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Chemical Complementarity in the Contacts for Nanoscale Organic Field-Effect Transistors

George S. Tulevski, Qian Miao, Ali Afzali, Teresita O. Graham, Cherie R. Kagan,* and
Colin Nuckolls*

*Department of Chemistry and the Nanoscience Center, Columbia University, New York, New York 10027, and
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598*

Received November 2, 2005; E-mail: cn37@columbia.edu; cheriek@us.ibm.com

Shrinking the device dimensions of polycrystalline thin film organic transistors to the nanoscale enables charge transport in single grains to be probed, eliminating grain boundaries that give rise to deleterious traps and poor electronic coupling. However, when the size of the devices is severely reduced, new challenges emerge because the resistance of the contact between metal and molecule exceeds the channel resistance and dominates the device properties.[1,2] The strategy described in this paper is to control this interface by directly coupling an organic semiconductor to the surface of the source and drain electrodes. These monolayers, depicted in Figure 1a, form a template on the metal surface and provide better electronic coupling between the electrode and the semiconductor. The important result is that superior nanoscale (40−100 nm) transistors form only when the monolayer functionality is complementary to the structure of the molecular semiconductor.

We fabricated field-effect transistor (FET) test structures using electron beam lithography on highly doped silicon wafers with 5 nm of thermally grown silicon oxide. Figure 1b,c shows a schematic and scanning electron micrograph of the devices. Au (19 nm) on Ti (1 nm) source and drain electrodes were deposited by e-beam evaporation and lithographically defined to form a range of sub-100 nm channel lengths. The organic semiconductors were deposited in the nanoscale channels by spin-coating and isolated from the remainder of the device using a thick SiO_2 layer (Figure 1c).

The source-drain contacts of these devices were derivatized from solutions (1 mM THF) of the monolayer-forming molecules (**1**−**3**) shown in Figure 1d. Polycrystalline pentacene films were formed by first spin-coating and then thermally initiating a retro-Diels−Alder reaction (Scheme 1) of the pentacene/*N*-sulfinylacetamide adduct (**4**).[3b] For micron-sized devices, this method produces hole mobilities that exceed 0.5 cm^2/Vs.[3] Table 1 compares the mobility (μ), current modulation (I_{ON}/I_{OFF}), and transconductance (g_m) for the unfunctionalized and functionalized devices.[4] Thiophenol (**1**)[5] and 2-mercaptoethanesulfonic acid (**2**)[5] show only modest improvement, while a monolayer of thioketone **3**[5] shows a dramatic performance increase in every aspect. The beneficial effect of the thioketone is a stark contrast to the few studies using self-assembled monolayers to modify micron-scale devices, which show only modest improvement.[6]

Figure 2a−d compares the electrical properties of 50 nm channel length FETs with and without molecular functionalization (using thioketone **3**) of the electrodes. In both cases, the devices were well-behaved with linear, ohmic regions followed by current saturation. The ease with which the *N*-sulfinylacetamide/pentacene adduct forms nanoscale transistors contrasts sharply with the nonideal IV characteristics reported for most sub-100 nm evaporated pentacene FETs.[1] The most striking difference upon modifying the electrodes with the thioketone template molecule is a 50-fold increase in the saturation current (Figure 2c). Covalently attaching the organic semiconductor to the electrode allows for better electronic coupling between the electrodes and organic semiconductor. This leads to an average mobility of 0.022 cm^2/Vs, around 2 orders of magnitude higher than that of unmodified devices.[7]

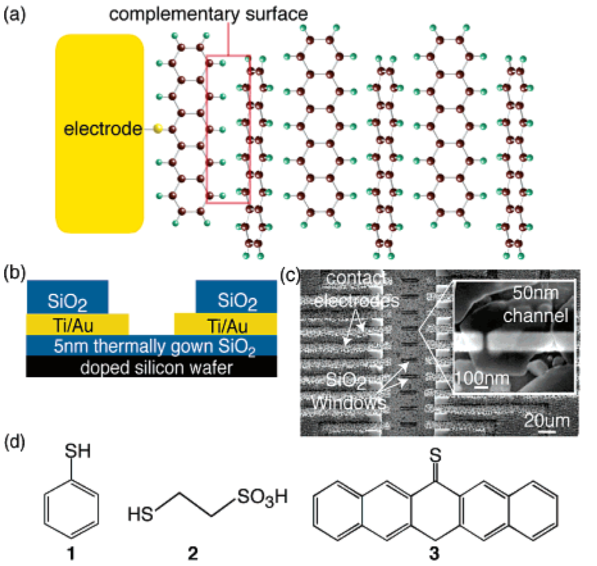

Figure 1. (a) Illustration of surface modification to form a template that recognizes a complementary surface. (b) Schematic of the device structure. (c) Scanning electron micrograph of devices and single device channel (inset). (d) Structures of compounds used to modify the electrodes.

Scheme 1. Retro-Diels−Alder to Pentacene

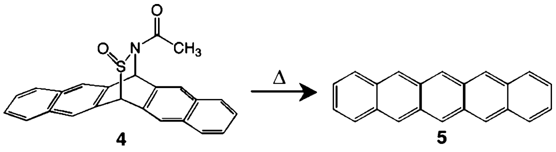

Table 1. Transistor or Characteristics[4] of Modified Devices[a]

modification	I_{ON}/I_{OFF}	μ (cm^2/Vs)	g_m (nA/V)
none	100	$1.4 \pm 0.3 \times 10^{-4}$	0.5 ± 0.1
1	50	$5.1 \pm 0.9 \times 10^{-4}$	1.3 ± 0.3
2	35	$7.6 \pm 1.1 \times 10^{-4}$	1.8 ± 0.2
3	8000	$2.2 \pm 0.7 \times 10^{-2}$	12.2 ± 1.4

[a] Values are an average of many devices (>10) with channel lengths ranging from 40 to 100 nm.

We evaluated the origin of the difference in device properties with the thioketone (**3**) through a quantitative study of the contact resistance.[8] Figure 2d shows a plot of normalized total resistance versus channel length for both modified and unmodified electrodes. In both cases, there is very little change in total resistance as a function of channel length, suggesting that the device resistance is dominated by the contact resistance.[9] Modifying the electrodes

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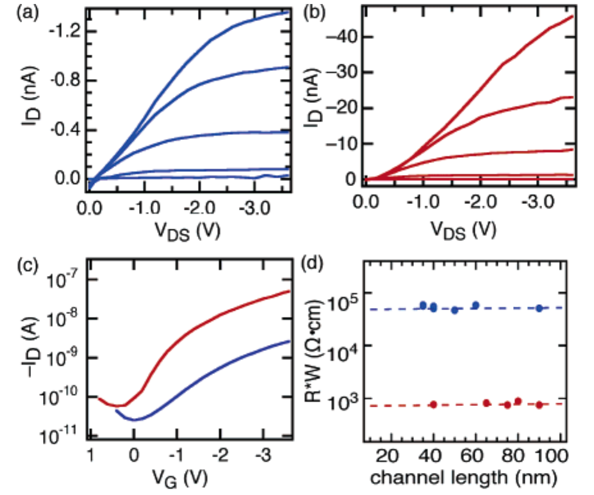

Figure 2. I_D versus V_{DS} curves ($V_G = 0$ to -3.6 V in -0.9 V steps) (a) unmodified and (b) electrodes modified with thioketone **3**. (c) I_D versus V_G curves ($V_{DS} = -3.6$ V) and (d) normalized total resistance as a function of channel length for both unmodified (blue) and modified (red) electrodes ($V_G = -3.6$ V).

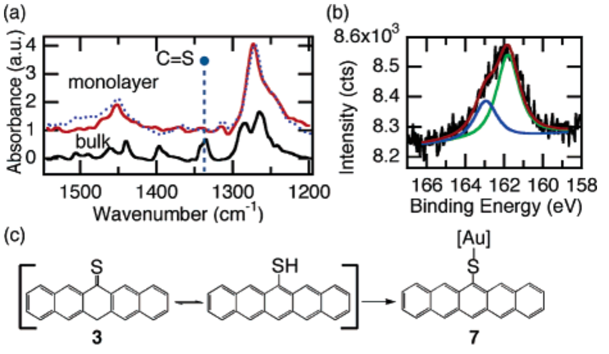

Figure 3. (a) Comparison of reflection−absorption IR spectra from bulk (black) and the monolayer from **3** before (red) and after heating for 2 min at 200 °C (dashed blue line). (b) Black trace shows the XPS spectrum of a sulfur bonded to gold. The colored traces are a curve fit with the expected 2:1 ratio for the sulfur 2p photoelectron from a gold−thiolate. (c) Tautomerization to 6-thiopentacene followed by binding to gold.

decreased the contact resistance by 2 orders of magnitude from the unmodified electrodes. This decrease in contact resistance is the origin of the improved device performance.

The important conclusion from the combination of reflection−absorption infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) is that thioketone **3** tautomerizes to 6-thiopentacene and binds to the gold surface (Figure 3). The infrared spectrum shows the loss of the C═S stretch (1340 cm^{-1}) upon monolayer formation (Figure 3a).[10] The XPS data reveal a single type of sulfur 2p doublet at 161.8 eV that is indicative of a gold−thiolate (Figure 3b).[11] In addition, the infrared spectrum shows aromatic stretching at 1450 and 1250 cm^{-1} that is indicative of linear acenes.[12] Binding through the sulfur atom would point the unencumbered acene edge into the gap, where it can act as a template[13] (Figure 1a). The contact angle of a water drop on these films was 58°. The contact angle and IR spectrum (Figure 3A) of the monolayers were unchanged after heating to 200 °C (2 min). These are the same conditions used to initiate the retro-Diels−Alder reaction to form the pentacene films.

In summary, using structurally and electronically similar compounds to modify the electrode surfaces leads to much better electronic coupling between the contacts and the semiconductor and dramatically decreases the contact resistance in nanoscale organic FETs. This strategy allows well-behaved devices to be made that have as little as 40 nm separating the source and drain electrodes. Combining this approach with metal−molecule linkages that are more conductive than gold thiolates[14] and acene-modified gate dielectric surfaces[1i] should further improve these devices.

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Supporting Information Available: Experimental details for the device preparation/characterization, infrared spectroscopy, and XPS. This material is available free of charge via the Internet at http://pubs.acs.org.

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