the case of  $n$ -channel  $\text{C}_{60}$  FET,<sup>5,6</sup> this analysis has been shown to be useful for the investigation of carrier injections in both  $n$ - and  $p$ -channel organic FET devices.

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