Field effects on electron conduction through self-assembled monolayers

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The electronic conduction through the self-assembled monolayer (SAM) can be modulated by the electric potential applied to the silicon gate electrode surrounding the SAM. The dependence of the current through SAM on the gate voltage can be explained that the renormalized molecular energy levels are swept through the window between the Fermi levels of the source and drain electrodes. The effects of the lowest unoccupied molecular orbital and a hybrid energy level near the Fermi level in the transmission spectrum can be identified. © 2006 American Institute of Physics.

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One of the major obstacles of the developments of the molecular electronics is the lack of stable designs of the devices that the field effects as well as the temperature dependence of the electronic conduction can be reproducibly studied.1 The field effects are of prime importance to the design of field effect transistors.2–7

In this letter, we present a design of three-electrode molecular device based on the preferential silicon etching in a heated KOH solution8–10 to create a nanopore on a silicon-on-insulator wafer. A schematic view of the three-electrode self-assembled monolayer (SAM) device is depicted in Fig. 1. Figure 1(a) shows the final form of the three-electrode molecular device. The enlarged central portion [the AA’ plane marked on Fig. 1(a)] of the nanopore is shown in Fig. 1(b). The square pore was filled with alkanethiol molecules that were adsorbed on the bottom Au electrode. The length of the edge of the gate oxide area in the AA’ plane is estimated to be 350 nm for a 200 nm thick gate oxide, which is at least seven times larger than the size of the nanopore, and hence ensures the uniformity11 of the electric potential experienced by the SAM. A scanning electron microscopy (SEM) image of the nanopore before the final thermal oxidation is illustrated in Fig. 1(c). The conductivity measurements were carried out at different temperatures with a commercial semiconductor characterization system.

Figure 2(a) displays the drain current ($I_d$) as a function of the positive value of drain voltage ($V_d$) for various gate voltages ($V_g$) in the range from −10 to 6.0 V at $T=210$ K. Whereas Fig. 2(b) shows several $I_g-V_d$ characteristics on the negative values of $V_d$ for different gate voltages from −2.0 to 1.0 V at 210 K. The reason to present them separately is because their drain current responses to the change of gate voltages are quite different in both the magnitude and the dependence on $V_g$. It is clear from the data shown in Figs. 2(a) and 2(b) that the $I_g-V_d$ curves vary strongly with $V_g$. The measurement ranges are carefully chosen to keep the drain currents from exceeding 10 μA, so as to avoid the local heating effects. With such a precaution, our data are highly reproducible for many temperature scans.

The dependence of $I_g$ on $V_g$ for $V_d>0$ V and that for $V_d<0$ V at $T=210$ K are demonstrated in Figs. 3(a) and 3(b), respectively. These data were taken in different runs of measurements from those shown in Fig. 2. For $V_d<0$ V [Fig. 3(b)], the drain current undergoes a steplike increase as the applied gate voltage is scanned from −2.0 to 0.5 V. Besides, the rising edge shifts positively as $V_d$ stepped from −2.00 to −0.80 V; meanwhile, the width of the rising region decreases. For $V_d>0$ V [Fig. 3(a)], one can find that $I_d$ first decreases as $V_g$ goes positively, reaches to a minimum, then increases to a plateau, and decreases again to a small value as $V_g$ scanned from −10 to 6 V.

In the following, we will use the assumption that the energies of the renormalized molecular levels12,13 can be shifted relative to the Fermi energy of the gold electrode by the scan of $V_g$ to explain the observed dependence of $I_d$ on $V_g$. The current $I_d$ flowing through the alkanethiol monolayer can be expressed as follows:1,13

$$I(V_g, V_d) = \frac{2e^2}{h} \int T(E + eV_g, V_d) \left[ f\left(E - \frac{eV_d}{2}\right) - f\left(E + \frac{eV_d}{2}\right) \right] dE,$$

(1)

where $T$ is the transmission function, $f$ the Fermi function of gold, and $E$ the energy of transmitting electron. The above expression can also be represented by the schematic energy diagram8 shown in Fig. 4. Only the transmission function is schematically drawn in Fig. 4. The initial conditions, where $V_g=0$ V and $V_d=0$ V, and the alkanethiol SAM sandwiched between the source and drain gold electrodes, are depicted in Fig. 4(a). Hybrid energy levels of the gold-alkanethiol-gold assembly are formed in the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital of the alkanethiol molecule, which, in terms, contribute a small peak to the transmission function just below the Fermi level of the whole assembly.

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When a negative bias of drain voltage $V_d$ is applied to the drain electrode, the energy of the Fermi level of the drain is raised by $eV_d$, as shown in Fig. 4. Once a rather large negative $V_g$, for example, $V_g = -2.0 \, \text{V}$ in Fig. 4, is applied to the gate electrode, the hybrid level is shifted up and out of the window between the two Fermi levels of source and drain electrodes. The drain current through the SAM would be very small due to the fact that there is no appreciable value of the transmission function in the window and the integration in Eq. (1) would be close to zero. As $V_g$ is increased positively, the hybrid level is shifted downward. Once the hybrid level overlaps with the window, the magnitude of the drain current would rise up and level off when the whole hybrid level is embedded in the window and the integration in Eq. (1) is constant.

The results shown in Fig. 3(a) can be explained with the energy-potential diagram depicted in Fig. 4(d). When a positive bias $V_d$ is applied to the drain electrode, the Fermi level of the drain electrode would be lowered, as shown in Fig. 4(d). One may start with a large value of positive $V_x$, for example, $V_x = 6 \, \text{V}$ in Fig. 3(a), the energy of LUMO will be shifted below the Fermi level of the drain electrode, and then moved upward as $V_x$ is scanned negatively. As LUMO overlaps with the window between the two Fermi levels, the drain current $I_d$ increases. A maximum rising rate occurs at $V_x = +0.9 \, \text{V}$ in the inset of (a).

FIG. 1. Schematics of the device structure. (a) Cross section of the three-electrode device, with a magnified top view of the cut through the AA' plane shown below. (b) Enlarged central region of the device. The top and bottom gold films serve as the drain and source electrodes, respectively. (c) SEM picture of the nanopore.

FIG. 2. $I_d$ vs $V_d$ curves of a three-electrode octanethiol SAM device for (a) $V_d > 0 \, \text{V}$ and (b) $V_d < 0 \, \text{V}$.

FIG. 3. $I_d$ vs $V_g$ curves for (a) $V_d > 0 \, \text{V}$ and (b) $V_d < 0 \, \text{V}$. The ranges of $V_g$ are different in (a) and (b). The absolute value of the derivative of $I_d$ with respect to $V_g$ for $V_d = +0.9 \, \text{V}$ is shown in the inset of (a).

FIG. 4. Energy-potential diagram of the three-electrode SAM device. (a) 3D energy bands of the SAM, showing the Fermi level of the silicon gate $E_F$. (b) The hybridization of the energy levels of the gate and drain electrodes at $V_g = -2.0 \, \text{V}$, resulting in a gap overlap. (c) The energy levels of the SAM and gate electrode at $V_g = 6 \, \text{V}$. (d) The energy levels of the SAM and drain electrode at $V_d = +0.9 \, \text{V}$.
FIG. 4. Energy-potential diagrams of the gold-SAM-gold system for (a) $V_d$ and $V_g$ are set to 0 V. (b) $V_d$ is set to 0 V, and a negative $V_g$ is applied to the drain electrode. (c) $V_g$ is set at $V_g$ = −2.0 V, and then is scanned toward positive potentials. (d) $V_g$ is set at 46 V, and then scanned toward negative potentials.

$V_g$ = 4.5 V for $V_d$ = 1 V when one takes the derivative of $I_d$ vs $V_g$, which is shown in the inset of Fig. 3(a). Then, $I_d$ levels off as LUMO is embedded in the window. The decrease in $I_d$ as $V_g$ scanned from 0 to −4 V may be due to the LUMO that is moved out of the window. This introduces a central peak in the curve of the absolute value of the derivative of the $I_d$ vs $V_g$, since the width of the window between two Fermi levels is equal to $V_d$, the above observations may provide information of the gating efficiency of the device. For example, for $V_d$ = 1 V, $V_g$ is scanned from 4.5 to −1.5 V to drive LUMO across the window with a 1 V width [Fig. 4(d)], thus the gating efficiency of 0.17 eV/V can be deduced. The same value of gating efficiency can also be obtained for the other $I_d$-$V_g$ curves in Fig. 3(a). Further negative scan of $V_g$ will cause $I_d$ to increase sharply, which may originate from the approach of the hybrid level to the window of Fermi levels from below as $V_g$ is scanned negatively. The maximum of the rising rate occurs at $V_g$ = −7 V that can be deduced from the inset of Fig. 3(a). This indicates that the hybrid level is entering the window of the Fermi levels between the source and drain electrodes.

In summary, we have observed clear field effects for the electric current conducted through SAM in a three-electrode nanopore device. The device is stable in both voltage and temperature scans, and the data observed are highly reproducible. The dependence of $I_d$ on $V_d$ and $V_g$ can be explained in the framework of Eq. (1) and the calculated transmission function.

$1$ S. Lindsay, J. Chem. Educ. 82, 727 (2005).